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The Crystal Structure of Monocalcium Phosphate Monohydrate, $Ca(H_2PO_4)_2.H_2O$

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A complete determination has been made of the positions of the calcium, phosphorus and oxygen atoms in the structure of monocalcium phosphate monohydrate. The crystal is triclinic with space group $P\bar{1}$, and the cell dimensions are:

$$a = 5{\cdot}61,\ b = 11{\cdot}89,\ c = 6{\cdot}46\ \text{Å};$$
$$\alpha = 98^\circ\ 36',\ \beta = 118^\circ\ 0',\ \gamma = 83^\circ\ 23'\ .$$

The atomic coordinates found are given in the paper.

The structure consists of parallel sheets of atoms of composition $CaPO_4$, these being identical with the corrugated sheets previously described in $CaHPO_4.2H_2O$ (brushite) and very similar to the sheets of $CaSO_4$ in gypsum. In the present structure the sheets are separated by PO_4''' ions and water molecules, instead of by water molecules alone as in brushite and gypsum, and this causes a lowering of the symmetry from monoclinic to triclinic. The crystal form, the twinning and the overgrowths on gypsum are nicely explained by the structure. These properties are expected to be of considerable significance in understanding more fully the reaction between sulphuric acid and apatite to give superphosphate or phosphoric acid, and in explaining the properties and behaviour of superphosphates.

Introduction

The crystal structure of monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2.H_2O$, was investigated as part of a programme of research into calcium phosphate structures of interest and use in fertilizer manufacture. This work is being undertaken in collaboration with the Research Department of Scottish Agricultural Industries Limited.

Structural determinations on fluorapatite (Beevers & MacIntyre, 1946), on dicalcium phosphate dihydrate (Beevers & Raistrick, 1954) and on anhydrous dicalcium phosphate (MacLennan & Beevers, 1955) have already been published. $Ca(H_2PO_4)_2.H_2O$ is the principal phosphate compound in the ordinary superphosphate fertilizer of commerce, and its structure is therefore of great practical interest.

The crystal morphology was first described by Haushofer (1883) as triclinic pinacoidal, and the optical properties and unit-cell dimensions have recently been determined (Lehr, Smith & Brown, 1952). The latter authors point out some similarities in cell dimensions with gypsum, and suggest that the structures may be analogous in some respects.

Experimental

Small platy crystals of $Ca(H_2PO_4)_2.H_2O$ were obtained by slowly cooling a solution of calcium hydroxide in phosphoric acid. The crystals are tabular on the (010) face, and microscopic examination revealed highly developed polysynthetic twinning according to the albite law, and contact twinning according to the Carlsbad law. No suitable single-crystal specimen could be found, and eventually a large plate, about 1 mm. square, was carefully cleaved into successively smaller fragments until an untwinned specimen was obtained. This was a lath-shaped fragment, $0{\cdot}7 \times 0{\cdot}2 \times 0{\cdot}1$ mm., elongated along the *a* axis. Oscillation and Weissenberg photographs were taken about the principal axes, using Cu $K\alpha$ radiation and a 5 cm.-radius Weissenberg camera. The unit-cell dimensions were obtained from high order $0kl$, $h0l$ and $hk0$ reflexions. The results were:

$$a = 5{\cdot}61 \pm 0{\cdot}01,\ b = 11{\cdot}89 \pm 0{\cdot}02,\ c = 6{\cdot}46 \pm 0{\cdot}01\ \text{Å};$$
$$\alpha = 98^\circ\ 36',\ \beta = 118^\circ\ 0',\ \gamma = 83^\circ\ 23'\ .$$

If this cell contains two molecules of $Ca(H_2PO_4)_2.H_2O$, the calculated specific gravity is 2·23, compared with an observed value of 2·22 (Bassett, 1908). The space group is $P\bar{1}$; and we have confirmed the presence of the morphological centre of symmetry by the statistical test of Howells, Phillips & Rogers (1950).

The reflexion intensities were estimated by visual comparison, using multiple exposures, and were corrected for Lorentz and polarization factors. They were placed approximately on an absolute scale by the method of Wilson (1942), though the curves obtained were rather unsatisfactory because of the high absorption. This also prevented measurement of the temperature factor.

Structure determination

In the space-group $P\bar{1}$ the general positions are two-fold, and, since there is one $Ca(H_2PO_4)_2.H_2O$ molecule in the unique volume of the cell, all the atoms can be in general positions. However, there are only three unique heavy atoms, giving rise to nine distinct non-

Table 1. *Values of* F_o *and* F_c *for the* (*hk*0), (*h*0*l*) *and* (0*kl*) *planes of* $Ca(H_2PO_4)_2.H_2O$

hkl	F_o	F_c
010	–	38
020	19	17
030	9	1
040	38	$\overline{43}$
050	22	24
060	48	$\overline{51}$
070	5	$\bar{2}$
080	24	26
090	11	11
0,10,0	33	33
0,11,0	34	29
0,12,0	16	15
0,13,0	22	$\overline{19}$
0,14,0	34	$\overline{31}$
0,15,0	24	$\overline{35}$
100	20	$\overline{16}$
110	20	17
120	59	97
130	35	28
140	40	48
150	10	$\bar{6}$
160	31	$\overline{27}$
170	12	12
180	42	$\overline{39}$
190	34	$\overline{27}$
1,10,0	6	6
1,11,0	18	15
1,12,0	50	46
1,13,0	40	31
1,14,0	10	9
1,15,0	8	8
$1\bar{1}0$	5	$\bar{2}$
$1\bar{2}0$	82	$\overline{98}$
$1\bar{3}0$	46	$\overline{47}$
$1\bar{4}0$	25	$\overline{21}$
$1\bar{5}0$	9	$\bar{7}$
$1\bar{6}0$	33	32
$1\bar{7}0$	20	12
$1\bar{8}0$	28	24
$1\bar{9}0$	30	24
$1,\overline{10},0$	16	$\overline{16}$
$1,\overline{11},0$	36	$\overline{30}$
$1,\overline{12},0$	30	$\overline{21}$
$1,\overline{13},0$	39	$\overline{29}$
$1,\overline{14},0$	10	$\overline{15}$
200	40	$\overline{40}$
210	0	$\bar{8}$
220	38	$\overline{36}$
230	15	$\overline{15}$
240	56	70
250	17	18
260	52	63
270	7	8
280	20	$\overline{21}$
290	4	5
2,10,0	60	$\overline{58}$
2,11,0	24	$\overline{11}$
2,12,0	18	$\bar{8}$
2,13,0	11	$\bar{8}$
2,14,0	32	29
$2\bar{1}0$	7	$\bar{8}$
$2\bar{2}0$	35	$\overline{24}$
$2\bar{3}0$	27	17
$2\bar{4}0$	47	42
$2\bar{5}0$	50	56
$2\bar{6}0$	23	29
$2\bar{7}0$	6	4
$2\bar{8}0$	9	$\bar{9}$
$2\bar{9}0$	50	$\overline{52}$
$2,\overline{10},0$	20	$\overline{10}$
$2,\overline{11},0$	27	$\overline{18}$
$2,\overline{12},0$	5	$\bar{4}$
$2,\overline{13},0$	24	18
$2,\overline{14},0$	7	$\bar{7}$
300	30	29
310	25	$\overline{17}$
320	35	$\overline{31}$
330	0	$\bar{6}$
340	46	$\overline{52}$
350	4	$\bar{5}$
360	20	26
370	36	46
380	52	69
390	4	$\bar{1}$
3,10,0	5	7
3,11,0	0	13
3,12,0	36	$\overline{20}$
3,13,0	13	$\bar{7}$
$3\bar{1}0$	22	17
$3\bar{2}0$	22	15
$3\bar{3}0$	22	22
$3\bar{4}0$	21	25
$3\bar{5}0$	4	$\bar{1}$
$3\bar{6}0$	28	$\overline{36}$
$3\bar{7}0$	46	$\overline{67}$
$3\bar{8}0$	21	$\overline{24}$
$3\bar{9}0$	6	$\bar{2}$
$3,\overline{10},0$	12	$\overline{13}$
$3,\overline{11},0$	30	20
$3,\overline{12},0$	10	6
$3,\overline{13},0$	12	14
400	6	$\bar{3}$
410	31	27
420	23	16
430	4	$\bar{5}$
440	25	$\overline{26}$
450	35	$\overline{44}$
460	30	$\overline{35}$
470	6	$\bar{9}$
480	0	$\bar{2}$
490	10	6
4,10,0	42	40
4,11,0	16	13
4,12,0	15	13
$4\bar{1}0$	31	29
$4\bar{2}0$	4	$\bar{3}$
$4\bar{3}0$	30	$\overline{44}$
$4\bar{4}0$	19	$\overline{19}$
$4\bar{5}0$	32	$\overline{45}$
$4\bar{6}0$	0	$\bar{6}$
$4\bar{7}0$	0	$\bar{2}$
$4\bar{8}0$	0	$\bar{9}$
$4\bar{9}0$	39	39
$4,\overline{10},0$	15	18
$4,\overline{11},0$	14	12
500	0	$\bar{1}$
510	15	13
520	20	19
530	30	34
540	21	15
550	0	3
560	11	0
570	14	$\overline{15}$
580	21	$\overline{30}$
590	9	$\overline{16}$
5,10,0	14	$\overline{20}$
$5\bar{1}0$	35	$\overline{44}$
$5\bar{2}0$	18	$\overline{19}$
$5\bar{3}0$	22	$\overline{22}$
$5\bar{4}0$	0	$\bar{5}$
$5\bar{5}0$	17	30
$5\bar{6}0$	0	$\bar{2}$
$5\bar{7}0$	24	23
$5\bar{8}0$	14	18
600	21	$\overline{28}$
610	24	$\overline{48}$
620	12	$\bar{9}$
630	2	4
640	0	$\bar{4}$
650	16	16
660	11	12
$6\bar{1}0$	16	$\overline{12}$
$6\bar{2}0$	0	$\bar{3}$
$6\bar{3}0$	17	17
$6\bar{4}0$	5	10
001	25	$\overline{28}$
002	39	$\overline{47}$
003	16	14
004	22	15
005	23	20
006	22	$\overline{17}$
007	11	$\overline{12}$
101	29	29
102	3	$\overline{12}$
103	0	3
104	51	43
105	15	$\overline{16}$
106	0	$\bar{2}$
$10\bar{1}$	10	$\bar{6}$
$10\bar{2}$	46	47
$10\bar{3}$	42	$\overline{33}$
$10\bar{4}$	10	5
$10\bar{5}$	8	1
$10\bar{6}$	48	39
$10\bar{7}$	15	17
201	13	17
202	54	85
203	33	$\overline{46}$
204	26	$\overline{24}$
205	12	6
$20\bar{1}$	35	14
$20\bar{2}$	22	17
$20\bar{3}$	58	49
$20\bar{4}$	16	$\bar{7}$
$20\bar{5}$	35	$\overline{29}$
$20\bar{6}$	50	37
$20\bar{7}$	8	$\overline{12}$
$20\bar{8}$	14	$\overline{10}$
301	7	10
302	0	0
303	13	16
304	16	$\overline{18}$
305	5	10
$30\bar{1}$	47	$\overline{45}$
$30\bar{2}$	0	4
$30\bar{3}$	16	$\overline{19}$
$30\bar{4}$	17	11
$30\bar{5}$	36	42
$30\bar{6}$	48	$\overline{38}$
$30\bar{7}$	4	$\bar{5}$
$30\bar{8}$	44	32
401	0	$\bar{2}$
402	24	$\overline{29}$
403	0	9
$40\bar{1}$	22	22
$40\bar{2}$	24	$\bar{9}$
$40\bar{3}$	22	$\overline{20}$
$40\bar{4}$	43	43
$40\bar{5}$	0	2
$40\bar{6}$	18	$\overline{23}$
$40\bar{7}$	4	5
$40\bar{8}$	24	$\overline{11}$
501	0	$\overline{17}$
502	11	19
$50\bar{1}$	4	0
$50\bar{2}$	4	$\overline{17}$
$50\bar{3}$	27	31
$50\bar{4}$	43	$\overline{39}$
$50\bar{5}$	0	$\overline{15}$
$50\bar{6}$	24	24
$50\bar{7}$	17	$\overline{12}$
$60\bar{1}$	13	$\overline{18}$
$60\bar{2}$	23	26
$60\bar{3}$	4	5
$60\bar{4}$	12	$\overline{19}$
$60\bar{5}$	5	6
$60\bar{6}$	14	$\overline{13}$
$60\bar{7}$	9	15
$70\bar{2}$	11	$\overline{21}$
$70\bar{3}$	17	$\overline{10}$
$70\bar{4}$	16	23
011	31	43
021	33	$\overline{39}$
031	8	6
041	4	7
051	29	$\overline{30}$
061	14	$\overline{13}$
071	32	$\overline{34}$
081	21	$\overline{15}$
091	12	14
0,10,1	4	$\bar{5}$
0,11,1	0	$\overline{10}$
0,12,1	8	1
0,13,1	16	$\overline{13}$
0,14,1	0	$\bar{3}$
$0\bar{1}1$	8	$\bar{9}$
$0\bar{2}1$	30	26
$0\bar{3}1$	25	$\overline{30}$
$0\bar{4}1$	33	42
$0\bar{5}1$	6	$\bar{3}$
$0\bar{6}1$	14	9
$0\bar{7}1$	40	41
$0\bar{8}1$	3	$\bar{4}$
$0\bar{9}1$	10	15
$0,\overline{10},1$	11	8
$0,\overline{11},1$	11	$\bar{4}$
$0,\overline{12},1$	10	6
$0,\overline{13},1$	7	$\bar{1}$
$0,\overline{14},1$	9	4
$0,\overline{15},1$	15	20
012	35	$\overline{47}$
022	37	$\overline{36}$
032	21	16
042	41	50
052	40	40
062	15	12
072	3	$\bar{7}$
082	8	$\bar{8}$
092	52	$\overline{51}$
0,10,2	17	$\overline{19}$
0,11,2	12	$\bar{8}$
0,12,2	3	$\bar{6}$
0,13,2	28	28
0,14,2	4	6
$0\bar{1}2$	0	$\bar{5}$
$0\bar{2}2$	59	$\overline{74}$
$0\bar{3}2$	35	$\overline{35}$
$0\bar{4}2$	36	37
$0\bar{5}2$	19	19
$0\bar{6}2$	47	65
$0\bar{7}2$	4	$\bar{1}$
$0\bar{8}2$	0	$\bar{8}$
$0\bar{9}2$	10	$\bar{8}$
$0,\overline{10},2$	52	$\overline{61}$
$0,\overline{11},2$	8	$\bar{6}$
$0,\overline{12},2$	14	$\bar{5}$
$0,\overline{13},2$	3	$\bar{4}$
$0,\overline{14},2$	26	19
$0,\overline{15},2$	2	7
013	16	$\overline{20}$
023	14	$\overline{11}$
033	6	2
043	20	20
053	3	0
063	0	$\bar{6}$
073	13	$\overline{10}$
083	9	8
093	22	21
0,10,3	27	$\overline{25}$
0,11,3	0	$\bar{5}$
0,12,3	9	$\bar{4}$
0,13,3	4	$\bar{4}$
$0\bar{1}3$	14	$\overline{14}$
$0\bar{2}3$	4	2
$0\bar{3}3$	41	41
$0\bar{4}3$	16	$\overline{19}$
$0\bar{5}3$	16	10
$0\bar{6}3$	30	$\overline{29}$
$0\bar{7}3$	0	$\bar{7}$
$0\bar{8}3$	29	31
$0\bar{9}3$	31	$\overline{34}$
$0,\overline{10},3$	19	15
$0,\overline{11},3$	0	7
$0,\overline{12},3$	11	1
$0,\overline{13},3$	19	20
$0,\overline{14},3$	18	$\overline{21}$
014	3	3
024	17	$\overline{16}$
034	33	$\overline{42}$
044	19	$\overline{18}$
054	29	$\overline{36}$
064	19	$\overline{20}$
074	21	23
084	13	10
094	33	31
0,10,4	30	24
0,11,4	7	1
$0\bar{1}4$	48	52
$0\bar{2}4$	27	22
$0\bar{3}4$	10	$\overline{14}$
$0\bar{4}4$	17	$\overline{12}$
$0\bar{5}4$	33	$\overline{41}$
$0\bar{6}4$	30	$\overline{34}$
$0\bar{7}4$	13	$\bar{9}$
$0\bar{8}4$	22	$\overline{25}$
$0\bar{9}4$	19	14
$0,\overline{10},4$	22	18
$0,\overline{11},4$	21	15
$0,\overline{12},4$	25	41
$0,\overline{13},4$	2	0
015	10	$\overline{12}$
025	4	3
035	30	30
045	5	$\bar{4}$
055	18	14
065	17	$\overline{17}$
075	0	$\bar{1}$
085	30	38
095	0	$\bar{1}$
0,10,5	2	9
$0\bar{1}5$	20	$\overline{17}$
$0\bar{2}5$	4	$\bar{4}$
$0\bar{3}5$	0	6
$0\bar{4}5$	0	$\bar{2}$
$0\bar{5}5$	8	$\bar{8}$
$0\bar{6}5$	19	$\overline{13}$
$0\bar{7}5$	6	$\bar{2}$
$0\bar{8}5$	13	14
$0\bar{9}5$	9	3
$0,\overline{10},5$	29	$\overline{29}$
$0,\overline{11},5$	0	$\bar{5}$
$0,\overline{12},5$	9	$\bar{9}$
016	22	19
026	11	12
036	28	29
046	35	37
056	9	8
066	13	14
076	19	$\overline{15}$
$0\bar{1}6$	23	$\overline{23}$
$0\bar{2}6$	14	$\overline{10}$
$0\bar{3}6$	17	$\overline{13}$
$0\bar{4}6$	14	10
$0\bar{5}6$	20	24
$0\bar{6}6$	24	24
$0\bar{7}6$	34	38
$0\bar{8}6$	18	22
$0\bar{9}6$	11	$\overline{12}$
$0,\overline{10},6$	3	$\bar{8}$
017	9	$\overline{10}$
027	5	1
037	4	$\bar{5}$
$0\bar{1}7$	11	10
$0\bar{2}7$	11	$\overline{11}$
$0\bar{3}7$	13	10
$0\bar{4}7$	13	22
$0\bar{5}7$	6	$\bar{8}$
$0\bar{6}7$	3	2

origin interatomic vectors, so that it seemed probable that two-dimensional Patterson syntheses would suffice to locate these atoms. The projections including the long b axis were likely to provide the best resolution of vectors. The (0*kl*) and the (*hk*0) Patterson functions were calculated at intervals of 30ths of a and c, and 60ths of b. For these and subsequent Fourier summations, an electrical analogue computer of the Hägg–Laurent type, built by Dr F. Stern, was employed.

The vector distribution obtained indicated that two of the heavy atoms must be superposed on the (*hk*0) projection, in positions separated by very nearly $(0, 0, \frac{1}{2})$. These must be the Ca atoms and one P atom since $\frac{1}{2}c$ (= 3·2 Å) is too small a separation between two PO_4 groups. Interpretation of the (*hk*0) projection was thus simplified to the case of two heavy atoms, ($Ca+P_1$) and P_2. There are only four vectors to identify, three of which involve the superposed atoms and so are much heavier than any others. These were easily identifiable and the fourth was located after examination of the three possible combinations utilizing the heavy vector peaks. The atomic positions thus chosen were used to calculate structure factors for the (*hk*0) projection, giving a factor $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ of 0·43. A Fourier projection, using 110 F_o terms which could be given signs, was then computed. Peaks corresponding to suitable oxygen positions were located on this map, and a complete trial structure on the (*hk*0) projection was thus obtained. Structure factors calculated on this basis gave $R = 0{\cdot}32$, after F_o had been multiplied by a scale factor given by $\Sigma|F_c|\div\Sigma|F_o|$. Refinement by difference Fourier syntheses indicated that the Ca and P_1 atoms should be separated slightly in the a direction, and attention was therefore given to the other projections in order to discover how these atoms should be moved.

The z parameters of the Ca and P atoms were obtained from the (0*kl*) Patterson map by comparison of the vector distribution with that determined on (*hk*0). Structure factors calculated for these atoms gave $R = 0{\cdot}48$, and the oxygen positions were obtained from a Fourier projection. For the complete trial structure, using the planes (0*kl*), R was 0·39, and five cycles of refinement were subsequently carried out. The best x and z parameters obtained from these were then used to calculate the (*h*0*l*) projection, which is unsuitable for detailed refinement because of the small area, several pairs of atoms being superposed. For this projection R proved to be 0·34, and a difference synthesis revealed the directions in which Ca and P should be moved along the a axis. When these shifts had been made, and the structure factors for all three projections had been recalculated using the mean parameters from the separate refinements, the following final residual errors were obtained:

$$R(0kl) = 0{\cdot}214,\ R(hk0) = 0{\cdot}230,\ R(h0l) = 0{\cdot}287\ .$$

For the reflexions in the three two-dimensional zones taken all together R was 0·235. This figure includes reflexions of observed zero intensity, and no corrections have been applied for extinction or for a temperature factor. The values of F_o and F_c for the three zones are given in Table 1. As a final check of the validity of the structure, structure factors for the planes with $h = 1$ were calculated. A satisfactory degree of agreement was obtained with $R = 0{\cdot}27$.

The final atomic parameters, in 360ths of the cell edges, are:

	x	y	z
Ca	262	37	278
P_1	270	35	99
P_2	127	134	222
O_1	216	9	123
O_2	324	9	63
O_3	336	63	183
O_4	204	69	33
O_5	135	90	216
O_6	60	147	261
O_7	228	150	282
O_8	81	147	135
H_2O	24	90	0

A two-dimensional Fourier synthesis for the final structure, projected down the a axis, is shown in Fig. 1.

The accuracy of the determination was estimated using the equations given by Cruickshank (1949). The standard deviation in electron density is $\sigma(\varrho) = 1{\cdot}2$ e.Å^{-2} on the $(0kl)$ projection. The standard deviation in atomic coordinates in the c direction is $\sigma(z) = 0{\cdot}008$ Å for Ca, 0·010 Å for P, and 0·036 Å for O. The standard deviations in bond lengths are:

$$\text{Ca–O} = 0{\cdot}037,\ \text{P–O} = 0{\cdot}039,\ \text{O–O} = 0{\cdot}050\ \text{Å}\ .$$

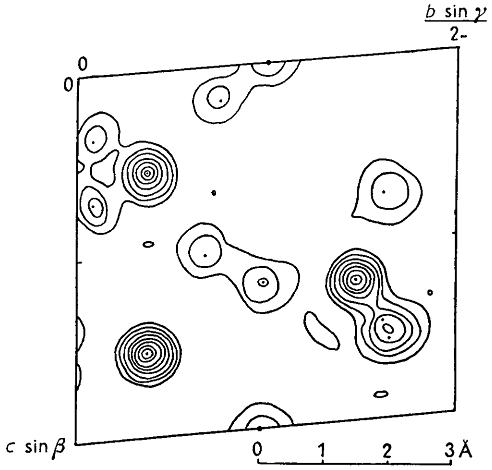

Fig. 1. Electron-density projection of $Ca(H_2PO_4)_2.H_2O$, viewed down the a axis. Contours at 5, 10, 15, ..., 45 e.Å^{-2}.

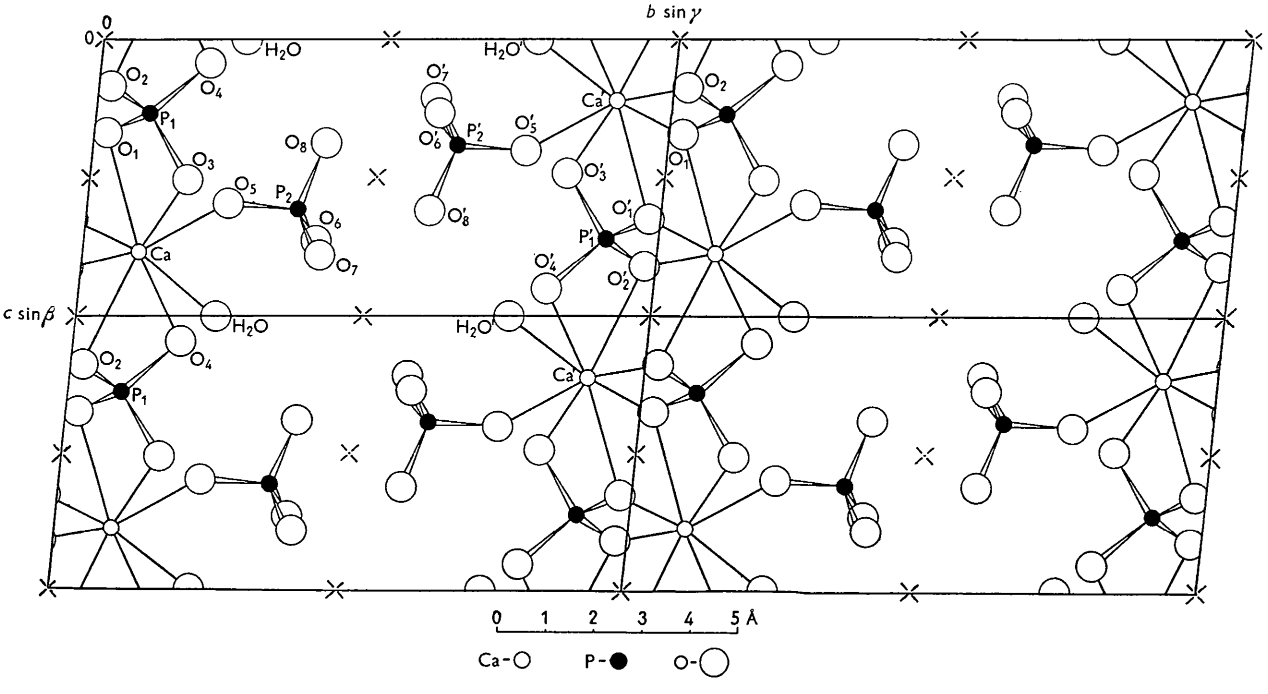

Fig. 2. Four unit cells of $Ca(H_2PO_4)_2 \cdot H_2O$, projected down the a axis.

Description of the structure

As in all orthophosphates, the structure of this one consists essentially of discrete PO_4''' tetrahedra and Ca^{++} ions, the latter coordinated by a shell of oxygen atoms. Fig. 2 shows a projection of the structure down the *a* axis, the contents of four cells being included. The outstanding feature is the presence of sheets of composition $CaPO_4$ in the (010) plane. These sheets are virtually identical with those found in $CaHPO_4.2H_2O$ (Beevers & Raistrick, 1954), and hence analogous to the sheets of $CaSO_4$ in gypsum (Wooster, 1936).

The sheets contain parallel chains of composition

$$=Ca=PO_4=Ca=PO_4=$$

along the *c* axis. Adjoining chains in the sheet differ in height along the *b* axis by 2·3 Å, to give a corrugation effect, the higher set of chains being related to the lower by centres of symmetry. The distance between sheets is equal to the (010) spacing, and the sheets are separated by the water molecules coordinated to the calcium ions, and by the remaining PO_4 tetrahedra, which face each other in pairs across the centres of symmetry, in a similar orientation to that reported in the structure of H_3PO_4 (Smith, Brown & Lehr, 1955).

Along the chains, the Ca atom is coordinated to O_1 and O_3 on the one side, and O_2 and O_4 on the other, and it is in contact with O_1' and O_2' of the neighbouring chain. Its total coordination of eight is made up by bonds to the water molecule and to O_5 belonging to the second phosphate group. In the structure of $CaHPO_4.2H_2O$, the place of O_5 is taken by the second water molecule, and the sheets are therefore closer together, being in fact at $\frac{1}{2}b = 7{\cdot}59$ Å apart. Successive sheets are rotated through 180°. This is the only major difference between the two structures, and gives rise to the change of symmetry from monoclinic to triclinic.

The observed bond lengths and angles are:

P_1–O_1 = 1·50 Å Ca–O_1 = 2·57 Å
P_1–O_2 = 1·43 Ca–O_2 = 2·59
P_1–O_3 = 1·59 Ca–O_3 = 2·74
P_1–O_4 = 1·64 Ca–O_4 = 2·65
P_2–O_5 = 1·44 Ca–O_5 = 2·44
P_2–O_6 = 1·50 Ca–O_1' = 2·30
P_2–O_7 = 1·54 Ca–O_2' = 2·36
P_2–O_8 = 1·49 Ca–H_2O = 2·49

O_1–P_1–O_2 = 109·0° O_5–P_2–O_6 = 105·5°
O_1–P_1–O_3 = 106·5 O_5–P_2–O_7 = 108·0
O_1–P_1–O_4 = 116·5 O_5–P_2–O_8 = 109·0
O_2–P_1–O_3 = 113·5 O_6–P_2–O_7 = 109·0
O_2–P_1–O_4 = 108·5 O_6–P_2–O_8 = 109·0
O_3–P_1–O_4 = 102·5 O_7–P_2–O_8 = 115·5

The average P–O bond length is 1·52 Å, the average Ca–O bond length is 2·52 Å, and the average O–O distance within the PO_4 group is 2·48 Å.

It has not been found feasible to identify the six hydrogen positions in a direct manner. It is probable that these atoms lie between oxygens of neighbouring phosphate tetrahedra and also near the oxygen of the water molecule, forming hydrogen bonds. The shortest O–O distances found are:

O_3–O_5 = 2·50 Å O_1–O_1' = 2·91 Å
O_7–O_8' = 2·79 O_2–O_2' = 2·92
H_2O–O_4 = 2·61 H_2O–O_6 = 3·00
H_2O–O_8 = 2·68

Some at least of these close contacts will correspond to hydrogen bonds, those which serve to link neighbouring sheets in the structure being especially likely.

The structure thus consists of parallel sheets of $CaPO_4$, identical with those in brushite, separated by water molecules and phosphate ions, the sheets being held together by hydrogen bonding. This description agrees with the observed crystal habit, which is tabular on (010) with elongation parallel to the *c* axis. The occurrence of oriented overgrowths of monocalcium phosphate on gypsum crystals, described by Lehr *et al.* (1952), forms additional confirmation of the presence of identical sheets in the two structures. The almost invariable presence of multiple twinning according to the albite law, i.e. with (010) as the twinning and composition plane, is also accounted for, since it corresponds merely to a misorientation of successive sheets by 180° around an axis perpendicular to (010). In brushite and gypsum there are screw axes already in this position so that alternate sheets are always disposed in this manner. The substitution of albite twinning for this regular alternation corresponds to the loss of monoclinic symmetry.

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