CLINOBARRANDITE AND THE ISODIMORPHOUS SERIES, VARISCITE-METAVARISCITE

Duncan McConnell, *The University of Texas, Austin, Texas.*

INTRODUCTION

In 1916, W. T. Schaller (1) suggested the existence of the isodimorphous series, variscite-metavariscite. Until recently no additional data were available to test the validity of this premise, so it seemed desirable to investigate the supposed members of the series by x-ray methods.

At an early stage of the investigation it became desirable to study one member of each group in some detail, because x-ray measurements had not been made on any of the members of the series. Investigations of phosphosiderite and scorodite were begun simultaneously, the latter in collaboration with Dr. L. J. B. LaCoste. The results for phosphosiderite have recently appeared (2). The work on scorodite led to the tentative selection of $Pcab - V_h^{15}$ as the probable space group, and this agrees with the results of P. Kokkoros (3).

When the intensity measurements failed to yield a plausible structure, the study of scorodite was temporarily discontinued, because specimens of sufficiently good quality to permit more accurate intensity measurements were not available. Furthermore, the crystals were not suitable to the production of Laue photographs which were desired in order to confirm the choice of the space group. Attention was then directed toward the measurement of the several remaining members of the series by powder diffraction methods.

Recently, H. Strunz and K. v. Sztrókay (4) have presented certain data on this mineral series. However, the results obtained in the present study are somewhat more complete and will serve to confirm their results* as well as to supplement them. In addition to giving measurements on metavariscite and variscite, the present work will show the existence of a monoclinic mineral having the composition $(Al, Fe)PO_4 \cdot 2H_2O$, clinobarrandite. The existence of this mineral has not been recognized previously, although its probable existence has been predicted by the writer (5) on the basis of the apparent discrepancies in the optical properties reported for barrandite.

The following specimens were examined in this study:

   I. Scorodite, from Ojuela mine, Mapimi, Durango, Mexico.
  II. Scorodite, from Djebel Debar (Constantine) Algeria. Purchased from Ward's Natural Science Establishment.
 III. Strengite and phosphosiderite, from Pleystein, Wildenau, Germany. U.S.N.M. 95538.
 IV. Variscite and metavariscite, from Lucin, Utah (part of type). U.S.N.M. 87485.

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* The choice of the probable space group for phosphosiderite is not confirmed for reasons mentioned below.

   V. Peganite [variscite] from Hot Springs, Arkansas. Kindly furnished by Dr. J. W. Gruner, Minneapolis.

  VI. Barrandite [intimate mixture of clinobarrandite and barrandite] from Manhattan, Nevada, U.S.N.M. 94669.

 VII. Barrandite, from Třenice, Bohemia. Furnished by the Field Museum of Natural History through the kindness of Dr. H. W. Nichols. M4144.

VIII. Barrandite, from Cerhovic, Bohemia. Purchased from Ward's Natural Science Establishment. No. 1069.

  IX. Phosphate [barrandite with quartz and mixture of dahllite-collophane] from island Gran Roque, Venezuela. Furnished by the Servicio Técnico de Minería y Geología, Caracas, through the kindness of Mr. S. E. Aguerrevere.

   X. Metavariscite and variscite [containing small amount of iron] from Candelaria, Nevada. Kindly furnished by Mr. S. E. Clabaugh.

Unless otherwise indicated the specimens were furnished by the U. S. National Museum through the kindness of Dr. William F. Foshag, to whom the writer is indebted. Some of the powder diffraction patterns used in this study were kindly prepared by Mr. Lynn Gardiner, of the University of Minnesota, Minneapolis.

Experimental Results

Powder diffraction diagrams were obtained for all of the specimens accessible through the use of unfiltered iron radiation and precision cameras (M. J. Buerger's model) with $r = 57.3$ mm. Some of the substances measured do not represent pure compounds (end-members) and for this reason the cell edges listed are not the determinations for any particular specimen, but are based on a number of measurements. Presumably, these values are for the pure compounds, or end-members, and are accurate within ± 0.05 Å. Specific gravity measurements from the literature are compared with the calculated densities.

		a_0	b_0	c_0	ρ	G
Orthorhombic—*Pcab*						
Variscite	$AlPO_4 \cdot 2H_2O$	9.85	9.55	8.50	2.61	2.5
Barrandite	$(Al, Fe)PO_4 \cdot 2H_2O$					
Strengite	$FePO_4 \cdot 2H_2O$	10.05	9.80	8.65	2.89	2.87
Scorodite	$FeAsO_4 \cdot 2H_2O$	10.30	10.00	8.90	3.32	3.3
Monoclinic ($\beta \rightarrow 90°$) — *P2₁/n*						
Metavariscite	$AlPO_4 \cdot 2H_2O$	5.15	9.45	8.45	2.53	2.54
Clinobarrandite	$(Al, Fe)PO_4 \cdot 2H_2O$					
Phosphosiderite	$FePO_4 \cdot 2H_2O$	5.30	9.80	8.65	2.74	2.76
[Clinoscorodite]	$FeAsO_4 \cdot 2H_2O$	—	—	—	—	—
? Vilateite	$(Fe, Mn)PO_4 \cdot 2H_2O$	—	—	—	—	2.75

In the present work the transformation suggested by Strunz and Sztrókay (4) for the variscite group has been adopted, because this permits a more direct comparison of the lattices of the two mineral groups, making the perfect cleavage (010) for both strengite and phosphosiderite. In both cases the imperfect cleavage is (001). This transformation is: Laubmann-Steinmetz to Strunz-Sztrókay 001/100/010.

As already pointed by Strunz and Sztrókay, however, the space group $P2_1/m$ is not a subgroup of $Pcab$, and the writer had considered this fact prior to the selection of $P2_1/m$ as the probable space group for phosphosiderite.

More recently it has been possible to obtain Weissenberg photographs of metavariscite and it has become quite apparent that the writer(2) and Strunz and Sztrókay (4) overlooked the absence of $h0l$ when $h+l$ is odd on the rotation photographs of phosphosiderite. Thus $P2_1/n - C_{2h}^5$ is the probable space group of metavariscite, clinobarrandite and phosphosiderite, and $P2_1/n$ is a subgroup of $Pcab$.

Measurement of a specimen from Manhattan, Nevada, has proven that this substance is not pure barrandite, but an intimate mixture of barrandite and the dimorphous form, clinobarrandite. In Table 1 the interplanar distances and estimated intensities are compared for clinobarrandite+barrandite VI, strengite and phosphosiderite. The interplanar distances for the monoclinic mineral are intermediate between those of phosphosiderite and metavariscite. Likewise the d values for the orthorhombic substance are intermediate between those of strengite and variscite. This proves that clinobarrandite and barrandite are present, rather than a mixture of phosphosiderite and variscite, or strengite and metavariscite. As neither the monoclinic nor the orthorhombic substance very closely approaches an end-member in composition, E. V. Shannon's analysis (6) will serve to demonstrate the intermediate composition of both substances.

A specimen from Candelaria, Nevada, has been examined and found to be an intimate mixture of variscite and metavariscite, although it contains a small amount of iron. Dr. R B. Ellestad kindly determined total iron as Fe_2O_3 and obtained 1.32%. The diffraction diagram of this specimen is given in Fig. 1, where the similarity between it and the mixture of clinobarrandite and barrandite is apparent. However, the spacings of the lines are slightly different because of the differences in the cell dimensions.

TABLE 1. COMPARISON OF POWDER DIFFRACTION DIAGRAMS*
(UNFILTERED Fe RADIATION—$r = 57.3$ MM.)

	Clinobarrandite +Barrandite			Strengite		Phosphosiderite	
No.	d	I	Key	d	I	d	I
	—			—		6.48	1
1	5.40	4	B_5	5.42	5	—	
2	4.87	3	B_4	4.92	4	—	
	—			—		4.88	1
3	4.65	2	C_5	—		4.67	5
4	4.50	2		—		—	
5	4.327	8	B_8+C_6	4.338	8	4.327	6
	—			—		4.089	2
6	3.979	1		—		—	
	—			—		3.965	2
	—			3.947	3	—	
	—			3.684	2	—	
7	3.581	1	C_5	—		3.592	5
8	3.522	1		—		—	
	—			3.378	1	—	
9	3.285	1	C_2+B_2	3.239	2	3.320	2
10	3.087	2	B_6	3.093	6	—	
11	3.044	2	C_3	—		3.052	3
12	2.948	4	B_{4+4} {	2.982	4	—	
				2.925	4	—	
	—			—		2.831	1
13	2.802	3		—		—	
14	2.752	8	$C_{10}+B_4$	2.782	4	2.771	>10
	—			2.675	1	—	
	—			—		2.651	1
	—			2.611	1	—	
15	2.533	5	B_8+C_5	2.514	8	2.557	5
16	2.437	2	B_4+C_1	2.426	4	2.452	1
17	2.332	2	C_2+B_2	2.346	2	2.338	2
	—			2.272	2	—	
	—			—		2.256	2
	—			—		2.221	2
18	2.077	1	B_5+C_3	2.121	5	2.123	3
	—			2.099	2	—	
	—			2.070	3	—	
	—			—		2.064	1
19	2.004	4	C_5+B_4	1.995	4	2.011	5

* The column marked "Key" indicates the source of the lines as clinobarrandite and/or barrandite, the subscripts indicating the relative intensities of comparable lines in the patterns of strengite and phosphosiderite. Beta lines and lines with estimated intensities less than one have been omitted from the table.
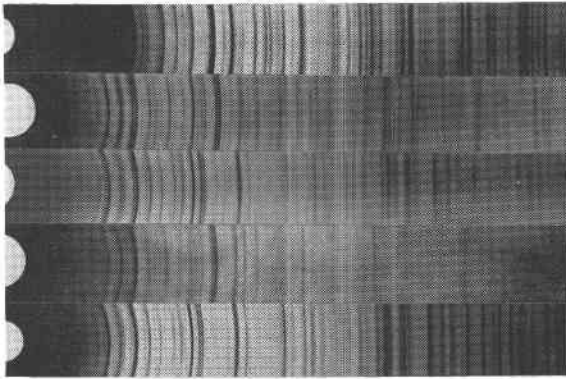
Fig. 1. Comparison of powder diffraction patterns of phosphosiderite, metavariscite +variscite X, barrandite VIII, clinobarrandite+barrandite VI, and strengite (reading from top to bottom).

The following aluminum-iron ratios for specimens of barrandite and clinobarrandite+barrandite are taken from the published analyses.

	Al/Fe
Clinobarrandite+barrandite	
Manhattan, Nevada	0.4
Barrandite	
Cerhovic, Bohemia	0.7
Gran Roque, Venezuela	2.5
Třenice, Bohemia	6.0

Several other minerals were investigated in order to discover any identities which might exist, but these studies have not been completed due to the difficulties in obtaining specimens. Zepharovichite has been found to be identical with wavellite. Callainite produces a pattern distinctly different from either variscite or metavariscite, but its existence as a species is not necessarily confirmed in the present work. S. G. Gordon (9) has suggested the probable identity of globosite and strengite but no opportunity to check this was afforded. The description of eggonite suggests its probable identity with either variscite or metavariscite. A specimen was not available for examination in this study, however.

Discussion

Barrandite is now known from seven localities, namely, Třenice (7) and Cerhovic (8) in Bohemia; Manhattan, Nevada (6); Moore's Mill, Pennsylvania (9); the island Gran Roque, Venezuela (5); the island Con-

nétable, French Guiana (10) and Ninghanboun, S. W. Australia (11).*
This suggests that barrandite is not as rare in its occurrence as previously
supposed. At Gran Roque it is the chief constituent of the phosphate
deposit, and it may be the iron- and aluminum-bearing constituent of
other rock phosphates.

Strunz and Sztrókay introduced the term "clinoscorodite" to apply to
the dimorphous form of scorodite. The evidence for the existence of this
dimorphous form is the variation in the optical properties observed by
E. S. Larsen (12). Although clinoscorodite has been included in the tabu-
lation, it is noteworthy that the goniometric measurements and refractive
index determinations by T. Ito and T. Shiga (13) do not support the
supposition that the material from Kiura mine, Bungo, Japan, is clino-
scorodite, unless both scorodite and clinoscorodite occur at this locality.
The association is probable, however, in view of the frequent association
of other dimorphous pairs.

The relation of vilateite to this series is not quite clear and a specimen
could not be obtained for investigation. If Himmelbauer's form (301) is
taken as (101) the following comparison results.

Phosphosiderite	Vilateite
$a:b:c=0.545:1:0.897$	$a:b:c=0.565:1:0.889$
$\beta = 89°24'$	$\beta = = 89°27'$
$G=2.76$	$G=2.75$
$n_\beta=1.725$	$n_\mu=1.74^a$
$r>v$ very strong	$r>v$ strong
negative	negative

It is to be remembered that the isodimorphism of the variscite—meta-
variscite series depends upon one assumption which seems to be well
founded: the degree of hydration is the same for the members of both
groups. The specimens studied in the present work were not suitable for
accurate determinations of the water of hydration.

SUMMARY

The name clinobarrandite is proposed for a new mineral which is
monoclinic and has the same composition as barrandite, $(Al, Fe)PO_4$
$\cdot 2H_2O$. The probable space group of metavariscite, clinobarrandite and
phosphosiderite is $P2_1/n$. Lattice dimensions are given for the members
of both groups of the isodimorphous series.

* This material, intermediate in composition between variscite and strengite, was de-
scribed as "variscite (redondite)." The term "redondite" carries no mineralogical con-
notation whatever. This so-called mineral is probably identical with barrandite which has
priority. If it is not identical, the term should not be applied until its properties have been
established. A chemical analysis made on heterogeneous material is not a sufficient basis
for the introduction of a new mineral name.

[a] $n_\mu=(n_\alpha+n_\gamma)/2$, or mean index.

Metavariscite is reported from Candelaria, Nevada thus recording a second locality, for this species.

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[b] Schaller's lucinite=variscite and variscite=metavariscite. See: Larsen, E. S., and Schaller, W. T.: *Am. Mineral.,* **10,** 23–28 (1925).