

Crystallography of Tetracalcium Phosphate*

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Tetracalcium phosphate, $\text{Ca}_4\text{O}(\text{PO}_4)_2$, has a monoclinic modification with the parameters $a = 11.99$, $b = 9.48$, and $c = 6.97$ Å, $\alpha = 90.8^\circ$, $z = 4$, and space group $\text{P}2_1$ or $\text{P}2_1/m$. From a comparison with the work of Trömel and Zamminer, it is concluded that this salt has monoclinic and orthorhombic modifications with the most probable space groups being $\text{P}2_1$ and $\text{P}2_122_1$, respectively.

The results support the view that tetracalcium phosphate has a layer-type structural relationship to hydroxyapatite, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. This would account, in part, for variations in the compositions of apatitic materials in which the ratio Ca/P is greater than 10/6, and it suggests that tetracalcium phosphate may be present in the mineral of tooth and bone.

Key Words: Hilgenstockite, tetracalcium phosphate, hydroxyapatite, bone mineral, tooth mineral, unit cell, symmetry, twinning.

1. Introduction

Tetracalcium phosphate (hilgenstockite), $\text{Ca}_4\text{O}(\text{PO}_4)_2$, the most basic calcium phosphate known, is a constituent of Thomas slag and of other basic calcium phosphate systems at high temperatures. Its major economic importance comes from the fact that it is a product of the reaction between phosphorus, oxygen and lime in the manufacture of iron [2, 22]³ and through this reaction has a significant role in controlling the properties of the metal. Since it has been prepared only at high temperatures and in systems substantially free of water, no biological significance has been attributed to it. The results of a single-crystal x-ray study reported here, however, give evidence that it has a structural relationship to hydroxyapatite, $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, the principal inorganic component of hard tissues, and as a result the possible involvement of tetracalcium phosphate in biological processes cannot be ruled out.

Early optical studies on tetracalcium phosphate have yielded somewhat divergent results. Its symmetry has been described as triclinic [18], as monoclinic [19], and as orthorhombic [8, 10, 16]. Prominent among its crystallographic properties is a pronounced tendency to twin polysynthetically. Its x-ray powder diffraction patterns have similarities to those of hydroxyapatite, and this has been taken to indicate that the two salts are structurally related [17, 20]. The two sets of powder patterns are sufficiently different, however, to indicate extensive structural dissimi-

larities. Trömel and Zamminer [23] reported approximate unit-cell constants for tetracalcium phosphate, but made no note of the similarities of the unit-cell dimensions and x-ray intensities of the two salts.

2. Experimental Methods

Equimolar mixtures of CaHPO_4 and CaCO_3 were heated at 1,500 °C. for 24 hr in a vacuum in platinum foil envelopes. The preparations obtained in this manner were very light green in color. In one instance the central portion of the fused mass was not discolored, indicating that the contamination may have been platinum from the foil. The crystals used in the petrographic and x-ray studies were fragments obtained by lightly crushing the fused product. Examination with the petrographic microscope revealed no significant contaminant phases; the characteristic OH-stretching frequency in the infrared spectrum of hydroxyapatite was completely absent as were peaks attributed to other known calcium phosphates and to carbonate [26].

A single setting (a axis) of a small crystal (largest dimension less than 0.1 mm) was used to collect five equi-inclination Weissenberg patterns ($h = 0$ through 4) and four precession photographs, $h0l$, $h1l$, $hk0$, and hkl , using Cu-K α radiation ($\lambda = 1.542$ Å). Several precession photographs were also obtained from a larger crystal with an [021] setting.

3. Results

3.1. Optical Results

The crystalline fragments were birefringent, positive, with indexes of refraction $N_\alpha = 1.644$, $N_\beta = 1.645$, $N_\gamma = 1.648$; wavy extinction was common; many displayed striations due to polysynthetic twinning.

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³ Italicized figures in brackets indicate the literature references at the end of this paper.

In some particles the twin domains were wedge shaped; in others the striations were parallel and uniformly spaced. The direction of minimum index in any view of a crystal showing twinning striations was always nearly perpendicular to the striations and closely approximated $N=1.644$. This shows that the composition plane of the twins studied optically was nearly perpendicular to the N_α direction. Extinction angles relative to the striations were variable and often unsymmetrical. The unsymmetrical extinction is believed to be due to the superpositioning of strain birefringence on the natural (and relatively weak) birefringence of the crystals. Variability in the extinction angle relative to the striations is in accord with the idea that the unique axis of the monoclinic crystal, a , lies in the composition plane. The extinction angles relative to the composition plane appeared to be smaller for the more birefringent views of the crystals.

The crystals for x-ray study were selected because they extinguished sharply and did not display twinning striations. Subsequent examinations showed, however, that most, if not all, of the particles would show twinning striations if rolled into the correct positions. On this basis alone it is probable, therefore, that the crystals used in the x-ray study were polysynthetic twins. As described below, the x-ray effects also revealed twinning.

3.2. X-Ray Results

The x-ray diffraction patterns were indexed on the basis of a monoclinic cell; unit-cell constants are summarized in table 1 along with the results of Trömel and Zaminer [23]. The axial notation was selected to conform with that for hydroxyapatite and the data of Trömel and Zaminer were converted to this notation by an interchange of their a and c axes. The cell dimensions of hydroxyapatite [12] and octacalcium phosphate, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ [7], are listed in table 1 for comparison.

TABLE 1. Unit-cell dimensions of tetracalcium phosphate, hydroxyapatite, and octacalcium phosphate

	Tetracalcium phosphate		Hydroxyapatite [11]	Octacalcium phosphate [7]
	This work	Trömel and Zaminer [21]		
a	11.99 Å	11.9 Å	9.432 Å	19.87 Å
b	9.48	9.4	9.432	9.63
c	6.97	7.0	6.881	6.87
α	90.8°	90°	90°	89.3°
β	90	90	90	92.2
γ	90	90	120	108.9
Cell contents	$\text{Ca}_{16}\text{O}_4(\text{PO}_4)_8$	$\text{Ca}_{16}\text{O}_4(\text{PO}_4)_8$	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$	$\text{Ca}_{16}\text{H}_4(\text{PO}_4)_{12} \cdot 10\text{H}_2\text{O}$
d_{calc}	3.07	3.10		
d_{obs} [8]	3.06	3.06		
Space group	$\text{P}2_1^a$ or $\text{P}2_1/\text{m}$	$\text{P}2_1/\text{m}$	$\text{P}6_3/\text{m}$	$\text{P}1$

^a In this work it is concluded that the most probable space groups are $\text{P}2_1$ and $\text{P}2_1/\text{m}$.

The only systematic absences noted were $h00$ with $h=2n+1$ and $00l$ with $l=2n+1$. In this instance, for the monoclinic cell, only the a axis can be a two-fold screw axis, and the indication of a two-fold screw axis

paralleled to c probably derives from a similarity of the monoclinic structure to one that is orthorhombic. The even orders of $00l$ were intense.

No significant deviation from orthorhombic symmetry was detected in the intensities of the spots; all differences were so slight that they could easily arise from absorption by the crystal or its mount. The 0.8° deviation in α from 90° was clearly visible in both the Weissenberg and the precession photographs; this, along with the optical properties, the inability to detect a deviation from 90° in β and γ in the $h0l$ and $hk0$ precession photographs, and the indication for a 2_1 axis parallel to a led to the conclusion that the symmetry of the crystals studied by us was monoclinic rather than triclinic or orthorhombic. The value of α listed in table 1 was calculated by the method of triangulation [9] using reflections 042 and $0\bar{4}2$ in the zero layer Weissenberg pattern. The values obtained by measuring the separation of the twin spots in the Weissenberg patterns and by direct measurement of the angle in the $0kl$ precession photograph were in agreement with this value for α . It was noted, also, that the 042 and $0\bar{4}2$ reflections appeared in the a -rotation photograph with the expected separation. This is proof that the unit cell of the crystals studied by us was not orthogonal; the separation of spots in the Weissenberg and precession photographs could not have been caused by a multiple crystal with orthorhombic symmetry.

In the Weissenberg patterns for the smaller crystal, the spots could be divided into two groups according to their appearance, and each group could be associated with one member of a twin. The $00l$ spots of the two members were divided by a constant angular separation of 1.6° , but the $0k0$ spots were superimposed. The $0kl$ spots of the two members (e.g., the strong pair 042 and $0\bar{4}2$) differed in both angular and radial position. The relative positions of the two sets of spots, as they appeared in the zero-layer pattern, persisted through the layers, $h=1$ through 4, indicating that the crystal could be described as a normal twin with b^* the twin axis, and (010) the composition plane, or, alternatively, as a parallel twin with c the twin axis and an $(hk0)$ the composition plane. The four precession photographs of the smaller crystal were fully in accord with these twin relationships; only the hkl photograph showed splitting of the spots. The larger crystal also appeared to be twinned, but in this instance the twinning appeared to be different, corresponding either to a normal twin with c^* the twin axis and (001) the composition plane, or a parallel twin with b the twin axis. Of these four possible types of twins, the normal twins with b^* and/or c^* the twin axes are best supported by the optical study. The other mechanisms could not be eliminated, however, because of difficulties inherent with the petrographic study of anhedral crystals. Usually one should be able to distinguish between normal and parallel twinning of these types in a monoclinic crystal by comparison of spot intensities. In this instance, however, the pseudo-orthorhombic character of tetracalcium phosphate prevented making a distinction.

A precession photograph of a third crystal revealed hexagonal symmetry; the positions and intensities of the spots resembled those of the $hk0$ net of hydroxyapatite. Since no section through the reciprocal lattice of tetracalcium phosphate could yield this net, the third crystal must have been an extraneous phase. Schneiderhöhn, [18] has described the occurrence of hydroxyapatite in tetracalcium phosphate. The indexes of refraction of these two salts are so similar that hydroxyapatite would be extremely difficult to detect in tetracalcium phosphate. The absence of an (OH)-stretching band in the infrared spectrum suggests that the phase may have been "oxyapatite", $\text{Ca}_{10}\text{O}(\text{PO}_4)_6$ [14].

4. Discussion

4.1. Unit Cell

Our cell dimensions agree with those of Trömel and Zaminer within their indicated accuracy (table 1). Our dimensions yield axial ratios, $c/a=0.581$ and $a/b=1.254$. Axial ratios of Termier and Richard quoted by Groth [11] and by Winchell and Winchell [25], $A/B=0.577$ and $C/B=1.255$ are in good numerical agreement with ours, but they are algebraically inconsistent with ours unless the reciprocal of C/B is used for the ratio 1.255. The inversion of this ratio is confirmed by the average of the interfacial angles quoted by Groth, $(011) \wedge (010)=51^\circ 36'$. This yields $B/C = \tan 51^\circ 36' = 1.262$.

The description of tetracalcium phosphate given in Groth and in Winchell and Winchell may be rewritten following the transformation cab/ABC as, "Monoclinic, $\alpha=90^\circ \pm$. Crystals (100) tablets with poor (100), (001) and (010) cleavages. Lamellar twinning on (010) and (001). $N_\beta = a$; N_γ near b .

4.2. Crystal Symmetry

The optical and x-ray results clearly show that the crystals studied by us had symmetry lower than orthorhombic. Three explanations would account for the discrepancy between our results and those of Trömel and Zaminer:

(1) Both monoclinic and orthorhombic modifications of tetracalcium phosphate may exist.

(2) Trömel and Zaminer [23] may have overlooked or discounted the evidence for monoclinic symmetry in the x-ray patterns.

(3) The crystals we studied may have been distorted because of thermal strain or impurities, or they may have been twinned mechanically when the fused mass was crushed.

The first possibility is strongly indicated by the high degree of pseudosymmetry apparent in our x-ray effects. On the other hand, it is easy to overlook the indications for lower symmetry in the x-ray patterns. The displacements between the twin spots, as seen in the Weissenberg pattern, are so slight that use of too large a crystal, or one that produced diffuse reflec-

tions, would make it difficult to detect distortion from orthorhombic symmetry. In this respect, the precession photographs are more revealing than Weissenberg photographs which display a 1.6° angular separation as a constant lateral displacement of only 0.8 mm. Evidence against the view that the lower symmetry is caused by distortion comes from three sources. First, the reflections in the single-crystal x-ray patterns appear too sharp to accord with a simple distortion mechanism. Second, the optical properties show a high degree of uniformity relative to the only morphological feature present (the composition plane) even though there is evidence of strain. Third, the twinning is inconsistent with orthorhombic symmetry; the indicated composition planes are pinacoids and twinning could not be detected optically. The twinning appears to be a persistent feature of tetracalcium phosphate preparations that has been frequently observed by optical methods [18, 19, 20]. Trömel and Zaminer indicate that an attempt to study the crystals with an optical goniometer was unsuccessful because the light reflections were not sharp. They attributed this difficulty to imbedded material. The unevenness in the crystal faces could be caused by polysynthetic twinning.

If, as seems likely, there is a high-temperature orthorhombic modification, and a low-temperature monoclinic modification, the two forms would differ by relatively minor atomic displacements. Of greater importance relative to the symmetry and structure of tetracalcium phosphate is the indication in our x-ray effects that c is a two-fold screw axis rather than a simple diad as reported by Trömel and Zaminer [23]. The presence of this two-fold screw axis would make the most probable orthorhombic space group $P2_12_1$ rather than $P2_12_2$. The absence of glide-plane effects in the diffraction patterns precludes all centrosymmetric orthorhombic space groups. The centrosymmetric monoclinic space group $P2_1/m$ is allowed by the x-ray effects observed by us. If tetracalcium phosphate truly exists in two modifications, it would be highly improbable that a centrosymmetric monoclinic space group is closely related to a noncentrosymmetric orthorhombic space group. It appears, therefore, that the most probable space groups are $P2_1$ and $P2_12_1$ for the monoclinic and orthorhombic situations, respectively.

4.3. Optical Properties

The indexes of refraction for tetracalcium phosphate reported here are in good agreement with the minimum and maximum values given by Schneiderhöhn [18] who also studied a synthetic preparation. Trömel and Zaminer [22] reported somewhat higher values ($N_\alpha = 1.649$, $N_\beta = 1.650$ and $N_\gamma = 1.658$) but these were for crystals obtained from a Thomas slag; it appears probable that the higher values were due to the presence of impurities. Trömel and Fix [21] reported that the indexes of refraction of a synthetic material were in agreement with those of Schneiderhöhn.

The negative birefringence reported by Schneiderhöhn is in disharmony with the positive birefringence found by Trömel and Zaminer [23] and by us.

There is complete disagreement between the optical directions of Termier and Richard ($N_\alpha \approx c$, $N_\beta = a$, and $N_\gamma \approx b$) [19] and those of Trömel and Zaminer ($N_\alpha = b$, $N_\beta = c$, and $N_\gamma = a$). It was noted above that N_α appeared to be normal to the composition plane. The two sets of indexes are in accord with this observation to the extent that in one N_α appears to be normal to (001) and in the other normal to (010), both of which are composition planes of the possible normal twins.

4.4. Twinning

Trömel and Zaminer state that the tabular plane is (110) although in their drawing it is given as (100) in agreement with Termier and Richard. Tabularity on (100) is consistent with a being the largest unit-cell dimension, since the long dimension of the cell is commonly the short dimension of the crystals.

Trömel and Zaminer give (100) as the plane of the polysynthetic twinning. This contrasts with the findings of Termier and Richard that (010) and (001) are the lamellar twin planes. The x-ray results described above for the two crystals are in accord with the findings of Termier and Richard in that the composition planes for the two normal twins would be (010) and (001). It is not unusual for pseudo-orthorhombic crystals (e.g., some feldspars) to have more than one twinning mechanism.

4.5. Structural Relationship to Hydroxyapatite

We attach considerable significance to the apparent structural relationship between hydroxyapatite and tetracalcium phosphate revealed by the comparison of unit-cell dimensions in table 1. The cell constants of octacalcium phosphate, which is known to have a structural relationship to hydroxyapatite [5], are also listed in table 1. It is apparent that the unit-cell lengths, b and c , and the enclosed angle, α , are very nearly the same for all three salts. It was this similarity between the dimensions of octacalcium phosphate and hydroxyapatite, that was initially taken [6] to indicate that the two salts were structurally related. This was later verified by the structure determination of octacalcium phosphate [5]. Analogously it appears that a layer parallel to (100) in tetracalcium phosphate is structurally similar to one parallel to (100) in hydroxyapatite. Differences in the lengths of the a axes and the β and the γ angles relate to the ways in which the layers are stacked. Another indication of similarity between the structures of tetracalcium phosphate and hydroxyapatite was noted in the intensities of the 00 l reflections. In hydroxyapatite, 00 l reflections with odd values of l are missing because of two-fold screw axes parallel to c , and the even values of l are strong because all the heavy atoms and 12 of the 26 oxygens have z parameters that are multiples of 1/4.

The intensities of the 00 l reflections of octacalcium phosphate are strikingly similar to those of hydroxyapatite because the heavy atoms and most of the oxygens have z parameters similar to those in hydroxyapatite even though there are no mirror planes restricting them to these positions. The same situation is believed to apply to tetracalcium phosphate, but verification of such a relationship must await determination of the structure.

As noted above, the powder pattern of tetracalcium phosphate, like that of octacalcium phosphate, bears considerable resemblance to that of hydroxyapatite. This makes difficult the detection of tetracalcium phosphate in the presence of hydroxyapatite. This difficulty is compounded by the facts that the indexes of refraction of tetracalcium phosphate are close to those of hydroxyapatite ($n_e = 1.640$, $n_w = 1.646$) [7], and the infrared spectrum of tetracalcium phosphate has no strong peaks that distinguish it in the presence of hydroxyapatite.

Tetracalcium phosphate is the most basic calcium phosphate known, having a Ca/P ratio of 2/1. Hydroxyapatite has a Ca/P ratio of 5/3 and octacalcium phosphate has a ratio of 4/3. It is well known that hydroxyapatite exhibits broad variations in its composition. Most of the materials having low Ca/P ratios, in the range 5/3 to 4/3, are adequately explained on the basis that they are intracrystalline mixtures of octacalcium phosphate with hydroxyapatite [7]. McConnell [15] has emphasized that biological materials tend to have Ca/P ratios higher than 5/3, and he has suggested that such crystals may contain (OH $^-$) $_4$ and CO $_3^{--}$ groups substituting for PO $_4^{--}$ ions in the hydroxyapatite crystal. In view of the apparent structural relationship between tetracalcium phosphate and hydroxyapatite, it appears that the two salts also may form interlayered mixtures; it would then not be necessary to postulate substitution in the hydroxyapatite lattice to account for high Ca/P ratios. Interlayered crystals of hydroxyapatite and octacalcium phosphate contain the two salts, with their b and c axes collinear. In this connection it is significant that the lamellae of tetracalcium phosphate crystals are reported by Trömel and Zaminer to be parallel to the (100) as they should be if they are caused by interlayering with hydroxyapatite. However, more complex mixtures are possible also. The length of a of tetracalcium phosphate, 11.99 Å, is very nearly 3/2 of $d(100)$ of hydroxyapatite, 8.16 Å. As a result, it may be hypothesized that a block of tetracalcium phosphate two unit cells in thickness could occupy a three unit-cell space in the hydroxyapatite lattice without much distortion. An arrangement of this type, if randomized within the hydroxyapatite, would more nearly fulfill the conditions for a "solid solution" than would an interlayered mixture of the two salts.

A structural similarity between tetracalcium phosphate and hydroxyapatite has bearing on another aspect of considerable importance to the chemistry of apatitic materials. Natural and biological apatites are notorious in their ability to pick up and retain impurities, notably carbonate. There is yet no clear

understanding of the nature of the sites in which the impurities are retained. It is generally accepted that the presence of carbonate influences the chemical properties and the unit-cell dimensions of hydroxyapatite, and is correlated with a decrease in caries resistance. The ease with which tetracalcium phosphate reacts with CO₂ and the suggested structural relationship with hydroxyapatite introduces a new possibility for the understanding of these phenomena.

There is at this time no evidence that tetracalcium phosphate can form from an aqueous system, but this cannot be ruled out. The solubilities of calcium hydroxide and the calcium phosphates in a basic solution are extremely low. The range of compositions where tetracalcium phosphate would be more stable than hydroxyapatite, if one exists, would have to be very basic; the low solubilities would make it difficult to prepare pure tetracalcium phosphate from such systems. The possibility should be kept in mind, however, that under suitable conditions, kinetic factors may facilitate the incorporation of tetracalcium phosphate into the hydroxyapatite crystal.

5. References

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