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The crystal structure of a mineral related to paulkerrite

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Abstract. An apparently new phosphate mineral (named "benyacarite") showing evident relationships with paulkerrite and mantienneite, but richer in Mn^{+2}, was found in granitic pegmatites in Argentina (Cerro Blanco, Tanti, Còrdoba) where it is associated with other phosphates such as triplite etc., and fluorides such as pachnolite. The unit-cell parameters are: $a_0 = 10.561(5)$ Å, $b_0 = 20.585(8)$ Å, $c_0 = 12.516(2)$ Å, orthorhombic, space group $Pbca$, $Z = 4$, $D_x = 2.37$ gcm^{-3}. The crystal structure has been refined to R(unweighted) = 0.034 and R(weighted) = 0.040 using 1023 independent reflections. It contains layers perpendicular to [010] of two kinds of octahedra, $M(2)O_5(O,F)$ and $TiO_5(O,F)$, the first essentially centered by Fe^{+3} atoms, with some Ti^{+4}; the fluorine atom shares vertices of both octahedra. On both sides of these layers there are 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 $M(1)O_6$ octahedron centered by

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

	Paulkerrite[a]	Mantienneite[b]	"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*, $Z=4$			

[a] Data from Peacor et al. (1984).
[b] Data from Fransolet 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 $(H_2O_{0.78}K_{0.16}Na_{0.03})_2Ti(Mn^{+2}_{0.75}Fe^{+2}_{0.21}Mg_{0.04})_2(Fe^{+3}_{0.68}Ti^{+4}_{0.28}Al_{0.07})_2(PO_4)_4$-$(O_{0.6}F_{0.4})_2 \cdot 14H_2O$. 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 (Fransolet, 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[1], was observed for the first time in a granitic pegmatite at Cerro Blanco, near Tanti, Còrdoba, 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,

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[1] 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[a]		Mantienneite[b]		"Benyacarite"[c]	
	theor.	obs.	theor.	obs.	theor.	obs.*
Na_2O	–	–	0.2	0.2	0.2	0.2
K_2O	4.5	4.4	2.8	2.8	1.6	1.6
Al_2O_3	1.7	1.6	10.6	10.5	0.7	0.7
Fe_2O_3	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_2	10.0	9.8	9.1	9.0	12.9	12.3
P_2O_5	29.9	29.4	32.1	32.0	29.6	28.1
F	0.9	0.9	–	–	1.6	1.5
H_2O	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^{+2}	–	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^{+3}	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	

[a] Observed data from electron microprobe analysis by Peacor et al. (1984).

[b] Observed data from chemical analysis by Fransolet et al. (1984).

[c] 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_2O_3/FeO ratio as required by the crystal structure determination.

mantienneite 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 MoK_a radiation ($\lambda = 0.71073$ Å). The refined unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections having a θ value in the range $12.1 - 13.6°$.

The intensity data collection was carried out using a θ-2θ 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 2θ angle of 50°; 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 $\Sigma w(F_o - k|F_c|)^2$ 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 Å^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 e/Å^3; the final values for R and R(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.[2]

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 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 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).

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[2] 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 $U_{eq} = 1/3\,(U_{11} + U_{22} + U_{33})$.

Atom	x	y	z	U_{eq} (Å^2)
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_6 and $M(2)O_6$, 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^{+3}, 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 ± 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: $\exp[-2\pi^2\{h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23}\}]$ 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 $S = \exp[(r_0 - r)/0.37]$ and a value of 1.705 Å for r_0 of Ti^{+4}-F (derived from recent data on substances containing the 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.

M(1) polyhedron			
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)−$O_{aver.}$	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)
M(2) polyhedron			
M(2)−F[a]	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)[b]	1.956(6)	F−M(2)−O(6)	92.7(3)
M(2)−O(6)[c]	2.017(6)	F−M(2)−O(8)	97.0(3)
M(2)−O(8)[d]	1.973(6)	F−M(2)−O(13)	173.5(2)
M(2)−O(13)[a]	2.154(5)	O(2)−M(2)−O(4)	89.6(2)
M(2)−$O_{aver.}$	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)
Ti polyhedron			
Ti−F[b,e]	1.942(4)	F−Ti-O(3)	91.0(3)
Ti−O(3)[f,g]	1.989(6)	F−Ti−O(3)	89.0(3)
Ti−O(7)[h]	1.999(6)	F−Ti−O(7)	88.7(3)
Ti−$O_{aver.}$	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
Phosphate tetrahedra			
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−$O_{aver.}$	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)

Phosphate tetrahedra			
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-$O_{aver.}$	1.533	O(6)−P(2)−O(8)	109.2(3)
S*	5.02	O(7)−P(2)−O(8)	108.9(4)
Hydrogen bonds			
O(1)...O(9)^{i}	2.781(11)	O(14)...O(4)	2.839(10)
O(2)...O(9)	2.904(10)	O(14)...O(7)^{m}	2.802(11)
O(10)...O(K)^{j}	2.735(9)	O(14)...O(10)	2.790(11)
O(11)...O(5)^{i}	2.798(10)	O(14)...O(12)^{i}	2.791(2)
O(11)...O(6)	2.859(10)	O(15)...O(13)^{n}	2.913(11)
O(13)...O(2)^{j}	2.713(8)	O(15)...O(K)^{j}	2.917(11)
O(13)...O(6)^{k}	2.775(8)	O(15)...O(6)^{i}	3.010(9)
O(13)...O(15)^{l}	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.

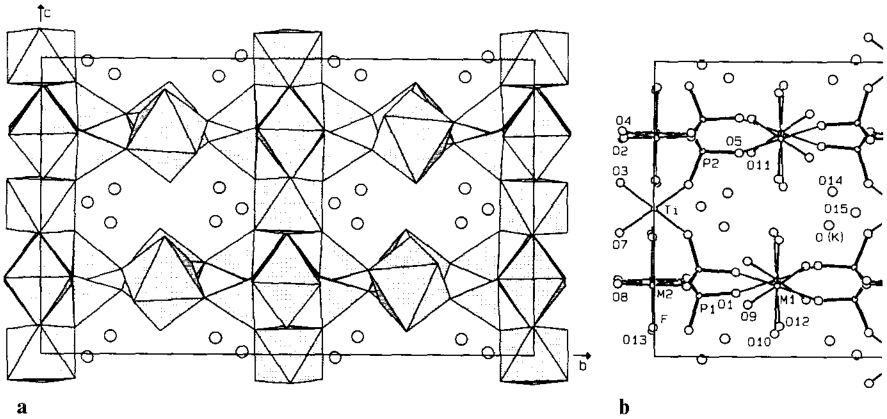

Fig. 1. a) A view of the coordination polyhedra along the *a* axis drawn by the POLIEDRI Program (Pilati, 1990). b) An ORTEP (Johnson, 1971) view of parts of the structure with atom labels.

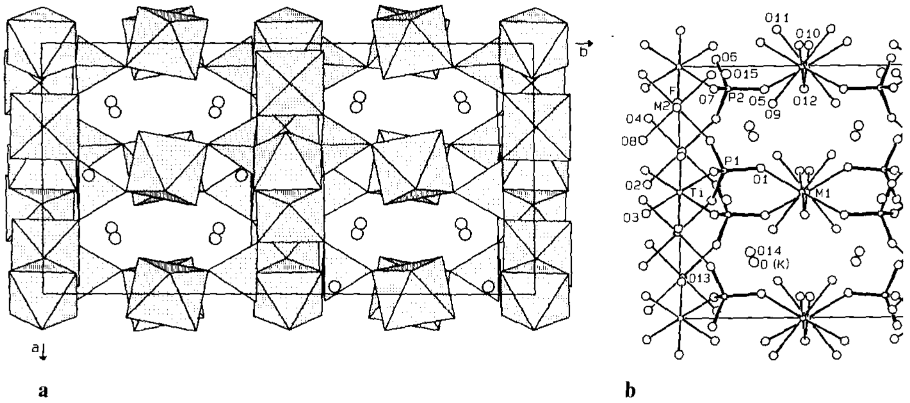

Fig. 2. a) A view of the coordination polyhedra along the *c* axis drawn by the POLIEDRI Program (Pilati, 1990). b) An ORTEP (Johnson, 1971) view of parts of the structure with atom labels.

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 $M(1)O_6$ octahedron, the average bond length with oxygen is 2.136 Å, a value substantially greater than the corresponding averages for the $TiO_5(O,F)$ or $M(2)O_5(O,F)$ 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^{+2} is by far the most likely, since the general average of $Mn^{+2}-O$ bond lengths (hexacoordinated) is 2.21 Å (Ondik and Smith, 1974), compared with much shorter general average values for $Ti^{+4}-O$ and $Fe^{+3}-O$ (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^{+2} 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 $Fe^{+2}-O$ 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 Fe^{+2} should also be present, contrasting with the assumption of Fransolet et al. (1984) who consider all iron to be present as 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 Mn^{+3}, an element sometimes occurring in phosphates from pegmatites like purpurite ($MnPO_4$), is very unlikely for two reasons: i) Some Fe^{+2} is present, and the equilibrium $Fe^{+2} + Mn^{+3} \leftrightarrows Fe^{+3} + Mn^{+2}$ in all known cases is definitely shifted to the right; ii) The colour of 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 Ti^{+3} should be virtually excluded, due to the presence of Fe^{+3} which indicates a relatively high oxygen activity at the time of formation of the mineral; the contemporary presence of Fe^{+3} and 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 Fe^{+3}) and titanium (as 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.

d) The Ti site

The attribution of this site to Ti^{+4} is in agreement with the relatively short value of the average metal–oxygen bond (1.994 Å); since the amount of Ti found by chemical analysis is in substantial excess (1.56 atoms instead of 1), an average of 0.56 atoms should occupy another site. Incidentally this is almost the exact amount corresponding to the complete occupation of the M(2) site. A similar situation occurs for paulkerrite; for mantienneite, however, the Ti content corresponds exactly to the filling of this site, with no extra titanium to occupy the M(2) site.

Due to the similarity of the metal–oxygen bond lengths, some mutual replacement of Fe^{+3} and Ti^{+4} between this "Ti" site and the "M(2)" site should be expected to occur; some evidence for it is given by the high refined occupation factor [1.100(2)] for the Ti atom in "benyacarite". This, however, is not enough to establish a precise value for such replacement and, in lack of such data, this substitution is not indicated in the chemical formula proposed here.

The oxygen atoms which are directly bonded to titanium in this site are only shared with two independent P atoms, and no water is present in the coordination sphere. The fluorine atom is not linked to the P atoms.

e) The potassium site

In all these minerals, significant amounts of potassium have been detected. From crystal structure refinement, a "water" position corresponds to a higher peak than the others in the Fourier synthesis; refinement of the occupation factor leads to a value of 1.28(2), in agreement with partial replacement by an atom of a heavier element. Here, potassium is the most likely candidate, since the shortest distance with the surrounding oxygen atoms is 2.735 Å [with O(10)], and the average distance with respect to the six closest neighbours is 2.942 Å. In agreement with the results of chemical analysis, for all these minerals, the occupation of this site by a K^+ ion is only partial, attaining a maximum value of 0.45 for paulkerrite. Here a small difference with respect to the previous assumptions can be noticed: according to the idealized formula $KTi(Mg,Mn)_2(Fe^{+3},Al,Ti,Mg)_2(PO_4)_4(OH)_3 \cdot 15H_2O$ proposed by Peacor et al. (1984), potassium is contained in equivalent amounts to Ti, whereas Fransolet et al. (1984) assume vacancies to be present in this site. Apart from packing energy considerations, which render the presence of a considerable number of vacancies unlikely in these compounds, the absence of vacancies (at least for "benyacarite") is also confirmed by the high value of the occupation factor.

The presence of ions such as H_3O^+ instead of water substituting for potassium seems unlikely: the contacts between the oxonium ions and the surrounding oxygen atoms are subject to strong hydrogen – bond formation and are considerably shorter than the K – O distances [the average O – O distance involving H_3O^+ is 2.57 Å (Lundgren and Olovsson, 1976)]. A similar situation was encountered by Demartin, Diella, Donzelli, Gramaccioli and Pilati (1991) for phosphuranylite $KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 8\,H_2O$, another phosphate where the potassium ion is partly replaced by water molecules.

f) The phosphate groups

The geometry of the two independent phosphate ions is in agreement with the general conformation of these groups. The average of the P – O bond distances is 1.533 Å; these range from 1.512 to 1.546 Å, thereby excluding the presence of P – OH bonds, which should be considerably longer (about 1.57 Å). The absence of ions such as $(PO_3OH)^{2-}$ is in agreement with other independent details, since e.g. no H atoms were observed linked to the oxygen atoms around P. The angles centered on the P atoms (106.4 to 111.3°) are near to the 'ideal' value for a regular tetrahedron (109.47°).

g) Hydrogen bonding

The structure contains five water molecules forming part of the coordination sphere around the M(1) and the M(2) sites, as we have seen. Besides these and the water molecule partially replaced by potassium, whose distances with the adjoining oxygen atoms correspond to hydrogen bonds (see Table 5), there are two more water molecules, situated in cavities, whose oxygen atoms are indicated here as O(14) and O(15). Around the former, the hydrogen atoms can still be observed in the difference Fourier synthesis, whereas the situation around the latter is less clear, probably owing to statistical distribution of the hydrogen atoms, as is observed in ice and in many hydrated salts. There are four $O \cdots O$ distances around O(14), ranging between 2.790 and 2.839 Å, which are consistent with H-bond formation, and there are also four distances ranging between 2.753 and 3.010 Å around O(15), which can also be considered as good evidence for hydrogen bond formation.

h) Conclusions

The above results and crystal-chemical considerations have led to the following chemical formula for the minerals related to paulkerrite: $(H_2O,K)_2TiM(1)_2M(2)_2(PO_4)_4(O,F)_2 \cdot 14H_2O$. Here M(1) and M(2) are essentially Mn^{+2}, Fe^{+2} or Mg, and Fe^{+3} or Al, respectively: some mutual replacement is also possible between Ti and Fe^{+3} in the "M(2)" site.

The differences between the above chemical formula and the one proposed by Peacor et al. (1984) or by Fransolet et al. (1984) for paulkerrite or mantienneite, respectively, are only minor; they concern the role of potassium (which is largely substituted by water molecules), the essential presence of some FeO (especially for mantienneite), and in particular the role of fluorine, which seems to be peculiarly important in these minerals: a redetermination of this element in mantienneite would be advisable. In particular for "benyacarite", where the Al content is low, a substantial part of the fluorine atoms must be necessarily bonded to atoms of iron and/or titanium, a unusual case for minerals; this also shows the unique character of these natural substances.

Some relationships to other phosphates from granitic pegmatites also containing iron (as Fe^{+3}) and potassium might be examined: for instance, leucophosphite $K_2[Fe_4(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$ could be useful for comparison. However, in the structure of this mineral (Moore, 1972), definite clusters of octahedral tetramers occur, but no chains as are found in "benyacarite"; moreover, there is no role for either titanium, fluorine, or Mn/Mg. A comparison could also be made with a 'classic' manganese-rich phosphate from granitic pegmatites, hureaulite $Mn_5(H_2O)_4[PO_3OH]_2$-$[PO_4]_2$; however, the structural motive of this mineral (Moore and Araki, 1973) is based on *edge*-sharing clusters (pentamers) of MnO_6 octahedra, and no indefinitely extended layers of octahedra are observed.

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