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The Crystal Structure of Manganese-Whitlockite, $Ca_{18}Mn_2H_2(PO_4)_{14}$

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Hexagonal, $R3c$, $a = 10\cdot438$ (2), $c = 37\cdot15$ (1) Å [rhombohedral setting: $a = 13\cdot757$ (5) Å, $\alpha = 44\cdot34$ (2)°], $Ca_{18}Mn_2H_2(PO_4)_{14}$, $Z = 3$, $D_x = 3\cdot106$ g cm^{-2}. The crystals were grown hydrothermally at 425°C and 52000 p.s.i.

Introduction

During attempts to grow single crystals of calcium hydroxyapatite doped with Mn^{2+} under hydrothermal conditions at 425°C and 52000 p.s.i. (Mengeot, Harvill & Gilliam, 1973) by the addition of $Mn_3(PO_4)_2$ to the stoichiometric charge, small pink crystals were recovered which were found to be β-$Ca_3(PO_4)_2$-like rather than apatitic.

It has been only in recent years that the structural relationship between β-$Ca_3(PO_4)_2$ (Dickens, Schroeder & Brown, 1974) and the mineral whitlockite, $Ca_{18}(Mg, Fe)_2H_2(PO_4)_{14}$, (Gopal & Calvo, 1972) has been resolved. Indeed, as we were in the final stages of our refinement, Gopal, Calvo, Ito & Sabine (1974) published a paper on synthetic Mg-whitlockite, and very recently Calvo & Gopal (1975) have completed a structural analysis of Palermo whitlockite. As a comparison with the available data we should like to present our results on the synthetic Mn analogue.

A small ($\sim 0\cdot15$ mm) well formed crystal was selected for data collection. Precession photographs allowed the space groups $R3c$ or $R\bar{3}c$; $R3c$ was chosen for refinement in analogy to the mineral. The lattice parameters were determined in a *PICK*-II least-squares refinement program using 48 reflections in the angular range $36° < 2\theta < 57°$, each automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation.

Diffraction intensities were measured using Zr-filtered Mo $K\alpha$ radiation at a take-off angle of $2\cdot5°$ with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1° min^{-1} over $1\cdot5°$ with allowance for dispersion and with 40 s background counts taken at both ends of the scan. Of the 1920 data investigated in the angular range $2\theta < 62°$, 1722 were considered observable according to the criterion $|F_o| > 1\cdot58\sigma_F$, where σ_F is defined as $0\cdot02|F_o| + [C + k^2 B]^{1/2}/2|F_o| Lp$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored and no random variations in intensity greater than 3 % were observed over each data collection period. Because of instrumental problems, four separate scale factors were used in the refinement representing the four essentially equal periods of data collection.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections were made with a computer program written by N. W. Alcock and modified by B. Lee for a crystal of general shape. Input for the program included the indices of the plane faces of the crystal, which were determined with the aid of precession photographs, and the orientation angles of the crystal coordinate system with respect to the diffractometer coordinate system, which were obtained from the program *PICK*-II. For the crystal with an average μR of $0\cdot5$, the maximum absorption correction applied was $9\cdot0\%$ of $|F_o|$.

The positional parameters of the mineral (Gopal & Calvo, 1972) were used as a trial structure with Mn at the origin. Analysis of the thermal parameters indicated

that the $P(1)O_4$ tetrahedron was not disordered and that the Ca(II A) site (Gopal & Calvo, 1972) was empty. The full-matrix least-squares refinement (Busing, Martin & Levy, 1962) using a $1/\sigma^2$ weighting scheme, zero-valent scattering factors for Mn, Ca, P and O (Cromer & Mann, 1968), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, converged to a residual $R = 0.068$ and a

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and anisotropic thermal parameters*

Numbers in parentheses are estimated standard deviations in the last significant figure.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(a)	0	0	0	0·68 (2)	B_{11}	0·73 (4)	$\frac{1}{2}B_{11}$	0	0
Ca(1b)	2954 (1)	1585 (1)	6721·6 (5)	2·85 (5)	1·49 (4)	1·42 (4)	1·65 (3)	−0·97 (3)	−0·68 (3)
Ca(2b)	2813 (1)	1464 (1)	5657·2 (4)	0·75 (3)	0·76 (3)	0·80 (4)	0·40 (2)	−0·03 (2)	−0·06 (2)
Ca(3b)	3874 (1)	1798 (1)	7678·4 (4)	0·91 (3)	0·69 (3)	0·82 (4)	0·42 (2)	−0·18 (2)	−0·07 (2)
P(1a)	0	0	7542·6 (8)	0·86 (11)	B_{11}	2·14 (10)	$\frac{1}{2}B_{11}$	0	0
P(2b)	3166 (1)	1431 (1)	8649·8 (4)	0·68 (4)	0·61 (3)	0·81 (4)	0·38 (3)	0·02 (3)	0·03 (3)
P(3b)	3524 (1)	1590 (1)	9673·7 (4)	0·59 (3)	0·68 (3)	0·67 (4)	0·27 (3)	0·03 (3)	0·06 (3)
O(1b)	2798 (4)	955 (4)	8259 (1)	1·62 (12)	1·45 (11)	0·89 (10)	0·91 (10)	0·13 (8)	0·14 (8)
O(2b)	2449 (4)	2318 (4)	8783 (1)	1·40 (11)	1·35 (11)	1·34 (11)	1·03 (10)	0·20 (8)	0·04 (9)
O(3b)	2708 (3)	6 (3)	8868 (1)	0·94 (9)	0·68 (9)	0·82 (9)	0·36 (7)	0·19 (7)	0·27 (7)
O(4b)	4868 (4)	2415 (3)	8711 (1)	0·73 (10)	0·57 (10)	1·50 (12)	0·26 (8)	0·22 (9)	0·03 (8)
O(5b)	4017 (4)	1953 (3)	75 (1)	1·61 (12)	1·05 (10)	0·79 (10)	0·69 (9)	−0·44 (8)	−0·12 (8)
O(6b)	4020 (4)	512 (4)	9542 (1)	1·14 (10)	1·29 (10)	1·04 (10)	0·84 (9)	−0·07 (8)	−0·03 (12)
O(7b)	4174 (4)	3063 (4)	9473 (1)	1·32 (11)	0·89 (10)	0·88 (10)	0·28 (8)	0·24 (8)	0·48 (8)
O(8b)	1817 (4)	802 (3)	9629 (1)	0·64 (9)	0·83 (9)	1·16 (11)	0·30 (8)	−0·05 (8)	−0·15 (8)
O(9a)	0	0	7972 (2)	2·82 (21)	B_{11}	1·84 (30)	$\frac{1}{2}B_{11}$	0	0
O(10b)	−182 (4)	1303 (3)	7425 (1)	1·34 (11)	0·81 (9)	2·25 (14)	0·74 (9)	0·62 (10)	0·40 (8)

Table 2. *Bond distances, polyhedral edge lengths and bond angles for the calcium polyhedra*

Numbers in parentheses are estimated standard deviations in the last significant figures.

(i) Interatomic distances (Å)

Ca(1)–O(6)	2·365 (4)	Ca(2)–O(7)	2·320 (3)	Ca(3)–O(3)	2·358 (3)
–O(3)	2·385 (3)	–O(5)	2·420 (4)	–O(1)	2·386 (4)
–O(2)	2·414 (4)	–O(4)	2·434 (3)	–O(10)	2·386 (3)
–O(5)	2·495 (3)	–O(6)	2·449 (4)	–O(8)	2·435 (3)
–O(1)	2·535 (4)	–O(10)	2·460 (4)	–O(2)	2·444 (3)
–O(5′)	2·572 (4)	–O(4′)	2·467 (3)	–O(8′)	2·465 (3)
–O(7)	2·618 (4)	–O(3)	2·527 (3)	–O(7)	2·654 (4)
–O(10)	3·008 (4)	–O(2)	2·789 (4)	–O(6)	2·681 (4)

Ca(1) polyhedron		Ca(2) polyhedron		Ca(3) polyhedron	
O(6)—O(3)	4·681 (5)	O(7)—O(5)	4·489 (5)	O(3)—O(1)	4·477 (5)
O(6)—O(2)	3·641 (5)	O(7)—O(4)	3·078 (5)	O(3)—O(10)	3·102 (5)
O(6)—O(5)	4·154 (4)	O(7)—O(6)	2·782 (5)	O(3)—O(8′)	3·207 (5)
O(6)—O(1)	3·965 (5)	O(7)—O(10)	3·211 (5)	O(3)—O(2)	2·789 (5)
O(6)—O(5′)	2·482 (5)	O(7)—O(4′)	4·168 (5)	O(3)—O(8)	4·382 (5)
O(6)—O(7)	2·782 (5)	O(7)—O(3)	4·539 (5)	O(3)—O(7)	4·733 (5)
O(6)—O(10)	4·727 (5)	O(7)—O(2)	2·999 (5)	O(3)—O(6)	2·772 (5)
O(3)—O(2)	2·789 (5)	O(5)—O(4)	3·324 (5)	O(1)—O(10)	3·319 (5)
O(3)—O(5)	3·044 (5)	O(5)—O(6)	4·549 (5)	O(1)—O(8′)	3·333 (5)
O(3)—O(1)	2·450 (4)	O(5)—O(10)	2·926 (5)	O(1)—O(2)	4·555 (5)
O(3)—O(5′)	4·492 (5)	O(5)—O(4′)	3·336 (5)	O(1)—O(8)	3·137 (5)
O(3)—O(7)	4·244 (5)	O(5)—O(3)	3·044 (5)	O(1)—O(7)	2·927 (5)
O(3)—O(10)	3·102 (5)	O(5)—O(2)	3·089 (5)	O(1)—O(6)	3·171 (5)
O(2)—O(5)	4·625 (5)	O(4)—O(6)	4·454 (4)	O(10)—O(8′)	4·667 (5)
O(2)—O(1)	3·844 (5)	O(4)—O(10)	4·307 (4)	O(10)-O(2)	2·918 (4)
O(2)—O(5′)	3·089 (5)	O(4)—O(4′)	2·802 (6)	O(10)-O(8)	4·504 (4)
O(2)—O(7)	4·951 (5)	O(4)—O(3)	4·424 (5)	O(10)-O(7)	3·211 (5)
O(2)—O(10)	2·918 (5)	O(4)—O(2)	2·477 (5)	O(10)-O(6)	3·698 (5)
O(5)—O(1)	3·247 (4)	O(6)—O(10)	3·556 (5)	O(8′)-O(2)	4·305 (5)
O(5)—O(5′)	4·128 (7)	O(6)—O(4′)	3·532 (5)	O(8′)-O(8)	2·837 (6)
O(5)—O(7)	2·483 (4)	O(6)—O(3)	2·772 (4)	O(8′)-O(7)	4·535 (6)
O(5)—O(10)	3·692 (5)	O(6)—O(2)	4·906 (5)	O(8′)-O(6)	2·473 (4)
O(1)—O(5′)	5·075 (5)	O(10)—O(4′)	4·803 (5)	O(2)—O(8)	3·428 (5)
O(1)—O(7)	2·927 (5)	O(10)—O(3)	3·820 (5)	O(2)—O(7)	2·999 (5)
O(1)—O(10)	4·997 (5)	O(10)—O(2)	2·918 (4)	O(2)—O(6)	4·768 (4)
O(5′)-O(7)	4·195 (5)	O(4′)—O(3)	2·453 (4)	O(8)—O(7)	2·468 (4)
O(5′)-O(10)	2·962 (5)	O(4′)—O(2)	4·600 (5)	O(8)—O(6)	4·544 (5)
O(7)—O(10)	5·224 (5)	O(3)—O(2)	5·110 (5)	O(7)—O(6)	5·119 (5)

Table 2 (cont.)

(ii) Angles (°) (e.s.d. = 0·1°)

Ca(1) polyhedron		Ca(2) polyhedron		Ca(3) polyhedron	
O(6)—Ca(1)-O(3)	160·5	O(7)—Ca(2)-O(5)	142·5	O(3)—Ca(3)-O(1)	141·3
O(6)—Ca(1)-O(2)	99·3	O(7)—Ca(2)-O(4)	80·7	O(3)—Ca(3)-O(10)	81·7
O(6)—Ca(1)-O(5)	117·5	O(7)—Ca(2)-O(6)	71·3	O(3)—Ca(3)-O(8')	84·0
O(6)—Ca(1)-O(10)	108·0	O(7)—Ca(2)-O(10)	84·3	O(3)—Ca(3)-O(2)	71·0
O(6)—Ca(1)-O(5')	60·2	O(7)—Ca(2)-O(4')	121·1	O(3)—Ca(3)-O(8)	130·6
O(6)—Ca(1)-O(7)	67·7	O(7)—Ca(2)-O(3)	138·9	O(3)—Ca(3)-O(7)	141·6
O(6)—Ca(1)-O(10)	122·8	O(7)—Ca(2)-O(2)	71·2	O(3)—Ca(3)-O(6)	66·4
O(3)—Ca(1)-O(2)	71·1	O(5)—Ca(2)-O(4)	86·4	O(1)—Ca(3)-O(10)	88·2
O(3)—Ca(1)-O(5)	77·2	O(5)—Ca(2)-O(6)	138·3	O(1)—Ca(3)-O(8')	87·5
O(3)—Ca(1)-O(1)	59·7	O(5)—Ca(2)-O(10)	73·7	O(1)—Ca(3)-O(2)	141·2
O(3)—Ca(1)-O(5')	130·0	O(5)—Ca(2)-O(4')	86·7	O(1)—Ca(3)-O(8)	80·6
O(3)—Ca(1)-O(7)	116·0	O(5)—Ca(2)-O(3)	75·9	O(1)—Ca(3)-O(7)	70·8
O(3)—Ca(1)-O(10)	69·1	O(5)—Ca(2)-O(2)	72·4	O(1)—Ca(3)-O(6)	77·3
O(2)—Ca(1)-O(5)	140·8	O(4)—Ca(2)-O(6)	131·6	O(10)-Ca(3)-O(8')	151·0
O(2)—Ca(1)-O(1)	101·9	O(4)—Ca(2)-O(10)	123·3	O(10)-Ca(3)-O(2)	74·3
O(2)—Ca(1)-O(5')	76·5	O(4)—Ca(2)-O(4')	69·7	O(10)-Ca(3)-O(8)	136·4
O(2)—Ca(1)-O(7)	159·3	O(4)—Ca(2)-O(3)	126·2	O(10)-Ca(3)-O(7)	79·0
O(2)—Ca(1)-O(10)	64·0	O(4)—Ca(2)-O(2)	56·1	O(10)-Ca(3)-O(6)	93·6
O(5)—Ca(1)-O(1)	80·4	O(6)—Ca(2)-O(10)	92·8	O(8')-Ca(3)-O(2)	123·9
O(5)—Ca(1)-O(5')	109·1	O(6)—Ca(2)-O(4')	91·9	O(8')-Ca(3)-O(8)	70·8
O(5)—Ca(1)-O(7)	58·1	O(6)—Ca(2)-O(3)	67·7	O(8')-Ca(3)-O(7)	126·0
O(5)—Ca(1)-O(10)	83·7	O(6)—Ca(2)-O(2)	138·9	O(8')-Ca(3)-O(6)	57·6
O(1)—Ca(1)-O(5')	167·1	O(10)-Ca(2)-O(4')	154·3	O(2)—Ca(3)-O(8)	88·6
O(1)—Ca(1)-O(7)	69·2	O(10)-Ca(2)-O(3)	100·0	O(2)—Ca(3)-O(7)	72·0
O(1)—Ca(1)-O(10)	128·5	O(10)-Ca(2)-O(2)	67·2	O(2)—Ca(3)-O(6)	136·9
O(5')-Ca(1)-O(7)	107·9	O(4')-Ca(2)-O(3)	58·8	O(8)—Ca(3)-O(7)	57·5
O(5')-Ca(1)-O(10)	62·7	O(4')-Ca(2)-O(2)	122·0	O(8)—Ca(3)-O(6)	124·0
O(7)—Ca(1)-O(10)	136·3	O(3)—Ca(2)-O(2)	148·0	O(7)—Ca(3)-O(6)	147·3

weighted residual $R_w = 0·100$. The anisotropic refinement, based on a data parameter ratio of 12·4 to 1 with 139 independently varied parameters, yielded a final $R = 0·035$ and $R_w = 0·050$ for the observed data.* The four scale factors refined to 1·98 (1), 2·12 (2), 2·10 (1) and 2·18 (2). There was a significant correlation (of the order of 0·4) between the scale factors and the thermal parameters $\beta_{11}, \beta_{22}, \beta_{33}$ of the metal atoms but for each atom the magnitude of the correlation was roughly the same for all four scale factors. The correlation between scale factors and metal occupancies (see below) was low. In the final refinement, the maximum extinction correction (Zachariasen, 1968) was 17% of $|F_o|$ for the 2,0,20 reflection.

Discussion

Table 1 represents the final atomic coordinates and anisotropic thermal parameters. Three Ca atoms on general positions are each eight-coordinated to O atoms at an average distance of 2·520 Å (2·320–3·008 Å). Table 2 lists the angles and distances for the Ca polyhedra which are comparable to those found in Mg-whitlockite and to the similar Ca sites in β-Ca₃(PO₄)₂ (Dickens *et al.*, 1974). The Mn atom is located at the origin on the threefold axis with two

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(×3) O atoms at 2·141 (4) Å. As summarized in Table 3, the octahedron is trigonally distorted. However, although the bond angles have a larger deviation from the ideal octahedral 90° than in the Mg analogue, the bond distances are essentially equal [they are 2·057 (5) and 2·077 (5) Å in Mg-whitlockite]. The two phosphate tetrahedra centered on general positions [P(2) and P(3)] are fairly regular with an average P–O distance of 1·535 Å and O–P–O angle of 109·2°. The third P atom [P(1)], located on the unique axis, has one (×3) O at 1·521 (3) Å and a unique O [O(9)] at 1·596 (9) Å. It is this O atom which is bonded to an H atom forming an HPO₄ group. Table 4 lists the bond angles and distances for the phosphate tetrahedra. The standard deviations for all bond lengths and angles were computed by the function and error program (*ORFFE*) of Busing, Martin & Levy (1964).

Table 3. *Bond distances, polyhedral edge lengths and bond angles for the manganese octahedron*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances (Å)

Mn–O(4) (3×)	2·141 (4)	Mn–O(8) (3×)	2·141 (4)
O(4)–O(4)	2·802 (6)	O(8)–O(8)	2·837 (6)
O(4)–O(8)	3·262 (4)	O(4)–O(8)	4·281 (4)
O(4)–O(8)	3·183 (4)		

(ii) Angles (°)

O(4)–Mn–O(4)	81·8 (1)	
O(4)–Mn–O(8)	99·3 (1)	
O(4)–Mn–O(8)	96·0 (1)	
O(8)–Mn–O(8)	83·0 (1)	
O(4)–Mn–O(8)	177·4 (3)	

Table 4. *Bond distances, polyhedral edge lengths and bond angles for the phosphate tetrahedra*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances (Å)

P(1)–O(9)	1·596 (9)	P(2)–O(1)	1·519 (4)	P(3)–O(7)	1·523 (4)
–O(10) (3×)	1·521 (3)	–O(2)	1·527 (3)	–O(6)	1·528 (3)
		–O(3)	1·540 (3)	–O(8)	1·546 (4)
		–O(4)	1·553 (4)	–O(5)	1·559 (4)

P(1) tetrahedron		P(2) tetrahedron		P(3) tetrahedron	
O(10)–O(10)	2·524 (5)	O(1)–O(2)	2·536 (5)	O(7)–O(6)	2·586 (5)
O(10)–O(9)	2·502 (8)	O(1)–O(3)	2·450 (4)	O(7)–O(8)	2·468 (4)
		O(1)–O(4)	2·544 (5)	O(7)–O(5)	2·483 (4)
		O(2)–O(3)	2·565 (5)	O(6)–O(8)	2·473 (4)
		O(2)–O(4)	2·477 (5)	O(6)–O(5)	2·482 (5)
		O(3)–O(4)	2·453 (4)	O(8)–O(5)	2·580 (5)

(ii) Angles (°)

P(1) tetrahedron		P(2) tetrahedron		P(3) tetrahedron	
O(10)–P(1)–O(10)	112·1 (1)	O(1)–P(2)–O(2)	112·7 (2)	O(7)–P(3)–O(6)	115·9 (2)
O(10)–P(1)–O(9)	106·7 (2)	O(1)–P(2)–O(3)	106·5 (2)	O(7)–P(3)–O(8)	107·1 (2)
		O(1)–P(2)–O(4)	111·8 (2)	O(7)–P(3)–O(5)	107·3 (2)
		O(2)–P(2)–O(3)	113·6 (2)	O(6)–P(3)–O(8)	107·1 (2)
		O(2)–P(2)–O(4)	107·2 (2)	O(6)–P(3)–O(5)	107·1 (2)
		O(3)–P(2)–O(4)	105·0 (2)	O(8)–P(3)–O(5)	112·5 (2)

As the details of the whitlockite structure have been adequately described (Gopal *et al.*, 1974), no further discussion is necessary. However, the question of the distribution of Mn atoms over the various cation sites has been raised (Calvo & Gopal, 1975). Varying only the metal occupancies in an anisotropic refinement resulted in occupancy parameters of 0·326 (2), 1·008 (5), 1·011 (5) and 0·984 (5) for Mn, Ca(1), Ca(2) and Ca(3) respectively. Furthermore, our e.s.r. data indicated a single Mn^{2+} ion on an octahedral site with rather broad ($\sim$20 G) line widths due to the relatively high concentration. No e.s.r. evidence was found for Mn^{2+} in other (eight-coordinated) sites. As expected, Mn^{2+} prefers the six-coordinated position.

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