

# WOLFEITE, XANTHOXENITE, AND WHITLOCKITE FROM THE PALERMO MINE, NEW HAMPSHIRE\*

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## ABSTRACT

Wolfeite, a new species, has the composition  $(\text{Fe}''', \text{Mn}'')_2(\text{PO}_4)(\text{OH})$  and occurs as a hydrothermal alteration product of triphylite at the Palermo pegmatite, North Groton, New Hampshire. Monoclinic prismatic, with  $a_0=12.20 \text{ \AA}$ ,  $b_0=13.17$ ,  $c_0=9.79$ ;  $\beta=108^\circ$ ;  $Z=16$ . Cleavage  $\{100\}$  good,  $\{120\}$  fair,  $\{010\}$  poor,  $\{110\}$  very poor. Specific gravity 3.79. Optically biaxial positive, with  $nX=1.741$ ,  $nY=1.742$ ,  $nZ=1.746$ ;  $r>v$  very strong;  $2V$  medium. Analysis gave: CaO 0.19, MgO 2.28, MnO 13.12, FeO 44.44,  $\text{Fe}_2\text{O}_3$  0.70,  $\text{P}_2\text{O}_5$  32.90,  $\text{H}_2\text{O}$  3.78, F 0.51,  $\text{Na}_2\text{O}$  0.14,  $\text{K}_2\text{O}$  0.05,  $\text{Li}_2\text{O}$  0.56, insol. 1.44; total 100.11. Wolfeite is isostructural with triploidite  $(\text{Mn}'', \text{Fe}'')_2(\text{P}_2\text{O}_7)(\text{OH})$ , and sarkinite  $\text{Mn}''_2(\text{AsO}_4)(\text{OH})$ , and forms an isomorphous series with triploidite extending from Fe:Mn=1:3.30 to Fe:Mn=3.39:1 at least, and probably to the pure iron end member. The name wolfeite is applied to that part of the triploidite-wolfeite series with  $\text{Fe}>\text{Mn}$ . Wolfeite also occurs at Cyrillhof, Moravia, at Skrumptetorp, Sweden, and at Hagendorf, Bavaria.

Xanthoxenite, hitherto known only from Rabenstein, Bavaria, on the basis of a partial description, occurs abundantly at the Palermo mine. Composition:  $\text{Ca}_2\text{Fe}'''(\text{PO}_4)_2(\text{OH}) \cdot 1\frac{1}{2}\text{H}_2\text{O}$  from the analysis: CaO 24.99, MgO 0.91, MnO 4.55,  $\text{Fe}_2\text{O}_3$  21.68,  $\text{Al}_2\text{O}_3$  0.01,  $\text{P}_2\text{O}_5$  37.62,  $\text{H}_2\text{O}+9.13$ ,  $\text{H}_2\text{O}-0.86$ , insol. 0.78; total 100.53. As crusts or masses of indistinct platy or lath-like crystals. Monoclinic or triclinic. One perfect cleavage. Hardness  $2\frac{1}{2}$ . Specific gravity 2.97. Color pale yellow to brownish yellow. Optically biaxial negative with  $nX=1.704$ ,  $nY=1.715$ ,  $nZ=1.724$ ;  $2V$  large,  $r<v$  strong.

Whitlockite crystals from a new find at Palermo gave on analysis: CaO 46.84, MgO 1.91, FeO 2.34, MnO 0.76,  $\text{Fe}_2\text{O}_3$  0.20,  $\text{Al}_2\text{O}_3$  0.11,  $\text{P}_2\text{O}_5$  45.94, Cl 0.03, F 0.07,  $\text{H}_2\text{O}$  0.66,  $\text{CO}_2$  0.14,  $\text{Na}_2\text{O}$  0.59,  $\text{K}_2\text{O}$  0.01, insol. 0.34; total 99.94. Specific gravity 3.09. The analysis confirms the accepted formula,  $(\text{Ca}, \text{Mg}, \text{Fe})_3(\text{PO}_4)_2$ . The new forms  $j\{20\bar{2}3\}$ ,  $k\{1.0.1.10\}$ ,  $g\{01\bar{1}3\}$  and  $h\{01\bar{1}8\}$  are noted, and a new habit tabular on  $\{0001\}$  is described.

Roscherite, hitherto known only from Ehrenfriedersdorf, Saxony, is noted from two new localities: the Nevel mine, Newry, Maine, and Black Mountain, Rumford, Maine. The mineral occurs as fibrous botryoidal masses with albite in pegmatite.

## WOLFEITE

Early in 1947, several huge triphylite crystals were encountered during mining operations for feldspar and beryl in the Palermo pegmatite at North Groton, New Hampshire. A cleavage mass of the mineral weighing about 1000 pounds was thrown on the dump heap of the quarry at that time, where it has been broken down and largely removed by mineral collectors during the course of the past two years. The triphylite, which was of a bluish gray color on fresh surfaces, locally contained irregular grains up to an inch or so in size of a reddish-brown cleavable mineral. This mineral was first noticed by Professor C. W. Wolfe of Boston University and was tentatively identified by him as triploidite. The mineral is a hydrothermal replacement of the triphylite and is associated with

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indistinct veinlets containing chlorite, sphalerite, pyrite and arsenopyrite. Several months later further operations in the quarry exposed another large triphylite crystal that had been partly reworked hydrothermally into a granular aggregate composed of residual triphylite, siderite, quartz, apatite, plagioclase, ludlamite and abundant columnar-fibrous masses of a dark clove-brown mineral. The latter mineral was found by the writer to afford an  $x$ -ray powder pattern identical with that of triploidite, but with smaller cell dimensions, and the indices of refraction proved to be considerably higher than those of the Branchville triploidite. These facts, together with the occurrence of the mineral as an alteration product of triphylite, rather than of lithiophilite as at Branchville, suggested that the material was the iron analogue of triploidite. A satisfactory analysis sample could not be obtained from this material by any reasonable effort due to admixture. An examination of the reddish-brown granular mineral mentioned above, however, proved it to be identical with the dark clove-brown mineral at hand, although with slightly lower indices of refraction, and an analysis sample was obtained therefrom without difficulty. The analysis, cited in Column 7 of Table 1, proves that the mineral is in fact the iron analogue of triploidite.

TABLE 1. CHEMICAL ANALYSES OF TRIPLOIDITE-WOLFEITE

	1	2	3	4	5	6	7	8
CaO		0.33	(~0.90)	0.56	2.00	1.27	0.19	
MgO				4.74		0.40	2.28	
MnO	63.95	48.45	43.46	29.85	21.73	17.92	13.12	
FeO		14.88	18.87	24.31	36.44	33.37	44.44	64.24
Fe <sub>2</sub> O <sub>3</sub>				4.26	0.22	7.78	0.70	
P <sub>2</sub> O <sub>5</sub>	31.99	32.11	32.62	30.89	34.20	32.44	32.90	31.73
H <sub>2</sub> O	4.06	4.08	4.14	4.20	4.50	4.48	3.78	4.03
F		none		tr.	0.09	0.88	0.51	
Rem.			1.09	0.94	1.27	2.47	2.19	
Total	100.00	99.85	100.18	99.75	100.45	101.01	100.11	100.00
G		3.697			3.78		3.79	
Fe:Mn		1:3.30	1:2.39	1:1.07	1.66:1	2.22:1	3.39:1	

1. Theoretical composition,  $Mn_2''(PO_4)(OH)$ . 2. Triploidite, Branchville. Brush and Dana (1878). 3. Triploidite, Branchville. Rem. is quartz, CaO estimated. Brush and Dana (1878). 4. Triploidite, Wien, Moravia. Herles analysis in Kovář and Slavík (1900). Fe<sub>2</sub>O<sub>3</sub> due to oxidation of FeO and calculated as such in the Fe:Mn ratio. 5. Wolfeite, Skrumptorp, Sweden. Rem. is Na<sub>2</sub>O 0.93, K<sub>2</sub>O tr., H<sub>2</sub>O—0.19, insol. 0.15. Berggren analysis in Mason (1941). 6. Wolfeite, Cryillhof, Moravia. Rem. is (Na, K)<sub>2</sub>O 0.17, insol. 2.30. Herles analysis in Kovář and Slavík (1900). Fe<sub>2</sub>O<sub>3</sub> due to oxidation of FeO and calculated as such in the Fe:Mn ratio. 7. Wolfeite, Palermo, N. H. Peck analysis, 1948. Rem. is Na<sub>2</sub>O 0.14, K<sub>2</sub>O 0.05, Li<sub>2</sub>O 0.56, insol. 1.44. 8. Theoretical composition,  $Fe_2''(PO_4)(OH)$ .

The derived formula is  $(\text{Fe, Mn, Mg})_2(\text{PO}_4)(\text{OH})$ , with  $\text{Fe}'':\text{Mn}'':\text{Mg} = 11.1:3.27:1$ . A partial analysis of the triphylite from which the mineral was derived gave  $\text{FeO}$  38.81 and  $\text{MnO}$  8.25 per cent, or  $\text{Fe}:\text{Mn}=4.65:1$ . The name wolfeite is proposed for the mineral and is particularly appropriate in view of Professor Wolfe's studies of iron and manganese phosphates from Palermo and other localities. Wolfeite is isostructural with triploidite and forms an isomorphous series with that mineral extending over the range  $\text{Fe}:\text{Mn}=1:3.30$  to  $\text{Fe}:\text{Mn}=3.39:1$  at least. The name wolfeite is properly applied to that part of the series with  $\text{Fe} > \text{Mn}$  in atomic per cent.

*Morphology and Structure Cell.* Euhedral crystals of wolfeite have not been found at Palermo. The mineral occurs either massive granular, or as slender columnar or coarse fibrous aggregates elongated [001] and ranging up to an inch or so in length. The columnar material sometimes shows a few crystal faces where it contacts quartz, and the forms {120} and {100} were identified. In the following section, it is shown that an unanalyzed mineral from Hagendorf, Bavaria, earlier described as triploidite, actually has  $\text{Fe} > \text{Mn}$  and hence is properly classed as wolfeite. This mineral was described morphologically by Müllbauer. His elements and forms are given in Table 2 in comparison with those of E. S. Dana obtained on Branchville triploidite with  $\text{Fe}:\text{Mn}=1:3.30$ . The elements of these workers are here given with the  $b$ -axis doubled to conform with the structure cell determined by Kokkoros on the Hagendorf material

TABLE 2. ANGLE TABLE FOR TRIPLOIDITE-WOLFEITE  
Monoclinic; prismatic  $-2/m$

$a:b:c=0.9258:1:0.7442$ ;  $\beta=108^\circ 18'$  (for Hagendorf wolfeite crystals with  $\text{Fe}:\text{Mn}>3:1$ ).  
 $a:b:c=0.9286:1:0.7463$ ;  $\beta=108^\circ 14'$ ;  $p_0:q_0:r_0=0.8037:0.7088:1$ ;  $r_2:p_2:q_2=1.4108:1.1338:1$ ;  $\mu=71^\circ 46'$ ;  $p_0'=0.8462$ ;  $q_0'=0.7463$ ;  $x_0'=0.3294$  (for Branchville triploidite crystals with  $\text{Fe}:\text{Mn}=1:3.30$  (?)).

Forms	Branch- ville triploi- dite	Hagen- dorf wol- feite	$\phi$	$\rho$	$\phi_2$	$\rho_2=B$	C	A
$c$ 001	*	*	90°00'	18°14'	71°46'	90°00'	—	71°46'
$b$ 010	*	*	0 00	90 00	—	0 00	90 00	90 00
$a$ 100	*	*	90 00	90 00	0 00	90 00	71 46	0 00
$n$ 120	*	*	29 33	90 00	0 00	29 33	81 07	60 27
$m$ 110		*	48 35	90 00	0 00	48 35	76 26	13 34
$e$ 021	*	*	12 26	56 48	71 46	35 12	54 48	79 36
$\rho$ 203		*	90 00	41 47	48 13	90 00	23 33	48 13
$p$ 221	*		-42 24	63 40	143 44	48 33	76 35	127 11

and verified by Richmond on the Branchville material and by the writer on the Palermo material. An angle table for the known forms of triploidite-wolfeite based on Dana's elements for the Branchville crystals is also given in Table 2.

The unit cell dimensions found for material in the triploidite-wolfeite series are listed in Table 3. The x-ray powder spacings are given in Table 4. The space group is  $P2_1/a$ .

TABLE 3. UNIT CELL DIMENSIONS OF TRIPLOIDITE-WOLFEITE

Locality	Triploidite Branchville (Richmond)	Wolfeite Palermo (Frondel)	Wolfeite Hagendorf (Kokkoros)
Fe:Mn	1:3.30(?)	3.39:1	>3:1
$a_0$	12.26 Å	12.20 Å	12.12 Å
$b_0$	13.38	13.17	13.16
$c_0$	9.90	9.79	9.73
$\beta$	108°4'	108°	108°18'
$a_0:b_0:c_0$	0.916:1:0.740	0.926:1:0.743	0.921:1:0.739

TABLE 4. X-RAY POWDER SPACING DATA FOR TRIPLOIDITE-WOLFEITE  
*Iron radiation ( $\lambda=1.937$ ), manganese filter. Some faint lines  
 have been omitted, and no lines are given below 1.70.*

Triploidite Fe:Mn 1:3.30(?)		Wolfeite Fe:Mn 3.39:1	Triploidite		Wolfeite
<i>I</i>	<i>d</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>d</i>
3	4.40	4.37	5	2.31	2.29
4	3.65	3.63	1	2.19	2.19
5	3.41	3.37	5	2.15	2.14
8	3.19	3.18	1	2.06	2.06
9	3.10	3.09	1	2.05	2.04
10	2.94	2.93	1	2.01	2.01
1	2.89	2.87	3	1.98	1.96
4	2.84	2.80	3	1.95	1.95
1	2.71	2.69	1	1.83	1.82
1	2.65	2.63	6	1.80	1.79
5	2.58	2.57	1	1.76	1.75
3	2.47	2.45	2	1.72	1.71
1	2.35	2.33			

*Physical Properties.* The hardness of wolfeite is  $4\frac{1}{2}$  to 5. The specific gravity of the reddish-brown analyzed material from Palermo is 3.79;

the variation in specific gravity with Fe:Mn ratio is shown in Fig. 1. The luster is vitreous but in columnar-fibrous types tends toward silky. The color varies in shades from reddish-brown to dark clove-brown and in general is similar to but darker than triploidite. Small grains are transparent.

Wolfeite from Palermo has four different cleavage directions in a single zone, [100], and probably is unique in this regard. A columnar cleavage fragment when measured goniometrically was found to give no less than 12 reflections from cleavage surfaces, corresponding to the forms {010}, {100}, {120} and {110}. Confirmatory measurements were obtained on a number of fragments, although not all of the equivalent cleavage directions were present on each. Optical and Weissenberg  $x$ -ray study of several such fragments gave no evidence of twinning or intergrowth. The quality of the cleavages is as follows: {100} good, {120} fair but interrupted, {010} poor and interrupted, {110} very poor and interrupted. Only the {100} cleavage has hitherto been reported; fragments of the Branchville triploidite, however, were found to show cleavage on {120} and {010} in addition to {100}. The fracture of wolfeite-triploidite is uneven to subconchoidal.

The indices of refraction of the granular and columnar types of wolfeite from Palermo are given in Table 5, together with Larsen's data on the Branchville triploidite (here verified) and new data on the Hagen-dorf material. The indices increase with increase in the Fe:Mn ratio as shown in Fig. 1. The graph is not entirely satisfactory since the data on

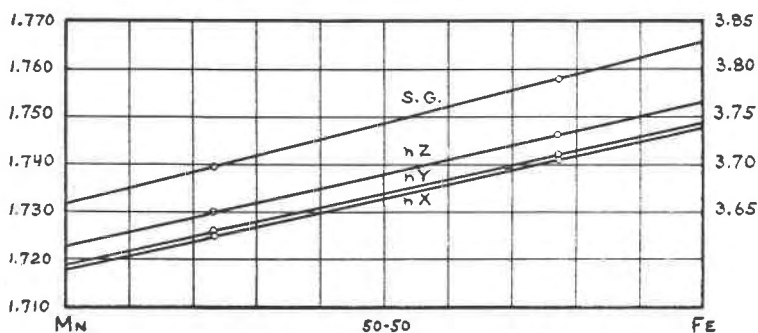


FIG. 1. Indices of refraction and specific gravity of the triploidite-wolfeite series.

the Branchville mineral was not obtained on an analyzed sample and it is known that the material from this locality, as at Palermo, varies somewhat in composition (see analyses 2 and 3 in Table 1). Further the linear variation assumed may not be correct, especially since the effect of the small amount of Ca and Mg present in substitution for (Fe, Mn) is not known.

*Wolfeite from Other Localities.* Material termed triploidite has been described from five localities, but several of these minerals have  $Fe > Mn$  and are properly classed as wolfeite. The original triploidite described by Brush and Dana from Branchville varies slightly in composition, with  $Fe:Mn = 1:3.30$  and  $Fe:Mn = 1:2.39$  in the two reported analyses (Table 1). The actual composition of the Branchville material studied optically by Larsen and used by Richmond in his  $x$ -ray study is not known; the data of Fig. 1 are plotted for a  $Fe:Mn$  ratio of  $1:3.30$  corresponding to the lighter colored, more common, material. The triploidite

TABLE 5. OPTICAL DATA FOR THE TRIPLOIDITE-WOLFEITE SERIES

Locality	Triploidite Branchville	Wolfeite Palermo (granular)	Wolfeite Palermo (fibrous)	Wolfeite Hagendorf
Fe:Mn	1:3.30(?)	3.39:1		> 3:1
$nX$	1.725	1.741	1.747	1.748
$nY$	1.726	1.742	1.748	1.749
$nZ$	1.730	1.746	1.752	1.753
$Z \wedge c$	$-4^\circ$		$-31^\circ$	

Dispersion  $r > v$ , very strong. 2V medium. Faintly pleochroic in very thick grains, with absorption  $Z > X, Y$ .

from Wien, Moravia, analyzed by Kovář and Slavík has  $Fe:Mn = 1:1.07$  and hence is true triploidite. On the other hand, the mineral from Cyrillhof, Moravia, described by these writers has  $Fe:Mn = 2.22:1$  and hence properly is wolfeite. Optical and  $x$ -ray data are lacking for the material of these two occurrences. It is not certain if the material from Cyrillhof, at least, actually belongs in the wolfeite-triploidite structure type and it may be an altered form of grastonite as suggested by Mason. The so-called triploidite from Skrumptetorp, Sweden, described by Mason also is wolfeite since it has  $Fe:Mn = 1.66:1$ . The indices of refraction given by Mason for this material ( $nX = 1.725$ ,  $nZ = 1.731$ ) are much too low for the composition and are believed to be in error. Finally, so-called triploidite also has been described by Müllbauer from Hagendorf, Bavaria. A chemical analysis of this material is lacking. The indices of refraction, however, correspond virtually to the pure iron compound according to the data of Fig. 1 and Table 5. The specific gravity, 3.78, and the unit cell dimensions (Table 3) also indicate a high-iron compound but these data probably contain relatively large errors and do not give a consistent  $Fe:Mn$  ratio.

*Chemistry.* A complete series extends between triploidite and wolfeite from  $Fe:Mn = 1:3.30$  (analysis 2) to  $Fe:Mn = 3.39:1$  (analysis 7) at

least. The series probably extends up to the nearly pure iron end member according to the optical data on the Hagendorf material. Both Ca and Mg substitute in small amounts for (Fe, Mn), with Ca:(Fe, Mn)=1:22.9 in analysis 5 and with Mg:(Fe, Mn)=1:6.92 in analysis 4. The composition of triploidite-wolfeite differs from that of triplite only in the presence of F in place of (OH). These species have in fact been earlier thought to be isostructural and isomorphous on the basis of this similarity in formula. X-ray powder diffraction study by the writer and by Mason and the single-crystal x-ray study of triplite by Heinrich and Wolfe indicates however, that these species are distinct. F apparently can substitute in small amounts for (OH) in the triploidite-wolfeite structure, with F:(OH)=1:5.37 in analysis 6; it is possible that part of the F in this particular analysis is due to admixed triplite. It may also be noted that considerable amounts of Fe<sub>2</sub>O<sub>3</sub> have been reported in triploidite-wolfeite. The largest amounts occur in more or less altered material from Wien and Cyrillhof in Moravia (analyses 4 and 6) and is due to partial oxidation of original Fe'' to Fe'''. Triploidite-wolfeite is isostructural with sarkinite, Mn<sub>2</sub>(AsO<sub>4</sub>)(OH), as shown by Hägele, but there is no evidence for an isomorphous series between these minerals.

#### XANTHOXENITE

Xanthoxenite occurs abundantly although inconspicuously at the Palermo mine as one of the last formed of the hydrothermal reworked products of triphylite. Open cavities in the triphylite crystals are variously lined with crystals of quartz, siderite, apatite, whitlockite, childrenite-eosphorite, amblygonite and other phosphates formed during the later stages of hydrothermal mineralization and it is upon these minerals that the xanthoxenite is deposited.

*Physical Properties.* Xanthoxenite occurs as crusts and masses composed of indistinct platy or lath-like crystals often aggregated in lamellar fashion. The hardness is about  $2\frac{1}{2}$  and the specific gravity is about 2.97; both values probably are somewhat in error because of the physical nature of the material. The color of the mineral is pale yellow to brownish yellow, and the luster is dull to slightly waxy. Under the microscope, xanthoxenite is pale yellow to slightly lemon yellow in color. Very thick grains are faintly pleochroic in yellow with absorption Y>X, Z. For the most part the mineral appears as shreds and flakes with a perfect cleavage but without definite outline. Occasionally lozenge-shaped grains are observed. These apparently are cleavage sections through crystals, and their optical orientation and plane angles are shown in Fig. 2. On edge the flakes show inclined extinction with Y' making a maximum angle with the elongation of about 43°. The mineral is either monoclinic with

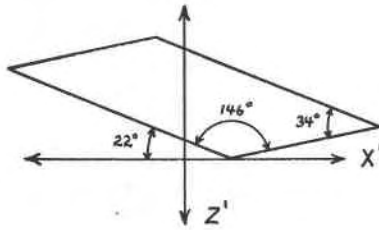


FIG. 2. Optical orientation of xanthoxenite.

the cleavage in the zone [010] or is triclinic. Dispersion is strong and some orientations show the ultra-blue. The optical properties are given below.

$n_X$ $1.704 \pm 0.003$	Optically negative (-)
$n_Y$ $1.715 \pm 0.003$	2V large
$n_Z$ $1.724 \pm 0.003$	Dispersion strong, $r < v$

Some variation may be expected in these characters since both Mn and Mg may substitute to some extent for the main cation, Ca. Xanthoxenite differs markedly in optical properties from calcioferrite, its closest neighbor chemically. The latter mineral is uniaxial negative with  $O=1.57$ ,  $E=1.575$ .

*Identity with Xanthoxenite.* The mineral at hand was originally thought to be a new species since a search of the literature revealed no known mineral with identical properties. Among the minerals which came under consideration was an ill-defined substance described under the name xanthoxenite by Laubmann and Steinmetz from the Hühnerkobel pegmatite near Rabenstein, Bavaria. This substance occurred as radial aggregates of unmeasurable gypsum-like crystals flattened on {010} with a clinodome making an angle with [001] of about  $41^\circ$  as seen under the microscope. Color wax-yellow to reddish brown. Specific gravity 2.844. Perfect cleavage {010}. Optically; biaxial negative with  $Z \wedge c = +36^\circ$  and a birefringence of about 0.05. Pleochroic, with Z bright yellow and Y light yellow. The mineral was said on the basis of qualitative tests to be a hydrated ferric phosphate with considerably smaller amounts of manganese and calcium, and demonstrable amounts of aluminum and magnesium. A partial chemical analysis gave  $P_2O_5$  32.61 per cent and  $H_2O$  16.10 per cent (by ignition). Three specimens labelled xanthoxenite from Hühnerkobel were available in the Harvard collection but these exhibited nothing that answered the description of the mineral. After this work was completed another specimen labelled xanthoxenite from Hühnerkobel fortunately came to hand through the interest of S. G. Gordon of the Philadelphia Academy of Natural Sciences. This specimen showed a small amount of a mineral



identical in appearance and properties with the Palermo mineral. No crystals or bounded cleavage flakes were observed. The conclusion thus seems forced that the Palermo mineral is identical with xanthoxenite, in spite of the discrepancies in the description of the two substances. The partial chemical analysis of the Hagendorf material was probably made on a micro-sample and may be considerably in error, and the seeming differences in crystal form and optical orientation may possibly be due to unlike crystal habits. The *x*-ray powder patterns of the two substances are identical. A complete re-examination of the type xanthoxenite from Hagendorf would, however, still be desirable.

An analysis of another mineral perhaps identical with xanthoxenite has been published by Schaller. This substance, labelled "near dufrenite," was found at Grafton, New Hampshire [about 25 miles from the Palermo mine]. The analysis affords ratios near those of xanthoxenite and mitridatite but closer to the suggested formula for the latter substance. Descriptive details are lacking, and it is impossible to obtain such data since the only known specimen has been lost.\*

*Composition and Systematic Relations of Xanthoxenite.* A chemical analysis, cited in Table 6, proves xanthoxenite to be a hydrated basic phosphate of calcium and ferric iron with the formula

TABLE 6. CHEMICAL ANALYSIS OF XANTHOXENITE

	1	2	3	4	5	6
CaO	30.31	25.22	24.99	.4456	.5324	4
MgO		0.92	0.91	.0226		
MnO		4.59	4.55	.0642		
Fe <sub>2</sub> O <sub>3</sub>	21.58	21.45	21.68	.1359	1	1
Al <sub>2</sub> O <sub>3</sub>			0.01			
P <sub>2</sub> O <sub>5</sub>	38.37	38.14	37.62	.2650	1.95	2
H <sub>2</sub> O+	9.74	9.68	9.13	.5116	3.76	4
H <sub>2</sub> O-			0.86			
Insol.			0.78			
	100.00	100.00	100.53			

1. Theoretical composition, Ca<sub>2</sub>Fe(PO<sub>4</sub>)<sub>2</sub>(OH) · 1½H<sub>2</sub>O. 2. Theoretical composition of (Ca, Mn, Mg)<sub>2</sub>Fe(PO<sub>4</sub>)<sub>2</sub>(OH) · 1½H<sub>2</sub>O with Ca:Mn:Mg=19.7:2.84:1. 3. Xanthoxenite, Palermo, N. H., H. J. Hallowell analysis, 1948. 4. Molecular quotients. 5. Oxide ratio. 6. Ideal oxide ratio.

Ca<sub>2</sub>Fe<sup>III</sup>(PO<sub>4</sub>)<sub>2</sub>(OH) · 1½H<sub>2</sub>O. Small amounts of Mn and Mg substitute for Ca, with Mg:Mn:Ca = 1:2.8:19.7 in the reported analysis.

\* W. T. Schaller, private communication, 1948.

The description of any phosphate of calcium and ferric iron is attended by much uncertainty, since no less than six minerals with this general composition have been already described and named and few of these can be said to be adequately defined. These minerals are listed and briefly described below. The closest relative to xanthoxenite appears to be the relatively well characterized mineral calcioferrite. Both minerals have the same metal:  $(\text{PO}_4):(\text{OH})$  ratio but in calcioferrite the ratio of Ca:Fe is 1:1 and in xanthoxenite Ca:Fe = 2:1. None of the other calcium iron phosphates listed shows any relation to xanthoxenite insofar as can be inferred from the available data. Their non-identity with xanthoxenite is supported particularly by the analytical evidence which in all cases shows a ratio of Ca:Fe of 1:2 or greater. Unfortunately, x-ray powder diffraction data are not available for any of the minerals listed. The powder data for xanthoxenite are given in Table 7.

TABLE 7. X-RAY POWDER DIFFRACTION DATA FOR XANTHOXENITE  
Iron radiation ( $\lambda=1.937 \text{ \AA}$ ), manganese filter.

<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
5	6.24	2	2.68	1	1.84
4	4.94	4	2.60	2	1.72
7	3.48	2	2.46	1	1.65
8	3.22	1	2.36	1	1.57
2	3.12	2	2.30	3	1.53
10	3.05	6	2.23	1	1.44
1	2.96	1	2.08	1	1.41
9	2.73	1	2.01	1	1.36
				1	1.30

*Borickite.*  $\text{CaFe}'''_5(\text{PO}_4)_2(\text{OH})_{11} \cdot 3\text{H}_2\text{O}$  (?). Compact reniform masses, in part opaline, with weak waxy luster. Color reddish brown. Isotropic, due to aggregate polarization, with a variable mean index of refraction, 1.57 to 1.67. In part as fibers with high birefringence. Efforts to obtain an x-ray powder pattern were unsuccessful. The name was originally applied by Bořický (1867) and von Hauer (1854) to material with the composition cited from Nenačovic, Bohemia, and Leoben, Austria. The mineral was later classed by some authors with type fouchérite and delvauxite and various chemically similar substances ascribed thereto.

*Calcioferrite.*  $\text{Ca}_3\text{Fe}'''_3(\text{PO}_4)_4(\text{OH})_8 \cdot 8\text{H}_2\text{O}$  (?). Found as foliated, nodular or reniform masses. Color sulfur-yellow to greenish yellow and yellowish white. Perhaps hexagonal in crystallization, with a perfect cleavage parallel to the foliation, another at right angles to this and traces of a third cleavage oblique to the same.  $H=2\frac{1}{2}$ .  $G=2.53$ . Optically uniaxial negative, with  $O=1.575$  and  $E=1.570$  (Larsen and Berman, 1934). Originally described by Blum (1858) from a Tertiary clay bed at Battenberg, Rhenish Prussia, x-ray data are lacking.

*Egüeite.*  $\text{CaFe}'''_{14}(\text{PO}_4)_{10}(\text{OH})_{14} \cdot 21\text{H}_2\text{O}$  (?). Described by Garde (1909) and Lacroix (1910) as occurring as fibrous-lamellar nodules in clay impregnated with trona and

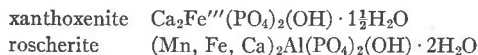
thenardite in the Eguéi region of Chad Territory in the Sudan. Friable. Luster vitreous to slightly greasy. Apparently monoclinic, but isotropic due to aggregate polarization with a mean index of refraction of 1.65 (Larsen, 1921). Brownish yellow in color, with  $G=2.60$ . *X*-ray data are lacking.

*Foucherite*.  $\text{Ca}(\text{Fe},\text{Al})_4(\text{PO}_4)_2(\text{OH})_8 \cdot 7\text{H}_2\text{O}$  (?). Compact, brownish red globules.  $H=3\frac{1}{2}$ .  $G=2.7$ . Found in sandstone at Fouchères, Champagne, France (see Lacroix, 1910). *X*-ray and optical data are lacking. Colloform minerals from Litošice ( $n=1.648$ ) and St. Benigna, Bohemia, described by Ulrich (1922) and Slavík (1918) have been ascribed to this ill-defined species. Foucherite may be identical with borickite.

*Mitridatite*.  $\text{CaFe}''''_2(\text{PO}_4)_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$  (?). A name given to various ill-defined metacolloidal substances found in oolitic iron ores on the Kerch and Taman peninsulas, southern Russia. Massive, as nodules, crusts and veinlets. Structure earthy and pulverulent or friable to dense and gum-like. Color greenish yellow to dark green; also brownish green to yellowish brown and brownish black. Luster earthy to resinous. Isotropic. Optical and *x*-ray data are lacking. Ten analyses have been reported (see Popoff, 1910; Chukhrov, 1937; Sidorenko, 1945). It is not certain if these analyses represent one or several different minerals, and some apparently were made on mixtures. A few analyses approach the formula cited.

*Richellite*.  $\text{Ca}_2\text{Fe}''''_{10}(\text{PO}_4)_8(\text{OH})_{12} \cdot n\text{H}_2\text{O}$  (?). Compact or foliated masses and radially fibrous globules.  $H=2-3$ .  $G \sim 2$ . Color reddish to yellowish brown. Luster greasy to horn-like. Described by Desprets and Cesàro (1883) from Richelle near Visé, Belgium, associated with halloysite, allophane and koninckite. Optical and *x*-ray data are lacking.

The only other hydrated basic phosphate of divalent and trivalent cations of the same formula type as xanthoxenite is the little-known mineral roscherite:



An authentic specimen of roscherite from Ehrenfriedersdorf, Saxony, the type locality, showed no similarities in optical characters or *x*-ray powder pattern to xanthoxenite. Two new localities for roscherite were found in the course of this work, at the Nevel mine, Newry, Maine, and at Black Mountain, Maine. At both localities the mineral occurs as fibrous botryoidal aggregates associated with albite in pegmatite. Roscherite probably has been mistaken at other pegmatite localities for the fibrous types of eosphorite-childrenite, which it greatly resembles.

#### WHITLOCKITE

Whitlockite, identical with the beta polymorph of  $\text{Ca}_3(\text{PO}_4)_2$  known from slag systems, was first found (8) in nature at the Palermo mine in 1941. The species was later described as a minor constituent of phosphate-rock from four localities in the West Indies (9), as a cave-deposit at Sebdu, Algeria (1), and as a constituent of urinary calculi and pathological concretions in the human body (10). Whitlockite occurs abundantly although only locally at Palermo, both as granular masses and as euhedral crystals in altered triphylite. The associated minerals include

siderite, quartz, apatite, ludlamite, brazilianite, amblygonite, xanthoxenite, childrenite-eosphorite, plagioclase. Wolfeite sometimes occurs in the triphylite as well, but is formed in a very early stage of the hydrothermal alteration as a replacement of that species and is not a crevice or cavity deposit as are the above mentioned minerals. In the original description of whitlockite mention was made of rhodochrosite and of an altered zeolite as associated minerals. The supposed rhodochrosite, based on the occurrence of iron and manganese oxide pseudomorphs after a scalenohedral mineral, has since been found to be siderite or a manganoan variety thereof, and the zeolite apparently is an altered fibrous iron phosphate.

Some newly found whitlockite comprised transparent water-clear crystals and afforded material for both a new chemical analysis and for morphological study. The analysis is cited in Table 8 in comparison with the original analysis on slightly weathered crystals from Palermo and with the material from Algeria. The new analysis confirms the original formula,  $\text{Ca}_3(\text{PO}_4)_2$ , and also indicates that the ferric iron reported in the

TABLE 8. CHEMICAL ANALYSES OF WHITLOCKITE

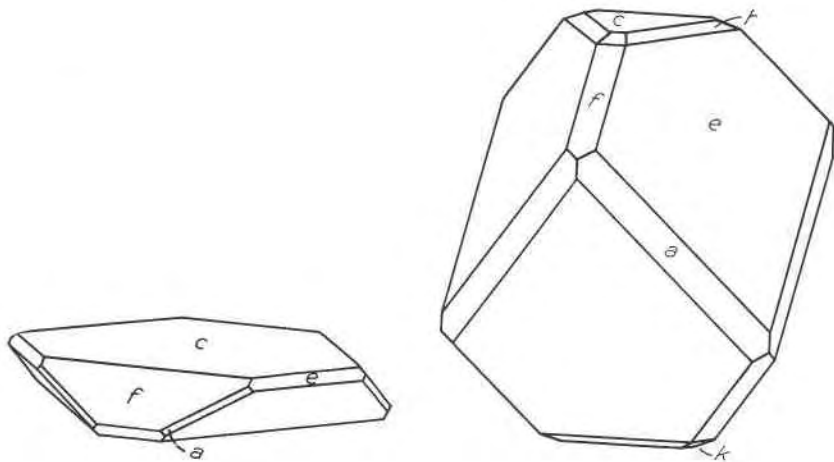
	1	2	3	4
CaO	54.22	46.84	46.90	48.15
MgO		1.90	2.53	3.53
FeO		2.34	1.91	
MnO		0.76		0.01
Fe <sub>2</sub> O <sub>3</sub>		0.20	1.73	0.05
Al <sub>2</sub> O <sub>3</sub>		0.11		0.06
P <sub>2</sub> O <sub>5</sub>	45.78	45.94	45.68	45.87
Cl		0.03	tr.	
F		0.07	0.06	
H <sub>2</sub> O $\pm$		0.66	0.48	2.00
CO <sub>2</sub>		0.14		
Rem.		0.94	0.51	0.04
Total	100.00	99.94	99.80	99.71
G	3.19	3.09	3.12	2.96

1. Theoretical composition,  $\text{Ca}_3(\text{PO}_4)_2$ . 2. Whitlockite, Palermo. Peck analysis, 1948. Rem. is  $\text{Na}_2\text{O}$  0.59,  $\text{K}_2\text{O}$  0.01, insol. 0.34. 3. Whitlockite, Palermo, Gonyer analysis in Frondel (1941). Rem. is insol. 4. Whitlockite, Sebdu, Algeria. Bennett analysis in Bannister (1947). Rem. is  $\text{SiO}_2$ .

first analysis is due to partial oxidation of ferrous iron present in substitution for calcium. The analysis affords  $\text{Mn}:\text{Fe}:\text{Mg}:\text{Ca} = 1:3.2:4.4:78$ , the small amount of  $\text{Fe}_2\text{O}_3$  present being converted into  $\text{FeO}$  for the purpose

of the calculation. It is also interesting to note that a small but significant amount of  $(\text{CO}_3)$  is present, presumably in substitution for  $(\text{PO}_4)$ . It has already been found (9) that some of the whitlockite from insular phosphate-rock contains relatively large amounts of  $(\text{CO}_3)$ , with an accompanying marked lowering of the indices of refraction, and constitutes a variety of the mineral, carbonate-whitlockite, analogous to carbonate-apatite.

Several well-formed whitlockite crystals also were measured goniometrically. An entirely new habit for the mineral is shown in Fig. 3.



FIGS. 3 and 4. Crystal habits of whitlockite.

Crystals of this type are rare and the usual habit is rhombohedral. Four new forms were observed,  $g$   $\{01\bar{1}3\}$ ,  $h$   $\{01\bar{1}8\}$ ,  $j$   $\{20\bar{2}3\}$  and  $k$   $\{1.0.\bar{1}.10\}$ , and their measured and calculated angles are given in Table 9. Several of the new forms are shown in Fig. 4. The most important form on whitlockite from the point of view of both relative size and frequency of occurrence is  $\{01\bar{1}2\}$ ; it usually comprises the dominant habit either alone or in combination with other faces. The next most important form is  $\{0001\}$ ; it is ordinarily small in size although present on the majority of crystals and only rarely is it developed to the extent shown in Fig. 3. The third and fourth most common forms,  $\{10\bar{1}4\}$  and  $\{11\bar{2}0\}$ , are comparable in frequency of occurrence; both are present only as small modifying facets.

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TABLE 9. NEW FORMS ON WHITLOCKITE

$$a:c=1:3.5473; \alpha=44^{\circ}40'; p_0:q_0=4.0961:1; \lambda=114^{\circ}33\frac{1}{2}'$$

Form	Calculated		Measured		Number of faces
<i>j</i> 2023	30°00'	69°53'	30°00'	69°41'	3
<i>k</i> 1.0.1.10	30 00	22 16½	30 00	22 14	10
<i>g</i> 0113	-30 00	53 47	-30 00	53 50	3
<i>h</i> 0118	-30 00	27 07	-30 00	27 24	6

the Palermo mine, generously presented to the Harvard collection many of the specimens examined in the course of this study.

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