

## The Crystal Structure of Whitlockite from the Palermo Quarry

C. CALVO, AND R. GOPAL

*Institute for Materials Research, McMaster University,  
Hamilton, Ontario, Canada, L8S 4M1*

### Abstract

Whitlockite from the Palermo pegmatite quarry, North Groton, New Hampshire, crystallizes in the rhombohedral space group  $R3c$  with lattice parameters  $a_R = 13.729(2)$  Å and  $\alpha = 44.20(5)^\circ$ . The equivalent hexagonal parameters are  $a = 10.330(2)$  and  $c = 37.103(5)$  Å. The structure has been refined by full-matrix least-squares methods to an  $R = 0.048$ , utilizing 1857 reflections. Site population analysis yields a rhombohedral unit cell composition of  $\text{Ca}_{18.10}(\text{Mg}_{1.17}\text{Fe}_{0.83})\text{H}_{1.02}(\text{PO}_4)_{14}$ . The Mg and Fe atoms are randomly distributed in octahedrally coordinated sites lying on three-fold axes.  $\text{Ca}_{1/2}\text{PO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  groups are randomly distributed in sites such that the phosphate groups are related by a pseudo-mirror plane perpendicular to  $c$  and slightly removed from the face of the tetrahedron. In cells containing  $\text{Ca}_{1/2}\text{PO}_4^{2-}$ , the oxygen atom lying on the three-fold axis is bonded to three calcium ions; in those containing  $\text{HPO}_4^{2-}$  groups, a hydrogen atom occurs on this oxygen. This change in bonding requires that the phosphate groups be reoriented. The structure can accommodate up to 22 cations per rhombohedral cell, upon the exclusion of the hydrogen atoms. This seems to correlate well with the meteoritic and lunar occurrences of whitlockite.

### Introduction

The mineral whitlockite from the Palermo pegmatite quarry near North Groton, New Hampshire, was described by Frondel (1941) as  $\text{Ca}_3(\text{PO}_4)_2$  on the basis of its chemical analysis. The water lost upon heating was regarded as non-essential. Later, he concluded that whitlockite and synthetically prepared  $\beta\text{Ca}_3(\text{PO}_4)_2$  are identical because they had similar X-ray powder patterns and optical constants (Frondel, 1943). Thus began a chain of events obscuring the relationship between the composition and structure of  $\beta\text{Ca}_3\text{P}_2\text{O}_8$  and its isostructures and whitlockite. This was recently unravelled (Gopal and Calvo, 1972).

The diffraction pattern of whitlockite is consistent with space groups  $R3c$  or  $\bar{R}3c$ . Frondel (1941) indicated no morphological evidence existed for the lower symmetry space group. In either case the glide plane, requiring atoms to occur as pairs, seemed incompatible with seven formula units of  $\text{Ca}_3(\text{PO}_4)_2$  in the rhombohedral cell.

Serious attempts at determining the structure of whitlockite were begun by Mackay (1952). A positive pyroelectric effect led to  $R3c$  as the space group. He suggested that the structure was related

to that of  $\text{Ba}_3(\text{PO}_4)_2$  (Zachariasen, 1948) but with the chains on the three-fold axis half as dense as expected by analogy with that structure. Keppler (1965) showed that the composition  $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$  satisfied the space group requirements since two hydrogen ions replaced one Ca ion. This formulation fits the density and the composition to at least the same degree as  $\text{Ca}_3(\text{PO}_4)_2$ . Later Keppler (1966, 1968) indicated that he found a model for the structure of synthetic Fe-whitlockite that fitted a limited subset of the diffraction data. Unfortunately, he proceeded to complete the circle by questioning the chemical identification of  $\text{Ca}_3(\text{VO}_4)_2$ , since it was regarded to be isotypic with whitlockite (Keppler, 1970a) and thus should be deficient in calcium. Calvo and Gopal (1970) reported the structure of  $\text{Ca}_3(\text{VO}_4)_2$  (1973) and  $\text{Ca}_3(\text{AsO}_4)_2$  (1971). Subsequently the structure of magnesium-containing  $\beta\text{Ca}_3(\text{PO}_4)_2$  (Dickens, Bowen, and Brown, 1971) was shown to have the same structure. Finally, Gopal and Calvo (1972) reported that whitlockite from the Palermo quarry was neither  $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$  nor  $\text{Ca}_3(\text{PO}_4)_2$  but had an intermediate composition and that it was distinguishable from synthetic  $\beta\text{Ca}_3(\text{PO}_4)_2$  by careful powder diffractometry.

The name whitlockite has been used to characterize the structure of a number of non-mineralogical species.  $\beta\text{Ca}_3(\text{PO}_4)_2$  prepared at high temperatures and devoid of hydrogen ions, as shown by Wallace and Brown (1971), is so designated as are various abnormal dental (Vahl, Hohling, and Frank, 1964), urinary (Lonsdale and Sutor, 1972), and other animal calcifications (Rowles, 1968) which yield powder patterns similar to that of the mineral. Synthetic Mg-whitlockite ( $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$ ) has been fully characterized (Gopal, Calvo, Ito, and Sabine, 1974), and Keppler (1966, 1968) has reported the preparation of the Fe analog.  $\beta\text{Ca}_3(\text{PO}_4)_2$  can be prepared without cations of small radii—i.e., Mg or Fe—but the hydrogen containing species seems to require them (Ito, personal communication, 1972). Skinner (1973) found "whitlockite but distinct from  $\beta\text{Ca}_3(\text{PO}_4)_2$ " as a disequilibrium metastable phase intermediate in some regions of the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  at 2 kbar  $\text{H}_2\text{O}$  pressure and  $300 \leq T \leq 600^\circ\text{C}$ .

Mason (1971) had indicated that even the mineralogical nomenclature is ill defined, although common usage prefers whitlockite over merrillite as the name for similar phosphates found terrestrially, in meteorites (Fuchs, 1962, 1969; van Schmus and

Ribbe, 1971) and in lunar samples (Albee *et al.*, 1970; Busche *et al.*, 1971; Fuchs, 1971). The chemical compositions of these are compared in Table 1. The hydrogen leaves both whitlockite from the Palermo quarry and synthetic Mg-whitlockite at the same temperatures (700 and  $1000^\circ\text{C}$ ) (Gopal *et al.*, 1974). The meteoritic and lunar samples are expected to lack hydrogen and thus are likely to have the  $\beta\text{Ca}_3(\text{PO}_4)_2$  structure type. In hindsight it appears that the literature regarding synthetic and biological calcium phosphate species of this kind would have been less confused if the name whitlockite had been restricted to those species containing essential hydrogen, and merrillite used for the others. It is interesting that Fleischer (1944) proposed that martinitite and whitlockite be distinguished in the sense that the former contained  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and that the latter designation should be restricted to  $\beta\text{Ca}_3\text{P}_2\text{O}_8$ .

### Experiments

Although the structure was solved using data from integrated precession photographs, all the data used in this refinement were recorded with a Syntex P1 automatic diffractometer. The crystal was provided by Professor C. Frondel who had obtained it from the Palermo pegmatite quarry in North Groton, New Hampshire.

The data were collected from a ground sphere with a radius of 0.025 cm. Graphite-monochromatized  $\text{MoK}\alpha$  radiation was used together with a scintillation counter. Fifteen moderately high angle re-

TABLE 1. Rhombohedral Unit Cell Contents of Whitlockites Based Upon Chemical Analysis and Scaled to Fourteen Phosphorus Atoms

Source	Number of atoms						
	Ca	Mg	Fe	Mn	Na	H	P $\text{H}_2\text{O}^+$
Palermo quarry*	18.19	1.17	0.03			1.62	14
Oran, Selrion, Algeria <sup>(a)</sup>	18.37	1.89	0.01			2	14 2.12
Sabinas Hidalgo, Mexico <sup>(b)</sup>	17.06	1.12	0.50**			2	14 0.84
Odegarden, Norway <sup>(c)</sup>	17.84	1.70	0.26		0.16	2 <sup>++</sup>	14
Djati-Pengilon <sup>(d)</sup>	17.43	1.75	0.28		1.92		14
Forksville <sup>(d)</sup>	17.46	1.82	0.14		1.96		14
Allegan <sup>(e)</sup>	16.66	2.00	0.09	0.00	0.70		14
Shergotty <sup>(f)</sup>	17.58	0.80	0.40	0.04	1.04		14

Morinite heated to near  $800^\circ\text{C}$  yields  $\text{Ca}_{9.3}(\text{Ca}_{0.97}\text{Na}_{9.27}\text{Al}_{6.53})(\text{Al}_{10.4}\text{PO}_3\text{F})_{3.47}(\text{PO}_4)_{7.06}$ <sup>(g)</sup>

Yttrian-cerian whitlockite from lunar rock 12036, has 19.47 to 22.05 cations per fourteen tetrahedral anions.<sup>(h)</sup>

Lunar rock 14310 is  $\text{Ca}_{17.40}\text{Mg}_{1.14}\text{Fe}_{1.26}\text{RE}_{1.14}\text{Na}_{0.06}(\text{PO}_4)_{13.50}(\text{SiO}_4)_{0.50}$ <sup>(c)</sup>

<sup>+</sup> $\text{H}_2\text{O}$  analysis has been separated in this table into  $2\text{H}^+$  and excess  $\text{H}_2\text{O}$ .

\*\* Calculated value.

\* See Table 2

\*\* Zn

(a) Bannister (1947).

(b) Cady, Hill, Miller and Magness (1952).

(c) Griffin, Amli, Heier (1972).

(d) Van Schmus and Ribbe (1969).

(e) Fuchs (1962).

(f) Fuchs (1969).

(g) Fisher and Volborth (1960).

(h) Busche, Conrad, Keil, Prinz, Bunch, Erlichman and Quaide (1971).

TABLE 2. Crystal Data for Whitlockite

$\text{Ca}_{18.19}\text{Mg}_{1.17}\text{Fe}_{0.83}\text{H}_{1.62}(\text{PO}_4)_{14}$					$\text{fw } 2134.98$
rhombohedral	$a_R = 13.729(2) \text{ \AA}$	$\alpha = 44.20(5)^\circ$	$Z = 1$		
hexagonal	$a = 10.330(2) \text{ \AA}$	$c = 37.103(5) \text{ \AA}$	$Z = 3$		
volume	$3428.05 \text{ \AA}^3$	$\rho_M = 3.12 \text{ g/cm}^3$	$\rho_{\text{CALC}} = 3.102 \text{ gm/cm}^3$		
composition (weight per cent)					
	CaO	$\text{P}_2\text{O}_5$	MgO	FeO	$\text{H}_2\text{O}^+$
predicted	47.77	46.53	2.20	2.79	0.68
found	47.15 <sup>(a)</sup>	46.87 <sup>(b)</sup>	2.37	2.45 <sup>(c)</sup>	0.65 <sup>(d)</sup>

<sup>+</sup>Frondel (1941)

(a) Included 46.90 CaO reported by Frondel (1941) and 0.48 SrO determined by Ito (1972).

(b) Includes 45.68  $\text{P}_2\text{O}_5$  reported by Frondel (1941) and 1.41  $\text{SiO}_2$  determined by Ito (1972).

(c) Includes 1.87 FeO and 0.58 MnO determined by Ito (1972).

(d) Determined by Gopal, Calvo, Ito and Sabine (1974) and does not include 0.20 non-essential  $\text{H}_2\text{O}$ .

flections provided the  $2\theta$  values used to calculate the lattice parameters reported in Table 2. All the reflections in a hemisphere defined by  $2\theta_{\max} = 50^\circ$  were scanned at rates dependent upon the peak intensity and over an angular range  $1^\circ$  in  $2\theta$  on either side of the peak. The observed limit was set at  $3\sigma$ , where  $\sigma$  was determined from the counting statistics for the peak and two backgrounds. Reflections whose intensity measures were less than zero were discarded in order to save computing time. The mean deviation between symmetry-related reflections was 2 percent. The data, consisting of 1857 independent reflections, were corrected for Lorentz and polarization effects. Absorption corrections, with  $\mu = 28.7 \text{ cm}^{-1}$ , were applied assuming the crystal to be a perfect sphere.

### Structure Solution

Initial atomic parameters were obtained from those of  $\text{Ca}_3\text{As}_2\text{O}_8$  (Gopal and Calvo, 1971) and  $\text{Ca}_3\text{V}_2\text{O}_8$  (Gopal and Calvo, 1973) with P replacing the pentavalent ion and with equal molar amounts of Mg and Fe at the octahedrally coordinated site located at the origin. This model is essentially the  $\beta\text{Ca}_3\text{P}_2\text{O}_8$  structure (Dickens *et al.*, 1971). Full-matrix least-squares refinement, initially with individual isotropic and subsequently anisotropic thermal parameters, led to an  $R$  value of 0.106. Scattering factors for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{P}^{5+}$  and  $\text{O}^-$  from the *International Tables for X-ray Crystallography* (1962), corrected for dispersion, were used. Weights,  $w$ , were chosen so that  $w|F_o - F_c|$  in local average, would be independent of  $|F_o|$ . The large thermal parameters for  $\text{Ca}(\text{II}A')$  suggested, at this stage, that this site was empty and that the rhombohedral unit cell composition was  $\text{Ca}_{18}(\text{Mg,Fe})_2(\text{PO}_4)_{14}$ . The cell was shy two positive charges and thus a hydrogen atom was added to each of the  $\text{O}(\text{IA})$  atoms of the phosphate groups lying on the three-fold axes. Because this oxygen atom is bonded to three Ca ions in the  $\beta\text{Ca}_3\text{P}_2\text{O}_8$  configuration, the  $\text{P}(\text{A})\text{O}_4$  groups were inverted so that the  $\text{O}(\text{IA})$  would be free to carry these protons.

This model refined to a minimum  $R$  value of 0.073; however, the  $\text{P}(\text{A})\text{--O}(\text{IA})(\text{--H})$  bond length, coincident with the three-fold axis, at  $1.70(2) \text{ \AA}$ , was substantially longer than expected ( $1.59 \text{ \AA}$ ). The difference electron density synthesis showed residual peaks which were interpreted as two phosphate configurations in the ratio of 7 to 1. Figure 1 indicates how  $\text{Ca}(\text{II}A')$

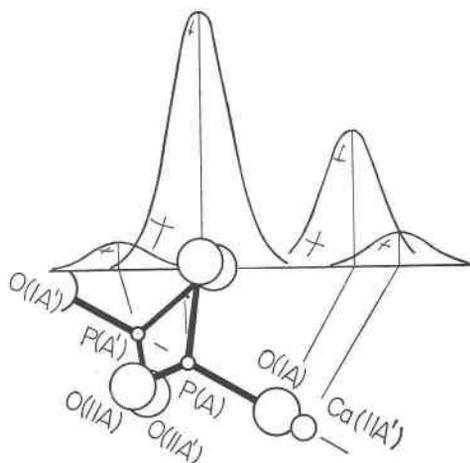


FIG. 1. The superposition of the electron density along the  $c$  axis. A ball and stick model of the atomic configuration is shown in the lower half of the diagram. The electron densities for each of the atoms, calculated from  $\rho = 2Z \exp -5r^2$ , is shown in the upper half of the diagram. An apparent shift of  $0.1 \text{ \AA}$  in the peak position of  $\text{P}(\text{A})$  is obtained by adding the electron densities of  $\text{P}(\text{A})$  and  $\text{Ca}(\text{II}A')$ .

near  $\text{O}(\text{IA})$  and  $\text{P}(\text{A}')$  near  $\text{P}(\text{A})$  act to enlarge the  $\text{P}(\text{A})\text{--O}(\text{IA})$  bond length. Subsequent difference syntheses and structure factor calculations were used to determine the  $\text{HP}(\text{A})\text{O}_4$  to  $\text{Ca}_{1/2}\text{P}(\text{A}')\text{O}_4$  and the  $\text{Fe}^{2+}$  to  $\text{Mg}^{2+}$  ratios. The configuration of the atoms in  $\text{Ca}_{1/2}\text{P}(\text{A}')\text{O}_4$  were essentially those in  $\text{Ca}_3\text{V}_2\text{O}_8$  with  $\text{V} \equiv \text{P}$ . The minimum  $R$  and  $R_w (= \{\sum w |F_o - F_c|^2 / \sum w F_o^2\}^{1/2})$  were 0.069 and 0.088 respectively ( $w = (30 - 0.1F_o + 0.004F_o^2)^{-1}$ ). The thermal parameters of the atoms in  $\text{Ca}_{1/2}\text{P}(\text{A}')\text{O}_4$  and  $\text{HP}(\text{A})\text{O}_4$  groups were restricted to isotropic values, and H was not inserted into the calculation. A constrained least-squares program written by Finger (1970) was used to determine the final ratio of the  $\text{P}(\text{A})\text{O}_4$  to  $\text{Ca}_{1/2}\text{P}(\text{A}')\text{O}_4$  and Mg to Fe. The final composition corresponds to  $\text{Ca}_{18.19}(\text{Mg}_{1.17}\text{Fe}_{0.83})\text{H}_{1.62}(\text{PO}_4)_{14}$  and agrees well with the results of chemical analysis (Table 2). The final  $R$  is 0.048. The atomic parameters are in Table 3, and the observed and calculated structure factors are compared in Table 4.

A large crystal was examined at temperatures near that of liquid  $\text{N}_2$  using a precession camera. No change in the relative intensity, compared with that at room temperature, was detected. The apparent change of whitlockite into a centrosymmetric structure, as suggested by the piezoelectric results of Mackay and Sinha (1967), was not detected. The same crystal used for the structure study when

TABLE 3. Final Atomic Parameters and Site Occupancies for Whitlockite with Estimated Standard Deviation in Parentheses

Atom	Site	x	y	z	$U_{11}(\text{\AA}^2)$	$U_{22}(\text{\AA}^2)$	$U_{33}(\text{\AA}^2)$	$U_{12}(\text{\AA}^2)$	$U_{13}(\text{\AA}^2)$	$U_{23}(\text{\AA}^2)$
M*	6	0	0	0	0.0059(6)	$U_{11}$	0.008(15)	$\frac{1}{2}U_{11}$	-	-
Ca(IIB1)	18	0.2794(1)	0.1457(1)	0.56639(5)	0.0091(3)	0.0036(3)	0.0105(6)	0.0051(3)	-0.0004(3)	-0.0009(3)
Ca(IIB2)	18	0.3871(1)	0.1794(1)	0.76866(5)	0.0095(3)	0.0075(3)	0.0102(6)	0.0042(3)	-0.0020(3)	-0.0007(3)
Ca(IA)	18	0.2887(2)	0.1545(1)	0.67371(6)	0.0358(6)	0.0176(4)	0.0182(8)	0.0206(5)	-0.0119(3)	-0.0086(4)
P(B1)	18	0.3166(2)	0.1426(2)	0.86517(5)	0.0090(4)	0.0079(4)	0.0090(8)	0.0053(3)	0.0006(3)	-0.0001(4)
P(B2)	18	0.3501(2)	0.1570(1)	0.96832(8)	0.0067(4)	0.0073(4)	0.0076(9)	0.0032(3)	0.0006(4)	0.0003(4)
O(1B1)	18	0.2728(6)	0.0910(6)	0.8261(2)	0.023(2)	0.022(2)	0.0115(30)	0.0138(17)	0.0011(18)	0.0009(2)
O(1IB1)	18	0.2456z(5)	0.2317(6)	0.8788(2)	0.017(2)	0.019(2)	0.0194(31)	0.0147(15)	0.0027(16)	0.0016(17)
O(1IB3)	18	0.2729(4)	0.0014(4)	0.8874(2)	0.011(1)	0.006(1)	0.0117(26)	0.0023(10)	-0.0026(13)	0.0017(11)
O(1IB5)	18	0.4889(4)	0.2417(5)	0.8698(2)	0.007(1)	0.008(1)	0.0225(31)	0.0032(11)	-0.0008(13)	0.0011(14)
O(1IB2)	18	0.3991(5)	0.0475(5)	0.9550(2)	0.011(1)	0.016(2)	0.0129(28)	0.0095(12)	-0.0012(14)	0.0003(15)
O(1IB4)	18	0.4158(5)	0.3034(4)	0.9476(2)	0.012(1)	0.008(1)	0.0205(30)	0.0022(11)	0.0030(15)	0.0044(14)
O(1IB6)	18	0.1779(4)	0.0783(5)	0.9642(2)	0.006(1)	0.010(1)	0.0157(28)	0.0034(10)	0.0017(12)	0.0020(14)
O(1B2)	18	0.4013(6)	0.1951(5)	0.0080(2)	0.023(2)	0.016(2)	0.0087(29)	0.0122(15)	-0.0015(16)	0.0006(15)
O(IA)	4.86	0	0	0.7982(6)	0.038(4)					
P(A)	4.86(6)	0	0	0.7547(1)	0.0106(4)					
O(IIA)	14.57	-0.0192(5)	0.1309(5)	0.7422(2)	0.0123(7)					
Ca(IIA)	0.57	0	0	0.8125(11)	0.019(4)					
P(A')	1.14	0	0	0.7344(3)	0.002(1)					
O(IA')	1.14	0	0	0.6934(14)	0.019(10)					
O(IIA')	3.43	-0.0001(20)	0.1374(18)	0.7499(7)	0.012(3)					

\*M contains 3.52(8) Mg<sup>2+</sup> and 2.48 Fe<sup>2+</sup> per cell

† $U_{ij}$  appear in the temperature factor as

$$\exp -[U_{11}a^2h^2 + \dots + 2U_{12}a^*b^*hk + \dots]$$

heated to 1200°C inverted to the  $\beta\text{Ca}_3\text{P}_2\text{O}_8$  structure.

### Description of the Structure

The  $\text{Ba}_3\text{P}_2\text{O}_8$  structure-type of whitlockite will be described in terms of the  $\text{Ba}_3\text{P}_2\text{O}_8$  (Zachariasen, 1948) structure-type. This is not only convenient, but provides a rational framework for understanding the relationships between the structures of  $\text{Ca}_3\text{X}_2\text{O}_8$  and  $\text{Pb}_3\text{X}_2\text{O}_8$ , as discussed by Calvo and Krishnamachari (1975).

### The $\text{Ba}_3\text{P}_2\text{O}_8$ Structure Types

The  $\text{Ba}_3\text{P}_2\text{O}_8$  structure-type is composed solely of translationally equivalent interconnected chains with the centric repeat unit being  $\text{PO}_4\text{-Ba(II)-Ba(I)-Ba(II)-PO}_4$  (Fig. 2a)<sup>1</sup>. Each chain has six neighboring ones leading uniquely to six  $\text{PO}_4$  groups around Ba(I), whose site symmetry is  $\bar{3}2m$ .

The non-equivalent oxygen atoms O(I) and O(II) lie at sites of  $3m$  and  $m$  symmetry respec-

tively. Ba(I) shares an O(II) ion with six symmetrically equivalent phosphates that lie on 3-fold axis (Fig. 2b). The O(II) ions form a distorted octahedron about Ba(I) such that  $\text{Ba(I)-O(II)} = 2.80 \text{ \AA}$ . The six O(I) ions in Figure 2b lie close to a plane, here called the equatorial plane of Ba(I), that contains Ba(I). The  $\text{Ba(I)-O(I)}$  distance equalling  $a(3)^{-1/2} = 3.23 \text{ \AA}$  indicates a weak bond between these atoms. A separation of about 0.5 Å between the strong and weak bonds in twelve-fold coordinate Ba seems characteristic, as it also occurs in  $\text{BaNaPO}_4$  (Calvo and Faggiani, 1975). Ba(II) coordinates to ten oxygen atoms (Fig. 2c) and lies on a site of  $3m$  symmetry. It shares three oxygen atoms (open circles, Fig. 2c) forming a face that is shared with the  $\text{Ba(I)O(II)}_6$  octahedron. This face is shown stippled in Figures 2b and 2c. Six of these oxygen atoms (solid black circles, Fig. 2c) are O(II) and form edges of the Ba(II) polyhedron that are shared with  $\text{PO}_4$  tetrahedra. The tenth oxygen atom coordinated to Ba(II) is an O(I) that is colinear with Ba(I) and Ba(II) lying on the same three-fold axis.

The instability of this structure-type, relative to

<sup>1</sup>The notation used by Süssle and Buerger (1970) for the atoms in  $\text{Ba}_3\text{V}_2\text{O}_8$ , isotypic with  $\text{Ba}_3\text{P}_2\text{O}_8$ , has been adopted with roman numerals substituted for the arabic ones.





TABLE 5. Bond Lengths and Angles in Whitlockite with Estimated Standard Deviations in Parentheses

distance	value(Å)	distance	value(Å)	distance	value(Å)
Ca(1B)-O(1B1)	2.550(5)	Ca(11B1)-O(11B1)	2.772(7)	Ca(11B2)-O(11B1)	2.387(7)
-O(11B1)	2.416(8)	-O(11B3)	2.501(5)	-O(11B1)	2.450(8)
-O(11B3)	2.383(6)	-O(11B5)	2.467(5)	-O(11B3)	2.371(6)
-O(11B2)	2.378(7)	-O(11B5)	2.445(6)	-O(11B2)	2.638(6)
-O(11B4)	2.658(8)	-O(11B2)	2.456(7)	-O(11B4)	2.630(5)
-O(1B2)	2.521(5)	-O(11B4)	2.313(7)	-O(11A)	2.395(5)
-O(1B2)	2.453(7)	-O(1B2)	2.426(7) <sup>a</sup>	-O(11B6)	2.460(6)
-O(11A)	2.928(7)	-O(11A)	2.452(4)	-O(11B6)	2.429(5)
Mg,Fe-O(11B5)	2.088(5) 3X	Ca(11A')-O(1B1)	2.536(10) 3X		
-O(11B6)	2.077(6) 3X	-O(11A')	2.722(27) 3X		
P(A)-O(11A)	1.616(5)	P(A')-O(1A')	1.515(15) 3X		
-O(11A)	1.532(7) 3X	-O(11A')	1.533(25) 3X		
angle	value(°)	angle	value(°)		
O(1A)-P(A)-O(11A)	107.7(3) 3X	O(1A')-P(A')-O(11A')	112.1(9) 3X		
O(11A)-O(11A)	111.3(4) 3X	O(11A')-O(11A')	106.7(12) 3X		
distance	value(Å)	distance	value(Å)		
P(B1)-O(1B1)	1.529(8)	P(B2)-O(1B2)	1.545(8)		
-O(11B1)	1.523(8)	-O(11B2)	1.533(7)		
-O(11B3)	1.533(5)	-O(11B4)	1.523(6)		
-O(11B5)	1.554(4)	-O(11B6)	1.550(4)		
angle	value(°)	angle	value(°)		
O(1B1)-P(B1)-O(11B1)	112.3(4)	O(1B2)-P(B2)-O(11B2)	107.3(4)		
-O(11B3)	106.3(3)	-O(11B4)	107.6(3)		
-O(11B5)	112.2(4)	-O(11B6)	112.6(4)		
O(11B1)-P(B1)-O(11B3)	113.2(4)	O(11B2)-P(B2)-O(11B4)	115.0(4)		
-O(11B5)	107.6(3)	-O(11B6)	107.3(3)		
O(11B3)-P(B1)-O(11B5)	105.1(3)	O(11B4)-P(B2)-O(11B6)	107.2(3)		

an edge with Ca(11B1). This relieves the oxygen atom congestion in the equatorial plane of Ca(1B) while reducing its coordination number to 8. It shares three O(1)-O(II) edges of three PO<sub>4</sub> groups on neighboring chains and two additional O(II) corners with two more PO<sub>4</sub> groups. One further Ca-O interaction of less than 3 Å is found, Ca(1B)-O(11A), occurring in those cells containing the HP(A)O<sub>4</sub> groups. The individual bond distances and angles are found in Table 5.

The Ca(11A') ions are bonded to six oxygen atoms and share a face with the P(A')O<sub>4</sub> group (Fig. 5). The three Ca(II)-O(1B1) and three Ca(II)-O(11A') distances are 2.54(1) Å and 2.73(3) Å respectively. This feature also occurs in the Ca<sub>3</sub>X<sub>2</sub>O<sub>8</sub> structures. The phosphate configurations on the A chain are related by pseudo-mirror plane ~1/8 Å removed from the plane of the O(II) oxygen atoms. The P(A)O<sub>4</sub> is also rotated by 7° about the c axis relative to P(A')O<sub>4</sub>.

Mg<sup>2+</sup> and Fe<sup>2+</sup> are octahedrally coordinated to

oxygen atoms of type O(II) as shown in Figure 6. The six O(I) atoms, however, lie either 3.60 or 3.57 Å from these cations and thus are not bonded. This fact allows for the displacement of the P(B)O<sub>4</sub> groups, relative to the Ba<sub>3</sub>P<sub>2</sub>O<sub>8</sub> structure, so as to accommodate for bonding constraints of the cations in the B chains.

### Discussion

The agreement between the chemical composition of the mineral as determined in this refinement and that determined by chemical analysis is satisfactory. In particular, the analysis for structural hydrogen, originally conceived as unessential water, is noteworthy. Since no separate distinction has been made for Sr<sup>2+</sup>, Si<sup>4+</sup>, and Mn<sup>2+</sup> in the X-ray refinement, their oxides have been expressed as equivalent amounts of CaO, P<sub>2</sub>O<sub>5</sub>, or FeO in the analysis. Mn is known, from an unpublished electron spin resonance study, to occur at a site on the three-fold axis and is likely to be substituted at the (Mg,Fe) site rather than the

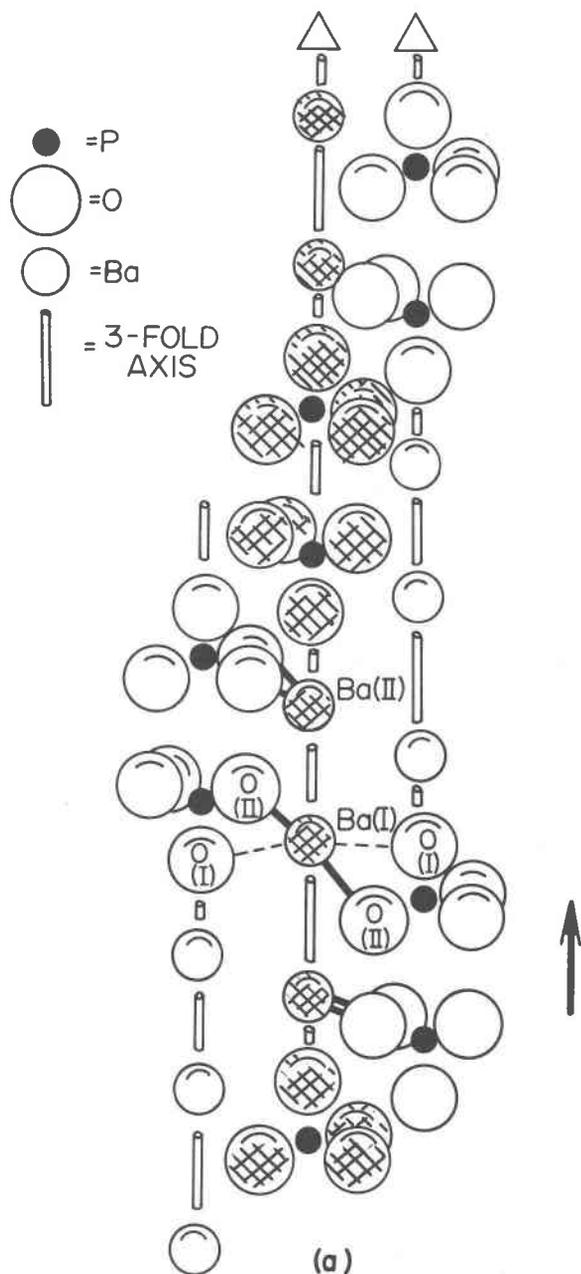


FIG. 2a. The interconnected chain structure in  $Ba_3P_2O_8$ . The large open circles represent oxygen atoms and the small filled circles represent phosphorus atoms. The intermediate size circles are barium atoms. The atoms of the central chain are shown stripped. Two of the six neighboring chains are shown. The Ba(I)-O(I) interactions and the Ba(I)-O(II) are indicated. The interaction of Ba(II) with one of the O(II)-O(II) edges is also shown. The entire environment of the stripped chain is generated by the three-fold axis coincident with the chain axis.

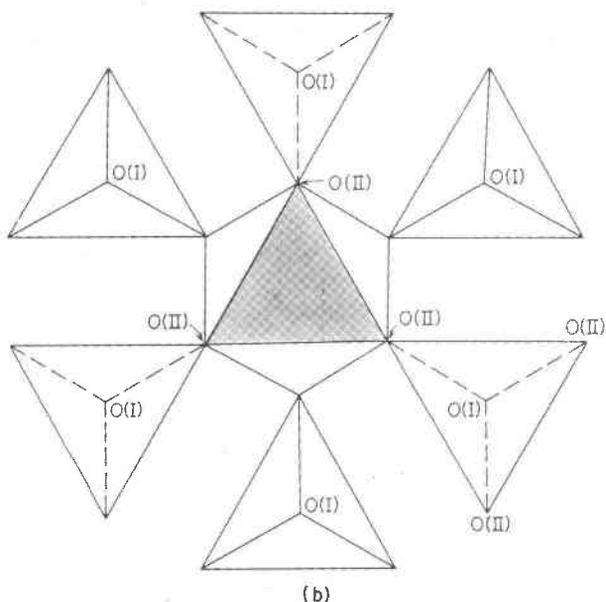


FIG. 2b. The environment of the Ba(I). Ba(I) lies at the center of the octahedron whose corners represent the oxygen atoms shared with the phosphate groups shown in projection. The stippled face is common to the stippled one in Figure 2c. The Ba(I) also bonds weakly to the six apical O(I) atoms and thus shares an O(I)-O(II) edge with each  $PO_4$  group. The equatorial plane of Ba(I) is parallel to the page.

Ca(IIA) site. However, this hypothesis has not been tested. One Sr ion occurs for every 180 calcium ions and would make an insignificant contribution to the scattering unless the Sr were to segregate into the Ca(IIA) site. In the latter case it might contribute to determining the  $Ca_{1/2}P(A')O_4$  to  $HP(A)O_4$  ratio in some unknown way. If all the Sr were in this site, the Ca(IIA') site would be half filled with Sr. Thus the thermal parameter for this cation should then be anomalously low in comparison with the remaining cations in the structure. This is not the case although the thermal parameters are about half those found for Ca(IIA') in  $Ca_3V_2O_8$  (Gopal and Calvo, 1973). Since this cation occurs near the O(IA) site (0.53 Å) in the model, their electron densities will be overlapped, possibly leading to higher errors than apparent from the least-squares analysis.

The chemical analysis for nafalwhitlockite, prepared by heating morinite to near 800°C in air (Fisher and Volborth, 1960) agrees as well with the concept of a non-hydrogen containing whitlockite.

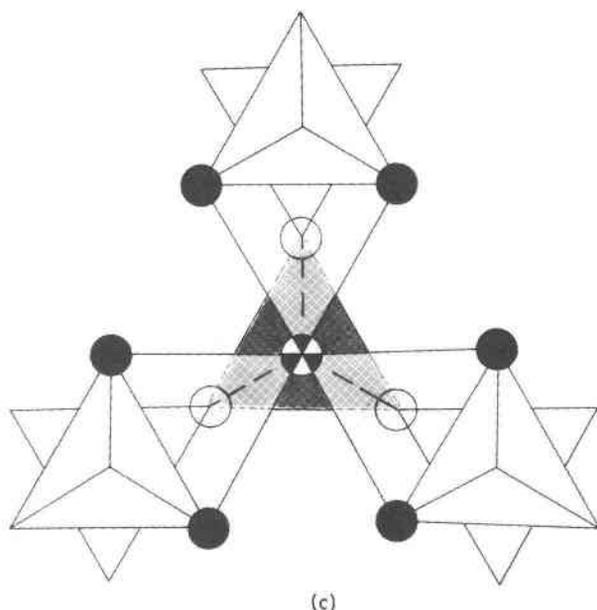


FIG. 2c. The environment of Ba(II). Ba(II) lies at the center of the diagram. The oxygen atoms to which it is bonded are shown as circles. The open circles lie below the plane of the diagram and represent those O(II) atoms shared with Ba(I) with the stippled face common with that one stippled in Figure 2b. The full circles, in pairs, are an O(II)-O(II) edge shared with phosphorus atoms. The equatorial plane of Ba(II) contain the 3 shared O(II)-O(II) edges and parallels the plane of the page. The phosphate groups on neighboring chains are shown in projection. The partially filled circles represent O(I) lying directly above Ba(II).

Morinite,  $\text{Ca}_4\text{Na}_2\text{Al}_4(\text{OH}_2\text{F}_{5-x})\text{PO}_4(5-x)\text{H}_2\text{O}$ , transforms to apatite by composition lying between  $\text{Ca}_8\text{Al}_2(\text{PO}_4)_5(\text{AlO}_4)\text{F}_2$  and  $\text{Ca}_6\text{Al}_4(\text{PO}_4)_4(\text{AlO}_4)_2\text{F}_2$  (Fisher and McConnell, 1969) and yields a whitlockite, as identified by powder pattern relatively rich in Na, F, and Al. Its composition corresponds to  $\text{Ca}_{28}(\text{Ca}_3\text{Na}_{16}\text{Al}_{10})(\text{PO}_3\text{F})_{11}(\text{AlO}_4)_{11}(\text{PO}_4)_{20}$  (Fisher and Volborth, 1960)<sup>2</sup>. Thus the hexagonal unit cell, containing one such formula unit, has all 42 tetrahedral anion sites and all 66 cation sites of the  $\text{Ca}_3\text{V}_2\text{O}_8$  structure type filled.

The P(A)-O(IA) bond, presumably with the proton on O(IA), is 1.615(5) Å, a value somewhat longer than the 1.580(9) Å found for the analogous

<sup>2</sup> The composition proposed by Fisher and Volborth has been rearranged in order to assign the fluorine ions to the fluophosphate ion. In addition, the number of Ca ions has been reduced by one, thus achieving better agreement with the results of chemical analysis.

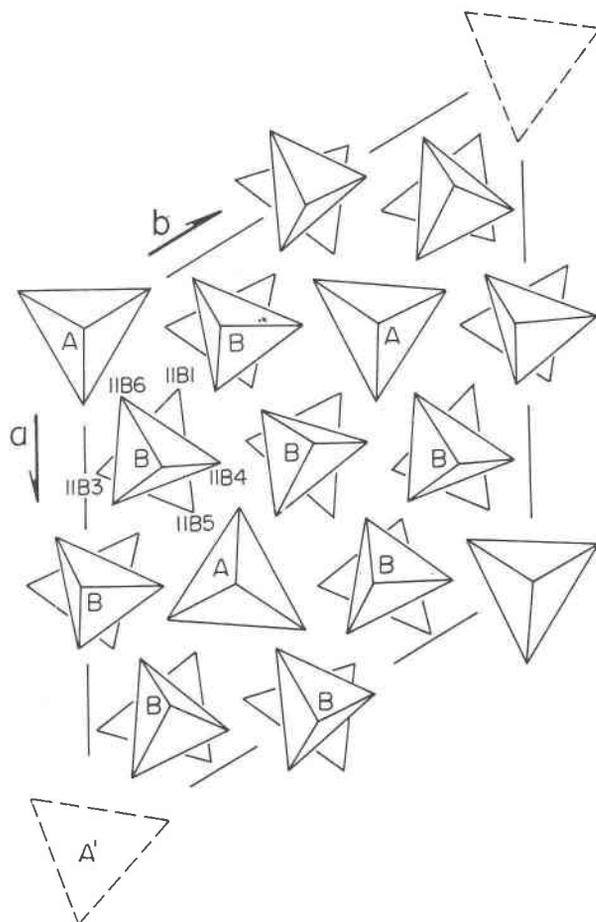


FIG. 3. A half cell projection of the whitlockite structure. The tetrahedra in the upper half cell of the whitlockite structure are shown. The dashed tetrahedron represents the configuration of the A' chain. The A and A' chains are separated by a unit cell length for clarity. The oxygen atoms, at the corners of two tetrahedra in the B chain, have been labelled.

distance in synthetic Mg-whitlockite (Gopal *et al*, 1974). The parameters of O(IA) may be influenced by the apparent close approach of the Ca(IIA') arising from the disorder of the A and A' chains. The P(A')-O<sub>4</sub> group, with the P(A'-O(IA')) bond equal to 1.52 Å, is consistent with the loss of the hydrogen. However, the O(IA')-P(A')-O(IIA') angles are larger than the O(IIA')-P(A')-O(IIA') angles, contrary to the results for synthetic Mg-whitlockite and for the analogous angles in  $\text{Ca}_3\text{V}_2\text{O}_8$ . The O(IIA) and O(IIA') are separated by less than 0.4 Å in the space averaged cell, and since the concentration of O(IIA') is small their positions may be affected substantially by systematic errors.

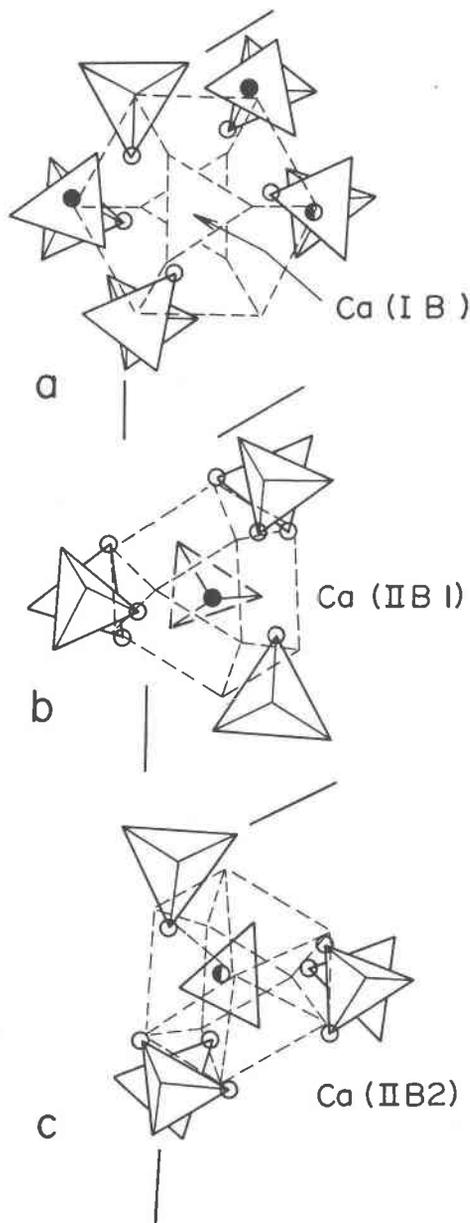


FIG. 4. The positions of the oxygen atoms around Ca(IB), Ca(II B1), and Ca(II B2) in whitlockite are represented by the apices of the solid (phosphate) tetrahedra. Those oxygen atoms bonded to Ca are shown as open circles [=O(II)], filled circles [=O(II B2)] or half-filled circles [=O(II B1)].

In the  $\text{Ba}_3\text{P}_2\text{O}_8$  structure the comparable positions of the oxygen atoms around Ba would be at the junctions of the dashed lines plus, in the case of (b), the single black circle. Thus (a) illustrates the octahedral environment around Ba(I) plus the six equatorial oxygen atoms whereas (b) and (c) illustrate the ten-fold environment around Ba(II) as viewed along two opposite directions. In (c) the half-filled circle is a member of the tetrahedron shown as a triangle at the center of the diagram.

TABLE 6. Total Bond Strengths Around the Oxygen Atoms in Whitlockite and Related Structures

Atom	whitlockite	Synthetic whitlockite	$\text{Ca}_3(\text{VO}_4)_2$
O(II B1)	1.986*	1.839*	2.018 <sup>†</sup>
O(II B1)	1.949	1.963	1.925
O(II B3)	2.110	2.094	2.115
O(II B5)	2.053	2.065	2.083
O(II B2)	1.979	1.969	1.952
O(II B2)	1.990	1.979	2.020
O(II B4)	1.981	1.950	1.992
O(II B6)	2.089	2.129	2.213
O(II A)	1.059*	1.137*	2.001 <sup>†</sup>
O(II A)	1.904	1.901	2.158
Average deviation in magnitude from two	0.058	0.066	0.054

\*Oxygen atoms involved in the hydrogen bonding have been excluded in the determination of the average deviation.

<sup>†</sup>Includes the contribution of the half occupied Ca(II A) site but with half weight.

The hydrogen atom is assumed to lie between O(II B) and O(II B1), which are separated by 2.892(8) Å compared with 2.748(6) Å in synthetic Mg-whitlockite. The hydrogen bond does not pull O(II B1) towards O(II A) since O(II B1) lies the same distance from the nearest three-fold axis as in  $\text{Ca}_3\text{V}_2\text{O}_8$ . The P(A)O<sub>4</sub> group is rotated slightly and displaced by 0.06 Å, relative to the origin, with respect to its position in synthetic Mg-whitlockite.

The atom positions of the P(B)O<sub>4</sub> groups differ by less than 0.1 Å in the two whitlockites. In fact, half of the individual atomic fractional coordinates differ by less than 3σ. All the O-P(B)-O bond angles and all the P-O bond lengths, save one, are not significantly different (<3σ). This latter interaction, P(B2)-O(II B6), differs by 0.017 Å in the two structures.

The average (Mg,Fe)-O bond length is 2.083 Å, a value 0.016 Å larger than the (Mg-O) bond length in synthetic Mg-whitlockite. If the bond lengths are assumed to reflect the local environment, rather than the long range structure forces, a concentration weighted average ionic radii difference between Mg<sup>2+</sup> and Fe<sup>2+</sup> (0.021 Å) should predict this difference between these mean bond lengths. Further, the separation between this cation site and O(II B6) is the same in both structures whereas the separations to O(II B5) differ by 0.031 Å. Thus the thermal parameters of O(II B5) in the mineral should reflect the disorder arising from the identity of the cation in the octahedral site and those of O(II B6) should

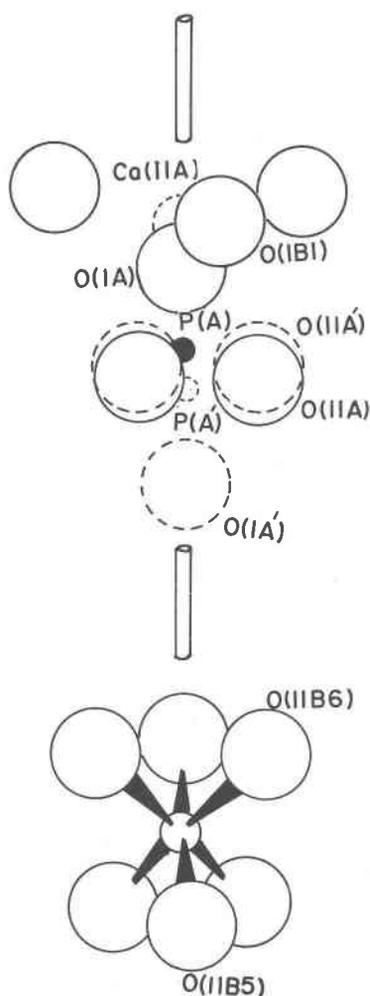


FIG. 5. A view of the average  $A$  chain. The large circles are represented oxygen atoms. The open small circles are Mg or Fe and the filled circle is phosphorus. The dashed circles represent atoms of the  $A'$  chain.

not. Although the value of  $U_{33}$  for O(IIB5) is larger in the mineral than in the synthetic crystal so is the  $U_{33}$  of O(IIB6), and by about the same proportion.

The Ca(IIA') fractional coordinates, relative to an origin at the octahedral coordinated cation site, are not significantly different from those in  $\text{Ca}_3\text{V}_2\text{O}_8$ . This cation shares a face of the  $\text{P}(A')\text{O}_4$  tetrahedron. The three Ca(IIA')-O(IIA') distances are 2.536(10), 2.61(7), and 2.68(2) Å in the mineral,  $\text{Ca}_3\text{As}_2\text{O}_8$  and  $\text{Ca}_3\text{V}_2\text{O}_8$  respectively. The remaining three distances, involving O(IB1), are 2.72(3), 3.04(7), and 3.00(1) Å in the same order. No obvious explanation for these differences exists. The six oxygen atoms about this cation are more like a distorted octahedron than a trigonal prism.

The coordination environments of Ca(IB), Ca(IIB1) and Ca(IIB2) are very similar in the two whitlockites. Exclusive of the Ca(IB)-O(IB1) bond, the bond lengths on average differ by less than 0.01 Å. The Ca(IB)-O(IB1) bond lengths at 2.550(5) and 2.503(4) Å in the mineral and the synthetic systems, respectively, differ significantly ( $9\sigma$ ). This oxygen is the hydrogen bond acceptor, and this change should be related to a change in the strength of the hydrogen bonding.

The Ca(IB) ion position is displaced by 0.19 Å from its position in synthetic Mg-whitlockite. The difference in the positional coordinates of Ca(IB) in these two whitlockites is about 50 percent larger than predicted by taking 19 percent (as suggested by the minerals composition) of the difference between the Ca(IB)'s position in synthetic Mg-whitlockite and  $\text{Ca}_3\text{V}_2\text{O}_8$ . The Ca(IIB1) and Ca(IIB2) positions differ by 0.06 Å and 0.04 Å, respectively, in the two whitlockites. Ca(IB) would be expected to have two mean positions: one in cells containing  $\text{Ca}_{1/2}\text{P}(A')\text{O}_4$  groups, where it is bonded to O(IA') and not O(IIA), and another in the cell containing  $\text{HP}(A)\text{O}_4$  groups where it is bonded to O(IIA) and O(IA') does not occur. This suggests that its thermal parameters would be anomalously large, as is indeed the case. In particular, the  $U_{11}$  value for this cation is more than three times larger than the thermal component of any other cation. In the synthetic sample Ca(IB) also has large thermal parameters ( $\frac{2}{3}$  the values in whitlockite) compared to the remaining cations. The hydrogen atom position must vary positionally or dynamically to be consistent with the crystallographic three-fold axis. In synthetic

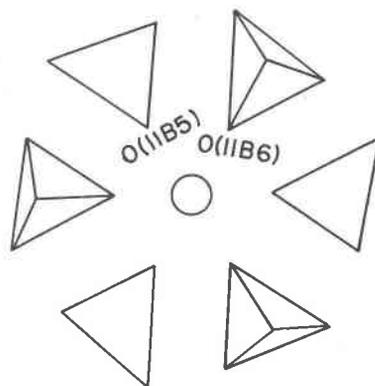


FIG. 6. The environment of Mg or Fe. The octahedra about this cation together with the surrounding phosphate tetrahedra are shown. The circle represents  $M = \text{Mg}$  or Fe.

whitlockite this is the only source of disorder aside from the thermal vibrations.

The atomic disorder in these structures should be reflected in the deviations of the bond strengths sums to the oxygen atoms from the expected value of 2 since different moments of the nuclear displacements are averaged. These sums in the mineral, calculated from the parameters proposed by Brown and Shannon (1973), are compared with those calculated for synthetic Mg-whitlockite and  $\text{Ca}_3\text{V}_2\text{O}_8$ . The average deviation from 2, excluding those involved in hydrogen bonding, are very similar, suggesting that these sums are not particularly sensitive to the effects of positional disorder in the structures.

This present study suggests that whitlockite can support compositions varying from  $\text{Ca}_{18}(\text{Mg,Fe})_2(\text{Ca},\square)(\text{PO}_4)_{14}$  to  $\text{Ca}_{18}(\text{Mg,Fe})_2\text{H}_2(\text{PO}_4)_{14}$ . If the hydrogen ion sites are disregarded, there are 22 cation sites in the first case and 20 in the second. All the terrestrial whitlockite contain hydrogen, which, at high temperatures, is lost as water. It should be noted, however, that the water in excess of that required by the above formula, as found by Bannister (1947) and Cady, Hill, Miller, and Magness (1952), can be inserted in the voids along the triad axis in the space vacated by the missing formula unit relative to the  $\text{Ba}_3\text{P}_2\text{O}_8$  structure-type. In this regard, Keppler (1968) has indicated that whitlockite and cerite are isotypic. Ito (1968) has shown that synthetic cerite has composition  $M^{2+}_3\text{Ln}_7\text{Si}_7\text{O}_{27}\cdot\text{OH}\cdot\text{H}_2\text{O}$  or  $M^{2+}_2\text{Ln}_8\text{Si}_7\text{O}_{28}\cdot 3\text{H}_2\text{O}$ . The former formulation agrees with the results presented here. Future structural research will show whether the postulate of such substitution in whitlockite is correct.

The meteoritic samples appear to support a formula near  $\text{Ca}_{18}(\text{Mg,Fe})_2\text{Na}_2(\text{PO}_4)_{14}$ . Lunar samples indicate that the whitlockites of extra-terrestrial origin can contain either 20, 21, or 22 cations per 14 tetrahedrally coordinated anions. However, it is unlikely that the phosphate groups on the three-fold axes have the  $\text{P}(A)\text{O}_4$  rather than the  $\text{P}(A')\text{O}_4$  configuration in those structures with less than 22 cations, since otherwise the  $\text{O}(IA)$  would be underbonded.

A relationship between the apatite and whitlockite structures is not unexpected, because apatite appears as a decomposition product of whitlockite and quartz in the Palermo quarry pegmatite (Fron del, 1941), morinite changes into apatite, followed by whitlockite, upon heating in air to successively higher temperatures (Fisher and Volborth, 1960),

and whitlockite has been identified as one of the products of carious attack on dental apatite (Johnson, Taylor, and Berman, 1969).

The crystal structures of apatite (Sudarsanan and Young, 1969) and whitlockite are, in fact, not closely related, although the Ca(I) site of apatite can easily be transformed into the  $M(I)$  site of the  $\text{Ba}_3\text{P}_2\text{O}_8$  structure type. The Ca(I) ions, comprising four of the ten cations in a unit cell of apatite, lie on three-fold axes. Its near environment consists of six phosphate groups with which this calcium ion shares one oxygen per  $\text{PO}_4$  group. These oxygen atoms form a slightly distorted trigonal prism, and this prism shares faces with its enantiomorphs, generated by mirror planes perpendicular to the three-fold axis. These prisms form chains parallel to  $c$  (Fig. 7a). Three of these phosphate groups each share an additional oxygen atom with the  $\text{Ca}^{2+}$ , capping the rectangular faces of the trigonal prism, and the other three phosphate groups cap faces of trigonal prisms in neighboring chains. Half of the environment about the  $M(I)$  site in  $\text{Ba}_3\text{P}_2\text{O}_8$  can be generated by the rotation by ninety degrees of

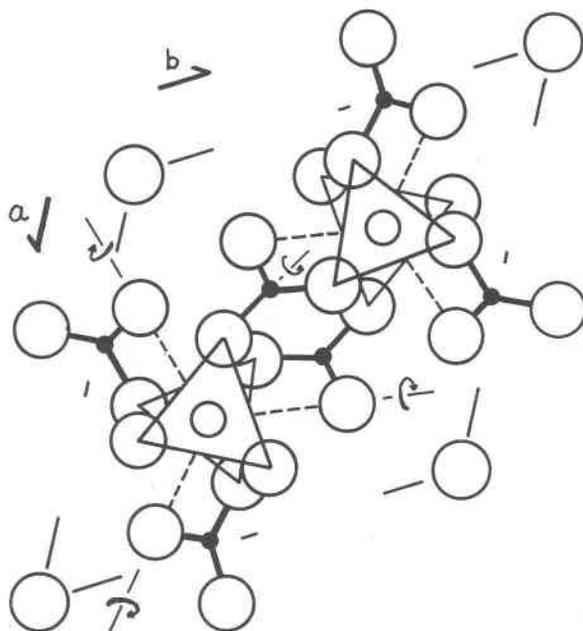


FIG. 7a. The apatite structure projected down the  $c$  axis. The phosphate tetrahedra and the trigonal prisms about  $M(I)$  are shown. The  $M(II)$  ion is not shown. The longer interactions capping the rectangular faces are shown dashed. The arrows indicate the direction of the rotation of the tetrahedra which will result in an environment like that of  $\text{Ba}(I)$  in  $\text{Ba}_3\text{P}_2\text{O}_8$ .

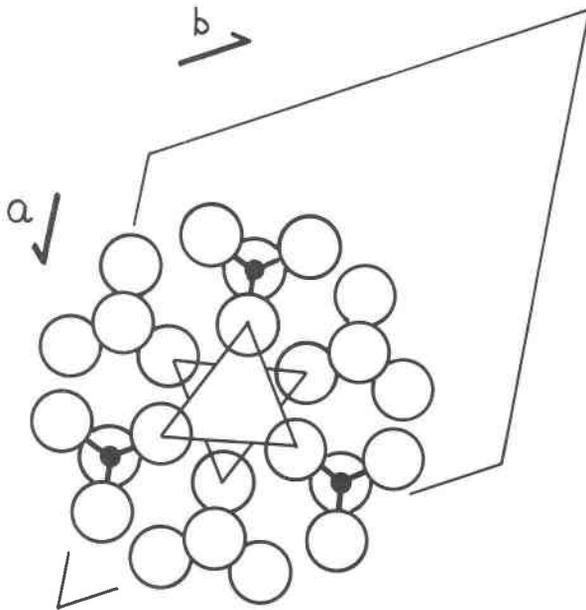


FIG. 7b. The transformed  $M(I)$  site of apatite.

the three phosphate groups, with which  $Ca(I)$  shares two oxygen atoms (Fig. 7b). The oxygen atom lying on the face of the trigonal prism becomes  $O(II)$  type oxygen atom. Similar changes involving the other three phosphate groups can be conceived, but these require new bonds between the calcium ions and those oxygen atoms that become  $O(I)$  type. Further, if the rotation of the phosphate groups are about one of the oxygen atoms rather than the phosphorus atoms, the triangular faces of the trigonal prism of the apatite structure will be rotated so as to look like an octahedron corresponding to the  $M(I)$  site of  $Ba_3P_2O_8$  structure type. Of course adjacent sites in the chain can no longer be enantiomorphic but can adopt the configuration for the group cations like those in glaserite. The relationship between glaserite and  $Ba_3P_2O_8$  structure type has recently been discussed by Moore (1973).

In apatite the infinite chains of trigonal prisms are arranged at edges of a prism with a hexagonal cross section having an edge equal to  $a(3)^{1/2} = 5.33 \text{ \AA}$ . The hydroxyl ions lie on a chain at the center of the prism. The hexagonal prism in whitlockite has an edge of  $3.3 \text{ \AA}$  formed by  $B$  type chains with the  $A$  chains at the center. The packing density in whitlockite normal to the prism axis is higher than in apatite, because the edges shared between  $P$  and  $Ca$  involve strong bonds, although the hexagonal prisms in the latter case are space filling.

The hexagonal prisms in whitlockite are interspersed with triangular prisms. The chemical change of apatite to whitlockite can not proceed without substantial bond breakage and reformation, however.

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