

CRYSTALLOGRAPHY OF MONOCALCIUM AND DICALCIUM PHOSPHATES

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ABSTRACT

Optics and lattice constants are reported for three triclinic calcium orthophosphates. The lattice constants are: anhydrous monocalcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, $a=5.55 \text{ \AA}$, $b=7.60 \text{ \AA}$, $c=9.07 \text{ \AA}$, $\alpha=121^\circ 54'$, $\beta=108^\circ 48'$, $\gamma=87^\circ 28'$; monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $a=5.67 \text{ \AA}$, $b=11.92 \text{ \AA}$, $c=6.51 \text{ \AA}$, $\alpha=99^\circ 50'$, $\beta=118^\circ 31'$, $\gamma=83^\circ 9'$; and anhydrous dicalcium phosphate, CaHPO_4 , $a=6.91 \text{ \AA}$, $b=6.66 \text{ \AA}$, $c=7.02 \text{ \AA}$, $\alpha=96^\circ 7'$, $\beta=103^\circ 53'$, $\gamma=89^\circ 11'$. A structural similarity between monocalcium phosphate monohydrate and dicalcium phosphate dihydrate is postulated.

INTRODUCTION

Primary and secondary calcium orthophosphates are major components of most of the phosphate fertilizer used in the world and are present also in other products of the chemical industry. The primary or monocalcium salt occurs in the anhydrous form, $\text{Ca}(\text{H}_2\text{PO}_4)_2$, and as the monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The secondary or dicalcium salt occurs in anhydrous form, CaHPO_4 , and as the dihydrate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. Both forms of the dicalcium salt are found as natural minerals—the anhydrous form as monetite and the hydrate as brushite.

X-ray studies of single crystals have been reported for only one of these crystalline calcium phosphates. Hill and Hendricks (1936) and Terpstra (1937) predicted from their x-ray study of single crystals that dicalcium phosphate dihydrate would be found essentially isostructural with gypsum—a prediction confirmed recently by Beevers and Raistrick (1954). X-ray powder diffraction patterns and refractive indices of the mono- and dicalcium phosphates were reported by Hill and Hendricks (1936) and by Bale *et al.* (1945). Haushofer (1883) and Schulten (1904) reported axial ratios and interaxial angles of monocalcium phosphate monohydrate and anhydrous dicalcium phosphate from goniometric measurements.

The results of x-ray measurements on single crystals of monocalcium phosphate—anhydrous and monohydrated—and of anhydrous dicalcium phosphate are presented here. The optical properties of the three compounds also are covered more completely than has been done heretofore.

OPTICAL AND X-RAY EXAMINATIONS

The crystals were synthetic. Their refractive indices were measured at 25°C . with calibrated oils and Corning filters. Optic angle $2V$ was computed from the refractive indices.

The x -ray photographs were made with a Weissenberg camera 57.3 mm. in diameter and with copper K_{α} radiation ($\lambda = 1.54 \text{ \AA}$). To the extent possible, the reciprocal angles were determined by the method of triangulation (Buerger, 1942). The axial lengths were determined to within ± 0.2 per cent and the angles to within $\pm 0.3^{\circ}$.

Single-crystal x -ray data and some of the optical data for the three compounds are shown in Table 1. Several additional points about the crystallography of each compound are given in the text. The optical descriptions are in terms of the axes selected from x -ray measurements.

TABLE 1. OPTICAL AND SINGLE-CRYSTAL X -RAY DATA FOR ANHYDROUS MONOCALCIUM PHOSPHATE, MONOCALCIUM PHOSPHATE MONOHYDRATE, AND ANHYDROUS DICALCIUM PHOSPHATE

	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	CaHPO_4
Symmetry	Triclinic, pinacoidal	Triclinic, pinacoidal	Triclinic, pinacoidal
Refractive indices:			
425 $m\mu$	$\begin{cases} N_{\alpha} & 1.543 \\ N_{\beta} & 1.567 \\ N_{\gamma} & 1.596 \end{cases}$	$\begin{cases} 1.492 \\ 1.512 \\ 1.526 \end{cases}$	$\begin{cases} 1.586 \\ 1.613 \\ 1.635 \end{cases}$
610 $m\mu$	$\begin{cases} N_{\alpha} & 1.548 \\ N_{\beta} & 1.572 \\ N_{\gamma} & 1.602 \end{cases}$	$\begin{cases} 1.496 \\ 1.515 \\ 1.529 \end{cases}$	$\begin{cases} 1.588 \\ 1.616 \\ 1.640 \end{cases}$
Birefringence (610 $m\mu$)	.054	.033	.052
Optic sign	Biaxial (+)	Biaxial (-)	Biaxial (-)
Optic angle $2V$ (610 $m\mu$)	$85^{\circ} 14'$	$81^{\circ} 30'$	$84^{\circ} 4'$
Dispersion	$r < v$, very weak	$r > v$, very weak	$r > v$, weak
Cleavage	None observed	(100) imperfect (001) imperfect	None observed
Space group	$P\bar{1}$ or $P1$	$P\bar{1}$ or $P1$	$P\bar{1}$ or $P1$
a	5.55 \AA	5.67 \AA	6.91 \AA
b	7.60	11.92	6.66
c	9.07	6.51	7.02
α	$121^{\circ} 54'$	$99^{\circ} 50'$	$96^{\circ} 7'$
β	$108^{\circ} 48'$	$118^{\circ} 31'$	$103^{\circ} 53'$
γ	$87^{\circ} 28'$	$83^{\circ} 9'$	$89^{\circ} 11'$
Cell contents	$2[\text{Ca}(\text{H}_2\text{PO}_4)_2]$	$2[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$	$4[\text{CaHPO}_4]$
Density- calc.	2.55	2.19	2.89
obs. ^a	2.546	2.22	2.89 ₂

^a Bassett (1908).

Anhydrous Monocalcium Phosphate

This salt crystallizes as colorless triclinic rods that are elongated parallel to the a -axis and as elongated tablets with $(01\bar{1})$, and sometimes (010) , as the tabular face. Twinning was not observed.

The N_α - N_β plane is perpendicular to (010) and essentially parallel to the a -axis, with N_β (the optic normal) inclined to (010) by 15° in obtuse γ .

The x -ray data in Table 1 are based upon rotation photographs and Weissenberg photographs (zero, first, and second layers) for the three primitive axial directions. The interaxial angles measured microscopically are in satisfactory agreement with those given in Table 1.

In a moist atmosphere the anhydrous crystal alters slowly to randomly oriented crystallites of the monohydrate. This observation and the apparently unrelated unit-cell dimensions of the two crystals indicate an absence of structural similarity.

Monocalcium Phosphate Monohydrate

This salt crystallizes as colorless triclinic (010) plates that are elongated parallel to the c -axis. Polysynthetic twinning according to the albite law is common, with (010) as the composition plane. Contact twinning on (001) with a as the twin axis, sometimes seen as penetration forms, is less common.

The obtuse bisectrix, N_γ , is parallel to (010) and is inclined to the a -axis by $2^\circ 40'$ in acute β . The N_α - N_β plane is perpendicular to (010) , with N_α inclined to (010) by 37° in obtuse α .

The lattice constants shown in Table 1 are based upon a rotation photograph and Weissenberg photographs (zero, first, second, and composite zero-second layers) from a c -axis setting. The tabulated values agree with those determined from a rotation pattern and a zero-layer Weissenberg photograph from an a -axis setting.

Haushofer (1883) reported the following interaxial angles and axial ratios for monocalcium phosphate monohydrate: $\alpha = 98^\circ 40'$, $\beta = 118^\circ 21'$, $\gamma = 83^\circ 16'$, $a:b:c = 0.4753:1:0.5448$. With the exception of the value for α , agreement with the x -ray values in Table 1 is good. The x -ray value for α was obtained from two different settings and is considered reliable.

Several of the crystals that were examined by the Weissenberg technique were twinned, and their reciprocal lattices proved that the twins were of the albite type.

A determination of the crystal structure may not be too difficult. If the usual dimensions of the phosphate ion are assumed and the positions of the hydrogens are ignored, a maximum of 18 parameters must be determined to specify the positions of the phosphate ions, calcium ions, and water molecules. The dimensions of the unit cell in the a and c

directions are relatively small, and most of the atoms therefore will be resolved clearly in Fourier projections. The weak intensities of the $0k0$ reflections for odd values of k suggest pseudosymmetry—a twofold screw axis or a layer-type structure with the layers perpendicular to b and with two similar but not identical layers for each unit cell. Monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, and gypsum have very similar lattice constants a , c , and β , as shown in Table 2. Haushofer (1883) also recognized a similarity between morphological elements of the two phosphates.

The structure of gypsum is known to comprise alternate layers of calcium sulfate and water molecules (Wooster, 1936). The a and c

TABLE 2. COMPARISON OF THE LATTICE CONSTANTS OF MONOCALCIUM PHOSPHATE MONOHYDRATE, DICALCIUM PHOSPHATE DIHYDRATE, AND CALCIUM SULFATE DIHYDRATE

Lattice Constant	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}^a$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}^b$
a	5.67 Å	5.812 Å	5.67 Å
b	11.92	15.180	15.15
c	6.51	6.239	6.51
β	118° 31'	116° 25'	118° 23'

^a Beevers and Raistrick (1954).

^b Simple alternative cell suggested by Bragg (1937).

directions of gypsum lie parallel to the plane of the calcium sulfate layers. The structure of monocalcium phosphate monohydrate apparently comprises similar layers—the shorter b resulting from an absence of two layers of water molecules. The stacking of the layers presumably results in a slight lateral displacement that shifts angles α and γ from 90°. The analogy may be extended to the striking similarity in the twinning of the two compounds. Both form contact twins with a as the twin axis. Gypsum does not form albite twins, because the twinning axis corresponds to one of its symmetry axes.

The similarities in crystallographic properties suggested a study of the overgrowth of the phosphate on gypsum. The phosphate was crystallized upon suspended blanks of gypsum that were cleaved along (010) from selected selenite stock. Thick, oriented overgrowths formed over large areas of the (010) faces of the gypsum. The overgrowths were predominantly of a type with the a and c axes of the two crystals parallel, and thus the (010) could be a composition plane. The relation of some of the

overgrowths to the substrate was analogous to the contact twinning exhibited by both compounds.

The confirmation of a close structural relation between the phosphate and gypsum would facilitate greatly a determination of the structure of the phosphate. Speculation on the basis of this structural analogy leads to a possibility that in monocalcium phosphate monohydrate the water of hydration occupies positions similar to the calcium sites, instead of the water sites, of gypsum—also that the phosphate structure comprises alternate layers with the respective compositions CaHPO_4 and $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$.

Anhydrous Dicalcium Phosphate

This salt crystallizes as colorless triclinic (010) tablets that are elongated parallel to the a -axis. Prismatic and rod habits also occur. The crystals are brittle with hackly fracture. Twinning was not observed.

The acute bisectrix, N_α , is oriented nearly perpendicular to $(11\bar{1})$ and is inclined 52° to the normal to (010) . The trace of the optic plane on $(11\bar{1})$ is inclined to the trace of (010) by 32° in obtuse γ . The extinction angles on the (010) are 15° with the (101) trace and 38° with the $(01\bar{1})$ trace. When the crystal is lying on (010) , a slight tilt in the direction of the fast component changes the extinction angle from 15° through the 23° -value reported by Hill and Hendricks (1936).

The x -ray data shown for this salt in Table 1 are based upon rotation and zero-layer Weissenberg photographs obtained from the three axes of the primitive cell. In addition, first- and second-layer Weissenberg photographs were obtained from the c -axis rotation. The x -ray data are brought into satisfactory agreement with Schulten's (1904) goniometric study of natural monetite through a transformation involving an assumption that the cell reported by him is b -centered with a b -axis twice that of the primitive cell. The comparison is shown in Table 3.

Hill and Hendricks (1936) noted a similarity between the powder patterns of anhydrous dicalcium phosphate and the orthorhombic anhydrous calcium sulfate (anhydrite). An additional similarity is evident from a comparison of the axial lengths:

	a	b	c
CaHPO_4	6.91 Å	6.66 Å	7.02 Å
CaSO_4	6.96	6.22	6.97

The similarity does not extend, however, to the axial angles. Although the general features of coordination in the two compounds may prove to be the same, considerable differences in structural details likely will be found.

TABLE 3. COMPARISON OF LATTICE CONSTANTS OF ANHYDROUS DICALCIUM PHOSPHATE AS DETERMINED FROM MORPHOLOGY AND FROM X-RAY MEASUREMENTS

Lattice Constant	Schulten Cell	Transformed X-ray Cell
$a:b:c$	0.647:1:0.824	0.645:1:0.824
α	84° 57'	85° 35'
β	90° 17'	90° 56'
γ	94° 22'	94° 20'

QUALITY OF SYNTHETIC MATERIALS

The chemical compositions of the synthetic crystals are compared with the theoretical compositions in Table 4. With the exception of liquid inclusions of negligible volume in the crystals of anhydrous monocalcium phosphate, extraneous phases were not detected in microscopic examinations.

Anhydrous monocalcium phosphate was crystallized over a 4-day period at 130° C. from a filtered solution that was prepared by dissolving 500 grams of recrystallized monocalcium phosphate monohydrate in 2000 ml. of an 81.5 per cent solution of phosphoric acid at the boiling point. The crystals were washed free of acid with anhydrous acetone on a heated funnel. They were oven-dried for 3 hours at 85° C. and then vacuum-dried for 4 days over anhydrous magnesium perchlorate.

Monocalcium phosphate monohydrate was thrice recrystallized from a 50 per cent solution of phosphoric acid. The final crystallization was done with slow cooling and constant stirring. The crystals were washed with acetone and vacuum-dried.

Anhydrous dicalcium phosphate was crystallized by slow interdiffusion of calcium nitrate and ammonium phosphate through a barrier of nitric acid at pH 3. Prepared from recrystallized reagents, the reactant solutions were 20 per cent $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (adjusted to pH 3 with nitric

TABLE 4. CHEMICAL COMPOSITION OF SYNTHETIC CRYSTALS

	CaO, per cent		P ₂ O ₅ , per cent	
	Found	Theoretical	Found	Theoretical
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	23.92 ^a	23.96	60.63 ^a	60.65
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	22.38 ^b	22.24	56.24 ^b	56.31
CaHPO_4	41.22 ^a	41.21	52.14 ^a	52.16

^a Average of four determinations.

^b Average of three determinations.

acid) and 20 per cent $\text{NH}_4\text{H}_2\text{PO}_4$. After 43 days of diffusion at 83°C . the resultant crystals were washed with hot water and then with acetone. They were dried at 105°C . for 72 hours. A chemical analysis showed an absence of nitrogen. The only significant impurity found in a spectrographic analysis was 0.03 per cent silica.

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