

## The crystal structure of a mineral related to paulkerrite

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Received: July 24, 1992; accepted December 21, 1992

### *Phosphates | Paulkerrite | Mantiennite | Benyacarite | Crystal structure*

**Abstract.** An apparently new phosphate mineral (named “benyacarite”) showing evident relationships with paulkerrite and mantiennite, but richer in  $\text{Mn}^{+2}$ , was found in granitic pegmatites in Argentina (Cerro Blanco, Tanti, Córdoba) where it is associated with other phosphates such as triplite etc., and fluorides such as pachnolite. The unit-cell parameters are:  $a_0 = 10.561(5) \text{ \AA}$ ,  $b_0 = 20.585(8) \text{ \AA}$ ,  $c_0 = 12.516(2) \text{ \AA}$ , orthorhombic, space group  $Pbca$ ,  $Z = 4$ ,  $D_x = 2.37 \text{ gcm}^{-3}$ . The crystal structure has been refined to  $R(\text{unweighted}) = 0.034$  and  $R(\text{weighted}) = 0.040$  using 1023 independent reflections. It contains layers perpendicular to  $[010]$  of two kinds of octahedra,  $\text{M}(2)\text{O}_5(\text{O},\text{F})$  and  $\text{TiO}_5(\text{O},\text{F})$ , the first essentially centered by  $\text{Fe}^{+3}$  atoms, with some  $\text{Ti}^{+4}$ ; the fluorine atom shares vertices of both octahedra. On both sides of these layers there are  $\text{PO}_4$  tetrahedra, with one face approximately parallel to the layers; the three corners of this face are shared with octahedra centered on Ti and M(2), whereas the remaining one is shared with another  $\text{M}(1)\text{O}_6$  octahedron centered by

**Table 1.** Unit-cell data for minerals related to paulkerrite.

	Paulkerrite <sup>a</sup>	Mantienneite <sup>b</sup>	“Benyacarite”
$a_0$ [Å]	10.49(7)	10.409(2)	10.561(5)
$b_0$ [Å]	20.75(13)	20.330(4)	20.585(8)
$c_0$ [Å]	12.44(2)	12.312(2)	12.516(2)

Space group: *Pbca*,  $Z=4$

<sup>a</sup> Data from Peacor et al. (1984).

<sup>b</sup> Data from Franolet et al. (1984).

$Mn^{+2}$  atoms (in part replaced by  $Fe^{+2}$ ). This network of octahedra and tetrahedra leaves cavities occupied by  $K^+$  and water molecules. According to these data, and to microprobe analysis the chemical formula corresponds to  $(H_2O_{0.78}K_{0.16}Na_{0.03})_2Ti(Mn_{0.75}^{+2}Fe_{0.21}^{+2}Mg_{0.04})_2(Fe_{0.68}^{+3}Ti_{0.28}^{+4}Al_{0.07})_2(PO_4)_4(O_{0.6}F_{0.4})_2 \cdot 14H_2O$ . On the basis of the knowledge of the structure of “benyacarite” and the strong similarities of its crystal chemistry with those of paulkerrite and mantienneite, a better characterization of these minerals is obtained. These species imply substitution of  $Mn^{+2}$  by Mg or  $Fe^{+2}$ , and of  $Fe^{+3}$  by  $Ti^{+4}$ , or Al, respectively.

## 1. Introduction

Eight years ago, two new phosphates were discovered almost simultaneously: the first of these, called paulkerrite, was found in the 7U7 Ranch pegmatite, Arizona (Peacor, Dunn and Simmons, 1984), together with other phosphates typical of granitic pegmatites. A recent occurrence of this mineral has been reported also at Bendada, Portugal (Schnorrer-Köhler and Rewitzer, 1991). The second new phosphate, named mantienneite (Franolet, Oustrière, Fontan and Pillard, 1984) comes instead from a sedimentary deposit at Anloua, Cameroun.

The analogy between these two minerals was already pointed out at the time of their discovery, and is evident both in the crystal data (see Table 1) and in the chemical composition (see Table 2). Particularly interesting is the presence of titanium, an element occurring rarely in natural phosphates.

Another related mineral, richer in  $Mn^{+2}$ , for which the name “benyacarite” has been proposed<sup>1</sup>, was observed for the first time in a granitic pegmatite at Cerro Blanco, near Tanti, Córdoba, Argentina (Gay, 1990), together with other phosphates and with species particularly rich in fluorine, such as fluellite and pachnolite. The unit-cell parameters for paulkerrite,

<sup>1</sup> The name and the status of “benyacarite” as a new mineral species have not been approved yet by the I. M. A. Commission on New Minerals and Mineral Names.

**Table 2.** Chemical composition (wt%) of the minerals related to paulkerrite. The analytical observed data are compared with the corresponding theoretical composition determined from crystal-structure analysis.

	Paulkerrite <sup>a</sup>		Mantienneite <sup>b</sup>		"Benyacarite" <sup>c</sup>	
	theor.	obs.	theor.	obs.	theor.	obs.*
Na <sub>2</sub> O	—	—	0.2	0.2	0.2	0.2
K <sub>2</sub> O	4.5	4.4	2.8	2.8	1.6	1.6
Al <sub>2</sub> O <sub>3</sub>	1.7	1.6	10.6	10.5	0.7	0.7
Fe <sub>2</sub> O <sub>3</sub>	12.4	12.2	1.6	5.6	11.2	11.0
FeO	—	—	3.7	—	3.1	2.8
MnO	7.2	7.1	0.2	0.2	11.0	11.2
MgO	4.7	4.6	6.5	6.5	0.3	0.3
CaO	—	—	0.3	0.3	0.1	0.1
TiO <sub>2</sub>	10.0	9.8	9.1	9.0	12.9	12.3
P <sub>2</sub> O <sub>5</sub>	29.9	29.4	32.1	32.0	29.6	28.1
F	0.9	0.9	—	—	1.6	1.5
H <sub>2</sub> O	29.5	(30.5)	32.9	33.0	28.9	(28.9)
—O=F	0.8	0.8	—	—	1.3	—
Total	100.0	100.0	100.0	100.0	100.0	—

Atomic ratios (P = 4)

	Paulkerrite		Mantienneite		"Benyacarite"	
Na	—	—	0.06	—	0.07	—
K	0.90	—	0.53	—	0.32	—
Fe <sup>+2</sup>	—	} 2.07	0.45	} 1.95	0.42	} 2.00 M(1) site
Mn	0.97		0.02		1.50	
Mg	1.10		1.43		0.07	
Ca	—		0.05		0.01	
Al	0.30	} 1.95	1.83	} 2.00	0.14	} 2.06 M(2) site
Fe <sup>+3</sup>	1.47		0.17		1.36	
Ti	0.18		—		0.56	
Ti	1.00	—	1.00	—	1.00	—
P	4.00	—	4.00	—	4.00	—
F	0.50	—	—	—	0.80	—

<sup>a</sup> Observed data from electron microprobe analysis by Peacor et al. (1984).<sup>b</sup> Observed data from chemical analysis by Fransolet et al. (1984).<sup>c</sup> Observed data from electron microprobe analysis by Diella and Mannucci in Gay (1990); new determinations on F, Na, Al, and Mg by EDX analysis (see text).\* Because of evident loss of water under the microprobe beam and the impossibility of determining the oxidation state of iron at the microprobe, the above data have been corrected by assuming an amount of water to be present and a Fe<sub>2</sub>O<sub>3</sub>/FeO ratio as required by the crystal structure determination.

mantiennite and “benyacarite” are reported in Table 1 for comparison. An X-ray powder pattern, reported by Gay (1990) is almost identical with the corresponding one of paulkerrite.

Apart from the problem of characterizing “benyacarite” better as a new mineral member of this series, an improved knowledge of the crystal chemistry of this interesting group of phosphates was considered useful. For instance, the crystal structure has not been reported yet in the literature, very probably due to the general poor quality of the crystals. Since “benyacarite” crystals are relatively more abundant and of better quality than the corresponding minerals from the other occurrences, a single crystal was selected from which a set of accurate X-ray diffraction intensities could be collected.

## 2. Experimental

The crystal used for the X-ray measurements was a small splinter of irregular shape, measuring about  $0.05 \times 0.05 \times 0.03$  mm; an EDX analysis was performed using a KEVEX Delta5 equipment attached to a S2700 Hitachi SEM microscope. This procedure showed the same ratios between corresponding peaks for this crystal and for the fragments whose analysis is reported in Table 2; for this reason the composition can be considered to be practically the same. In addition to the old data, significant amounts of fluorine were detected, the measured O/F ratio corresponding to approximately 0.8 atoms of F per formula unit.

X-ray crystal data were collected at room temperature (298 K), using a Nonius CAD4 automatic diffractometer and graphite monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The refined unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections having a  $\theta$  value in the range  $12.1 - 13.6^\circ$ .

The intensity data collection was carried out using a  $\theta$ - $2\theta$  scan mode and variable scan speed (maximum scan time for each reflection: 90 s). A total of 2742 independent diffracted intensities were collected by exploring the octant of the reciprocal lattice with  $0 < h < 12$ ,  $0 < k < 24$ ,  $0 < l < 14$  out to a maximum  $2\theta$  angle of  $50^\circ$ ; of these, 1023 for which  $I > 2\sigma(I)$  were used in the crystal structure determination and refinement. The diffracted intensities were corrected for Lorentz, polarization and background effects.

An empirical absorption correction was applied according to the procedure already described in Demartin, Pilati and Gramaccioli (1992), i.e. by performing a psi-scan correction [North, Phillips and Mathews (1968)], followed by a DIFABS correction [Walker and Stuart (1983)]. Transmission factors: 0.92 – 1.00 (psi-scan); 0.91 – 1.09 (DIFABS). Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from Cromer and Waber (1974) and Cromer (1974), respectively.

For the atoms in the sites labelled as M(1) and M(2) (see below) the scattering factors of Mn and Fe have been used, respectively. The structure was solved by direct methods, applying the MULTAN routine (Main, 1977); the final cycles of the refinement were carried out by full-matrix least squares, minimizing the function  $\sum w(F_o - k|F_c|)^2$  and considering anisotropic displacement parameters for all the non-hydrogen atoms. The weight  $w$  assigned to each individual observation was  $1/\sigma^2(F_o)$ , where  $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oL_p$ ,  $\sigma^2(I)$  is the standard deviation derived from counting statistics,  $k$  ( $= 0.04$ ) is a coefficient for improving the goodness of fit and  $L_p$  is the Lorentz-polarization factor. No empirical extinction coefficients were considered in the refinement.

Eleven (out of 14) hydrogen atoms were located in a difference Fourier map, and were introduced in the last structure-factor calculation, assuming a general value of  $0.05 \text{ \AA}^2$  for their isotropic thermal parameter  $U$ : their coordinates are reported at the end of Table 3. All the calculations were performed on a PDP11/73 computer using the SDS-Plus Structure Determination Package (Frenz, B. A. and Associates, 1980). After the location of the hydrogen atoms, the maximum residual in the final difference Fourier synthesis is  $0.43 \text{ e/\AA}^3$ ; the final values for  $R$  and  $R(\text{weighted})$  are 0.034 and 0.040, respectively. The final atomic coordinates (with their e. s. d.) are listed in Table 3, and the atomic displacement parameters in Table 4. Bond distances and angles are reported in Table 5.<sup>2</sup>

### 3. Discussion

A view of the crystal structure along the  $a$  axis is given in Figure 1, and a view along the  $c$  axis is shown in Figure 2. There are layers perpendicular to  $b$  containing two different kinds of octahedra (whose central atoms are referred to as "Ti" and "M(2)", respectively), joined at the vertices and also sharing other vertices with  $\text{PO}_4$  tetrahedra: these tetrahedra have one face practically parallel to the layer of octahedra.

Octahedra sharing vertices (opposed to each other) with only the  $\text{PO}_4$  tetrahedra are also present; the central atom of these octahedra will be referred to as "M(1)" here onwards. This network of octahedra and tetrahedra leaves relatively large cavities which are occupied by water and potassium ions (see below).

<sup>2</sup> Additional material to this paper can be ordered referring to the no. CSD 57004, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

**Table 3.** Fractional atomic coordinates and isotropic equivalent thermal parameters  $U_{\text{eq}} = 1/3 (U_{11} + U_{22} + U_{33})$ .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ (Å <sup>2</sup> )
M(1)	0.5033(2)	0.24517(6)	0.23961(9)	0.0162(5)
M(2)	0.6625(1)	−0.00457(7)	0.26007(9)	0.0123(5)
Ti	1/2	1/2	0	0.0128(7)
P(1)	0.4152(2)	0.0894(1)	0.2940(2)	0.0132(9)
P(2)	0.5892(2)	0.4027(1)	0.1965(2)	0.0104(9)
F	0.1434(4)	0.5030(3)	0.5970(3)	0.033(2)
O(K)	0.7802(5)	0.1481(3)	0.9454(5)	0.047(3)
O(1)	0.4054(6)	0.1629(3)	0.2853(5)	0.022(3)
O(2)	0.5333(5)	0.0646(3)	0.2363(4)	0.019(3)
O(3)	0.4174(6)	0.0683(3)	0.4119(4)	0.019(3)
O(4)	0.2954(5)	0.0616(3)	0.2402(5)	0.018(3)
O(5)	0.5939(6)	0.3293(3)	0.1906(4)	0.021(3)
O(6)	0.4709(5)	0.4261(3)	0.2581(4)	0.015(2)
O(7)	0.5894(6)	0.4307(3)	0.0826(4)	0.020(3)
O(8)	0.7087(5)	0.4261(3)	0.2549(5)	0.020(3)
O(9)	0.6503(6)	0.1869(3)	0.1761(6)	0.037(3)
O(10)	0.4172(6)	0.2401(3)	0.0779(5)	0.031(3)
O(11)	0.3544(6)	0.3044(3)	0.3072(5)	0.033(3)
O(12)	0.5926(6)	0.2500(4)	0.3962(5)	0.037(3)
O(13)	0.1624(5)	0.5050(3)	0.9120(4)	0.022(3)
O(14)	0.2394(8)	0.1405(3)	0.0602(5)	0.047(4)
O(15)	0.0306(8)	0.4059(3)	0.0091(6)	0.053(5)
H(9A)	0.6406	0.1483	0.1953	0.05
H(9B)	0.7500	0.1816	0.1953	0.05
H(10A)	0.3887	0.2832	0.0820	0.05
H(11A)	0.3594	0.3495	0.3046	0.05
H(11B)	0.2773	0.3163	0.3339	0.05
H(12A)	0.6406	0.1992	0.4180	0.05
H(12B)	0.5565	0.2500	0.4727	0.05
H(13A)	0.6406	0.0332	0.0566	0.05
H(13B)	0.7227	0.0010	0.0293	0.05
H(14A)	0.7500	0.0996	0.3887	0.05
H(14B)	0.6934	0.1172	0.4707	0.05

**a) The fluorine atom and its site**

In two coordination octahedra [TiO<sub>6</sub> and M(2)O<sub>6</sub>, respectively] around the metal atoms, the former has metal-ligand distances ranging from 1.942 to 1.999 Å (average: 1.977 Å), and the latter (centered essentially around Fe<sup>+3</sup>, see below) has metal–ligand distances ranging from 1.801 to 2.154 Å (average: 1.983 Å). For both of these octahedra, the smallest distance is notably smaller than the others (see Table 5), and corresponds in both cases to the same ligand, suggesting this atom to be different from the others; this hypothesis is confirmed by the value of the refined occupation factor ( $1.07 \pm 0.01$ ) if this atom is considered as oxygen. On applying bond valence

**Table 4.** Anisotropic thermal parameters –  $U$ s.

Name	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
M(1)	0.0166(5)	0.0115(4)	0.0204(5)	−0.0014(6)	0.0018(6)	0.0017(6)
M(2)	0.0081(5)	0.0134(5)	0.0155(5)	−0.0014(8)	0.0007(5)	−0.0031(8)
Ti	0.0173(7)	0.0142(7)	0.0070(7)	0.000(2)	0.0051(7)	0.0002(9)
P(1)	0.016(1)	0.0137(9)	0.0100(9)	−0.002(1)	−0.002(1)	−0.0001(9)
P(2)	0.0074(9)	0.0141(9)	0.0096(9)	0.0016(9)	−0.0004(9)	0.0005(8)
F	0.029(2)	0.042(3)	0.028(2)	0.003(4)	−0.001(2)	0.002(3)
O(K)	0.051(4)	0.036(3)	0.054(3)	0.014(3)	−0.007(3)	0.018(3)
O(1)	0.027(3)	0.018(3)	0.022(3)	0.002(3)	0.003(3)	0.001(3)
O(2)	0.018(3)	0.024(3)	0.016(3)	0.000(3)	0.000(3)	0.000(3)
O(3)	0.023(3)	0.022(3)	0.013(3)	0.002(3)	−0.001(3)	0.001(2)
O(4)	0.014(3)	0.021(3)	0.019(3)	−0.004(3)	−0.004(3)	0.000(3)
O(5)	0.020(3)	0.018(3)	0.024(4)	0.002(3)	−0.003(3)	−0.002(3)
O(6)	0.014(3)	0.020(2)	0.011(2)	0.003(2)	0.004(3)	0.005(3)
O(7)	0.017(3)	0.030(3)	0.013(3)	0.007(3)	0.000(3)	0.002(3)
O(8)	0.018(3)	0.024(3)	0.017(3)	−0.004(3)	−0.005(3)	−0.001(3)
O(9)	0.028(3)	0.026(3)	0.056(4)	0.001(3)	−0.009(4)	−0.008(3)
O(10)	0.037(3)	0.025(3)	0.031(3)	0.005(4)	−0.003(3)	0.003(3)
O(11)	0.026(3)	0.022(3)	0.051(4)	0.006(3)	0.012(3)	0.003(3)
O(12)	0.035(4)	0.042(4)	0.033(3)	0.002(4)	−0.001(3)	0.003(3)
O(13)	0.019(3)	0.030(3)	0.017(2)	−0.004(4)	−0.005(2)	0.006(3)
O(14)	0.081(5)	0.036(4)	0.023(4)	−0.024(4)	−0.018(4)	0.007(3)
O(15)	0.061(7)	0.047(4)	0.052(4)	0.006(4)	0.019(4)	0.004(4)

The form of the general temperature factor expression is:  $\exp[-2\pi^2\{h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23}\}]$  where  $a^*$ ,  $b^*$ , and  $c^*$  are reciprocal lattice constants.

considerations (Brown and Altermatt, 1985) and supposing this atom to be oxygen, a value of  $S = 1.60$  for the bond valence is obtained, which is notably different from the range of values calculated in the same way ( $S = 1.72$  to  $1.89$ ) for all the oxygen atoms coordinated to the metal atoms in this structure.

Accordingly, and considering also the results of our analysis, we thought this ligand could be essentially a mixture of oxygen and fluorine, with the average occupation of 0.6 and 0.4, respectively. Substantial amounts of F (0.9 wt%) have been shown to be also present in paulkerrite by Peacor et al. (1984), and for mantienneite traces of fluorine (not quantitatively determined) have been reported to be present by Fransolet et al. (1984). If this atom is assumed to be fluorine, using Brown and Altermatt's formula  $S = \exp[(r_o - r)/0.37]$  and a value of 1.705 Å for  $r_o$  of  $\text{Ti}^{+4}$ -F (derived from recent data on substances containing the  $\text{TiF}_6^{2-}$  ion) an estimate of 1.24 for the bond valence may be deduced. This also supports the idea that the site is actually occupied by a statistical distribution of fluorine and oxygen.

It is difficult to ascertain whether the fluorine atom is substituted by an oxygen atom or instead by an OH group. However, apart from bond-

**Table 5.** Interatomic distances (Å), angles (°) and bond valence calculations.

<i>M(1) polyhedron</i>			
M(1)–O(1)	2.064(7)	O(1)–M(1)–O(5)	177.4(3)
M(1)–O(5)	2.072(7)	O(1)–M(1)–O(9)	90.4(3)
M(1)–O(9)	2.117(9)	O(1)–M(1)–O(10)	90.5(3)
M(1)–O(10)	2.222(6)	O(1)–M(1)–O(11)	89.4(3)
M(1)–O(11)	2.163(8)	O(1)–M(1)–O(12)	90.3(3)
M(1)–O(12)	2.178(7)	O(5)–M(1)–O(9)	91.4(3)
M(1)–O <sub>aver.</sub>	2.136	O(5)–M(1)–O(10)	87.6(3)
S*	2.30	O(5)–M(1)–O(11)	88.9(3)
		O(5)–M(1)–O(12)	91.6(3)
		O(9)–M(1)–O(10)	86.1(3)
		O(9)–M(1)–O(11)	179.0(4)
		O(9)–M(1)–O(12)	92.7(3)
		O(10)–M(1)–O(11)	94.9(3)
		O(10)–M(1)–O(12)	178.5(3)
		O(11)–M(1)–O(12)	86.4(3)
<i>M(2) polyhedron</i>			
M(2)–F <sup>a</sup>	1.801(4)	F–M(2)–O(2)	93.4(3)
M(2)–O(2)	1.994(6)	F–M(2)–O(4)	94.0(3)
M(2)–O(4) <sup>b</sup>	1.956(6)	F–M(2)–O(6)	92.7(3)
M(2)–O(6) <sup>c</sup>	2.017(6)	F–M(2)–O(8)	97.0(3)
M(2)–O(8) <sup>d</sup>	1.973(6)	F–M(2)–O(13)	173.5(2)
M(2)–O(13) <sup>a</sup>	2.154(5)	O(2)–M(2)–O(4)	89.6(2)
M(2)–O <sub>aver.</sub>	2.019	O(2)–M(2)–O(6)	90.6(2)
S*	3.24	O(2)–M(2)–O(8)	169.6(3)
		O(2)–M(2)–O(13)	81.6(3)
		O(4)–M(2)–O(6)	173.3(3)
		O(4)–M(2)–O(8)	90.5(2)
		O(4)–M(2)–O(13)	90.1(3)
		O(6)–M(2)–O(8)	88.1(3)
		O(6)–M(2)–O(13)	83.3(3)
		O(8)–M(2)–O(13)	88.0(3)
<i>Ti polyhedron</i>			
Ti–F <sup>b,c</sup>	1.942(4)	F–Ti–O(3)	91.0(3)
Ti–O(3) <sup>f,g</sup>	1.989(6)	F–Ti–O(3)	89.0(3)
Ti–O(7) <sup>h</sup>	1.999(6)	F–Ti–O(7)	88.7(3)
Ti–O <sub>aver.</sub>	1.994	F–Ti–O(7)	91.3(3)
S*	3.52	O(3)–Ti–O(7)	90.6(2)
		O(3)–Ti–O(7)	89.4(2)
		F–Ti–F	180
		O(3)–Ti–O(3)	180
		O(7)–Ti–O(7)	180
<i>Phosphate tetrahedra</i>			
P(1)–O(1)	1.521(6)	O(1)–P(1)–O(2)	110.7(4)
P(1)–O(2)	1.529(7)	O(1)–P(1)–O(3)	110.5(3)
P(1)–O(3)	1.537(6)	O(1)–P(1)–O(4)	106.4(4)
P(1)–O(4)	1.544(6)	O(2)–P(1)–O(3)	110.3(4)
P–O <sub>aver.</sub>	1.533	O(2)–P(1)–O(4)	109.8(3)
S*	5.02	O(3)–P(1)–O(4)	109.0(4)

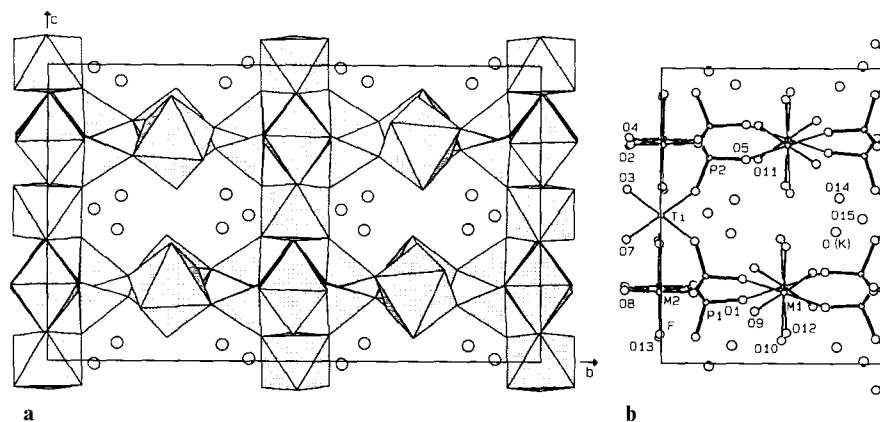
**Table 5.** (Continuation)

<i>Phosphate tetrahedra</i>			
P(2)–O(5)	1.512(6)	O(5)–P(2)–O(6)	111.3(4)
P(2)–O(6)	1.546(7)	O(5)–P(2)–O(7)	109.2(3)
P(2)–O(7)	1.538(6)	O(5)–P(2)–O(8)	108.0(4)
P(2)–O(8)	1.536(6)	O(6)–P(2)–O(7)	110.2(4)
P–O <sub>aver.</sub>	1.533	O(6)–P(2)–O(8)	109.2(3)
S*	5.02	O(7)–P(2)–O(8)	108.9(4)
<i>Hydrogen bonds</i>			
O(1)...O(9) <sup>i</sup>	2.781(11)	O(14)...O(4)	2.839(10)
O(2)...O(9)	2.904(10)	O(14)...O(7) <sup>m</sup>	2.802(11)
O(10)...O(K) <sup>j</sup>	2.735(9)	O(14)...O(10)	2.790(11)
O(11)...O(5) <sup>i</sup>	2.798(10)	O(14)...O(12) <sup>i</sup>	2.791(2)
O(11)...O(6)	2.859(10)	O(15)...O(13) <sup>n</sup>	2.913(11)
O(13)...O(2) <sup>j</sup>	2.713(8)	O(15)...O(K) <sup>j</sup>	2.917(11)
O(13)...O(6) <sup>k</sup>	2.775(8)	O(15)...O(6) <sup>l</sup>	3.010(9)
O(13)...O(15) <sup>l</sup>	2.753(10)		

Symmetry codes:

a =  $1/2 + x, 1/2 - y, 1 - z$ ; b =  $1/2 + x, y, 1/2 - z$ ; c =  $1 - x, y - 1/2, 1/2 - z$ ; d =  $3/2 - x, y - 1/2, z$ ; e =  $1/2 - x, 1 - y, z - 1/2$ ; f =  $1 - x, 1/2 + y, 1/2 - z$ ; g =  $x, 1/2 - y, z - 1/2$ ; h =  $1 - x, 1 - y, -z$ ; i =  $-1/2 + x, y, 1/2 - z$ ; j =  $-1/2 + x, 1/2 - y, 1 - z$ ; k =  $1/2 - x, 1 - y, 1/2 + z$ ; l =  $x, y, 1 + z$ ; m =  $-1/2 + x, 1/2 - y, -z$ ; n =  $-x, 1 - y, 1 - z$ .

\* Bond valence calculated according to Brown and Altermatt, 1985.



**Fig. 1.** a) A view of the coordination polyhedra along the *a* axis drawn by the POLIEDRI Program (Pilati, 1990). b) An ORTEP (Johnson, 1971) view of parts of the structure with atom labels.

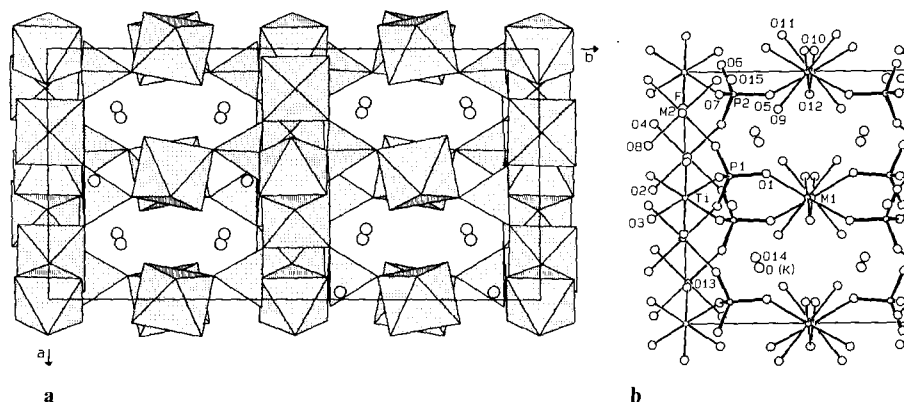


Fig. 2. a) A view of the coordination polyhedra along the  $c$  axis drawn by the POLIEDRI Program (Pilati, 1990). b) An ORTEP (Johnson, 1971) view of parts of the structure with atom labels.

valence considerations, or from evidence based on the Fourier map (of little value here, due to partial substitution of the site) the metal–OH bond should be longer than the corresponding metal–O bonds (and not shorter, as happens here). For these reasons, which support the bond-valence arguments, we are inclined to consider the presence of an oxygen instead of a hydroxyl group.

#### b) The M(1) site

In the M(1)O<sub>6</sub> octahedron, the average bond length with oxygen is 2.136 Å, a value substantially greater than the corresponding averages for the TiO<sub>5</sub>(O,F) or M(2)O<sub>5</sub>(O,F) octahedra (1.994 and 2.019 Å, respectively). The most reasonable assumption about the nature of the metal is, that of all the possible candidates (Mn, Fe or Ti), Mn<sup>+2</sup> is by far the most likely, since the general average of Mn<sup>+2</sup>–O bond lengths (hexacoordinated) is 2.21 Å (Ondik and Smith, 1974), compared with much shorter general average values for Ti<sup>+4</sup>–O and Fe<sup>+3</sup>–O (1.954 and 2.01 Å, respectively). Moreover, since there are good reasons for considering Mn to be in the +2 state (see below), this is the only available site for this element in this structure. Since the amount of Mn found by microprobe analysis is not sufficient for complete occupation of the site, then Fe<sup>+2</sup> and minor amounts of Mg and Ca should partially replace Mn, as shown in Table 2, thereby accounting for the relatively short value for the Mn–O bond (the general average value for hexacoordinated Fe<sup>+2</sup>–O bonds is 2.14 Å, according to Ondik and Smith, 1985). If this atom is considered as Mn, then the refined occupation factor is 0.985(2), a value that confirms our assumptions.

For paulkerrite and mantienneite, substantial amounts of Mg should be present in the M(1) site; for the latter mineral, these amounts are not sufficient for complete occupation, and for this reason some  $\text{Fe}^{+2}$  should also be present, contrasting with the assumption of Fransolet et al. (1984) who consider all iron to be present as  $\text{Fe}^{+3}$ . However, our assumption about the distribution of Fe in two oxidation states fits the requirements of both the M(1) and the M(2) sites very nicely (see Table 2 and below).

Of the six oxygen atoms directly bonded to the metal, only two [O(1) and O(5)] belong to phosphate groups, although not to the same one; the rest [O(9) to O(12)] are water molecules. The attribution of O(10) to a water molecule, rather than to an OH group, is mainly based on the M(1)–O(10) bond length, which is the largest in the coordination sphere. This is supported by charge-balance considerations.

### c) The M(2) site

The average M(2)–O distance (2.019 Å) excludes the presence in this site of Mn and Fe in the +2 state. The possible presence of  $\text{Mn}^{+3}$ , an element sometimes occurring in phosphates from pegmatites like purpurite ( $\text{MnPO}_4$ ), is very unlikely for two reasons: i) Some  $\text{Fe}^{+2}$  is present, and the equilibrium  $\text{Fe}^{+2} + \text{Mn}^{+3} \rightleftharpoons \text{Fe}^{+3} + \text{Mn}^{+2}$  in all known cases is definitely shifted to the right; ii) The colour of  $\text{Mn}^{+3}$  containing minerals is dark, ranging from black to deep purple, with strong pleochroism, a phenomenon which is not observed here. Besides, there are good reasons (see above) to consider all the Mn to occupy the M(1) site.

Similarly, the presence of  $\text{Ti}^{+3}$  should be virtually excluded, due to the presence of  $\text{Fe}^{+3}$  which indicates a relatively high oxygen activity at the time of formation of the mineral; the contemporary presence of  $\text{Fe}^{+3}$  and  $\text{Ti}^{+3}$  is also excluded by the light colour of the substance.

Of the two possible prevalent candidates for the M(2) site, i.e. iron (as  $\text{Fe}^{+3}$ ) and titanium (as  $\text{Ti}^{+4}$ ; see above), the former is the most likely, because the M(2)–O distance is relatively large; a minor substitution by aluminium, supported by the chemical analysis, is in line with the presence of more substantial amounts of Al in either paulkerrite or mantienneite. However, in “benyacarite” and in paulkerrite the observed amounts of Fe and Al are not sufficient for a complete occupation of the site; a reasonable assumption is that the “missing” element is titanium. This is reflected in a value of 0.840(2) for the refined occupation factor of this site, if the atom is considered as Fe.

Of the oxygen atoms around the central atom, two [O(2) and O(4)] are shared with P(1), and two [O(6) and O(8)] with P(2); the fluorine atom is not shared with P atoms, in agreement with the non-existence of fluophosphates in minerals, due to facility of hydrolysis. The longest bond [to O(13)] concerns a water molecule.