NATIONAL BUREAU OF STANDARDS REPORT

10 062

Progress Report

on

THE CRYSTALLOGRAPHY OF OTHER BIOLOGICALLY SIGNIFICANT INORGANIC COMPOUNDS



U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

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THE CRYSTALLOGRAPHY OF OTHER BIOLOGICALLY SIGNIFICANT INORGANIC COMPOUNDS

by

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U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

THE CRYSTALLOGRAPHY OF OTHER

BIOLOGICALLY SIGNIFICANT INORGANIC COMPOUNDS

INTRODUCTION

Calcium and phosphate are present in vivo mainly as calcium hydroxyapatite (HA), which is the prominent topic of the symposium. Since hydroxyapatite is held together by ionic bonds, the ions in the structure can readily be replaced shape by other ions of roughly the same size,/and charge. Some change in charge can be tolerated provided the crystal as a whole is kept electrically neutral. In a simple example, substitution of Na⁺ for Ca²⁺ could be compensated for electrically by substituting SO_4^{\pm} for PO_4^{\pm} . Thus compounds crystallizing in ionic lattices, and in the apatite structure in particular, need not be completely homogeneous as is well known. The apatite structure is apparently so stable that it is not only common among compounds with the same type of formula, but will also form as layers in a crystal interleaved with layers of differing stoichiometry, e.g., HA interlayered with octacalcium phosphate (see later). Substitutions in general, and in the HA structure in particular, can be envisioned on three levels:

- (i) interleaved layers (epitaxy)
- (ii) parts of one or more unit cells of related compounds replacing parts of the HA structure

(iii) substituted ions

It is therefore desirable to systematically study compounds related to HA with a view to revealing how the apatite structure can incorporate these substitutions or 'defects', and/or to gain enough structural knowledge to allow us to make predictions about the method of 'defect' incorporation.

The likelihood of epitaxy or other intergrowth can be considered from examinations of the crystal structures of appropriate compounds. Appropriate compounds, in turn, can be suggested from an observation of the types of coordination and bonding of ions. A formal evaluation of epitaxy has not yet been accomplished. In fact, only recently has a least squares computer program (Busing, 1968) been written to refine the various parameters required in a calculation of lattice energy from their initial estimates (by the method of steepest descents, using determined crystallographic parameters such as the cell dimensions and atomic positional parameters as observations). It may be feasible to calculate an approximation to the interfacial energy of two possibly epitaxial layers if the various energetic parameters above are "known". This, however, lies in the future.

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Besides searching for structural features which may be significant in the incorporation of defects or nonstoichiometry into apparently homogeneous crystal structures, it is also significant to examine appropriate structures, which will probably be of hydrated salts (see below), for features which may be important in determining the identity of a precursor phase during crystallization. Hydrated salts may be important in the nucleation and growth of anhydrous species from aqueous environments for the following reasons (Dickens and Brown, 1968), mentioned briefly below:

- (i) For small particles such as the nucleating particles during crystallization, the surface energy is a large factor in determining the identity of the particles. The high energy attractions between ions are reduced, and the surface energy in an aqueous environment hydrated salt. is lowered when the nucleus is formed from a highly/
- (ii) Because of kinetic factors, hydrated salts often crystallize more rapidly than the anhydrous counterparts, even when the latter are thermodynamically more stable.

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- (iii) Crystal growth poisons such as polyphosphates, magnesium and sugar, all of which are present in biological systems, apparently repress the growth of anhydrous calcium carbonates, and perhaps of HA, and allow hydrated forms to grow.
 - (iv) Most nucleation processes are thought to be heterogeneous rather than homogeneous. In the case of biological mineralization such nucleation is thought to be on collogen and other proteins, which, because of their hydrophilic nature, would presumably reduce the surface energy of a hydrated salt to a lower value than that of an anhydrous salt.

In this chapter, we report on the comtemporary structural knowledge of several compounds of interest. The structures of some of these have not been determined; some others are known except for the hydrogen atoms. In general much further work needs to be done.

The compounds have been chosen to indicate the relationship of that particular structural type to HA. If a particular compound or ion sounds unlikely as a biological agent, a more acceptable compound with a high probability of having the same or a related crystal structure can often be thought of by

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juggling the identities of the constituent ions while keeping the overall formula electrically neutral.

1. COMPOUNDS NOT ISOMORPHOUS WITH HYDROXYAPATITE BUT POSSIBLY RELATED TO IT. These compounds are relevant to hydroxyapatite in the context of possible ion substitution, unit cell substitution or interlayering.

(a) $Na_2M_8(SiO_4)_6F_2$ M = La, Pr, Nd

Rare earth compounds with the general formula $Na_2M_B(SiO_4)_{\odot}F_2$ have been prepared from molten fluxes by Ito (1967). The cell dimensions (Bowen, 1967; Swanson, McMurdie, Morris and Evans, 1969) are seen (Table 1) to be very closely related to those of HA (Posner, Perloff and Diorio, 1958) and fluorapatite (FA) (Naray-Szabo, 1930). The reciprocal lattice extinctions 000ℓ = 2n+1 indicate the space groups P6₃ or P6₃/m. The Ca ions in FA and HA are in positions 4f and 6h of space group $P6_3/m$ (Table 2). The rare earth compounds probably have the space group P63, a subset of P63/m. Six rare earth ions thus probably occupy general positions in P63 in a configuration like that of the 6 Ca ions in positions 6h of P63/m for FA and HA. The remaining two rare earth ions and the two Na ions probably occupy the 2b positions in P6,, and thus lie in columns analogous to the columns of Ca ions in the 4f positions in FA and HA. Since the electrostatic repulsive energy of a chain of M³⁺...M³⁺... $Na^{+}...Na^{+}...M^{3^{+}}$ will be 9 + 3 + 1 + 3 = 16 units/unit cell (Table 3) whereas that of a chain M³⁺...Na⁺...M³⁺...Na...M³⁺ will be 3 + 3 + 3 + 3 = 12 units/unit cell, these columns are expected to have Na and rare earth ions alternating. This may be relevant to the incorporation of foreign cations into hydroxyapatite.

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| Na ₂ La ₈ (SiO4) ₆ F ₂ | 9.6890(2)Å | 7.1805(2)Å | Г |
| $\operatorname{Na_2Pr_8(SiO_4)}_{6^{\mathrm{F}}2}$ | 9.5830(2) | 7.0728(2) | Т |
| $\operatorname{Na_2Nd_8(SiO_4)}_{6^{\mathrm{F}}2}$ | 9.51 | 7.02 | Г |
| $	ext{calo} (ext{Po}_4) 	ext{6F}_2$ | 9.37 | 6.88 | Г |
| са ₁₀ (Ро ₄) ₆ (он) ₂ | 9.432 | 6,881 | Г |

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Table 2

Comparison of $Na_2M_8(SiO_4)_6F_2$ with $Ca_{10}(PO_4)_6F_2$ *

Space group P63 Space group P63/m 6c 1 x, y, z 6h m x, y, .25 x, y, .75 x, y, .5+2 y, x-y, .25 y, x-y, z y, y-x, .75 y, y-x, .5+z $y-x, \bar{x}, z$ y-x, x, .25 x-y, x, .5+z x-y, x, .75 2b 3 .33, .67, z 4f 3 .33, .67, z .67, .33, .5+z .67, .33, .5+z .67, .33, z .33, .67, .5-z 2a 6 0, 0, .25 2a 3 0, 0, z 0, 0, z 0, 0, .75 $Na_2M_8(SiO_4)_6F_2$ $Ca_{10}(PO_4)_6F_2$ 6 M in (6c) with x - .25, 6 Ca in (6h) with x = .2466, y ≈ 0., z ≈ .25 y = .00312 M in (2b) with z = 0. 4 Ca in (4f) with z = .00142 Na in (2b) with z = .524 0 in general position (6c) 12 0 in general position with x = .3433, y = .2579z = .07056 O in (6h) with x = .3283y = .4846, z = .256 O in (6h) with x = .5876y = .4652, z = .252 F in (2a) with z -2.25 2 F in (2a)

* Kay, Young and Posner (1964).





(b) $CaK_3H(PO_4)_2$

The structure of $CaK_{3}H(PO_{4})_{2}$ (Frazier, Smith, Lehr and Brown, 1962; Brown and Fowler, 1967) is very closely related to that of $NaK_{3}(SO_{4})_{2}$ (glaserite). The formal relation between the type structure / $NaK_{3}(SO_{4})_{2}$ /and HA has been discussed by Wondratschek (1963).

CaK₃H(PO₄)₂ is unusual in that although it contains a phosphate group with an acid hydrogen, it is formed from solutions with a pH of 10-11. Presumably the packing in the structure is so efficient that the structure is able to remove a proton from such an alkaline environment in order to achieve the correct charge balance. In water, CaK₃H(PO₄)₂ hydrolyzes to HA. It has not been found in physiological situations, but here

The usual unit cells of $CaK_{3}H(PO_{4})_{2}$, $NaK_{3}(SO_{4})_{2}$ and HA are shown in Table 4 and are redefined in Table 5 to bring out their close correspondence.

That $CaK_{3}H(PO_{4})_{2}$ and $NaK_{3}(SO_{4})_{2}$ must have similar structures can be seen from

(1) the similarities of their formulae except for the H.

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Table 4

The Unit Cell Dimensions of $CaK_3H(PO_4)_2$,

$NaK_3(SO_4)_2$ and HA

| a | CaK ₃ H(PO4) ₂ 9.93 Å | NaK ₃ (SO ₄) ₂ 5.66 Å | Ca ₅ OH(PO ₄) ₃ (HA) 9.43 Å |
|-------------|--|--|--|
| b | 5.72 | 5.66 | 9.43 |
| C | 7.44 | 7.33 | 6.88 |
| α | 90 ° | 90° | 90 ° |
| β | 92.3 | 90 | 90 |
| Υ | 90 | 120 | 120 |
| Z | 2 | l | 2 |
| space-group | C²/m | P3ml | P6 ₃ /m |

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Table 5

The Unit Cells from Table 4, Redefined

| | $Ca_3K_9H_3(PO_4)_6$ | Na_3K_9 (SO ₄) ₆ | $Ca_{10} (PO_4)_6 (OH)_2$ |
|---|----------------------|---|---------------------------|
| a | 9.93 Å | 9.80 Å | 9.43 Å |
| b | 9.92 | 9.80 | 9.43 |
| С | 7.44 | 7.33 | 6.88 |
| α | 91.6° | 90° | 90° |
| β | 91.6 | 90 | 90 |
| γ | 120 | 120 | 120 |

(2) The similar dimensions of their ions

Na ionic radius = 0.96 Å Ca ionic radius = 0.99 Å K ionic radius = 1.33 Å P-O bond distance = 1.56 Å S-O bond distance = 1.44 Å

- (3) CaK₃H(PO₄)₂ is pseudo-trigonal in morphology, twinning, cell dimensions and in the intensities of supposedly non-equivalent reflections on all layers. The trigonal space-group which will most easily accommodate one formula weight of CaK₃H(PO₄)₂ is P3ml, which is the space-group of NaK₃(SO₄)₂. The actual space-group of CaK₃H(PO₄)₂, C²/m, is a subgroup of P3ml.
- (4) the x-ray intensities of CaK₃H(PO₄)₂ indicate a subcell with the heavy atoms at the corners as is found in NaK₃(SO₄),.
- (5) the x-ray powder patterns of $CaK_3H(PO_4)_2$ and $NaK_3(SO_4)_2$ are very similar.

Thus, the NaK₃(SO₄)₂ structure can be used as a first approximation to the actual structure of CaK₃H(PO₄)₂ with in CaK₃H(PO₄)₂ the exception of H, which is probably to be found/across the 0....0 close approach, i.e., across a center of symmetry in NaK₃(SO₄)₂. This hydrogen bond will destroy the three-fold axis of the PO₄ group, but will keep the mirror plane of C²/m. By analogy with other structures containing an O-H...O hydrogen bond across a nominal center of symmetry. This conclusion is supported by IR and NMR evidence (Brown and Fowler, 1967).

In the NaK₃(SO_4)₂ structure (Fig. 1) there are columns of SO₄ groups and K ions related by a $\overline{\mathbf{3}}$ axis. Thus, adjacent columns have the SO₄ groups pointing "up" and "down". The remaining ions, Na and K, are packed into columns designated by small circles in Figure 1. The formula balance is kept because there are twice as many SO₄/K columns as there are Na/K columns.

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Figure 1. The crystal structure of glaserite, NaK₃(SO₄)₂. The columns with the dark dots may be considered to have the 0 of the SO₄ group above the S on the three-fold axis, the others to the real unit have the O below the S. The light line corresponds /-cell, the heavy line is the refined cell. The small circles are columns of Na and K ions. One of these columns may be considered to have replaced the OH⁻ column in HA. The effect of changing the sign of the ions in the central column may be seen by comparing the structure of $NaK_3(SO_4)_2$ with that of HA (Fig. 2). In HA the Ca ions have been pulled in by the OH⁻, and the PO₄ groups have moved out so that they can coordinate to the Ca's through their oxygens while keeping the repulsion with OH⁻ within tolerance. Further, the PO₄ groups have tilted over about 35° which puts two oxygens near the centers of two Ca triangles (Fig. 3), in the Ca/O configuration found in aragonite (Bragg, 1924) and each of puts/the other two oxygens near the center of a Ca...Ca line in

the configuration found in calcite (Bragg, 1913).

 $CaK_{3}H(PO_{4})_{2}$ could exhibit epitaxial growth on HA or interchange with HA on a unit cell level and thus have relevance to the mechanism of crystal growth, to the poisoning of crystal growth and in the incorporation of impurities and defects.



Figure 2. The crystal structure of HA, $Ca_{10}(PO_4)_6(OH)_2$, projected down the <u>c</u> axis.



(c) Silico-carnotite $Ca_5(PO_4)_2(SiO_4)$

Silico-carnotite, which is apparently named more after its discoverer, Carnot, than by analogy with the mineral carnotite, is found in basic slags rich in phosphorus. Since it is readily soluble in dilute acids, it has been used for has been reported to many years directly as a plant fertilizer. It/exist over a range of composition of about 55% to 83% $Ca_3(PO_4)_2$ by weight at 1125°C (Nurse, Welch and Gutt, 1959) and has been found in several high temperature investigations (Nurse, et al, 1959; Berak and Wojciechowska, 1956; Vol'fkovich, Illarionov, Ozerov and Remen, 1960) of the Ca-PO₄-SiO₄ system. Since stoichiometric silico-carnotite is unstable below about 750° (Nurse et al, 1959) it must be preserved by quenching. Keppler (1968) has performed microprobe analyses on various crystals of silico-carnotite and has concluded that it is a definite compound.

The crystallographic properties of a representative specimen are given in Table 6 (Riley and Segnit, 1948; Tromel Dickens and Brown, 1969) and Zaminer, 1959; Keppler, 1968)/. There is good correspondence dimensions between the unit cell /of hydroxyapatite and silico-carnotite, and especially between the volumes of one formula weight (Table 7). Although silico-carnotite has the same cation/anion ratio (5/3) as the garnets $(A_3B_2(XO_4)_3$ where A and B are cations and probably XO₄ is an anion), the garnet structure is/too dense for silicocarnotite since the garnets invariably have for B some small cation which can form B....O distances of about 2 Å. In the garret Ca₃Al₂(SiO₄)₃ (Abrahams and Geller, 1958) B is Al, Ca...O distances are usually greater than 2.3 Å. which forms Al....O distances of 1.95 Å./

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Table 6

Silico-carnotite data

$$Ca_{\rm S} (PO_4)_{2} \text{SiO}_4$$

 $N_{\alpha} = 1.641 \| \underline{C}, N_{\beta} = 1.655 \| \underline{b}, N_{\gamma} = 1.663 \| \underline{a},$
measured on {001} plates

orthorhombic, space-group Pnma or Pn21a

<u>a</u> = 6.737 ± .001, <u>b</u> = 15.508 ± .004, <u>c</u> = 10.132 ± .002 Å

A Comparison of the Unit Cells of HA, a Garnet, Silico-Carnotite and Pyromorphite

Table 7

| | НА Са ₅ (Ро₄) ₃ (ОН) | $\begin{array}{c} \text{Garnet} \\ \text{Ca}_{3}\text{Al}_{2}(\text{S10}_{4})_{3} \end{array}$ | $\begin{array}{c} \text{Silico-}\\ \text{carnotite}\\ \text{Ca}_5(\text{PO}_4)_2\text{SiO}_4 \end{array}$ | Pyromorphite Pb ₅ (P0 ₄) ₂ S1 0 ₄ |
|------------------|---|--|---|---|
| a ا | 9.43 Ă | 11.87 Å | 15.508Å | 9.79 Å |
| ام | £#*6 | 11.87 | 10.132 | 9.79 |
| 01 | 6.88 | 11.87 | 6.7 37 | 7.32 |
| X | 120° | ° 06 | ° 06 | 120° |
| vol. | 530 ă ³ | 1672 Å ³ | 1059 Å ³ | 608 Å ³ |
| Z | Ŋ | 8 | 7 | Q |
| density | 3.14 | 3.58 | 3.10 | 7.20 |
| vol.of l F.wt | 265 Å ³ | 209 Ă ³ | 265 Å ³ | 304 Å ³ |

 $\frac{a}{B_{SC}} = 15.47$ Å $\sqrt{3}a_{HA} = (2d_{100}) = 16.34$ Å

(a) with permuted axes

Dickens and Brown (1969) have very recently determined the crystal structure (R = 0.05) of silico-carnotite using a crystal from sample D (British Museum sample 1919,64) in Riley and Segnit's paper (1948). Silico-carnotite was expected to follow in the HA-glaserite series as a member where the structure is essentially the HA structure with an empty column where the OH's are found in HA. The actual structure of silicocarnotite may be considered to be a distorted form of the above. The column Ca's in HA are represented by a Ca zig zag in silicocarnotite. The six $Ca(2)/PO_4$ chains along c (surrounding the OH column) in HA are represented by four Ca/PO4 and two Ca/SiO4 in silico-carnotite chains. A further distortion/is that the Ca's in the SiO_4 chain have been pulled in towards the OH site in HA to form a central zig zag of cations. The structure of silico-carnotite thus also approaches the NaK₃ (SO₄), structure and is intermediate between HA and $NaK_3(SO_4)_2$.

The structure principles found in silico-carnotite may be used in an appropriate calcium phosphate $(Ca_4Na(PO_4)_3)$ is one possibility) to allow the stoichiometry and properties of HA to change locally. $Pb_{5} (PO_{4})_{2}SiO_{4}$ (pyromorphite) has been reported by Wondratschek (1963) from x-ray data to be hexagonal with cell dimensions (Table 7) similar to those of hydroxyapatite. Presumably the lead atoms are in a hexagonal array perpendicular to <u>c</u> and either dominate the scattering so that deviations from hexagonal symmetry because of the non-equivalence of the PO_{4} and SiO_{4} groups are unnoticed, or the PO_{4} and SiO_{4} groups are statistically disordered. The formula of $Pb_{5} (PO_{4})_{2}SiO_{4}$ relates it to silico-carnotite, and it may have a closely related structure, perhaps made hexagonal or more nearly so by the effect of the increased size $(Pb^{2+} = 1.20 \text{ Å}, Ca = 0.99 \text{ Å})$ of the cation. The structure of $Pb_{5} (PO_{4})_{2}SiO_{4}$ is of great interest, and would be best determined by neutron diffraction.

(d) Tetracalcium phosphate, Ca₄O(PO₄)₂, TCP

Tetracalcium phosphate (Bookey, Richardson and Welch, 1952; Tromel, Fix and Fritze, 1961; Brown and Epstein, 1965) or Hilgenstockite, is prepared at high temperatures in systems free of water. It may not be found <u>in vivo</u> but may have a structural relationship to HA (Table 8) where it can be seen that the cell volume of HA and the <u>a</u> and <u>c</u> axes and hence the (010) faces of the two compounds are very closely related.

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A Comparison of the Unit Cells of Hydroxyapatite and Tetracalcium Phosphate

| I | $ca_4 o(Po_4)_2$ |
|---|--|
| 8 | ca ₁₀ (Po ₄) ₆ (OH) ₂ |

| ş | | | | | |
|-------|--------|-------|-------|--------------------|--------|
| 9.462 | 11.965 | 7.023 | 90°8° | 795 Å ³ | $P2_1$ |
| | | | | | dnoıf |
| 2 Ă | 5 | 1 | | vA | Space |
| 9.43 | 9.43 | 6.88 | 120° | 530 | |
| | | | | 01. | |
| a) | മ്പ | U | ~ | Ň | |

= 12.27 Å = 795 Å³

 $d_{1 \circ \circ}$ (HA) x $1.5 = 530 \text{ Å}^3 \times 1.5 =$

Although the crystals are nearly always twinned, we have collected x-ray data from an apparently untwinned single crystal. Statistical tests on the quasi-unitary structure factors indicate that the space group is non-centrosymmetric, and must therefore be P2₁ from the x-ray extinctions. We have tried to solve the structure by superposition techniques, son using an unsharpened Patter/ map, but obtained a trial structure for the Ca and P atoms which would not refine satisfactorily. This trial structure has four layers roughly equally spaced along <u>b</u>. We plan further effort in the solution of the structure using statistical methods on the quasinormalized structure factors (Dickinson, Stewart and Holden, 1966).

TCP takes up CO_2 , especially at high temperatures when the 0= presumably becomes CO_3^{--} . This is of considerable interest to the problem of carbonate-apatites, and suggests that carbonation of apatite can take place by making an OH⁻⁻ into HCO₃⁻⁻ or CO_3^{--} and expelling water if necessary. Since two cells of TCP can, on spatial considerations, readily replace three cells of HA, TCP may fit easily into the HA lattice and thus substitution of TCP for HA may provide a mechanism of defect incorporation

and/or carbonate incorporation in HA.

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(e) $\operatorname{Sr}_{6}\operatorname{H}_{3}(\operatorname{PO}_{4})_{5} \cdot 2\operatorname{H}_{2}O$ and $\operatorname{Sr}_{3}(\operatorname{PO}_{4})_{2} \cdot 4\operatorname{H}_{2}O$

These two compounds (Collin , 1959, 1960, 1964, 1966) are of interest because of the mechanism of incorporating Sr^{90} in the body. Also, $Sr_6 H_3 (PO_4)_5 \cdot 2H_2 O$ has been shown to immediately precede the formation of SrHA <u>in vitro</u> and there is evidence, quoted below, that the same may be true <u>in vivo</u>. $Sr_3PO_4 \cdot 4H_2 O$ may be related to the "amorphous phase" (Eanes, Gillessen and Posner, 1965, 1967; Weber, Eanes and Gerdes, 1967) found in the precipitation of calcium phosphates from aqueous solution.

In an examination (Johnson, Armstrong and Singer, 1966) of the tooth enamel of rats fed on a strontium-rich diet, the cell dimensions of the hydroxyapatite present were found to have increased from $\underline{a} = 9.47$, $\underline{c} = 6.86$ Å in enamel from Srpoor animals to $\underline{a} = 9.48$ Å, $\underline{c} = 6.91$ Å in Sr-rich animals. Extra lines in the powder patterns of the tooth enamel could $Sr_6 H_3 PO_4)_5 \cdot 2H_2O$ be attributed to $Sr_6 H_3 (PO_4)_5 \cdot 2H_2O$. otherwise has a powder pattern very similar to HA and, because of its Sr/Pratio of 1.2, could lower the apparent stoichiometry of (Ca, Sr) HA by interlayered growth in the way suggested (Brown, Smith, Lehr and Frazier, 1962) for octacalcium phosphate, $Ca_6 H_2 (PO_4)_6 \cdot 5H_2O$, (OCP). The formulae of $Sr_6 H_3 (PO_4)_5 \cdot 2H_2O$ and OCP are compared in Table 9. The Sr salt is obviously more acidic than OCP and contains less water. $Sr_6 H_3 (PO_4)_5 \cdot 2H_2O$ is the sole solid phase formed (Collin, 1966) (at pH 7.7) when 2.3 equivalents of $Sr(OH)_2$ are added to 1 equivalent of H_3PO_4 . It often forms as a disordered intergrowth of crystals from aqueous solution.

 $Sr_3PO_4 \cdot 4H_2O$ is formed (Collin, 1966) when more than 2.6 equivalents of $Sr(OH)_2$ are added to 1 equivalent of H_3PO_4 , and is stable for many days at 0°C. At 25°C and 37°C it very easily changes into SrHA (Collin, 1966). Its high degree of hydration make it of great interest. It has a variable water content as does OCP. The strong reflection at 20 = 6° (CuKa radiation) is dependent on the degree of hydration and suggests that the structure has a layer structure with a repeat distance of about 14 Å (Collin, 1964). OCP has a layer structure with a repeat of about 18.7 Å. Table 9

OCP is
$$Ca_{B}H_{2} (PO_{4})_{6} \cdot 5H_{2}O = Ca_{1} (H)_{25} (PO_{4})_{75} (H_{2}O)_{63}$$

 $Sr_{6}H_{3} (PO_{4})_{5} \cdot 2H_{2}O = Sr_{1} (H)_{5} (PO_{4})_{83} (H_{2}O)_{33}$

Thus $Sr_3 (PO_4)_2 \cdot 4H_2O$ is of interest to biological mineralization both as a possible candidate for a direct analogy to amorphous calcium phosphate, and as another structure which can incorporate several water molecules with alkaline earth and phosphate ions perhaps arranged in layers. Other examples of the latter are CaHPO_4 \cdot 2H_2O and Ca(H_2PO_4)_2 \cdot H_2O.

(f) Octacalcium phosphate, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, OCP

The possible importance of OCP in reducing the apparent Ca/P ratio of CaHA and in the growth mechanism of HA has been discussed by Brown (1966). The unit cells of OCP and HA are compared in Table 10. Since the <u>b</u>, <u>c</u> and α dimensions are very similar in the two compounds, their unit cells can easily share a common face.

The structure of OCP has been determined (Brown, 1962) but the hydrogen atoms have not been located because the x-ray data contain the effect of large corrections for absorption. Good large (0.1-0.2 mm) single crystals of OCP are very difficult to grow. We are attempting to grow suitable single crystals in order to recollect the data. We are also reprocessing the photographic x-ray data collected earlier and plan to describe the structure in much more detail when the fine details are better known. The structure of OCP is shown in Figure 4 and consists of apatitic layers between x = -.25 to +.25 interlayered by a hydrated layer with some Ca and PO₄ ions.

Table 10

A Comparison of the Unit Cells of OCP and HA

| | $Ca_8H_2(PO_4)_6 \cdot 5H_2O(OCP)$ | $Ca_{10}(PO_4)_6(OH)_2$ (HA) |
|---|------------------------------------|------------------------------|
| a | 19.87 Å | 9.42 Å |
| b | 9.63 | 9.42 |
| C | 6.87 | 6.88 |
| α | 89° 17' | 90° |
| β | 92° 13' | 90° |
| γ | 108° 57' | 120° |

.


Figure 4. The crystal structure of octacalcium phosphate.

The corners of the two hexagons are the phosphorus and calcium positions as they occur in projection in HA. (The hexagon in HA is a trigonal antiprism in three dimensions.) Two Ca ions and two PO_4 groups occur at each level of the trigonal antiprism in OCP. The environments of the Ca ions are very similar to those of the corresponding ions in HA. The OH groups in columns in HA have been replaced by the 0(42) water molecule and O(35) of the $P(14) PO_4$ group,⁴ The O(41) water has replaced a Ca ion in HA and presumably hydrogen bonds to the groups that Ca would have bonded to electrostatically with roughly similar distances (Ca- 0^{-2} .4 Å, O-H... O = 2.5... 2.8 Å). The Ca(1) and Ca(2) ions in OCP are almost exactly analogous to the column Ca's in HA. The other column has been distorted considerably with Ca(3) roughly in the same position as a column with moved by about 1.5 Å along the b of Ca's in HA but/Ca(4) axis to bond to O(41) which has replaced a Ca ion in the HA The detailed atomic arrangement around these ions structure. is part way between the environment of the Ca (5,6,7,8) ions and the environment of the Ca(1,2) ions. Hayered intergrowth of OCP and HA has been observed directly and the crystal habit of HA has been correlated with that of OCP by topotactic change (Brown, Smith, Lehr and Frazier, 1962).

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2. <u>CALCIUM CARBONATES</u>. The calcium carbonates are the other great body of biological minerals. The anhydrous forms have been found in the shells of marine life (K. M. Wilbur, 1964) and in humans in gallstones (Sutor and Wooley, 1968). Bone can contain (Neuman and Neuman, 1958) up to 6% carbonate ion.

(a) Calcite, CaCC₃

Calcite is the most stable form of CaCO₃ at normal temperatures. It is abundant in nature in such forms as the shells of several sea creatures, including oysters, and in gallstones, as well as a mineral. It is the final form precipitated from aqueous solutions at room temperature in the absence of crystal growth poisons such as polyphosphates, Mg²⁺ and sugars. It crystallizes in a hexagonal unit cell, a = 4.989, c = 17.062 Å, spacegroup R3c, and the structure is well known (Bragg, 1913; Sass, Vidale and Donohue, 1957). The oxygens are hexagonally closed packed and the Ca's are in octahedral coordination. As shown in Figure 5, each oxygen is coordinated to two Ca's. Calcite is isomorphous with NaNO3 and with the carbonates of Mg, Mn, Fe, Zn, Cd and Co, which are all small ions with ionic range of radii in the / 0.65 to 1.0 Å.

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A. CO_3 environment in calcite. B. CO_3 environment in aragonite. From Bragg (1924).

Figure 5.

(b) Aragonite, CaCO₃

Aragonite is the next most stable form of CaCO₂ at room It is denser than calcite and presumably is more temperature stable than calcite at low temperatures and/or high pressures. When heated it changes into calcite (Subba Rao and Yoganarashimhan, 1965) with the [001] of aragonite becoming the [0001] of calcite and [100] and [110] of aragonite being parallel to [1010] and / respectively of calcite (Dasgupta, 1964). Thus, during the transition the CO₃ group in aragonite is rotated 30° about c and moved to halfway between the Ca layers. The Ca layers must also change to become an ABCABC sequence in calcite instead of the ABABAB sequence in aragonite. $\mathcal{H}_{\text{Aragonite is found in coral}}$ clams and gallstones, and is isomorphous with the carbonates of Ba, Sr and Pb. Aragonite is precipitated preferentially to calcite from aqueous environments at temperatures above about 40°C. The unit cell is compared to that of calcite in Table 11. The structure (Fig. 6) is known formally (Bragg, 1924) but apparently not well by modern standards.

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Table 11

A Comparison of the Unit Cells of Calcite and Aragonite

*

| | Calcite | Aragonite |
|---|---------|-----------|
| a | 4.989 | 4.959 |
| b | 4.989 | 7.968 |
| C | 17.062 | 5.741 |
| V | 120° | 90° |

*ASTM card 5-0453



Figure 6. Crystal structure of aragonite perpendicular to <u>c</u> (twinned on (110). From Bragg (1924).

In aragonite, the oxygens are coordinated equally to three Ca's instead of two as in calcite (Fig. 5). Aragonite twins easily in the way explained by Bragg and has been reported (Hiragi, Kachi, Takeda and Nakanishi, 1966) to exist in fine particles ($0.5 - 1.0 \mu$) which have, at least in part, a superstructure (Fig. 7) with space-group Pbca and cell dimensions $\underline{a} = 8.420$, $\underline{b} = 9.385$, $\underline{c} = 5.741$. The relationship of the superstructure (<u>As</u>, <u>Bs</u>, <u>Cs</u>) to the normal structure (\underline{a} , \underline{b} , \underline{c}) of aragonite is <u>As</u> = $\underline{a} - \underline{b}$, <u>Bs</u> = $3/2\underline{a} + 1/2$ <u>b</u>, <u>Cs</u> = \underline{c} .

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(c) High pressure phases of CaCO₃

X-ray diffraction studies (Davis, 1964) at high pressures on powdered calcite (calcite I) have indicated the existence of two more phases of CaCO₃. CaCO₃ (II), a modified calcite type, is probably isostructural with KNO₃ (III) (Davis, 1963) apparently which is/related to calcite (Table 12) but has only unidirectional order of the NO₃ ion (about the 3-fold axis).

Calcite I is considered to transform into Calcite II at about 15.5 Kb pressure. Calcite III is stable at higher pressures (about 17.6 Kb to 27 Kb). Its powder pattern has been indexed (Davis 1964) as a KNO₃-IV aragonite type (Table 13) though this is still not certain.

Table 12

Comparison of the Proposed Unit Cells of the High Pressure Forms KNO_3 (III) and $CaCO_3$ (II) With Calcite

| Calcite (I) | KNO ₃ (III) | CaCO ₃ (II) |
|-------------|------------------------|------------------------|
| 4.989 Å | 5.44 Å | 4.98 Å |
| 17.062 | 18.25 | 16.83 |

Table 13

Comparison of the High Pressure Forms

KNO3 (IV) and Calcite (III) with Aragonite

| Aragonite | KNO ₃ (IV) | Calcite(III) |
|-----------|-----------------------|--------------|
| 5.741 Å | 11.04 Å | 8.90 Å |
| 4.959 | 8.36 | 8.42 |
| 7.978 | 7.40 | 7.14 |



Figure 7. The (001) plane projection of the model for the superstructure, including atoms from 0 to <u>c</u>/2. The solid lines show the unit cells of the superstructure, and the structure broken lines a unit cell of normal aragonite. The / is no longer periodic within the broken lines. From Hiragi, Kachi, Takada and Nakanishi (1966). The structures of the disordered KNO₃ and CaCO₃ forms are still not known. These disordered forms may be important in understanding the mechanisms of defect incorporation in calcium carbonates and in studying the kinetics of calcareous reactions.

(d) Vaterite, CaCO₃

Vaterite has been found as a mineral (McConnell, 1960), in the repaired part of mineralized tissue (Wilbur and Watabe, 1964) and in gallstones (Meier and Moenke, 1961). It has been recognized as the end member of the series of rare earth fluoride carbonate-calcium carbonate series bastnaesite-roentgenite-synchisite...vaterite (Donnay and Donnay, 1953). Structures have been given by Meyer (1959) and Kahmi (1963). Vaterite often grows in a spherulitic form; spherulitic vaterite has been discussed by Donnay and Donnay (1967). Kahmi used crystals which under high magnification could be seen to be aggregates of uniformly oriented hexagonal plates. Meyer proposed a structure in an orthohombic space a group with/primitive ortho-hexagonal unit cell. His space group and structure are incompatible with the results of other workers who have assigned vaterite to the hexagonal crystal system.

Optical studies (Bunn, 1945) had shown that the c axis of the hexagonal system must be in the plane of the CO_3 group. (This is presumably the major difference between vaterite and calcite and aragonite. The CO₃ groups are perpendicular to the hexagonal axis in the case of calcite and the correspseudo hexagonal ponding/c axis in the case of aragonite.) The vaterite structure can not exist in the cell a = 4.13, c = 8.49 Å because this contains only two CO₃ groups, vertically arranged, the and with only two CO3 groups in/unit cell the structure can not accommodate a three-fold axis. McConnell (1960) found evidence for the real cell $\underline{a}' = \sqrt{3a}$, $\underline{c}' = \underline{c}$. Kahmi found $\underline{a}' =$ $\sqrt{3a}$, c' = 2c (Table 14). Because most of the x-ray scattering is from the psuedo-cell, Kahmi analyzed the structure in terms of this cell in space group P6,/mmc and gave positions for the carbon and oxygens in the CO3 group which are the result of averaging three orientations (Fig. 8). For Kahmi's structure R = 0.16 which is about the limit of the data. Single crystals of vaterite good enough to extend Kahmi's averaged

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Table 14

Pseudo-Cell and "True" Cell of Vaterite

| Pseudo-Cell | "True" Cell (Kahmi) |
|-----------------|---------------------------------|
| <u>a</u> 4.13 Å | $\sqrt{3} \times 4.13 = 7.16$ Å |
| <u>c</u> 8.49 | $2 \times 8.49 = 16.98$ |
| z 2 | 12 |



Figure 8. Kahmi's structure for the vaterite pseudo-cell. From Kahmi (1963).

structure into a three-dimensional structure have not yet been grown. Other routes to the vaterite structure may be through the structure of an isomorph or by lattice energy calculations on various models.

Various rare-earth borates apparently isostructural with vaterite have been studied (Battram and Felton, 1962; Newnham, Redman and Santoro, 1963; Bradley, Graf and Roth, 1966) and a structure for the high temperature form of $YbBO_3$ has been suggested (Bradley, Graf and Roth, 1966) which is reported to be very close to Kahmi's for vaterite. Bradley, et al give x = .39, y = .78 for oxygen and Kahmi gives x =.38, y = .76, all for the vaterite subcell. Bradley et al give the space group as probably being P6322 for their "real" cell a = 6.99, c = 8.34 Å, z = 6. Their suggested structure for the YbBO3 'isomorph' is given in Fig. 9. Since their cell is only half the vaterite cell along c, the structure of vaterite may consist of layers of the proposed YbBO3 structure displaced perpendicular to c to double the c translation.

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The structure proposed by Bradley, Graf and Roth (1966) for the

Figure 9.

 YbO_3 . This is a

form of/ \underline{c} -axis projection of edge-sharing nets of YbO₆ octahedra. The profiles of triangular borate ions above this net are indicated by heavy lines to the corners which they share with octahedra, and the positions of ions below the net by light lines.

(e) $CaCO_3 \cdot 6H_2O$

CaCO₃.6H₂O may be an important compound in the nucleation of calcium carbonates in precipitation from aqueous solutions. It is the final form of calcium carbonate produced in an aqueous environment near 0°C in the presence of polyphosphates, (Brooks, Clark and Thurston, 1951). The CaCO₃·6H₂O initially formed slowly redissolves with concommitant formation of CaCO3 • 6H2O. CaCO3 • 6H2O crystallizes in the unit cell $\underline{a} = 8.87 \pm .02 \text{ Å}, \underline{b} = 8.23 \pm$.01 Å, c = 11.02 ± .02 Å, β = 110.2 ± .1° (at about -120°C) with space group C2/c and four formula weights per cell. The structure (R = 0.10, Figures 10 and 11) was determined (Dickens and Brown, 1968a) from photographic x-ray data collected from a crystal held at about -120 °C. It is of great interest because it contains discrete [CaCO₃] ion-pairs even though the structure contains enough water to coordinate Ca octahedrally. Each ion-pair is isolated from other ion-pairs by an envelope of 18 water molecules. Such ion-pairs may have a significant concentration in solutions saturated with respect to the calcium carbonates and may be important in mechanisms of biological transport. One factor preventing the formation of Ca(OH₂) a "complexes" may be the difficulty in packing such complexes using only CO3 ions. However Ca does not have the afinity for water



Figure 10. The $CaCO_3$ ion-pair and the Ca ion environment in $CaCO_3 \cdot 6H_2O$. From Dickens and Brown (1968a).



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From Dickens and Brown (1968a).

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of the increased importance, relative to the Ca...O term, of the Ca...H repulsion in the Ca...OH₂ electrostatic compared with the corresponding terms in the interaction when/Mg....OH₂/. It is also noteworthy in this interaction respect that the highest stable hydrated Mg carbonate presently recognized is MgCO₃ ⁵H₂O, where Mg is probably coordinated to the five H₂O molecules and either a CO₃ 'apex' or 'edge'. Thus even Mg, with its many known instances of complete water coordination, may preferentially coordinate to CO₃⁻ in the presence of water molecules.

At atmospheric pressure, the reactions

- (a) $CaCO_3$ (calcite) + $6H_2O$ (liq.) = $CaCO_3 \cdot 6H_2O$ (solid)
- (b) CaCQ(aragonite) + $6H_2O(liq.) = CaCO_3 \cdot 6H_2O$ (solid)

(c) $CaNa_2(CO_3)_2(solid) + 5H_2O(liq.) = CaNa_2(CO_3)_2 \cdot 5H_2O(solid)$ would be accompanied by 20, 18 and 13 percent decreases in volume, respectively, suggesting that at high hydrostatic pressures (such as those that occur in the abyssal layer

of the oceans or in hydrostatic vessels) CaCO3 6HgO in particular, and hydrated salts in general, may not only be present as nucleating particles for the reasons mentioned earlier, but may actually be the most stable forms. It is noteworthy in this connection that/most deep sea animals have little or no calcareous materials in their skeletons (Svendrup, Johnson and Fleming, 1942) suggesting that anhydrous calcium carbonates are not easily formed at these 2) depths, and/that CaCO₃ is essentially absent from sediments collected at depths greater than 5,000 m (Arrhenius, 1963) and Laughton, presumably because of its increased solubility (Heezen / 1963). It has been suggested (Riedel, 1963) from an electron microscopic examination that almost all the calcium carbonate in deep sea sediments is of organic origin and has not been changed by recrystallization after deposition. However, the possibility must be considered that at great depths the calcium carbonates in such sediments can be

converted in part into hydrated forms which prevent the formation of normal skeletons and which rapidly decompose to the anhydrous forms at normal temperatures and pressures (.i.e., during sample recovery).

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(f) $CaCO_3 \cdot H_2O$

 $CaCO_3 \cdot H_2O$ usually has a spherulitic habit (Brooks, Clark and Thurston, 1951) and its structure is unknown at present. It is the first macroscopic phase obtained in the preparation of $CaCO_3 \cdot 6H_2O$ and $CaNa_2(CO_3)_2 \cdot 5H_2O$ (gaylussite) by precipitation from aqueous solution in gel form in the presence of polyphosphates. $CaCO_3 \cdot H_2O$ has been grown as single crystals by Lippmann (1959) by hydrolysing KCNO in aqueous solution with MgCl₂ and CaCl₂ in a closed vessel at $20^{\circ}C$. The structure has a pronounced pseudo-cell (Table 15). CaCO₃ $\cdot H_2O$ is of considerable interest since it is so readily produced (in spherulitic form) in the presence of crystal growth poisons which inhibit the formation of calcite. It is stable for several months at $20^{\circ}C$ in air.

(g) <u>Gaylussite CaNa₂ (CO₃)₂ • 5H₂O</u>

Gaylussite is found as a mineral and in the solid phase eventually formed/at room temperature from aqueous solution when a large excess of Na₂CO₃ solution is added to CaCl₂ solution in the presence of polyphosphate. The unit cell has dimensions <u>a</u> = 14.361(2)Å, <u>b</u> = 7.781(4) Å, <u>c</u> = 11.209(2) Å and β = 127.84(1)°, with space group C2/c. The structure has been determined (Dickens and Brown, 1968 b), (R₁ = 0.043),

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Table 15

The "True" and Pseudo Cells of $\text{CaCO}_3\cdot\text{H}_2\,\text{O}$

<u>a</u> 10.62 Å pseudo cell <u>a'</u> = 6.13 Å <u>c</u> 7.54 <u>c</u> = 7.61 z 9 2 a = $\sqrt{3a}$ ' space-group D₃ (4,6) P3,21 or D₃ (3,5) P3,21 density 2.38 g/ml and the hydrogen atoms have been located approximately. Specific details are shown in Fig. 12 and 13. The structure contains CO₃-Ca-CO₃ ion triplets isolated from each other but coordinated to Na ions and water molecules. These triplets could be of importance in biological transport. The structure is more fully discussed by Dickens and Brown (1968b).

(h) Pirssonite, $CaNa_2(CO_3)_2 \cdot 2H_2O$

Pirssonite is found as a mineral and is the solid phase formed instead of gaylussite when the reactants are maintained at 50°C. The cell data are given in Table 16. Its structure has been determined from natural (Corazza and Sabelli, 1967) and synthetic (Dickens and Brown, 1968 b) material. For the latter determination $R_w = 0.029$. Despite the resemblance of its cell dimensions to those of Na_2CO_3 . $NaHCO_3 \cdot 2H_2O$, trona, it is not structually related. The structure (Fig. 14, 15) contains ion triplets (Fig. 14) very much like those in gaylussite except that the triplets are further coordinated together (Fig. 14, 15) because there are not enough water molecules in the structure to complete the

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Table 16

Cell Data for Pirssonite

| Evans | Dickens and Brown (1968b) |
|----------------------------------|------------------------------|
| $\underline{a} = 11.32$ | 11.340(4) |
| b = 20.06 | 20.096(5) |
| $\underline{c} = 6.00 \text{ Å}$ | 6.034(2) |
| Space group Fdd2 | |

z = 8

density = 2.367 g/ml



Figure 12. The CO₃CaCO₃ triplet and the Ca environment in CaNa₂(CO₃)₂.5H₂O (gaylussite). From Dickens and Brown (1968b).



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and Brown, (1968b).



and Brown (1968b).



Figure 15. The detailed bonding in $CaNa_2(CO_3)_2 \cdot 2H_2O$ (pirssonite). From Dickens and Brown (1968b).

coordination round the Ca ions. Other features of the coordination are shown in Fig. 14 and 15. The structure is more fully discussed by Dickens and Brown (1968b). Pirssonite may be important in the otoliths of benthic which are found fishes (Morris and Kittleman, 1967) /to be well stratified into distinct species in the sea. The otoliths are strongly piezo-electric and it has been suggested that this may be the mechanism by which the fishes perceive their depth, since they do not have gas bladders. The major inorganic component of the otoliths is aragonite, which, being centrosymmetric, cannot be piezo-electric. Pirssonite, however, is non-centrosymmetric and consists of ions commonly present in sea water, although it is not normally formed under conditions expected in sea water (Bury and Redd, 1933). Organic components in the otoliths also may be responsible for the piezo-electricity, however, as has been Lavine and Shamos, 1963 /). Other possible candidates suggested for bone (Shamos are shortite and $Na_2CO_3^{H_2}O_1$. Using a crude apparatus we have found both pirssonite and shortite to exhibit piezoelectricity. Our sample of small plates of Na₂CO₃·H₂O did not give a positive test under these conditions, although Harper (1936) observed such an effect.

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(i) Shortite Ca₂Na₂(CO₃)₃

Shortite is found mainly as a mineral and, because it is non-centrosymmetric, may, like pirssonite, be of importance in generating the piezo-electricity of some otoliths. Its structure has been determined (Wickman, 1949) but there are some large discrepancies between the calculated and the qualitatively observed structure factors and the structure needs refining. 3. OTHER STRUCTURES OF INTEREST

(a) Brushite CaHPO₄ • 2H₂O

Brushite was first found in 1865 by G. E. Moore (1865) in druses in phosphate rock from Avis Island in the Caribbean Sea. It frequently occurs as encrustations on ancient human and animal bones (Frondel, 1943) and is found in human urinary calculi /(Lonsdale, Sutor and Wooley, 1968). The structure is related to that of gypsum, CaSO₄ • 2H₂O (Atoji and Rundle, 1958), and was first refined (Beevers, 1958) in the same centrosymmetric space group I2/a. Chemical considerations and the observance of a pronounced piezoelectric effect prompted refinement to (R = 0.164) in the non-centrosymmetric space group Ia (Jones and Smith, 1962). The refinement used Beever's original data which was uncorrected for what must have been appreciable absorption. More recent work (Jones, 1968) using an incomplete set of neutron data collected from a large single crystal of brushite retains the overall structural similarity of CaHPO4 • 2H2O to CaSO4 • 2H2O, including the hydrogen bonding of the water molecules, although the detailed atomic distances in the two cases are different. The 'acid' hydrogen in CaHPO4 • 2H2O, which presumably distorts the space group from I2/a to I/a, is suggested to be located between 0(1) and 0(4') (Jones, 1968), i.e., in the CaPO₄ layer. The positions

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of the heavy atoms have not yet been refined from those in Jones and Smith (1962). Further refinment with new data is necessary. The structure (Figure 16) consists of $CaPO_4$ sheets like those which have been found in several other calcium phosphate structures (in gypsum there are similar $CaSO_4$ sheets). The sheets consist of neighboring chains of alternating Ca and PO_4 ions and are linked together by interleaved layers of water molecules. The water molecules hydrogen bond to the oxygens of the PO_4 ions on the surfaces of the $CaPO_4$ sheets and are electrostatically bonded to the Ca's. The structure may be rationalized from Figure 17 which is the monetite ($CaHPO_4$) structure idealized into a tetragonal structure. Figure 17 is also essentially Hohne, 1962; the anhydrite ($CaSO_4$) structure (Cheng and Zussman, 1963).

In CaSO₄, the structure is orthorhombic with <u>a</u> = 6.991, <u>b</u> = 6.996, <u>c</u> = 6.238 (Swanson, Fugat and Ugrinic, If A/IS alcentral Ca/PO₄ in CaHPO₄ · 2H₂O 1955). B and C are CaHPO₄ chains and D and E are water molecules. Similarly, in CaHPO₄ · 2H₂O the Ca's in the B and C chains are coordinated to water molecules on the side away from the A chain so that the layer in both brushite and gypsum is a zigzag interlocking of chains. In brushite, presumably there is distortion of the chain by the hydrogen bonding between PO₄ groups.



Figure 16. Projection of the structure of brushite on to a plane perpendicular to [101]. From Beevers (1958).



Figure 17. An idealized tetragonal $Ca(H)PO_4$ structure.


(b) Monetite CaHPO₄

The crystal structure of monetite has been determined (MacLennan and Beevers, 1955; Jones and Cruickshank, 1961) with moderate precision (R = 0.15) from photographic x-ray data uncorrected for what must have been appreciable absorption. The hydrogen positions have been determined (Curry, Denne and Jones, 1968) using neutron data and are consistent with observed P-O lengths and NMR data. The heavy atom positions have not been refined from the positions reported in Jones and Cruickshank (1961). Further work (Curry, Denne and Jones, 1968) is continuing on monetite.

The structure (Figure B) contains sheets of $CaHPO_4$ which are bonded to one another by Ca...O electrostatic bonds and by hydrogen bonds. The shortest O...O distance in the structure is $O(7)...O(7') = 2.44 \pm .03$ Å across the center of symmetry. The hydrogen is disordered about this center of symmetry so that the bond contains half a hydrogen on average on each side of the center. The reamaining "half" hydrogen is similarly disordered in the O(1)...O(5) region, where the

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Figure 18. Monetite: projection of one layer of the crystal structure on to the plane perpendicular to [001]; the other layer (of which only O_7 and O_8 is shown) is related to this by a center of symmetry. The smallest circles represent probable hydrogen sites.

From Jones and Cruickshank (1961).

interatomic distance is 2.58 \pm .02 Å. The remaining hydrogen in the unit cell is on O(6) and forms an essentially linear hydrogen bond to O(8) with O(6)...O(8) = 2.66 \pm .02 Å. The structure of monetite is essentially the structure given in Figure 17 distorted to triclinic by the hydrogen bonding and perhaps by the lack of fit of the O 'cage' and the Ca ionic radius.

(c) $Ca(H_{g}PO_{4})_{2} \cdot H_{2}O$

The structure of $Ca(H_2PO_4)_2 \cdot H_2O$ (Figures 19, 20) has been determined (MacLennan and Beevers, 1956; Jones and Cruickshank, 1961) with moderate precision (R = 0.16) from photographic x-ray data uncorrected for absorption. The hydrogens have been placed (Jones and Cruickshank, 1961) provisionally from considerations of the P-O bond lengths in the PO_4 group and of $O_{\bullet\bullet\bullet}O$ distances in the structure. In the P(1) PO4 group, two statistically disordered hydrogens have been suggested, from 0(1) to 0(1') (2.67 \pm .05 Å) across the center of symmetry and (a little less likely) from O(4)to O(9) (O(4)... $O(9) = 2.60 \pm .03 \text{ Å}$). O(3) is assigned a hydrogen which is hydrogen bonded to 0(5) (0(3)...0(5) =2.48 \pm .03Å). In the P(2) PO group, the P-O distances suggest the assignment of one hydrogen to O(6), forming a hydrogen bond to 0(8) (0(6)...0(8) = 2.72 ± .04 Å), and one hydrogen



Figure 19. Four unit cells of $Ca(H_2PO_4)_2 \cdot H_2O$, projected down the <u>a</u>axis. From MacLennan and Beevers (1956).



Figure 20. Projection of the crystal structure of $Ca(H_2PO_4)_{B}H_2O$ onto the plane perpendicular to [100]. From Jones and Cruickshank (1961). to O(7), forming a hydrogen bond to O(8) (O(7)...O(8) =2.58 \pm .04 Å). The hydrogens of the water molecules hydrogen bond to O(4) (O(9) ... $O(4) = 2.60 \pm .03$ Å) and to O(8) $(0(9)...0(8) = 2.74 \pm .03 \text{ Å})$. Neutron data on a twinned crystal of $Ca(H_2PO_4)_2 \cdot H_2O$ are being collected (Curry, Denne and Jones, 1968). The CaPO, layer structure for Ca(HPO4)2.H20 is very similar to that for CaHPO4 • 2H2O, if the hydrogen atoms are ignored. One of the water molecules, say position in Figure 17, in CaHPO₄ \cdot 2H₂O is the oxygen O(5) of a PO₄ group which is hydrogen bonded to its centro-symmetrically related partner (Figures 19,20). Successive sheets in Ca(H₂PO₄) 2H₂O crystallographically are not/related by a rotation about 180° as they are in gypsum and brushite and the occasional crystallization of layers rotated by 180° explains the observed twinning of Ca(H2PO)2.H2O The fact that there are similar (MacLennan and Beevers, 1956). /sheets in the above compounds account for their observed intergrowths (Lehr, Smith and Brown, 1952).

The structure of $Ca(H_2PO_4)_2 \cdot H_2O$ is also related (Brown, Smith, Lehr and Frazier, 1958) to several other calcium phosphate compounds as shown in Table 17.

(d) Ca₂PO₄Cl chlorospodiosite

The crystal structures of Ca_PO4Cl (Figure 21) and its analog Ca₂CrO₄Cl have recently been determined (Greenblatt, Banks and Post, 1967) with R = 0.043 and 0.041, respectively. The structure of Ca₂PO₄Cl contains CaPO₄ layers which are easily constructed from Figure 17 by taking a planar sheet consisting of the ABC chains and replacing those oxygens in chains by Cl- ions D and E which are coordinated to the Ca in the A chain/ The Cl ions are in turn coordinated to another planar sheet on thier far side. The voids left between adjacent CaPO₄ sheets and in the Cl- layer are filled by Ca ions. The whole structure undergoes some slight rearrangement, seemingly based on the second type of Ca being coordinated most efficiently to the two PO, edges in the six oxygen atoms in its coordination environment . The other two oxygens in this environment are PO₄ apices. These six oxygens from a cyclo-hexane shaped boat with the Ca just above the 'deck' and with two Cl ions at right angles to the prow-stern line completing the Ca coordination as a 'sail'. The oxygen 'boats' share a common side and adjacent ones are inverted. The CaPO chains, apart from being

| a_2 (NH ₄) H ₇ (PO ₄) ₄ • 2H ₂ O | Ca ₂ (K) H ₇ PO ₄ • 2H ₂ O | Ca_2H_8 (PO ₄) $\circ 2H_2O$ | cacl(H2PO4)2•H2(|
|---|--|--|------------------|
| 5.79 Å | 5.72 Å | 5.67 Å | 5.76 Å |
| 12.52 | 12°13 | 11.92 | 17。14 |
| 6.50 | 6.46 | 6.51 | 6。41 |
| 97057 * | 144°98 | 11 . 86 | °06 |
| 117045" | 118°1° | 118°31' | 119° |
| ∎0 ∘ 86 | 95°54 ° | 83°91 | •06 |
| lensity 5.99 | 5,90 | 5 . 89 | 8.57 |
| 'W/cell 1 | 1 | 2 | 4 |
| | | | |

The Unit Cell Data of Several Compounds Related to Ca($\rm H_2PO_4$) $_2\cdot\rm H_2O$

Table 17

-



Figure 21. The unit-cell contents of Ca_2PO_4Cl viewed along <u>a</u>. Large open circles, Cl; atoms shaded up and down, P; double circles, Ca; smaller open circles, O. Bonds between the atoms in $PO_4^{3^-}$ tetrahedra are represented by broken lines. From Greenblatt, Banks and Post (1967).

slightly rotated about their axis by coordination to interlayer Ca ions, are regular because no hydrogens are present to distort them through hydrogen bonding.

(e) $\alpha - Ca_{3}(PO_{4})_{2}$

 α -Ca₃ (PO₄)₂ is the form of Ca₃ (PO₄)₂ stable above 1180°C MacKay (1953) assigned to it the monoclinic cell $\underline{a} = 12.86 \pm$.02, <u>b</u> = 9.11 ± .01, <u>c</u> = 15.23 ± .02, β = 125.3 ± .2° and the space group $P2_1/a$ with z = 8. A pseudo-orthorhombic cell a = 15.22, b = 20.71, c = 9.109 Å has been reported (DeWolff). MacKay noted considerable hexagonal pseudo-symmetry in the hkO layer of the reciprocal lattice, i.e., in the projection of the structure along c. In three dimensions the structure is not pseudo-hexagonal. From two-dimensional Patterson syntheses he suggested the structure contained 12 columns of Ca and PO4 ions parallel to c, the columns being spaced about 3 Å apart with the heavy atoms Ca and P about 3.8 Å apart in the columns. More recently, Epstein (1968) has found that the <u>b</u> axis is invariably tripled in samples he has examined, and we have confirmed this. He found trial positions for the heavy atoms but could not find positions for the light atoms which would allow the structure to refine. He considered two structures with packings similar to the chains of Ca and PO4 ions in structures such as CaHPO4.

(f) $\beta Ca_3 (PO_4)_2$

 $\beta Ca_2 (PO_4)_2$ is the form of $Ca_3 (PO_4)_2$ stable at temperatures below 1180° and is trigonal (Frondel 1941, 1943; Mac ay, 1952) with <u>a</u> = 10.32 Å, <u>c</u> = 37.0 Å, space group R3c and z = 7. It exists as the mineral whitlockite and is often a pathological calcified deposit in the body. There is an anomaly in that 21 Ca's (in 7 formula weights of $Ca_3 (PO_4)_2$) cannot fit in space group R3c without statistical disordering. Brown and Wallace have recently (1968) shown by heating mixtures of $CaCO_3$ and $CaHPO_4 \cdot 2H_2O$ to form $\beta Ca_3 (PO_4)_2$ and $Ca_4P_2O_7$ and subsequently analyzing for $P_2O_7^{4-}$ that the ratio of Ca/P in $\beta Ca_3 (PO_4)_2$ is 21/14 and not 20/14 (which would fit in space group R3c). The structure of $\beta Ca_3 (PO_4)_2$ is not yet known.

(g) $Ca_4 Mg_5 (PO_4)_6$

The structure of $Ca_4Mg_5 (PO_4)_6$ has recently been determined by Dickens and Brown to the point of final refinement (R = 0.08). The formula is really $Ca_{3.5}Mg_{4.5}$ (Ca, Mg) (PO₄)₆. Ca and Mg are present in the variable site in about equal amounts in our crystal, making the empirical formula $Ca_4Mg_5 (PO_4)_6$. When the structure is reviewed along [201] an approximate $\overline{3}$ axis can be discerned if small shifts in the atomic positions and the difference between Ca and Mg are ignored. A pseudohexagonal cell <u>a'</u> = 6.86 Å, <u>b'</u> = 9.99 and <u>c'</u> = 14.88 Å can be defined. Similarities between this cell and that of NaK₃(SO₄)₂ (glaserite) can be seen. As in glaserite, there are cation columns and cation-anion columns in Ca₄Mg₅(PO₄)₆. The cation-anion columns in Ca₄Mg₅(PO₄)₆ have every other cation site vacant.

One of the main objectives in our study of $Ca_4Mg_5 (PO_4)_6$ is to find relationships between it and the two better known tricalcium phosphates, $\beta-Ca_3 (PO_4)_2$, and $\alpha-Ca_3 (PO_4)_2$, neither of which has a known structure. The dimensions of the pseudoorthohexagonal cell of $Ca_4Mg_5 (PO_4)_6$ strongly suggest that there are relationships between it and the two tricalcium phosphates. For example, whitlockite is known to have a prominent repeat of c/10 (i.e., 3.74 Å) in its cell structure. The pseudoorthohexagonal described above has a similar repeat of c'/4(i.e., 3.72 Å). The <u>a</u> axis of whitlockite, 10.43 Å, is quite similar to <u>b</u>' of $Ca_4Mg_5 (PO_4)_6$, 9.99 Å. The dimensions of the pseudo-orthorhombic cell of $\alpha-Ca_3 (PO_4)_2$, <u>a</u> = 15.23, <u>b</u> = 20.71 and $\underline{c} = 9.11$ Å, are also similar to those of the pseudoorthohexagonal cell of $Ca_4Mg_5 (PO_4)_6$. It now appears that no two of these compounds are isostructural, but it is likely that they will share important structural features. The unit cell and related data of $Ca_4Mg_5 (PO_4)_6$ are compared with those of $\alpha Ca_3 (PO_4)_2$, $\beta Ca_2 (PO_4)_2$ and $NaK_3 (SO_4)_2$ (glaserite) in Table 18.

(h) Calcium Oxalates

Other important constitutents of human urinary calculi are the compounds $Ca(COO)_2 \cdot H_2O$ (whewellite) and $Ca(COO)_2 \cdot 2$ - $2 \cdot 2H_2O$ (weddellite), which are also found as minerals. The structures of both have been determined. Whewellite is monoclinic, <u>a</u> = 6.24, <u>b</u> = 14.58, <u>c</u> = 9.89, 8 = 107°, z = 8 with space group $P2_1/c$, R = .13-.15. Its structure (Cocco and Carobbi, 1961; Cocco and Sabelli, 1962) is shown in Figure 22. The Ca's are coordinated by the longer edge of the oxalate anion, which presumably allows each oxygen to coordinate to two Ca's more easily. Apparently the hydrogen atoms were not located.

| | Ta | ble 18 | | |
|----------------------|----------------------------------|--|---------------------------|---------------------|
| A | Comparison of | the Unit Cel | l Data of | |
| | α and $\beta Ca_3 (PO_4)$ |) ₂ ,and Ca ₄ Mg | 5(PO4) ₆ and | |
| N | $a_{3}K_{9}(SO_{4})_{6}$ (g | laserite) α C | a ₃ (PO4) 2 | |
| Monoclinic cell) | pseudo- orthorhombic cell) | $\beta Ca_3 (PO_4)_{2}$ | $Na_{3}K_{9}(SO_{4})_{6}$ | $Ca_4Mg_5 (PO_4)_6$ |
| <u>a</u> 12.86 Å | 20.71* | 10.32 Å | 9.80 Å | 22.84 Å |
| <u>b</u> 27.33 | 9.109 | 10.32 | 9.80 | 9.994 |
| <u>c</u> 15.23 | 15.22 | 37.0 | 7.33 | 17.09 |
| β 125°20' | | Y:120° | γ :120° | β :99.96° |
| space group | P2 ₁ /a | R3c or R3c | PJml | C2/c |
| Vol. 4367 Å | 3 | 3412 Å ³ | 610 Å | 3841 |
| density 2.81 | g/ml | 3.12 g/m l | | 3.13 g/ml |
| Fwt/cell 24 | | 21 | 1 | 8 |
| Vol. $M_{2}(XO_{4})$ | . 182.0 Å ³ | 162.5 Å ³ | 203 Å ³ | 160 Å ³ |

* 2 x 12.86 cos (125°20') = 20.98 Å



Figure 22. Projection of half of the structure of whewellite on a plane roughly normal to [010].

Weddellite is tetragonal with $a = 12.30 \pm .02$, $c = 7.34 \pm$.02 and space group I 4/m. Its structure (Sterling, 1965) is shown in Figure 23. For this structure, R = 0.13. The Ca... oxalate coordination is similar to that in whewellite An unusual feature in the structure is the O(7) water, which is not in a position to form well defined hydrogen bonds and which is held in a zeolitic manner to a variable extent. The refinement suggests (Sterling, 1965) 0.4 of a water in this position, which in turn suggests the formula Ca(COO) 2.2.2H2O, close to the measured value of 2.17H₂O. Crystallographically, the maximum amount of water the structure can hold is 2.5H2O, which agrees with the suggestion of Philipsborn (1952). The hydrogen positions were not determined but possible hydrogen bonds have been suggested from inter-oxygen distances and angles.

(i) Newberyite MgHPO₄•3H₂O

Newberyite is often found with struvite, of which it may be a decomposition product. It is found in various types of guano and in urinary calculi. The structure has been determined (Sutor, 1967) (R = 0.044) and is shown in Figure 24. The acid hydrogen has been assigned on the basis of the P-O bond lengths and the 0...O distances; the remaining hydrogens have not been assigned unequivocally.

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Figure 23. Cell of weddellite. Atoms of primitive cell have bolder outlines or are solid. Smallest atoms are calcium, next larger ones are carbon, and largest are oxygen. Atoms of oxalate groups are connected with solid lines. Broken lines connect calcium ions in primitive cell with the oxygen atoms which they are coordinated. Solid oxygen atoms represent water molecules, 5 and 6 lying in the mirror plane (001). The solid calcium atoms also lie in (001).



Figure 24. Bounded projection of the structure of $MgHPO_4 \circ 3H_2O$ from $y = 0 \rightarrow 0.5$ on (010), showing the magnesium coordination. The magnesium atoms which are approximately coplanar are sandwiched by two planes of phosphorus atoms. In the bounded projection from $y = 0.5 \rightarrow 1.0$ which completes the structure, the atoms are related to these by 1/2 - x, 1/2 + y, z.

(j) Struvite MgNH₄PO₄•6H₂O

Struvite is apparently almost ubiquitous, having been found in canned crabmeat, shrimp, lobster, in peat bogs, in a mammoth's tooth and in bat guano. Its structure has been determined (Whitaker, 1965). The magnesium ion is coordinated by water molecules only, as one would expect from the similar situation in $MgSO_4 \circ 7H_2O$ (Baur, 1964). Struvite may be produced <u>in vivo</u> by bacterial action (Palache, 1923; Ayres, 1942). It seems probable that most or all of the newberyite found in calculi results from the decomposition of struvite (Lonsdale and Sutor, 1966).

(k) Calcium Arsenates

We have seen earlier that hydrated salts may be important in general as precursors in precipitation from aqueous solution. In the case of calcium phosphate hydrates, the calcium arsenates are a rich source of structural information by analogy.

Various hydrated calcium arsenates are thought to (See for example, Pierrot (1964) and references therein.) exist./ While several are related to known hydrated calcium phosphates, other have no analogy among the stable calcium phosphates. The structures of these arsenates may shed light on the possible composition of the highly hydrated amorphous phase (or on other possible precursors in the calcium/phosphate/ water system.

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Table 19

Hydrated Calcium Arsenates

| Ca(H ₂ AsO ₄) ₂ •nH ₂ O | n = 0, 1, 2, 3 |
|--|--------------------|
| CaHAsO ₄ •nH ₂ O | n = 0, 1, 2, 3 |
| $Ca_5H_2(AsO_4)_4 \cdot nH_2O$ | n = 4, 5, 9 |
| Ca ₃ (AsO ₄) _{2 • nH₂O} | n = 0, 2, 4, 8, 10 |
| $Ca_{10}(OH)_{2}(AsO_{4})_{6}$ | |

 Ca_2 (OH) $AsO_4 \cdot 2H_2O$

| 0 |
|-------------------------|
| $\overline{\mathbf{N}}$ |
| |
| |
| U |
| -1 |
| ⁱ |
| 4 |
| n |
| FH |

Unit Cell Data on Some Hydrated Calcium Arsenates

| | Mineral | Crystal | Cell | | |
|---|------------------------|---------|--|---------------------|--|
| Formula | Name | System | Parameters | Space Group | |
| CaHAsO4。2H20 ^a | Pharmacolite | ш | 6.001,15.58, 114°43' | Ia | |
| $CaHAsO_4 \bullet H_2O$ | Haidingerite | 0 | 6。946,16。14, 7.930 | P cnb | |
| caHAsO ₄ b | Weilite | თ | 7.11,6.94,7.15, 94°19'.101°35'.87°22' | | |
| Ca ₃ (AsO ₄) ₂ • 4H ₂ O | | ш | 22.75,10.19,4.81, 97°19' | | |
| $ca_{3}AsO_{4} \bullet 10H_{2}O$ | Rowenthalite | ц | | | |
| $ca_{s}H_{2}$ (AsO $_{4}$) $_{4}$ • 4H $_{a}$ O | Sainfeldite | ш | 18.64,9.81,10.12, 97° | C2/C | |
| Ca ₅ H ₂ (AsO ₄) ₄ • 5H ₂ O | Vladimirite | ш | 5.81,10.19,22.7, 82.41' | $P2_1/c$ | |
| Ca ₅ H ₂ (AsO4) 4 • 9H ₂ O | Guerinite | ш | | | |
| (CaMg) $_{3}$ (AsO $_{4}$) $_{2} \cdot 6H_{2}O$ | Picropharma colite | ш | 13°7,13•5,6•75, | | |
| Ca ₂ Mg (AsO ₄) ₂ • 2H ₂ O | Belovite Talmessite | ກ | 112°38°,70°49°,119°25° | | |
| (Ca,CO) ₂ (Co,Mg) (AsO ₄) ₂ 。2H ₂ O | Roselite | Ħ | 5.60,12.80,5.60, 100°45' | P21/c | |
| ^a cf CaHPO ₄ •2H ₉ O (br | ushite) Structure: | Binas, | 1966; Cassien, Herpin an | d Permingeat, 1966. | |

ł. . ^b_{cf} CaHPO₄ (monetite) 2 4

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