

CRYSTALLOGRAPHIC STUDIES IN THE VIVIANITE GROUP

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ACKNOWLEDGMENT

By courtesy of Professor Charles Palache the present writer, when still a regular staff member of the Geophysical Laboratory, was enabled to spend about five weeks of the summer of 1935 in the laboratories of the Mineralogical Museum at Harvard University. The chief object was to study a rock series from Iceland and the Faeroe Islands; but a visit to Harvard, this centre of crystallographic research, afforded also unique opportunities for studies in classical crystallography. When the writer expressed a desire to do some research work in this field, Dr. Palache kindly suggested a re-study of erythrite; he supplied the necessary material from the collections of the Museum, and himself selected some of the best crystals for goniometer measurements.

Dr. M. A. Peacock kindly offered to teach the writer the new methods and schemes of presentation worked out for the new edition of Dana's *Mineralogy*.

For the hospitality and the stimulating influence he received at the Mineralogical Museum the writer wishes to express his sincere appreciation.

All x-ray work was done at the Geophysical Laboratory. As usual Dr. W. F. Foshag kindly supplied the necessary mineral specimens from the U.S. National Museum. Thanks are also due to Mr. C. J. Ksanda for having taken many of the x-ray photographs.

The experimental part of the present paper was done while the writer was connected with the Geophysical Laboratory of the Carnegie Institution of Washington. A preliminary report on some of the results was given at the Sixteenth Annual Meeting of the Mineralogical Society (1935); but owing to various circumstances the writing of the final paper has been delayed for one year.

MEASUREMENTS WITH THE TWO-CIRCLE GONIOMETER

Erythrite, Cobalt bloom, $\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. The crystals are prismatic, show few faces, and are always striated vertically, usually also parallel to [101]. For these reasons few good goniometer measurements exist and the crystallographic constants are not known with any great accuracy. The results of measurements by Des Cloizeaux (1908) and Green (1910) are given below. Later studies by Lincio (1914) and Shannon (1926) did not lead to new values for the geometrical elements.

New measurements were carried out on erythrite crystals supplied by Prof. Palache from the Karabacek Collection in the Mineralogical Museum of Harvard University. Table 1 gives the crystal elements derived from the best measurements and the mean measured and calculated angles for the accepted forms. The orientation of V. Goldschmidt for vivianite has been retained.

TABLE 1. ERYTHRITE FROM SCHNEEBERG, SAXONY; TWO-CIRCLE MEASUREMENTS ON EIGHT CRYSTALS

Monoclinic; $a:b:c=0.7648:1:0.7122$; $\beta=105^\circ 02'$
 $p_0:q_0:r_0=0.9312:0.6878:1$; $\mu=74^\circ 58'$
 $p'_0=0.9642$, $q'_0=0.7122$, $x'_0=0.2686$

Forms	No. of Faces	Measured				Calculated	
		Range		Mean		ϕ	ρ
		ϕ	ρ	ϕ	ρ		
<i>c</i> 001	—	—	—	—	—	90°00'	15°02'
<i>b</i> 010	16	—2°40' to 3°30'	—	0°27'	90°00'	0 00	90 00
<i>a</i> 100	}	Vertical zone very poor. No faces could be determined uniquely, but there are broad chains of reflections very roughly corresponding to the positions of 100, 110 and 610				90 00	90 00
<i>m</i> 110						53 33	90 00
<i>n</i> 610						82 59	90 00
<i>w</i> $\bar{1}01$	6*	—85 48 to 93 02	34°50'	—89 40	34 50	—90 00	34 49½
<i>p</i> 111	6	61 16 to 59 50	54 16 to 55°10'	59 50	54 57½	59 59	54 55
<i>v</i> $\bar{1}11$	5	—44 17 to —44 25	44 48 to 44 58	—44 21	44 53	—44 19½	44 52½
<i>q</i> $\bar{6}16$	2†	—80 16 to —82 21	35 03 to 35 11	—81 18	35 01	—80 19	35 12½
<i>n</i> 101	1	—	—	89 41	51 07	90 00	50 57

* Vicinals.

† Vicinals to ($\bar{1}01$), indications of faces were seen throughout the zone from ($\bar{1}01$) to ($\bar{6}16$).

These figures and their relative accuracy will be discussed in a later section after the presentation of the *x*-ray studies.

Fig. 1*a* depicts the typical crystal habit, the large *b*-face is characteristic, the relative size of the upper terminal faces is however subject to some variations, but very regularly the same combination of faces is

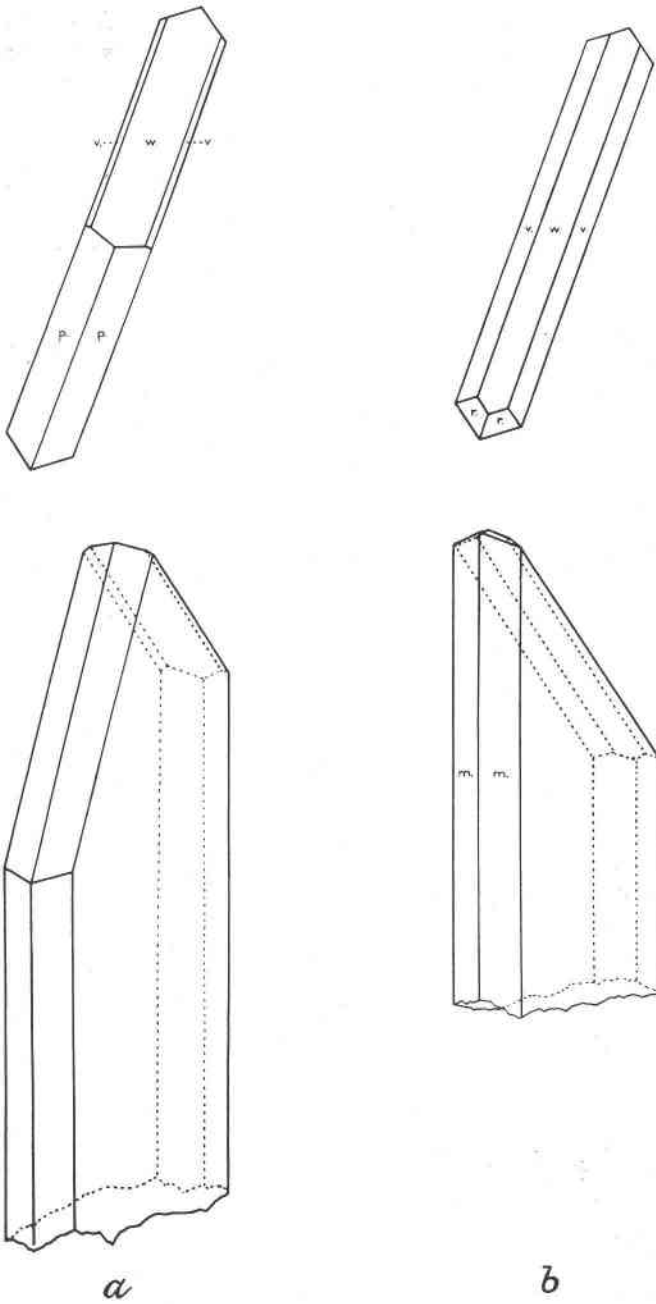


FIG. 1. (a) Erythrite from Schneeberg, Saxony. (b) "Cabrerite" (=annabergite) from Laurion, Greece.

present. Vertical striation is universal and affects all faces of the zone [001]; striation parallel to [101] is also practically always present and affects especially the faces $b(010)$, and $w(\bar{1}01)$. This is why good measurements are so difficult to obtain.

The pinacoidal cleavage (010) in erythrite is well known; in addition to it a prismatic cleavage or slipping was found parallel to $r(\bar{1}12)$.

Cabrerite, supposed to be $(\text{Ni, Mg})_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, but proved to contain no Mg. Like erythrite in habit. Good crystals for measurements have never been found. No reliable figures for the axial ratio exist; those given by Sachs (1906): $a:b:c=0.82386:1:0.77677$; $\beta=106^\circ 29'$ are at great variance with the present results; his material must have been very poor, therefore, or else his orientation of the crystal was different. His paper does not give any information regarding this question, however.

Table 2 gives the geometrical elements derived from new measurements on cabrerite crystals from the Karabacek Collection in Harvard University.

TABLE 2. CABRERITE FROM LAURION, GREECE; TWO-CIRCLE MEASUREMENTS ON THREE CRYSTALS

Monoclinic: $a:b:c=0.7874:1:0.7223$; $\beta=104^\circ 31\frac{1}{2}'$
 $p_0:q_0:r_0=0.9195:0.6993:1$; $\mu=75^\circ 28\frac{1}{2}'$
 $p_0'=0.9498$; $q_0'=0.7224$; $x_0'=0.2591$

Forms	No. of faces	Measured range		Calculated	
		ϕ	ρ	ϕ	ρ
c 001	—	—	—	$90^\circ 00'$	$14^\circ 31\frac{1}{2}'$
b 010	}	—	$90^\circ 00'$	0 00	90 00
a 100		Broad chains of reflections	90 00	90 00	90 00
m 110			90 00	52 45	90 00
w $\bar{1}01$		3	$-90^\circ 00'*$	34 40 to $34^\circ 47'$	90 00
p 111	—	—	—	59 $08\frac{1}{2}$	54 $37\frac{1}{2}$
v $\bar{1}11$	3	-42 24 to $-43^\circ 55'$	44 35 to 46 15	-43 43	44 59
r $\bar{1}12$	5	-30 11 to -32 18	22 04 to 22 20	-30 $51\frac{1}{2}$	22 49

* Because of the poor development of the prism zone the azimuth of this face was taken as zero.

Fig. 1b depicts the characteristic crystal habit; the small faces $r(\bar{1}12)$ are, however frequently missing. Perfect pinacoidal (010) cleavage. Striation parallel to [101].

Annabergite, $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, and *Köttigite*, $\text{Zn}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, are additional minerals belonging to the vivianite family. Much time was spent in search for small crystals suitable for goniometer measurements, but without much success. With the kind assistance of Dr. Harry Berman of the Mineralogical Museum at Harvard we finally succeeded in getting

a few faceted crystals which could be oriented and measured on the goniometer. Within the rather large error of measurement the observed interfacial angles were found to correspond to the analogous angles of erythrite and cabrerite. Although the number of faces was insufficient for establishing the geometrical elements, it can be concluded from these measurements that the constants must be very similar to those of erythrite and cabrerite.

X-RAY MEASUREMENTS

By optical goniometry the crystallographic constants of a mineral can be established only if a sufficient number of external faces is developed; if there are few or poorly developed faces, no values or uncertain values for the constants will result. By using an *x*-ray goniometer accurate values can be obtained even though no external faces may be present. The Weissenberg arrangement is ideally suited to this purpose. The instrument used for the present investigation was constructed by Brækken (1932) of the Fysisk Institutt of Norges Tekniske Høiskole at Trondheim, and was modified at the Geophysical Laboratory so as to render it more readily available for the application of the equi-inclination technique in accordance with the scheme of Buerger (1934). By this method the lattice spacings and the angles between planes in the crystal were directly measured. As will be seen, the accuracy of the method is very satisfactory. It is believed that greater accuracy can be secured with the reflection goniometer only if the crystal faces are of a high degree of excellence. It is also obviously possible to build a Weissenberg apparatus for very high precision of determination of spacings and angles and thereby, of course, the axial ratio. The construction of such an apparatus with an accuracy said to exceed that of an optical goniometer was announced by Buerger at the last (seventeenth) annual meeting of the Mineralogical Society (1936). But even with the ordinary Weissenberg arrangement the results are very satisfactory. By this method the following minerals were studied: vivianite, erythrite, cabrerite, and bobierrite. Unfiltered Cu-radiation was used throughout, the wave lengths are: $\lambda_{\alpha_1}=1.5373$, $\lambda_{\alpha_2}=1.5410$; in case of superposition of the α_1 and α_2 spot the average wave length $\lambda=1.5388$ was used. Other symbols used are: θ =glancing angle, μ' =separation of layer lines; a_0 , b_0 , c_0 are the periods along the corresponding crystallographic axes; d_{hkl} is the spacing between consecutive structure planes of the set (*hkl*).

Vivianite, monoclinic, $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. Small needle-like, transparent crystals from Monserrat Mine, Bolivia, kindly supplied by Dr. W. F. Foshag of the U.S. National Museum, Washington, D.C., were used in the present röntgenographic investigation. The habit of the crystals permitted an easy orientation of the *c*-axis, and they were therefore

mounted on the Weissenberg goniometer for rotation around this axis. Ordinary rotation, equator, and layer-line photographs were obtained. The diffraction spots were measured and indexed, and the lattice spacings determined in the usual way, see table 3. Particularly useful for an exact determination of the crystallographic angle β are diffraction spots from faces of the form $(h0l)$, and the glancing angles of these faces are most accurately determined from the rotation diagrams around the c -axis.

TABLE 3. VIVIANITE FROM MONSERRAT, BOLIVIA; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES
 $a_0=10.039$, $b_0=13.388$, $2c_0=9.374$; $\beta=104^\circ 18'$

Indices	θ°	b_0
0 2 0	6.61	13.368
0 4 0	13.29	13.388
0 8 0	27.37	13.388
0 10 0	35.04	13.388
0 12 0	43.57	13.386
0 16 0	66.72	13.389
Average		13.388

Indices	θ°	d_{100}
2 0 0	9.32	9.723
4 0 0	18.44	9.730
6 0 0	28.33	9.728
8 0 0	39.21	9.727
10 0 0	52.20	9.728
12 0 0	71.48	9.723
Average		9.728

	μ°	c_0
1st layer	19.17	4.687
2nd layer	41.05	4.687
Average		4.687

Indices	θ°	$(\beta-90)^\circ$
0 0 1	9.765	14°23'
2 0 1	11.61	14 18
2 0 1	15.00	14 17
Average		14 18

The table shows that the c -dimension of the structural lattice is halved as compared with the morphological lattice. Consequently:

$$a:b:c = \frac{a_0}{b_0} : \frac{b_0}{b_0} : \frac{2c_0}{b_0} = 0.7499:1:0.7002$$

$$\beta = 104^\circ 18'; \text{ density} = 2.711.$$

The probable error of the axial ratio can be estimated by inspection of table 3. A further check on these figures is supplied by a recent paper by Yamaguti (1936) which became available to me after the present manuscript was written. By the cathode ray diffraction method he determined the crystallographic constants of vivianite as follows:

$$a_0 = 9.997 \text{ \AA}, b_0 = 13.37 \text{ \AA}, c_0 = 4.696 \text{ \AA}; \beta = 104^\circ 16'.$$

Vivianite is not a rare mineral and is frequently encountered in well

TABLE 4. LINEAR GEOMETRICAL ELEMENTS OF VIVIANITE

$a:b:c$	β	Author
0.7488:1:0.7029	104°33'	Cesàro
0.7498:1:0.7017	104 26	Goldschmidt
0.7499:1:0.7002	104 18	<i>x</i> -ray (Barth)

developed faceted crystals which at various times have been measured with the reflection goniometer. As seen from table 4 the results obtained from the present *x*-ray study agree closely with the crystallographic elements of vivianite as determined on the reflection goniometer by earlier workers, e.g., Cesàro (1897), Goldschmidt (1913).

Personally the writer believes that the geometrical elements of a crystal can be more accurately determined with the present *x*-ray goniometer than is usually possible with a reflection goniometer. This is, of course, especially true for crystals with few or poorly developed faces. Several members of the vivianite group are encountered in such imperfect crystals that no determination of the crystallographic constants have been attempted. For other members the constants were known only approximately. In such cases the *x*-ray method is indispensable.

Erythrite, $\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. Thin crystal fragments flattened after (010)

TABLE 5. ERYTHRITE FROM SCHNEEBERG, SAXONY; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$$a_0 = 10.184, b_0 = 13.340, 2c_0 = 9.460; \beta = 105^\circ 01'$$

Indices	θ°	b_0
0 8 0	27.48	13.331
0 10 0	35.18	13.343
0 12 0	43.79	13.325
0 14 0	53.77	13.340
0 16 0	67.03	13.356
Average		13.340

Indices	θ°	d_{100}
4 0 0	18.23	9.838
8 0 0	28.00	9.832
10 0 0	51.38	9.839
Average		9.836

	μ°	c_0
1st layer	18.99	4.729
2nd layer	40.58	4.730
Average		4.730

Indices	θ°	$(\beta - 90)^\circ$
$\bar{2}$ 0 1	11.40	15°11'
$\bar{4}$ 0 1	18.36	14 51
2 0 1	14.94	15 00
6 0 1	32.58	15 05
8 0 1	43.55	14 59
Average		15 01

were used. They were mounted on the Weissenberg goniometer and x-ray pictures were obtained in the same way as for vivianite. The most important measurements are given in table 5.

The x-ray data lead to the following constants:

$$a:b:c = \frac{a_0}{b_0} : \frac{b_0}{b_0} : \frac{2c_0}{b_0} = 0.7633:1:0.7092; \beta = 105^\circ 01'$$

$$\text{Density} = 3.182^1$$

Since crystals of erythrite are never well suited for measurements with the reflection goniometer it is probable that the most accurate values for the crystallographic elements are those obtained from the present x-ray measurements; the probable limit of error can be estimated by inspection of table 5. Table 6 gives a comparison of all available independent determinations of the geometrical elements of erythrite.

TABLE 6.—LINEAR CRYSTALLOGRAPHIC ELEMENTS OF ERYTHRITE

<i>a</i>	<i>b</i>	<i>c</i>	β	Author
0.7937	1	0.7356	105°09'	Des Cloizeaux
0.7502	1	0.7006	105 01	Green
0.7648	1	0.7122	105 02	Barth (optical)
0.7633	1	0.7092	105 01	Barth (x-ray)

Cabrerite, $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ (proved to be annabergite). Only thin and flaky crystals were available; they are always very flexible and proved to be more or less bent and distorted and gave relatively poor x-ray photographs. The results are therefore not as accurate as those for vivianite or erythrite. It was possible in this case to mount a flaky little crystal on the Weissenberg goniometer for rotation around the *b*-axis. The crystallographic angle β could thus be measured directly and graphically on the film. Various spacings necessary for computation of the crystallographic elements were determined from additional Weissenberg photographs as shown in table 7.

Consequently:

$$a:b:c = \frac{a_0}{b_0} : \frac{b_0}{b_0} : \frac{2c_0}{b_0} = 0.7619:1:0.7073; \beta = 104^\circ 45'$$

Although these figures are not very accurate they probably represent the most accurate values of the geometrical elements of cabrerite thus far available. They probably are superior to those deduced from reflection goniometer measurements.

¹ Previous density determinations are: 2.912 Kersten (1893); 2.948 Dana (1892); 3.178 de Schulten (1903).

TABLE 7. CABRERITE FROM LAURION, GREECE; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$$a_0 = 10.122, b_0 = 13.284, 2c_0 = 9.396; \beta = 104^\circ 45'$$

Indices	θ°	d_{100}
2 0 0	8.99	9.847
4 0 0	18.38	9.760
6 0 0	28.14	9.802
10 0 0	51.86	9.773
12 0 0	70.28	9.799
Average		9.7835

Indices	θ°	$2d_{001}$
0 0 1	9.64	9.189
0 0 2	19.84	9.068
0 0 3	30.51	9.093
0 0 5	57.80	9.084
Average		9.0815

	μ°	b_0
1st layer	6.60	13.387
2nd layer	13.40	13.280
3rd layer	20.37	13.262
4th layer	27.60	13.286
5th layer	35.40	13.281
6th layer	44.07	13.277
7th layer	54.15	13.289
8th layer	67.90	13.287
Average		13.284

Bobierite, $Mg_3P_2O_8 \cdot 8H_2O$. Occurs in aggregates of minute, white, needle-like crystals. Much time was spent in search of a crystal suited for measurements with the reflection goniometer, but in vain. Nor are any older measurements on record. In order to determine the crystallographic constants of this mineral we have therefore in this case the choice between the x-ray method and no method at all. Material for the present study was supplied from both Harvard University (Dr. Palache) and U. S. National Museum (Dr. Foshag). The needle-like crystals permit orientation on the Weissenberg goniometer only of one zone, the *c*-axis. Without changing the orientation of the crystal a set of Weissenberg photographs was produced from which all the crystallographic constants were determined as shown in table 8.

This table demonstrates an interesting fact: the doubling of the *b*-axis as compared with vivianite, erythrite, and cabrerite. Thus we obtain:

$$a:b:c = \frac{a_0}{\frac{1}{2}b_0} : \frac{\frac{1}{2}b_0}{\frac{1}{2}b_0} : \frac{2c_0}{\frac{1}{2}b_0} = 0.7193:1:0.6671; \beta = 104^\circ 01'$$

as the geometrical elements of bobierite. The density is 2.169. These

TABLE 8. BOBIERRITE FROM MEXILLONES, CHILE; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$$a_0=9.946, \frac{1}{2}b_0=13.827, 2c_0=9.279; \beta=104^{\circ}01'$$

Indices	θ	b_0
0 4 0	6.42	27.656
0 8 0	12.86	27.654
0 16 0	26.44	27.646
0 20 0	33.81	27.654
Average		27.654

Indices	θ	d_{100}
2 0 0	9.12	9.7082
4 0 0	18.62	9.6387
6 0 0	28.55	9.6587
8 0 0	39.62	9.6520
10 0 0	52.83	9.6470
Average		9.650

	μ°	c_0
1st layer	19.37	4.640
2nd layer	41.56	4.639
Average		4.6395

Indices	θ°	$(\beta-90)^{\circ}$
2 0 1	15.06	13.75
2 0 1	11.72	14.28
Average		14.02

values are, however, susceptible of improvement. All crystals studied proved to be more or less distorted and composed of several fibres of slightly different orientation. Furthermore, all reflections from planes of the form $(h0l)$, which are particularly useful for the determination of the angle β , are either absent or very weak. The rotation photographs could not be used, therefore, for this determination; instead the zone curves were sketched on the first layer-line photographs, and the position of the wanted reflections thus fixed. But, of course, this procedure cannot give results as accurate as those for vivianite or erythrite.

UNIT CELL AND CRYSTALLOGRAPHIC ORIENTATION

In his *Atlas der Krystallformen* V. Goldschmidt has set the standard crystallographic orientation of the minerals of the vivianite family. In the present x -ray study the unit cell has been chosen so as to correspond to the orientation of Goldschmidt. It is not possible, however, to bring the unit cell demensions into exact agreement with the axial ratio of Goldschmidt. In vivianite, erythrite, and cabrerite the c -axis of the structural lattice is halved as compared with the morphological lattice, otherwise there is exact correspondence. However, the unit cell so far considered is not the "true" unit cell. As mentioned before it was thus chosen in order to make the results of the x -ray analyses directly comparable with those of the reflection goniometer. The interrelation of the three cells thus far mentioned: (1) the morphological cell, (2) the unit

cell used in the present study, and (3) the true unit cell, is brought out by fig. 2.

The question has recently been discussed by several American crystallographers whether the geometrical elements of a compound determined with the reflection goniometer should necessarily be exactly the same as those obtained from the unit cell dimensions established by *x*-ray analyses (Donnay, Tunell & Barth 1934). In 1933 George Tunell and the present writer expressed the belief that it is not desirable to

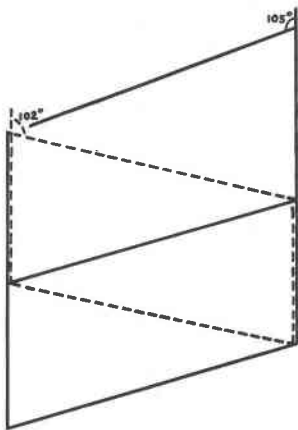


FIG. 2. Projection on (010) showing the mutual relationship of the three different cells mentioned in the text. The morphological cell is not a structural unit, it is represented by the full drawing, angle β is about 105° . The unit cell used in the present investigation is half the morphological cell and has the same orientation and the same angle β as the morphological cell; it is shown by full lines. The true unit cell is shown by stippled lines; the orientation is different from that of the morphological cell, angle β is about 102° , its volume is half that of the morphological cell.

stretch the results of the two methods of inquiry—with the reflection goniometer and the *x*-ray goniometer—into exact correspondence, although there should be a simple relation between them in all cases, and an exact correspondence in many.

If the morphological description of crystals of the vivianite type could be simplified by use of the true unit cell, a re-orientation of vivianite would seem desirable. However, no such advantage exists. The transformation: morphological cell (hkl) \rightarrow true unit cell, ($h'k'l'$) is:

$$h' = -(h + \frac{1}{2}l); k' = k; l' = \frac{1}{2}l.$$

If this transformation is tried, e.g., for erythrite or vivianite (all known faces are given by V. Goldschmidt) it is seen that no simplification of the indices results. Thus the present mineral group seems to constitute a case where the crystal morphology should not be described in terms of the true unit cell.

In bobierite the true unit cell is similar to that of the other minerals except that the b -axis is doubled. But since very few crystal faces have been observed in bobierite it is impossible to tell which lattice would best suit the morphology. It seems natural, however, to use the same morphological lattice for bobierite as for the other members of this mineral family.

SPACE GROUP DETERMINATION

Crystallographic measurements on vivianite, erythrite, and "cabrerite," indicate that these minerals belong to the holohedral class of the monoclinic syngony. The x -ray diffraction spots indicate a base-centered underlying lattice, consequently C_{2h}^6 and C_{2h}^3 are possible space groups. But C_{2h}^6 is excluded by the fact that diffraction spots from faces of the form $(00l)$ with l odd and $(h0l)$ with h even and l odd are present in the diagrams. All space group criteria are however in agreement with C_{2h}^3 , which is therefore regarded as the correct space group of these minerals.

Bobierite is not isomorphous with the same space group (as indicated e.g., by the presence of diffraction spots from faces of the form $(0kl)$ with both k and l odd). The ordinary space group criteria lead to C_{2h}^5 , but in addition to the extinctions demanded by this space group, there are a few additional systematic extinctions probably due to the doubling of the b -axis.

No endeavour was made to elucidate the atomic arrangement of any of these minerals.

OPTICAL STUDIES

Natural minerals as well as artificial products were examined. The following compounds were synthesized: $Ni_3As_2O_8 \cdot 8H_2O$ (annabergite), $Mg_3As_2O_8 \cdot 8H_2O$ (hörnesite), and $Mg_3P_2O_8 \cdot 8H_2O$ (bobierite). The procedure of de Schulten (1903) was followed. The synthetic crystals were too small, however, for measurements with the goniometer, but their optical constants could be determined with the microscope. A survey of the optical properties of the minerals of the vivianite group has been given by Larsen (1921), by Ulrich (1926), and by Larsen and Berman (1934). For comparison some of their data are included in table 9.

Several interesting points are brought out by this table: First we shall consider the data for bobierite. In this mineral as well as in artificial $Mg_3P_2O_8 \cdot 8H_2O$ the crystallographic b -axis coincides with the direction of the optical normal. This is contrary to the data given by Lacroix (1888), by Ulrich, and by Larsen and Berman who state that the plane of the optical axes is normal to (010) .² But new, careful comparative

² In the first issue of Larsen (1921) the optical orientation of bobierite is given as: $V = \beta$, which is in agreement with the new measurements by the present writer. The different statement in the second edition is therefore probably a misprint:

TABLE 9. OPTICAL PROPERTIES OF SOME MINERALS OF THE VIVIANITE GROUP

Mineral	α	β	γ	$c:\gamma$	Orient.	Author
Cabrerite	1.62	1.654	1.689	33°	$b = \alpha$	Larsen
Cabrerite	—	1.650	1.688	36	$b = \alpha$	Barth
Annabergite	1.622	1.658	1.687	36	$b = \alpha$	Larsen
Annabergite	—	1.651	1.689	30	$b = \alpha$	Barth
$Ni_3As_2O_8 \cdot 8H_2O$	—	1.655	1.688	32	$b = \alpha$	Barth
Hörneseite	1.563	1.571	1.596	31	$b = \alpha$	Larsen
$Mg_3As_2O_8 \cdot 8H_2O$	—	1.570	1.594	45	$b = \alpha$	Barth
Bobierite	1.510	1.520	1.543	29	$b = \beta^*$	Larsen
Bobierite	1.510	—	1.543	30	$b = \beta$	Barth
$Mg_3P_2O_8 \cdot 8H_2O$	1.510	—	1.543	30	$b = \beta$	Barth
$Mg_3P_2O_8 \cdot 8H_2O$	—	—	—	—	$b = \alpha$	Ulrich

* Larsen and Berman (1934) give $b = \alpha$.

studies of bobierite, vivianite, annabergite, etc. proved beyond doubt that the b -axis coincides with the direction of index β in all bobierite material used in the present investigation, both natural and synthetic. In this respect bobierite differs from all other minerals of the vivianite group (fig. 3). The fact that the spacing of the b -axis is doubled in bobierite, as compared with the other minerals of this group, may have something to do with the difference in optical behaviour.

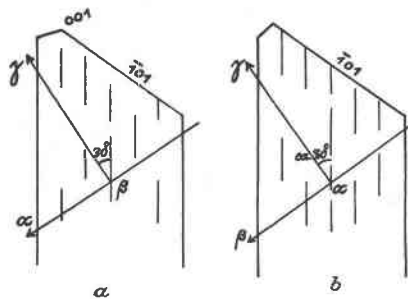


FIG. 3. (a) Optical orientation of bobierite. (b) Optical orientation of all other minerals of the vivianite group.

In this connection mention should be made of an old paper by Michel (1893) who introduces the name *hautefeuilleite* for a bobierite-like mineral which, according to his analysis, differs from bobierite in that it contains 5.71% CaO, and in its optical orientation. However, the redetermined optical properties of bobierite correspond to those of *hautefeuilleite* as given by Michel, viz.: “Le plan des axes optiques est compris dans $g^1(010)$ ”, and “L’indice moyen $n_m = 1.52$ (raie D)” (1893, p. 39). It may be reasonable to suppose, therefore, that Michel’s *hautefeuilleite* is not a new mineral, but ordinary bobierite. The presence of CaO in the analy-

sis is easily explained by contamination of apatite with which it is associated in nodular intergrowths. Michel's chief argument for establishing a new mineral species was the fact that the optical orientation of his mineral differed from that of bobierrite as given by Lacroix. But the results of the present study indicate that Lacroix was wrong in his optical determination, and that Michel thus was the first to establish the correct optical orientation of bobierrite. However, it is not impossible that bobierrite can take up a certain amount of CaO, although an isomorphous

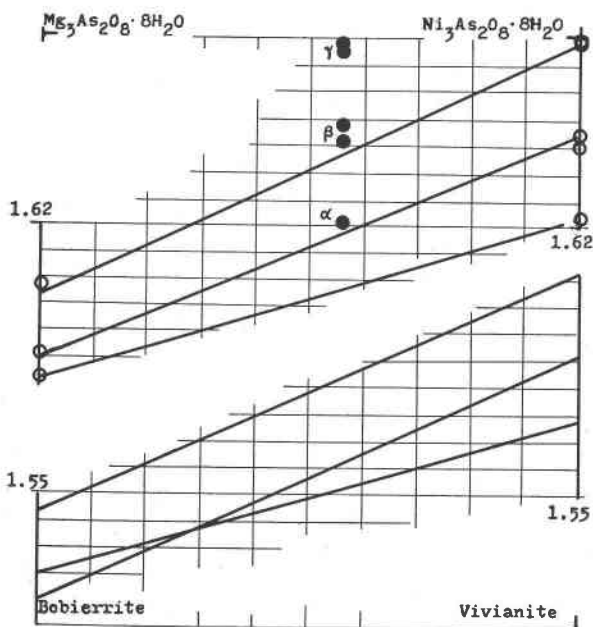


FIG. 4. Refractive indices of mixed crystals of the system $Mg_3As_2O_8 \cdot 8H_2O - Ni_3As_2O_8 \cdot 8H_2O$. ○ = Hörnesite. ○ = Annabergite ● = Cabrerite from Laurion. The alleged composition of cabrerite from Sierra Cabrera is approximately the same as that of cabrerite from Laurion.

replacement of Mg by Ca is rather unlikely from a crystallochemical point of view. Nor is the existence of lime-bearing bobierrites sustained by the present study. Until more convincing evidence is produced, therefore, it seems best to discard hautefeuillite as a mineral name.

It might be added that surprisingly little is known about the formation of mixed crystals in the vivianite family. For crystallochemical reasons one would, for instance, expect bobierrite to take up FeO (not CaO) with formation of mixed crystals towards the composition of vivianite. It is much more probable that such crystals exist than that hautefeuillite

exists. It is worth noticing that owing to the different optical orientation of the two end components certain members of the iron-bearing bobierite series in all probability would be optically uniaxial (fig. 4).

Another interesting point brought out by table 9 is the position of cabrerite in the binary system $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ — $\text{Mg}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. In fig. 4 a graphical survey is given of the optical properties of minerals and artificial compounds belonging to the system. The minerals annabergite and hörnesite are supposed to represent essentially the Ni-bearing and the Mg-bearing end-member respectively, and their optical properties are in complete agreement with this. Cabrerite is supposed to be a mixed crystal between these end-members,³ but its optical properties are in direct conflict with this assumption. To be sure, the optical properties of so-called cabrerite are practically identical with those of annabergite and of pure $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. We can conclude, therefore, that cabrerite from Laurion which has been studied both by Larsen and by the present author, is essentially pure $\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, i.e. annabergite, in spite of the analyses by Damour and by Sachs; for even a small amount of MgO would have evinced its presence in this mineral by decreasing the refractive indices. In this type of mixed crystals with very close crystallographic relationship between the two end-members (for the crystallography of hörnesite see Zambonini, 1919) the values of the refractive indices are directly proportional to the change in the composition (Barth, 1930).

The only other known occurrence of so-called cabrerite is Sierra Cabrera in Spain. The establishment of the mineral species rests on two very old analyses, one by Ferber (1863), and one by Frenzel (1874), which may or may not be trustworthy. Ferber's analysis shows 9.29% MgO, that of Frenzel 6.94% MgO—a rather large difference on presumably the same material—the corresponding contents of $\text{Mg}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ in the mix-crystal is 46 and 34 mol. per cent respectively. The refractive indices of a mixed crystal of about this composition is shown by fig. 4. Unfortunately no optical data on cabrerite from Sierra Cabrera are on record, nor has material been available for new studies. It is highly desirable that an optical analysis of this material be carried out. If the values of the refractive indices should support the assumption of a magnesia-rich mixed crystal (cabrerite) this would be the first example of a mineral series of mixed crystals with extensive replacement of Ni by Mg. However, before such data are available it seems best to discard cabrerite as a mineral name.

De Schulten (1903) claimed to have made synthetic cabrerite by drop-

³ Analyses by Des Cloizeaux and Damour (1878) and by Sachs (1906) on cabrerite from Laurion show 4.64 and 9.34% MgO respectively.

ping into a dilute solution of $\text{HNa}_2\text{As}_4 \cdot 7\text{H}_2\text{O}$ first magnesium sulphate, whereby hörnesite forms, then a mixture of magnesium sulphate and nickel sulphate whereby the hörnesite crystals are said to grow bigger and turn green—thereby becoming cabrerite. There is hardly any doubt, however, that this procedure would lead to the formation of zoned crystals, the total composition of which, as determined by de Schulten, has no direct relation to the actual composition of the various solid phases.

SUMMARY

The geometrical elements of a crystal can be more accurately determined with an x -ray goniometer than is usually possible with a reflection goniometer. This is, of course, especially true for crystals with few or poorly developed faces. Several members of the vivianite group are encountered in such imperfect crystals that no determination of the crystallographic constants had been attempted. For other members the constants were known only approximately.

New x -ray measurements as well as reflection goniometer measurements on this series of minerals have been carried out, and the crystallographic constants of the several members have been established (table 10).

TABLE 10. LINEAR GEOMETRICAL ELEMENTS OF THE MINERALS OF THE VIVIANITE GROUP

Mineral	Composition	a	b	c	β	Method
Vivianite	$\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7499	1	0.7002	$104^\circ 18'$	x -ray ¹
Symplectite	$\text{Fe}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7806	1	0.6812	107 17	reflect. gon. ²
Bobierite	$\text{Mg}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7193	1	0.6671	104 01	x -ray ¹
Hörnesite	$\text{Mg}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7676	1	0.7182	104 25	reflect. gon. ³
Erythrite	$\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7634	1	0.7092	105 01	x -ray ¹
Erythrite	$\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7648	1	0.7122	105 02	reflect. gon. ¹
Annabergite	$\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7619	1	0.7073	104 45	x -ray ¹
Annabergite	$\text{Ni}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7874	1	0.7223	$104\ 31\frac{1}{2}$	reflect. gon. ¹
Köttigite	$\text{Zn}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$	0.7	1	0.7	105	

¹ New data.² Krenner (1886).³ Zambonini (1919).

The unit cell used in this x -ray study was chosen so as to have the same crystallographic orientation as the morphological cell. The absolute dimensions of this cell are given in table 11. But it should be borne in mind that this cell is not the same as the so-called true unit cell (fig. 2).

A survey of the optical properties of minerals and artificial products belonging to the vivianite group is given in table 9. The mineral names

TABLE 11. ABSOLUTE DIMENSIONS OF THE UNIT CELL OF VIVIANITE, BOBIERRITE, ERYTHRITE, AND ANNABERGITE

Mineral	a_0	b_0	c_0	β	Density
Vivianite	10.039	13.388	4.687	104°18'	2.711
Bobierite	9.946	27.654	4.6395	104 01	2.169
Erythrite	10.184	13.340	4.730	105 01	3.182
Annabergite	10.122	13.284	4.698	104 45	3.231

hautefeullite and cabrerite have been discarded. They were supposed to stand for Ca-bearing bobierite and Ni-bearing annabergite, respectively. But it has been demonstrated that in their optical properties, as far as the determinations go, they do not differ from those of the end-members; and that thus far no compelling evidence has been produced proving the existence of any such mixed crystals either in Nature or among artificial products.

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