

# WHITLOCKITE: A NEW CALCIUM PHOSPHATE, $\text{Ca}_3(\text{PO}_4)_2$

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## ABSTRACT

Whitlockite is a tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ . Rhombohedral, probably scalenohedral— $\bar{3} 2/m$ , with  $a:c=1:3.547$ . Habit rhombohedral  $\{01\bar{1}2\}$ , with subordinate  $\{0001\}$ ,  $\{10\bar{1}4\}$ ,  $\{1120\}$ . Structure cell (in hexagonal coordinates):  $a_0=10.25\pm 0.03$ ,  $c_0=36.9\pm 0.1$ ;  $a_0:c_0=1:3.600$ ;  $a_{rh}=13.65$ ,  $\alpha=44^\circ 6\frac{1}{2}'$ . Cell contents in the rhombohedral unit  $\text{Ca}_{21}\text{P}_{14}\text{O}_{36}$ . Space group probably  $R\bar{3}c$ . No cleavage. Hardness 5. Specific gravity 3.12 (obsvd.), 3.19 (calc.). Colorless and transparent. Uniaxial negative, with  $\omega=1.629\pm 0.002$  and  $\epsilon=1.626\pm 0.002$  (for Na).

Found as a late hydrothermal mineral in granite pegmatite at the Palermo quarry, near North Groton, New Hampshire, in the following association and sequence: whitlockite and quartz—rhodochrosite—apatite—zeolite. Whitlockite is structurally distinct from graptomite, caryinite, fillowite and apatite. Named in honor of Herbert P. Whitlock, Curator of Minerals and Gems in the American Museum of Natural History.

## INTRODUCTION

The new mineral here described was found in the Palermo pegmatite quarry on Bald Face Mountain, near North Groton, Grafton Co., New Hampshire. The writer is indebted to Prof. Charles Palache for the opportunity to examine the material, and to Mr. Harold J. Verron, who found the first specimens, for guidance on a visit to the occurrence. The name whitlockite is proposed for the mineral in honor of Herbert Percy Whitlock, a former Secretary and President of the Mineralogical Society of America, and at present Curator of Minerals and Gems in the American Museum of Natural History.

## CRYSTALLOGRAPHY

Occurs as coarse granular masses with small open cavities lined with crystals. The crystals range in size from about 1 mm. to 1.5 cm. along the  $c$ -axis. An embedded partially developed crystal measured about 3 cm. across a rhombohedral face. The crystals usually are simple rhombohedra with the form  $e\{01\bar{1}2\}$ , as shown in Fig. 1, but sometimes are modified by small faces of  $c\{0001\}$  and  $f\{10\bar{1}4\}$ , as shown in Fig. 2. Many doubly terminated individuals were observed and no evidence was found of less than holohedral symmetry (rhombohedral scalenohedral— $\bar{3} 2/m$ ), although general forms are not present. The value for the  $a:c$  ratio was obtained from the average of the best angular readings on  $\{10\bar{1}4\}$  and

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$\{01\bar{1}2\}$ . The form list as given in Table 1 is in conformity with the structural cell as determined by  $x$ -ray Weissenberg study.

The smallest of the single crystals on the specimens was examined by the Weissenberg  $x$ -ray method, using Cu radiation. The  $[0001]$  period

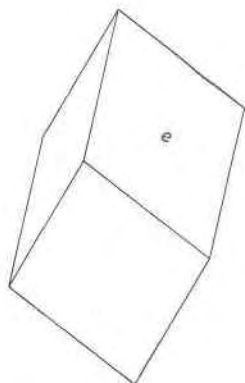


FIG. 1

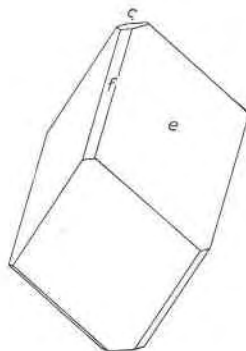


FIG. 2

proved to be extremely large. A 0-layer photograph taken about  $[0001]$  with a layer-screen slit opening of  $ca.$  1.5 mm. registered both the 0-layer reflections and a number of additional reflections belonging to the 1-layer. All of the 0- and 1-layer reflections on this film were measured and plotted with a Z scale marked for  $\beta=0^\circ$ . The 1-layer reflections were readily recognized on the projection by their slight inclination to the

TABLE 1. WHITLOCKITE: ANGLE TABLE

Forms	Hexagonal— $R$ ; scalenohedral— $\bar{3}2/m(?)$			
	$\phi$	$\rho$	$A_1$	$A_2$
$c$ 0001	—	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
$a$ 1120	$0^\circ 00'$	90 00	60 00	60 00
$f$ 10 $\bar{1}$ 4	30 00	45 41	51 43	90 00
$e$ 0112	$-30$ 00	63 58 $\frac{1}{2}$	90 00	38 54

0-layer net and by their geometrical relations, and proved to be offset  $\frac{1}{3}$  of a net diagonal from those of the 0-layer. The direct lattice type is thus established as rhombohedral. Rotation, 0- and 1-layer photographs were also taken about the  $[11\bar{2}0]$  axis. The 0-layer and especially the 1-layer films were not very satisfactory due mostly to the relatively large size of the crystal examined. The  $[0001]$  period appeared to be doubled on the 0-layer, indicating a glide plane with component  $c/2$ , but there is no

certainty of this due to marked absorption effects. Admitting the validity of the glide and accepting the point-symmetry as holohedral, the space group is  $D_{3d}^6 = R\bar{3}c$ .

The following cell dimensions were obtained (in hexagonal coordinates):

$$a_0 = 10.25 \pm 0.03; c_0 = 36.9 \pm 0.1; a_0 : c_0 = 1 : 3.600; a_{rh} = 13.65; \alpha = 44^\circ 6\frac{1}{2}'.$$

The value for  $a_0$  was calculated from the 0-layer about [0001]. The value for  $c_0$  is taken from the 12th (36.88), 14th (36.94) and 16th (36.90) orders on the rotation picture about [0001]. The rotation value is preferred to those obtainable on the 0-layer photograph about  $[11\bar{2}0]$  because of absorption and crystal-imperfection effects on this film. The value for  $c_0$  and possibly also that for  $a_0$  may be somewhat low. The cell contents in the hexagonal unit are  $21(\text{Ca}_3(\text{PO}_4)_2)$ , and are derived and itemized in Table 2. The difference between the calculated specific gravity of 3.19 and the observed specific gravity of 3.12, and the relatively low calculated cell contents as given in column 4, Table 2, indicate the calculated cell volume to be low.

#### PHYSICAL PROPERTIES

No cleavage was observed. Fracture is sub-conchoidal to uneven. Brittle. Hardness 5; it does not scratch apatite and is not scratched by apatite. Observed specific gravity is  $3.12 \pm 0.02$  (Berman microbalance); calculated specific gravity = 3.19. Luster is vitreous, inclining to sub-resinous on fracture surfaces; the luster very closely resembles that of apatite. The mineral is colorless and transparent. The larger crystals and the fractured masses are white or grayish-white and are translucent *en masse*. Optically, uniaxial negative. Indices (for Na):  $\omega = 1.629 \pm 0.002$  and  $\epsilon = 1.626 \pm 0.002$ . It does not fluoresce.

#### CHEMISTRY

Whitlockite is an anhydrous tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , as shown by the analysis cited in Table 2. Small amounts of Mg (Mg:Ca = 1:13) and of Fe (Fe:Ca = 1:31) are present replacing the calcium. The role of the ferric iron reported is uncertain, but is included with calcium in the calculation of the cell contents. About one-third of the small amount of water present is lost upon short heating at  $140^\circ \text{C}$ . and all of it is considered to be non-essential. The water apparently has come from minute liquid-filled cavities scattered through the crystals and visible under moderate magnification.

TABLE 2. ANALYSIS AND CELL CONTENTS OF WHITLOCKITE

	1.	2.	3.	4.	5.
CaO	46.90	47.47	Ca 0.8465	53.8	55.6
MgO	2.53	2.56	Mg 0.0635	4.0	4.2
FeO	1.91	1.93	Fe 0.0487	3.1	3.2
Fe <sub>2</sub> O <sub>3</sub>	1.73	1.75	P 0.6509	41.4	42
P <sub>2</sub> O <sub>5</sub>	45.68	46.23	O 2.5989	165.1	168
Cl	tr.	tr.			
F	0.06	0.06			
insol.	0.51				
H <sub>2</sub> O	0.48				
	99.80	100.00			

1. Analysis of whitlockite by F. A. Gonyer, October, 1940, on Harvard spec. no. 95031.
2. Analysis recalculated to 100 per cent after deduction of insoluble material and water.
3. Atomic proportions.
4. Actual number of atoms in the unit cell (hexagonal coordinates) calculated from the measured molecular weight of 6354.
5. Theoretical number of atoms in the unit cell for  $21(\text{Ca}, \text{Mg}, \text{Fe})_3(\text{PO}_4)_2$ , with  $\text{Ca}:\text{Mg}:\text{Fe} = 846:63:49$ .

Whitlockite does not appear to have any close relatives among either anhydrous or hydrous minerals of the  $\text{A}_3\text{X}_2\text{O}_8$  type. Graftonite,  $(\text{Fe}, \text{Mn}, \text{Ca})_3(\text{PO}_4)_2$ , is similar chemically. The optical and little known crystallographical properties of this species, however, indicate it to be monoclinic, and the  $x$ -ray powder pattern is quite different from that of whitlockite. The powder pattern of the orthorhombic mineral caryinite,  $(\text{Ca}, \text{Pb}, \text{Mn})_3(\text{AsO}_4)_2$  (?), is unlike those of whitlockite, graftonite and fillowite. Fillowite,  $(\text{Mn}, \text{Fe}, \text{Ca}, \text{Na})_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (?), is described as monoclinic, pseudo-rhombohedral. The crystals closely simulate a steep rhombohedron terminated by  $\{0001\}$ , which is a habit typical of whitlockite. A type specimen (Yale 3093) of fillowite from Branchville, Connecticut, was examined for purposes of comparison. Optically this material was biaxial positive, with small  $2V$  and with the acute bisectrix approximately perpendicular to the perfect cleavage ( $= \{0001\}$  in rhombohedral pseudo-symmetry). Indices:  $\alpha = \beta = 1.671 \pm 0.002$  and  $\gamma = 1.676 \pm 0.002$ . These data confirm the data for fillowite given by Larsen (1921). The  $x$ -ray powder pattern is entirely different from that of whitlockite. A sample of alleged merrillite from the Waconda meteorite was found to have a powder pattern different from both whitlockite and apatite, but there is no certainty as to the validity of the specimen. The  $x$ -ray powder patterns of apatite and whitlockite also are completely different, as

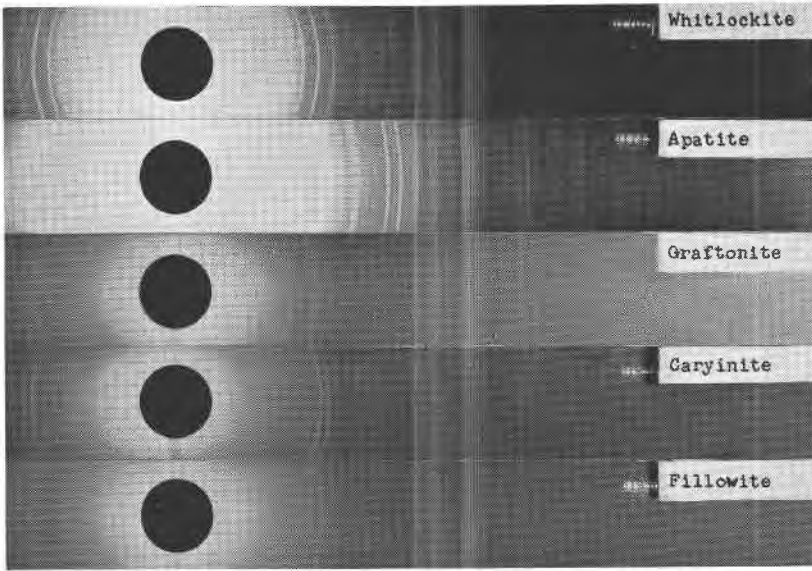


FIG. 3. X-ray powder photographs of whitlockite, apatite, graftonite, caryinite, fillowite. Cu radiation.

shown in Fig. 3, and there is no question but that the two species are structurally dissimilar. There is, however, a near identity in the physical properties of the two minerals, as is seen from the following tabulation:

	<i>Whitlockite</i>	<i>Apatite</i>
$\omega$	1.629	1.633–1.644
$\epsilon$	1.626	1.632–1.640
Hardness	5	5
Specific gravity	3.12	3.18 $\pm$
Fracture	Sub-conchoidal to uneven	
Luster	Vitreous to sub-resinous	

Dimensionally, apatite and whitlockite compare as follows:

	<i>Whitlockite</i>	<i>Fluor-apatite</i>
Space group	$R\bar{3}c$ (?)	$C6_3/m$
$a_0$ (hex. coords.)	10.25	9.37 ( $\sim 10.25$ )
$c_0$	36.9	$6.88 \left( \sim \frac{36.9}{6} \right)$

## OCCURRENCE AND ASSOCIATION

Whitlockite was found as a few small masses on the waste heap of the Palermo quarry. The material was weathered and stained and disintegrated readily under the hammer. The principal constituent of the masses was whitlockite as granular aggregates, and as crystals lining cavities. No feldspar or mica was present on the specimens, and the relation of the whitlockite to the main pegmatite body is not known. The nature of the associated minerals suggests that the whitlockite was a late low temperature hydrothermal product.

Colorless to pale smoky, doubly terminated quartz crystals ranging from microscopic dimensions up to 2–3 mm. in size are scattered through the whitlockite and in part project out into cavities. Rarely, small rhombohedrons of rhodochrosite occur perched upon whitlockite crystals and usually are slightly embedded in the surface of that mineral. Apatite is present as drusy crystals deposited upon whitlockite. In places the whitlockite was deeply etched and corroded before the apatite deposition. The apatite crystals range in size from about  $0.2 \times 0.5$  mm. to  $4 \times 2$  mm., and are inwardly colorless but outwardly have a pearly white zone with a brownish surface film. The last of the primary minerals to form was a zeolite in fibrous tufts and bundles and fan-like aggregates. The mineral is badly altered and chalky, and its identity is unknown. Thin brown and black crusts of hydrous iron and manganese oxides are present as weathering products. The sequence of deposition is:

whitlockite and quartz → rhodochrosite → apatite → zeolite.

The Palermo granite pegmatite was a large producer of muscovite for many years. The general geology of the occurrence and the quarry and underground workings have been described by Sterrett (1914). Details of the mineralogy are lacking, aside from the description by Berman (1927) of graftonite from this locality, and the following brief list of the more unusual minerals of the pegmatite may be of interest. Amblygonite was observed as pale yellow transparent platy crystals 1 to 5 mm. in width implanted on drusy white apatite crystals. Lazulite occurs as granular blue patches in interlocking aggregates of muscovite and feldspar adjacent to masses of triphylite. Triphylite occurs in large masses 15 or more feet long in single exposures. The mineral has yielded by its alteration: heterosite, vivianite and incrusting and stalactitic masses of dufrenite. The dufrenite itself alters readily to limonite. Graftonite formerly was abundant on the dump, in masses up to 18 inches in size. The graftonite is interlaminated with triphylite (or heterosite derived from the alteration of the triphylite) and occurs in close association

with the large triphylite masses. Zinnwaldite is said by Sterrett to occur in zoned brown and bluish-green crystals. Beryl is abundant in green and yellow-green prismatic crystals about 4 to 6 inches in length. The tourmaline observed at the locality was black and coarsely crystalline. Cyrtolite occurs in small crystals with triphylite. Apatite occurs as thin platy white crystals flattened on {0001} and aggregated into crusts over drusy crystals of colorless quartz. An early formed greenish-blue manganian variety of apatite also occurs.

## REFERENCES

- BERMAN, H., *Am. Mineral.*, **12**, 170 (1927).  
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## NOTE ADDED IN PRESS

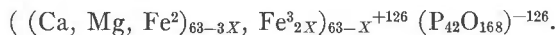
After the above described work was completed, a small and relatively perfect crystal-fragment of whitlockite was prepared and was re-examined by the Weissenberg method. This study verified both the rhombohedral character of the direct lattice and the existence of a glide along [0001]. A superior value of  $a_0$  also was obtained, viz., 10.32Å. This value brings the x-ray and the observed or theoretical crystal constants into very close agreement, as is seen from the following tabulation:

	S.G.	$a:c=1:$	Cell Contents (hex. coords.)				
			Ca	Mg	Fe	P	O
	3.12 (obs.)	3.547 (morph.)	55.6	4.2	3.2	42	168 (theor.)
(new) $a_0=10.32, c_0=36.9$	3.15	3.576	54.5	4.1	3.1	41.9	167.4
(old) $a_0=10.25, c_0=36.9$	3.19	3.600	53.8	4.0	3.1	41.4	165.1

Attention may be directed to the fact that the space group of whitlockite,  $R\bar{3}c$ , can not be reconciled with the theoretical cell contents,  $\text{Ca}_{21}\text{P}_{14}\text{O}_{56}=7(\text{Ca}_3(\text{PO}_4)_2)$ , since an odd number of cations are present and only equivalent positions occurring in pairs are available.\* At least two lines of explanation are available: (1) Chemically different atoms occupy structurally equivalent positions. This interpretation seems improbable in the present instance. (2) Sufficient positions are vacant in the structure to satisfy the symmetry requirements. A possible explanation on this basis may be suggested. In general, in order to have  $X$  missing Ca ions in the whitlockite structure, then either  $2X$  atoms of a trivalent cation such as  $\text{Fe}^3$  must be present in substitution among the

\* Remarkd to the writer by Dr. Duncan McConnell, Jan., 1941.

remaining cations, or corresponding omissions or substitutions must occur among the anions, in order to compensate the loss in positive valence. The cell contents in the former view may be represented as



The following calculation of the cell contents definitely suggests that one of the Ca positions is vacant, giving 62 instead of 63 cations in the cell. However, there is not quite enough  $\text{Fe}^{3+}$  present to compensate the loss of valence, although the agreement probably can be regarded as satisfactory in view of experimental error.

*Observed number of atoms in cell with  $a_0=10.32$ ,  $c_0=36.9$ , as  
re-calculated to 168 oxygen atoms*

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$$= 61.9, \text{ or } 63 - X \left\{ \begin{array}{l} \text{Ca} = 54.7 \\ \text{Mg} = 4.1 \\ \text{Fe}^{2+} = 1.72 \\ \text{Fe}^{3+} = 1.38 \\ \text{P} = 42.0 \\ \text{O} = 168 \end{array} \right. \left. \begin{array}{l} \\ \\ \\ = 2X, \text{ with } X = 0.69 \\ \\ \end{array} \right\} = 60.5, \text{ or } 63 - 3X$$

with  $X = 1.1$                       with  $X = 0.83$