

X-RAY DATA ON SEVERAL PHOSPHATE MINERALS.

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ABSTRACT. Pseudowavellite and dussertite are shown to be members of the alunite and jarosite groups, respectively. A new analysis shows that dussertite is an arsenate of barium (not calcium) and iron. The alunite group is composed of aluminum-containing sulfates, sulfate-phosphates, and phosphates; similar iron-bearing minerals are jarosites. Sarcopside is not directly related to triplite, although an isodimorphous relationship may exist in view of the chemical similarities. Callinite, coeruleolactite, and zepharovichite should be dropped as mineral names. Several minerals are amorphous with respect to X-rays; namely, kehocite, evansite, richellite, borickite, and diadochite. Some so-called amorphous minerals produce excellent diffraction patterns.

INTRODUCTION.

DURING the past few years considerable new information has appeared on the classification of phosphate minerals. H. Strunz and J. Schroeter (1) have presented a more general classification based on morphological data as well as those X-ray data which were available. W. E. Richmond (2) and C. W. Wolfe (3) furnished X-ray determinations for numerous mineral species of the types $A_2XO_4(Z)$ and $A_3(XO_4)_2 \cdot nH_2O$, respectively.

Incidental to the writer's investigations of phosphate minerals, information has been obtained which was not directly related to the isomorphous series then under consideration. These results are presented in order to supplement the more general classifications just mentioned.

Most of the mineral specimens examined in this work represented type material or material from type localities, but specimens of this sort were not available in every instance. Those cases in which such materials were not used, although suggestive, obviously cannot be regarded as conclusive.

Almost without exception the results presented here are based entirely upon measurements of X-ray powder diffraction patterns. Precision cameras (M. J. Buerger's model (4)) and a tube with iron anticathode were used, no filtration having been

applied to the radiation. In some instances optical examinations and qualitative microchemical determinations were used to confirm the labelled identifications when sufficient material was available, but these tests will not be discussed.

THE ALUNITE AND JAROSITE GROUPS.

An important contribution to the mineralogy of the alunite group was that presented by W. T. Schaller (5) in 1912. More recently, S. B. Hendricks (6) has described the structures of several of these minerals. Consideration of these works and numerous others permits the generalization: Sulfates, sulfate-phosphates, phosphates, and sulfate-arsenates of K, Na, Ca, Sr, Ba, Ag, Pb, Ce, etc. occur in combination with aluminum or iron to form rhombohedral crystals. All of these possible combinations are not known to occur; that is, there are no recognized iron phosphates of any of the several cations. Furthermore, the possible occurrence of intermediate compounds containing both iron and aluminum must be recognized, but the analyses suggest that a greater preponderance of one of these elements almost universally occurs.

In an attempt to obtain a simplified classification, those substances containing iron are referred to the jarosite group and those containing aluminum to the alunite group when appropriate crystallographic properties exist. This form of classification seems more fundamental than separation as sulfates, phosphates, etc. and the number of divisions is thereby considerably reduced. The existing arrangement is already inconsistent insofar as both sulfate-phosphates and sulfate-arsenates are included in the beudantite group. Dussertite would constitute the only member of a seventh (possibly eighth) group if the classification according to anionic groups were followed to its logical conclusion.

The members of the alunite and jarosite groups are as follows:

Alunite Group

Sulfates: Alunite [=loewigite?], natroalunite.

Sulfate-phosphates: Hinsdalite, woodhouseite, svanbergite
[=harttite?=tikhvinite?].

Phosphates: Goyazite [=hamlinite], pseudowavellite, gorceixite, plumbogummite, florencite, stiepelmannite, (?) beaverite.

Jarosite Group

Sulfates: Jarosite, karpfösidierite, borgströmite, natrojarosite, ammoniojarosite, argentojarosite, plumbojarosite [=vegasite?].

Sulfate-phosphates: Corkite.

Phosphates: (?) calcium ferri-phosphate (7), (?) egueiite (8).

Sulfate-arsenates: Beudantite [=lossenite?].

Arsenates: Dussertite.

Pseudowavellite and dussertite are referred to the alunite and jarosite groups, respectively, on the basis of the X-ray diffraction patterns they produce. In Table 1, pseudowavellite and dussertite are compared with woodhouseite (9). It is noticeable (Table 1) that the patterns of woodhouseite and pseudowavellite are so similar as to be almost indistinguishable and this prevents the identification of these minerals by X-ray methods alone.

Pseudowavellite has recently been found by the writer (10) to occur at a second American locality. The patterns of pseudowavellite from all three known localities are virtually indistinguishable.

Diffraction patterns were obtained for a considerable number of species of the alunite and jarosite groups, including alunite, gorceixite, hinsdalite, and borgströmite. However, these need no further consideration as their mutual relationships are already well recognized.

The diffraction pattern of dussertite shows similarity to that of woodhouseite, to be sure, but the resemblance to the pattern of borgströmite is more pronounced as might be expected from the fact that borgströmite and dussertite contain Fe^{3+} whereas woodhouseite contains Al^{3+} . It seems, however, unnecessary to give the measurements for a member of the jarosite group for comparison with dussertite; the comparison with woodhouseite will suffice.

The knowledge that pseudowavellite is a member of the alunite group requires some revision of the formula; it may be written $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$. This formula conforms with that of alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, and corresponds in a satisfactory manner to E. V. Shannon's analysis (11). The theoretical compositions of pseudowavellite and dussertite, which are required by the proposed formulas, are compared with the analytical determinations in Table 2.

TABLE I.
Comparisons of Powder Diffraction Patterns.
(Unfiltered Fe radiation— $r=57.3$ mm.).

Line No.	Woodhouseite		Pseudowavellite I		Dussertite		Sarcopsidite II	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	5.61	< ½	5.65	< ½	5.95	< ½	6.00	1
2	4.81	½	4.82	½	5.13	½	4.33	2
3	3.83	< ½	3.83	½	4.07	½	3.90	3
4	3.46	1	3.48	2	3.69	1	3.51	6
5	3.28	1	3.43	1	3.010	2
6	3.21	2	3.23	1	3.32	½	2.957	½
7	2.960	2	2.980	3	2.880	2
8	2.908	6	2.918	6	3.107	6	2.849	1
9	2.997	½	2.804	3
10	2.683	1	2.681	1	2.906	1	2.700	1
11	2.418	1	2.571	1	2.555	3
12	2.370	2	2.366	2	2.555	1	2.471	2
13	2.198	3	2.204	2	2.399	½	2.403	1
14	2.152	4	2.150	4	2.324	4	2.383	1
15	2.284	½	2.284	1
16	2.068	2	2.082	½	2.208	1	2.173	½
17	1.918	2	1.923	1	2.041	1	2.131	½
18	1.886	5	1.888	3	2.004	4	2.050	2
19	1.740	4	1.747	4	1.849	4	1.891	1
20	1.638	1	1.643	½	1.773	1	1.876	1
21	1.619	1	1.622	½	1.736	2	1.830	2
22	1.600	1	1.597	½	1.720	3	1.818	2
23	1.573	1	1.571	½	1.684	1	1.759	4
24	1.515	1	1.513	1	1.621	½	1.686	2
25	1.486	2	1.490	1	1.563	3	1.678	2
26	1.464	2	1.465	1	1.533	3	1.624	3
27	1.426	3	1.426	3	1.503	1	1.603	2

Inasmuch as the composition originally assigned to dussertite (12) did not correlate with the type formula for the jarosites, a new analysis seemed desirable. Dr. Harry Berman kindly prepared a sample of dussertite from the type locality (Harvard Mineralogical Museum No. 86739). The original material he found to be badly contaminated and to contain only about 20 per cent of dussertite. The purified material was given to Mr. F. A. Gonyer for analysis and his results are shown in Table 2.

It is apparent that dussertite is not an arsenate of iron and calcium, as originally reported, but contains barium as a principal constituent instead of calcium. Thus the formula for dussertite is $\text{BaFe}_3(\text{AsO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$. The analysis shows

TABLE 2.
Analyses of Dussertite and Pseudowavellite.

	1	2	3	4
CaO	0.08	13.8	13.5
BaO	20.93	22.37
Al ₂ O ₃	36.8	37.0
Fe ₂ O ₃	34.57	34.93
P ₂ O ₅	30.3	34.3
As ₂ O ₃	31.23	33.51
H ₂ O	9.30	9.19	18.0	15.2
Insol.	4.10	*	...
	100.21	100.00	100.0	100.0

1. Dussertite from Algeria. F. A. Gonyer, analyst.
2. BaFe₃(AsO₄)₂(OH)₆·H₂O.
3. Pseudowavellite from Utah. E. V. Shannon, analyst. Analysis of oölitic material "corrected for impurities."
4. CaAl₃(PO₄)₂(OH)₆·H₂O.

* Additional constituents: MgO 0.7, Na₂O 0.3 and K₂O 0.1.

excellent agreement with the theoretical composition derived from this formula.

Furthermore it is noticeable that the properties of dussertite are not dissimilar to those of other jarosites; that is, the rhombohedral (or hexagonal) symmetry, basal cleavage* solubility in HCl, etc. Likewise, the optical properties are similar to what would be expected for a jarosite of this composition.

The specimens examined were the following:

Pseudowavellite I, from Amberg, Oberpfalz, Bavaria (type locality). U. S. N. M. R-4271.

Pseudowavellite II, from Fairfield, Utah. U. S. N. M. The powder diffraction pattern was kindly furnished by Professor J. W. Gruner, University of Minnesota.

Pseudowavellite III, with Graphite, from near Harney City, South Dakota, U. S. N. M.

Dussertite, from Djebel Debar, Constantine, Algeria (type locality). Purchased from Ward's Natural Science Establishment.

Woodhouseite, from Mono County, California (type material). Kindly furnished by Dr. Dwight M. Lemmon, U. S. Geological Survey.

* See: Larsen, E. S., and Berman, Harry: 1934, U.S.G.S. Bull. 848, p. 91.

SARCOPSIDE.

The pattern obtained for sarcopside from Deering, New Hampshire, is virtually indistinguishable from the pattern produced by the specimen from Silesia. This confirms the identification of the material from New Hampshire and lends considerable weight to the conclusion that sarcopside is a distinct species. The diffraction lines of sarcopside II are listed in Table 1 and will serve as a means of identifying this mineral.

It has been suggested (1 and 2) that sarcopside is related to triplite and, therefore, a member of the wagnerite group. This was not found to be the case, however, as the diffraction patterns of sarcopside bear no resemblance to that of wagnerite. The possibility of a dimorphous relationship to triplite suggests itself because of the similarities of the chemical compositions, but this requires further justification in terms of additional chemical evidence. A closer resemblance of the pattern of sarcopside to that of triphylite was observed, but the resemblance is not sufficiently close to permit the conclusion that sarcopside and triphylite are isomorphously related.

The specimens examined were the following:

Sarcopside I, from Silesia (type material). U. S. N. M. (received from M. Websky).

Sarcopside II, from Deering, New Hampshire. Harvard University.

Wagnerite, from near Werfen, Salzburg, Austria (type locality). Purchased from Ward's N. S. E.

Triphylite, from Rochester, New Hampshire. Same source.

PSEUDONYMS OF WAVELLITE AND TURQUOIS.

Several specimens have been found to yield diffraction patterns almost identical with those of wavellite or turquoise or the combined patterns of both.

Zepharovichite is identical with wavellite and the name should be dropped. Callainite, from Montebrias, France, produces a pattern that can be satisfactorily accounted for only by assuming a mixture of wavellite and turquoise. Coeruleolactite, from Pennsylvania, is merely turquoise. Here again, the turquoise is associated with wavellite but they are not intimately intergrown, the wavellite occurring as single crystals. Wavell-

ite diffraction lines were not observed in the pattern of coeruleolactite.

The patterns of both wavellite and turquoise contain a large number of lines, but they exhibit variations in the intensities which are quite characteristic and permit conclusive identification, regardless of superficial similarities. It seems hardly necessary to give the measurements of these substances, particularly in view of their complexity.

Only the specimen of zepharovichite is from the type locality, although the occurrence of coeruleolactite in Pennsylvania is well known and material from this locality has been analyzed.

The specimens used were as follows:

Turquoise, from Nye County, Nevada. University of Texas collection.

Wavellite, from Arkansas.

Zepharovichite, Třenic near Cerhovic, Bohemia, (type locality). Harvard University.

Callainite, Montebrias, Creuze, France. Harvard University.

Coeruleolactite, East Whiteland Township, Chester County, Pennsylvania. F.M.N.H. M-14646.

MINERALS AMORPHOUS TO X-RAYS.

Although the term "amorphous" is frequently erroneously used to describe substances which appear isotropic under the microscope, nevertheless, there seem to be a few naturally-occurring phosphates which are amorphous (not crystalline) or very nearly so with respect to X-rays. The criterion used to establish the amorphous nature of these substances is their failure to produce resolvable diffraction lines during exposures up to four times those normally employed under comparable conditions. Notations on the diffraction patterns are given under the descriptions of the specimens.

Kehoeite, from Merrit mine, Galena, South Dakota (type material). U. S. N. M. R-5652. This specimen produced a very poor diffraction pattern unsuitable for measurement.

Evansite, from Zceleznik, Hungary (type locality). U. S. N. M. R-5609. This produced about three very diffuse bands.

Richellite, from near Visé, Liége, Belgium (type locality). A. M. N. H. 15719. No discernible lines or bands were produced.

Diadochite, New Idria mine, San Benito County, California. Specimen kindly furnished by Prof. A. Pabst, University of Cal-

ifornia. No visible lines or bands were obtained. This material is undoubtedly similar to the material from the same locality described by A. F. Rogers (13).

"*Diadochite*" from Styria, Austria. U. S. N. M. 48450. This substance produced an excellent diffraction pattern very similar to that of borgströmite.

Borickite, from Toellinggraben, near Leoben, Styria, Austria (type locality). Purchased from R. M. Wilke. This produced a number of the more intense lines of quartz, which occurs as an admixture. A few lines in addition to those of quartz were observed but these apparently were contributed by muscovite. The phosphatic constituent is separable from the contaminating substances only with great difficulty, but there is little reason to believe that it would produce a satisfactory diffraction pattern even if it were possible to obtain a sample that was entirely free from contamination.

Excellent diffraction patterns are obtained from several substances which have been presumed to be amorphous, notably, collophane,* griphite, delvauxite, and palmerite. Collophane (14) and griphite (10) have been classified on the basis of the diffraction patterns they produce, but the relationships of delvauxite and palmerite to other minerals are not yet known.

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* The term "collophane" does not denote a particular mineral species but, nevertheless, like "limonite," it is a useful term applicable to apatite-like substances of sedimentary or organic origin the exact chemical compositions of which are not known. When accurate chemical data are available a specific name (francolite, dahllite, dehrnite, etc.), is appropriate.

If it is argued that "collophane" is specifically reserved for an amorphous mineral with a composition similar to apatite, the term is a *nomen nudum* because the existence of such an amorphous substance has never been demonstrated. All of the specimens of collophane which have been examined by X-ray methods by the writer yield diffraction patterns; this statement is true for conodonts (see C. R. Stauffer: *Jour. Paleo.*, 12, 414, 1938), phosphatic brachiopods, fossil bones, rock phosphates, so-called quercyite, etc.

Bryant Mather. Specimens of diadochite and woodhouseite were kindly furnished by Prof. Adolf Pabst and Dr. Dwight M. Lemmon.

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