ALKALINE EARTH PHOSPHATES

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I. INTRODUCTION

The most important alkaline earth phosphates are those of calcium, because of their presence in the mineral phase of bone and the use of phosphatic compounds as soil and body foods. As a result, the chemistry of the calcium phosphates has been reviewed extensively and authoritatively (65, 77, 152, 153, 211). Comparable reviews on the strontium and barium phosphates do not exist.

The alkaline earth phosphates have assumed greater importance in recent years in view of their use as phosphor matrices. This usage has flourished since the discovery of the alkaline earth halophosphate family of phosphors (103), whose most important member is calcium chlorofluoroapatite, commonly known as calcium halophosphate. Other alkaline earth phosphate phosphors—namely, barium titanium phosphate (84, 89), tin-activated strontium pyrophosphate (134, 173, 179), and tin-activated modified calcium and strontium orthophosphates (42, 113, 199)—have also been developed for use in commercial fluorescent lamps. From the earliest work on phosphate phosphors it has been realized that the properties of the final phosphor depend to some extent upon the characteristics of the initial phosphate compounds used in the solid-state reactions, and recent work has been directed toward a study of such characteristics (2, 48, 116, 144).

This review is, therefore, directed toward a comparison of the phase relationships, chemistry, structure, and properties of the alkaline earth phosphates, with emphasis on the phosphates of strontium and barium wherever the data permit. It avoids the controversial subject of the nature and composition of calcium hydroxyapatite except from the crystallographic viewpoint. It also omits detailed discussion of the kinetics of phosphate reactions, since reliable experimental evidence is fragmentary and there is little or no agreement on results. In general, the discussion of phase relationships and structures considers only the systems $MO–P_2O_5–H_2O$ and $MO–P_2O_5$, where M is calcium, strontium, or barium, so neither quaternary phase diagrams nor mixed alkali–alkaline earth phosphates are considered. It does include, however, important thermodynamic and crystal structure work on the calcium phosphates in order to permit comparisons with the strontium and barium systems and to make the review complete through 1959.

II. NOMENCLATURE

The early literature on the alkaline earth phosphates is often difficult to interpret in view of (*1*) lack of precise methods for identifying and characterizing the species involved and (*2*) lack of universally accepted nomenclature. The experimental problems have been largely overcome in recent years by the use of x-ray diffraction and chromatographic techniques to define the phosphates uniquely, while the problems of nomenclature have been clarified by the increasing acceptance of standard terminology.

The orthophosphates should be straightforward, but even here the names used are sometimes ambiguous. For instance, the compound $Ca(H_2PO_4)_2$ is sometimes called by the old double-salt-derived name of monocalcium phosphate, sometimes by the common name of monobasic calcium orthophosphate, and sometimes by the preferred name (210) of calcium tetrahydrogen diorthophosphate. The common names will be used for the orthophosphates in this review because of their wide use and acceptance in the literature. The preferred names are completely unambiguous but, as a consequence, are cumbersome and give no immediate picture of the phosphate groups involved. The old names originating from the double-oxide type of formula will not be used, as they frequently lead to serious misinterpretation, an extreme case being the use of "tricalcium phosphate" (an orthophosphate) and "calcium triphosphate" (a polyphosphate) as synonyms. When referring to the apatites, formulas of the type $M_{10}(X)_2(PO_4)_6$, where X is OH, F, or Cl, will be used to denote the stoichiometric compounds, in keeping with current preferred practice.

The general structural theory and nomenclature of the condensed phosphates have been reviewed by several authors (43, 130, 196, 197, 214). The system followed herein is that of Van Wazer and Griffith (214) and Markowitz (130). Thus, the phosphates are defined in terms of their $M^{II}O/P_2O_5$ ratio (table 1).

The polyphosphates are straight-chain compounds having the formula $M^{II}_{(n+2)/2}P_nO_{3n+1}$, whose first member is the tribasic orthophosphate $M_3(PO_4)_2$ and whose second member is the dipolyphosphate or pyrophosphate $M_2P_2O_7$. Tripolyphosphate ($P_3O_{10}^{5-}$, $n = 3$), tetrapolyphosphate ($P_4O_{13}^{6-}$, $n = 4$), and pentapolyphosphate ($P_5O_{16}^{7-}$, $n = 5$) compounds are also found in the alkaline earth phosphates. The metaphosphates

TABLE 1

$M^{II}O/P_2O_5$ *ratios and general formulas of alkaline earth phosphates*

Phosphates	$M^{II}O/P_2O_5$ Ratio	General Formula
Polyphosphates..........	$1 < \text{ratio} \leq 3$	$M_{(n+2)/2}P_nO_{3n+1}$
Metaphosphates..........	1	$M_n(P_nO_{3n})_2$
Ultraphosphates..........	$0 < \text{ratio} < 1$	

having the formula $M^{II}_n(P_nO_{3n})_2$ occur in rings with only the trimetaphosphate ($P_3O_9{}^{3-}$, $n = 3$) and the tetrametaphosphate ($P_4O_{12}{}^{4-}$, $n = 4$) well established. Long-chain polyphosphates result from repeated linking of PO_4 groups in chains such that the metaphosphate composition is ultimately reached, as indicated by equation 1.

$$\lim_{n \to \infty} M_{(n+2)/2}P_nO_{3n+1} = M_n(P_nO_{3n})_2 \qquad (1)$$

The ultraphosphates, which have an MO/P_2O_5 ratio between 0 and 1, will not be considered here, but have been reviewed by Van Wazer (211).

III. Phase Relationships at Equilibrium

A. ORTHOPHOSPHATES FROM AQUEOUS SOLUTION

The phase diagrams at 25°C. for the systems $CaO-P_2O_5-H_2O$ (211), $SrO-P_2O_5-H_2O$ (acid region) (194), and $BaO-P_2O_5-H_2O$ (11, 83, 194) are given in figures 1, 2, and 3. In a three-component system, $MO-P_2O_5-H_2O$, at constant temperature and pressure (25°C., atmospheric pressure) the number of degrees of freedom, F, may be derived from the well-known phase rule.

$$(F)_{T,p} = 3 - P \qquad (2)$$

Hence the system becomes invariant when three phases (two solid, one liquid) are present. With only one salt present, the composition of the solution at equilibrium cannot be constant and will vary until a second solid phase appears.

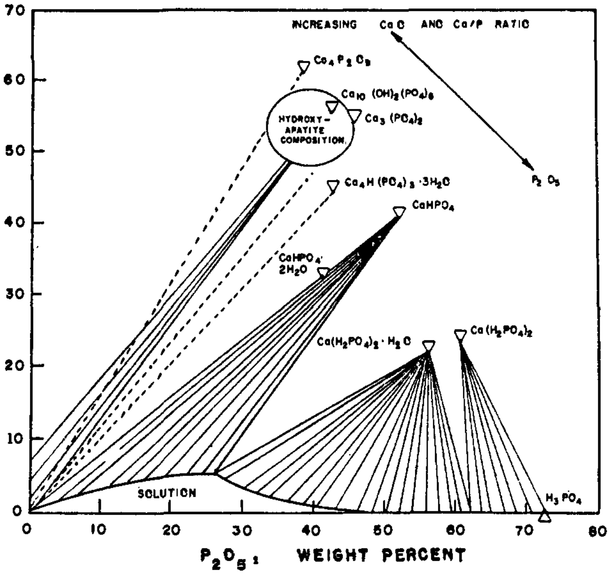


FIG. 1. Phase diagram of the system $CaO-P_2O_5-H_2O$ at 25°C. A dotted line indicates that existence of the phase at equilibrium is uncertain. Adapted from Van Wazer (211); reproduced by permission of Interscience Publishers, Inc., New York.

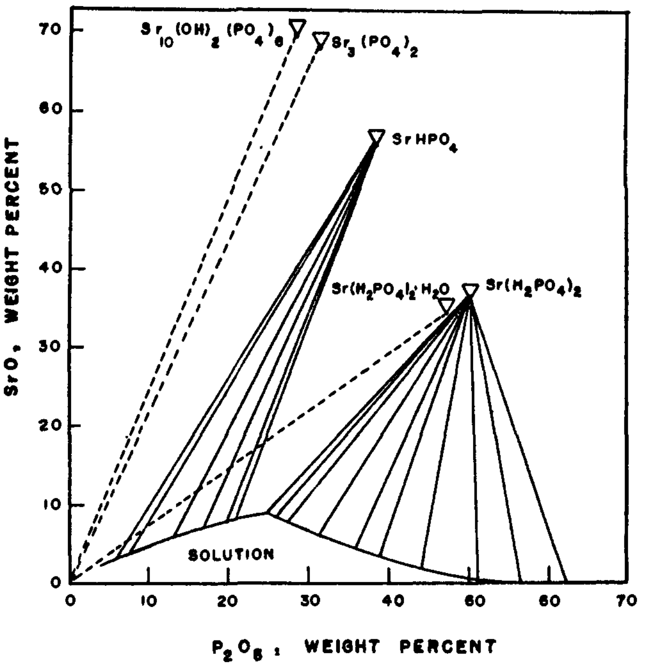


FIG. 2. Phase diagram of the system $SrO-P_2O_5-H_2O$ at 25°C. A dotted line indicates that existence of the phase at equilibrium is uncertain. Adapted from Tartar and Lorah (194); reproduced by permission of the American Chemical Society and the authors.

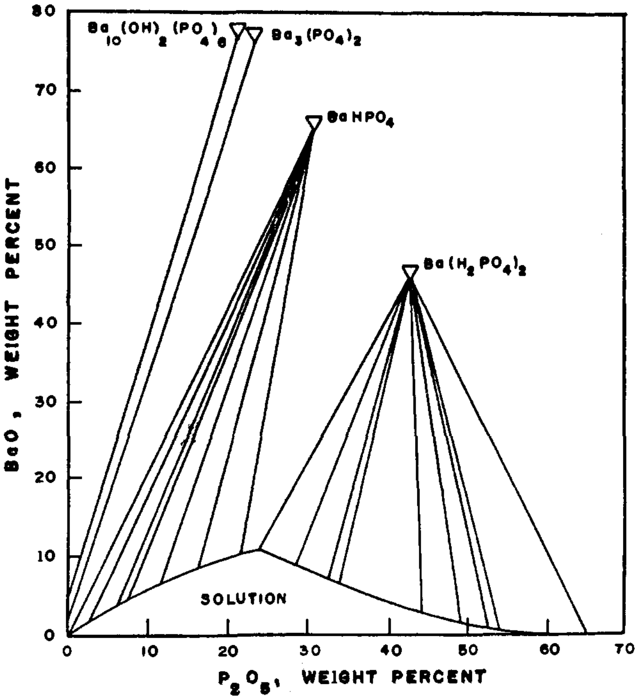


FIG. 3. Phase diagram of the system $BaO-P_2O_5-H_2O$ at 25°C. Adapted from Tartar and Lorah (194) and Arthur (11); reproduced by permission of the American Chemical Society and the authors.

1. Calcium orthophosphates

Many phase studies of the system $CaO-P_2O_5-H_2O$ have been made. Eisenberger, Lehrman, and Turner (65) have critically discussed the basic region in detail, and Van Wazer (211) has recently given the entire phase diagram based on work up to 1953. Both of these reviews show greatly expanded approximations of the region near the origin, which is of especial interest in the study of dilute solutions of the calcium orthophosphates. In addition, Bassett (17) has reviewed his original space diagram (15, 16) and finds that after fifty years of additional research, only minor modifications are required in his early work to bring it in line with more recent results.

(a) Octacalcium phosphate

Although not shown in previous phase diagrams, octacalcium phosphate, $Ca_4H(PO_4)_3 \cdot 3H_2O$, has been established as a distinct orthophosphate occurring with the controlled hydrolysis of $CaHPO_4 \cdot 2H_2O$ in sodium acetate buffer at 40°C. (39). Its occurrence as a distinct equilibrium phase at 25°C. is still uncertain, although there is supporting evidence dating back to 1866 (224). Octacalcium phosphate is perhaps so named (10) since its formula may be written as $Ca_8H_4(OH)_2(PO_4)_6 \cdot 4H_2O$, by analogy with the apatite formula.

It has been suggested (39) that the formation of bones and teeth may occur via the path shown in equation 3.

$$CaHPO_4 \cdot 2H_2O \rightarrow Ca_4H(PO_4)_3 \cdot 3H_2O \rightarrow \text{hydroxyapatite} \quad (3)$$

However, a series of papers by Tovborg-Jensen (200–205) indicates that the chemical progression shown may also include tribasic calcium orthophosphate as a product of calcification. In fact, there are instances where pure β-$Ca_3(PO_4)_2$ (whitlockite) is deposited on the teeth, whereas octacalcium phosphate occurs only as a minor constituent of dental calculi (202, 203).

(b) Tribasic calcium orthophosphate

While there has been much uncertainty about the existence of nonapatitic "tricalcium phosphate" (more properly tribasic calcium orthophosphate) in aqueous solutions (9, 65), it has been proved (7, 86, 207) that β-$Ca_3(PO_4)_2$ is precipitated from aqueous solution in the presence of magnesium, as suspected for many years. When found in nature as the mineral whitlockite, β-$Ca_3(PO_4)_2$ contains a small amount of magnesium (6.8 atom per cent) and a smaller amount of ferrous iron (2.9 atom per cent) (75), while in pathological calcifications 6–8 atom per cent magnesium is found (204). Impurities that stabilize the β-$Ca_3(PO_4)_2$ structure under conditions that ordinarily produce the much more common hydroxyapatite are magnesium (0.1 to 1 per cent), manganese (about 1 per cent), bivalent iron (about 10 per cent), and aluminum in decreasing order of effectiveness (86). Hayek and Newesely (86) postulate that only cations smaller than Ca^{2+} produce stabilization of β-$Ca_3(PO_4)_2$ (Ba^{2+} stabilizes $CaHPO_4$), and that the effect is one of seeding, since solid tribasic magnesium orthophosphate has the same effect as aqueous solutions of magnesium(II) salts in promoting formation of β-$Ca_3(PO_4)_2$ instead of hydroxyapatite. As is discussed later, magnesium, zinc, aluminum, calcium, and cadmium (in that order) also exhibit the ability to stabilize the β-$Ca_3(PO_4)_2$ structure in $Sr_3(PO_4)_2$ prepared by solid-state synthesis (113).

Perloff and Posner (160) prepared well-crystallized β-$Ca_3(PO_4)_2$ by hydrothermal synthesis at 300°C., using $CaHPO_4$ and water which became contaminated with iron and chromium when the platinum lining of their bomb cracked. Under normal conditions, only hydroxyapatite was produced. It has also been reported that β-$Ca_3(PO_4)_2$ is a constituent of "stones" found in the kidneys, bladder, and other parts of the body (25, 205), as well as a frequent constituent of dental calculi (200–205). Although tribasic calcium orthophosphate may not be precipitated from pure aqueous solutions of calcium and phosphorus, it is encountered in certain aqueous calcium phosphate systems containing impurities, particularly magnesium, manganese, iron, aluminum, and possibly chromium. Biological serums and soils are practical examples of such systems.

(c) Tetracalcium phosphate

Tetracalcium phosphate, or hilgenstockite, is well known in the $CaO-P_2O_5$ phase diagram, where $Ca_4P_2O_9$ forms a eutectic with α-$Ca_3(PO_4)_2$ at about 1550°C. (211). However, no convincing proof of the existence of $Ca_4P_2O_9$ in solution at normal temperatures has been presented as yet. Sanfourche (183) claimed the existence of hydroxyphosphoric acid, $H_8P_2O_9$, in solution under certain conditions and in the case of calcium (but not of strontium or barium) he obtained a "tetrabasic phosphate" on the basis of chemical analyses. However, this explanation is not plausible, since $Ca_4P_2O_9$ below about 1500°C. is known to react with water to form the hydroxyapatite (65).

$$3Ca_4P_2O_9 + H_2O \rightarrow Ca_{10}(OH)_2(PO_4)_6 + 2CaO \quad (4)$$

Thus, there are no x-ray data or other physical evidence to support the existence of $Ca_4P_2O_9$ in aqueous solutions under equilibrium conditions. Nevertheless, in a recent phase study d'Ans and Knütter (9) claim the occurrence of $Ca_4P_2O_9 \cdot 4H_2O$ and higher basic phosphates at 25°C. with an excess of $Ca(OH)_2$ present.

2. Strontium orthophosphates

Tartar and Lorah (194) studied the acid region of the aqueous strontium orthophosphate system at equilibrium and found only anhydrous $Sr(H_2PO_4)_2$ and $SrHPO_4$. There has been no systematic study of the basic region, although the basic salts $Sr_3(PO_4)_2$ and Sr_{10}-

$(OH)_2(PO_4)_6$ are well known (110, 143, 232). The direct precipitation of $Sr_3(PO_4)_2$ is difficult and normally both the dibasic phosphate and hydroxyapatite are formed (110, 178), as with the calcium orthophosphates. The hydrated $Sr_3(PO_4)_2$ of various researchers (5, 32, 33, 162) is probably a defect apatite, as found in the calcium system (168), and its existence as a well-defined compound has not been proved by single-crystal x-ray data. It shows an apatite x-ray powder pattern and forms anhydrous $Sr_3(PO_4)_2$ upon ignition (5, 32, 162), analogous to the β-$Ca_3(PO_4)_2$ formed by so-called "hydrated tricalcium phosphate" and other calcium-deficient hydroxyapatites (14, 153, 220). It appears then that the strontium orthophosphates are similar to the calcium orthophosphates, although the only phase study for SrO–P_2O_5–H_2O did not show strontium analogs for $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$, and $Ca_4H(PO_4)_3 \cdot 3H_2O$ (octacalcium phosphate).

Evidence for $Sr(H_2PO_4)_2 \cdot H_2O$ has been reported (136, 178, 198), but this hydrate does not appear to be stable under normal atmospheric conditions (178). It has been prepared in this laboratory by adding $SrCO_3$ to a very large excess of concentrated H_3PO_4 and then filtering at room temperature under vacuum overnight. Large crystals found in the filtrate gave the chemical analysis of the monohydrate, and the x-ray powder pattern was very similar to the pattern given by $Ca(H_2PO_4)_2 \cdot H_2O$.

The $SrHPO_4 \cdot 2H_2O$ reported by Plumier and Brasseur (164) has never been confirmed by chemical or single-crystal analysis and does not appear valid in the light of current evidence. Instead of exhibiting a dibasic dihydrate (i.e., $SrHPO_4 \cdot 2H_2O$), $SrHPO_4$ is dimorphic, with the lower-temperature form, β-$SrHPO_4$, predominating at room temperature (143).

Since no systematic study of the region lying between $SrHPO_4$ and $Sr_3(PO_4)_2$ has been made, it cannot be said that an "octastrontium phosphate" does not exist. Klement's hydrolysis studies (110) indicate that a gradual change of $SrHPO_4$ to strontium hydroxyapatite occurs with digestion at 40°C. in phosphate buffer solution of pH 11.0, but no change occurs in buffers at pH 6.8 and 8.3. Sodium acetate buffer solution (pH 8.8) at 40°C. produces no change in β-$SrHPO_4$ after thirty days of treatment (1), whereas $CaHPO_4 \cdot 2H_2O$ is converted to octacalcium phosphate in a few days (39). A thorough x-ray study of the intermediates obtained with the hydrolysis of $SrHPO_4$ in buffer solutions at pH 11.0 is more likely to prove or disprove the existence of a strontium analog of octacalcium phosphate.

3. Barium orthophosphates

The phase diagram for BaO–P_2O_5–H_2O in the acid region was also reported by Tartar and Lorah (194). As with strontium, only two acid salts, both anhydrous, were found: namely, $Ba(H_2PO_4)_2$ and $BaHPO_4$. Guérin and Artur (11, 83) confirmed the earlier findings and established two salts, $Ba_3(PO_4)_2$ and $Ba_{10}(OH)_2(PO_4)_6$, as the only phases stable in basic solution. The domains of stability for the various salts are summarized in table 2 from Artur's data (11).

TABLE 2

Domains of stability of the barium orthophosphates at 25°C.

Solid Phase	Liquid Phase		
	P_2O_5	BaO	Maximum pH
	per cent	*per cent*	
$Ba(H_2PO_4)_2$	65.3 to 21.4	0.55 to 11.4	1.0
$BaHPO_4$	21.4 to 0.0013	11.4 to 0.0047	7.2
$Ba_3(PO_4)_2$	0.0013 to trace	0.0047 to 0.26	12.0
$Ba_{10}(OH)_2(PO_4)_6$	Trace	0.26 to 3.05	13.3
$Ba(OH)_2 \cdot 8H_2O$	Trace	>3.05	—

Unlike the tribasic calcium and tribasic strontium orthophosphates, the tribasic barium orthophosphate is easily precipitated from solution, at least at 25°C. It appears that Stocklasa's $Ba(H_2PO_4)_2 \cdot H_2O$ (190) and Woyczinski's tetrabarium phosphate (229) do not exist as stable phases in water at 25°C. The "tetrabarium phosphate" was a mixture of $Ba_3(PO_4)_2$ and $BaCO_3$, as later determined by x-ray analysis (111).

An interesting feature of the barium orthophosphates is the marked stability of $BaHPO_4$ and $Ba_3(PO_4)_2$. Boiling $BaHPO_4$ in distilled water (111, 112) or in sodium hydroxide solution (194) produces very slow hydrolysis to $Ba_3(PO_4)_2$, but not to $Ba_{10}(OH)_2(PO_4)_6$. On the contrary, when Artur boiled barium hydroxyapatite in carbon dioxide-free water, he noted a *drop* in the Ba/P mole ratio of the solid from 1.66 to 1.58, with microscopic evidence for the formation of $BaHPO_4$ (11). During the experiment, the pH of the solution remained constant at 9.3 after eleven washes; according to table 2 this places it in the region where only $BaHPO_4$ and $Ba_3(PO_4)_2$ are the stable solid phases at 25°C.

The domain of stability of $BaHPO_4$ increases with temperature, according to Artur (11), since at 50°C. he precipitated $BaHPO_4$ when he combined 3 moles of BaO [as $Ba(OH)_2$] with 1 mole of P_2O_5 (as H_3PO_4), whereas at 25°C. he obtained $Ba_3(PO_4)_2$. This experiment conflicts with the more plausible observation (162, 175, 183) that in neutralizing phosphoric acid with barium hydroxide, the tribasic barium orthophosphate is obtained more quickly from hot solutions than from cold solutions. It is very difficult to prepare pure barium hydroxyapatite in aqueous solution (11, 111, 183, 194), since the tribasic barium orthophosphate is stable up to pH 12.0 and exists in an extremely limited domain (table 2); hence it readily precipitates. The hydroxyapatite precipitates only when the BaO in solution is between 0.26 and 3.05 per cent, and owing to the low solubility of the barium phosphates this condition is achieved only after many months (11).

B. *Orthophosphates in the solid state*

The $CaO–P_2O_5$ phase diagram has been fully reported, and the results have been summarized by Van Wazer (211). In addition to the known tribasic calcium orthophosphates, a new high-temperature form termed α'-$Ca_3(PO_4)_2$ has been found resulting from the inversion of α-$Ca_3(PO_4)_2$ at 1430°C. (155). The complete $SrO–P_2O_5$ and $BaO–P_2O_5$ phase systems remain unreported. The results of several fragmentary studies are discussed in Section IV,A,3, which deals with preparations by solid-state reaction.

IV. CHEMISTRY AND PREPARATION OF ALKALINE EARTH PHOSPHATES

A. ORTHOPHOSPHATES

1. *Generalized behavior in aqueous solution*

The complexity of the chemical behavior of alkaline earth compounds varies inversely with the ionic radius of the cation. The aqueous phase diagrams show two stable orthophosphate hydrates for calcium, one unstable hydrate for strontium plus dimorphic modifications of $SrHPO_4$, but no hydrates or polymorphism for barium. The tendency to form hydrates is associated with the tendency of the solid orthophosphates to hydrolyze on extended contact with water. Although no quantitative comparison of the hydrolysis of calcium, strontium, and barium orthophosphates has been made under conditions of equivalent particle size, the available data support the expected progression with respect to water (110, 111, 124, 143), i.e., the calcium orthophosphates are easiest and the barium orthophosphates most difficult to hydrolyze.

Several alkaline earth ammonium orthophosphates are known: $CaNH_4PO_4 \cdot 7H_2O$ (12, 185); the analogous barium salt, $BaNH_4PO_4 \cdot 7H_2O$ (12); other calcium salts including $Ca_2NH_4H_7(PO_4)_4 \cdot 2H_2O$ (40), previously known as $Ca_9(NH_4)_4H_{32}(PO_4)_{18} \cdot 10H_2O$ (71, 72), and $Ca(NH_4)_2(HPO_4)_2$, cited by Mellor (136). However, no pure strontium ammonium orthophosphates have been reported, despite several efforts by Auger and Ivanoff (12), who found that the strontium phosphate crystals that they obtained using the methods established for $CaNH_4PO_4 \cdot 7H_2O$ and $BaNH_4PO_4 \cdot 7H_2O$ were converted on washing to "a gel of strontium phosphate." Since $SrHPO_4$, as well as $CaHPO_4$ and $BaHPO_4$, is dissolved by solutions of ammonium salts such as ammonium citrate, chloride, and nitrate (136), and since $SrHPO_4$ is hydrolyzed more readily than $BaHPO_4$ (110), the absence of strontium ammonium phosphates is anomalous. Methods cited by Mellor (136) for calcium, such as the exposure of the monobasic salt, i.e., $Sr(H_2PO_4)_2$, to dry ammonia gas, may prove useful in showing the existence of strontium ammonium phosphates as a matter of academic interest.

A generalization of the chemistry of the alkaline earth orthophosphates in aqueous media is given by figure 4. Lithium phosphates have been excluded, owing to their markedly different behavior (211, 226). The ionization of phosphoric acid is the dominant factor in the formation of the ammonium, alkali metal, and organic orthophosphates (shown horizontally), as well as in the precipitation of the much less soluble alkaline earth orthophosphates (shown vertically).

As would be expected from the ionization of phosphoric acid, the reactions are reversible and extremely dependent on pH. However, the problem of preparing pure alkaline earth orthophosphates from solution should not be oversimplified, since strong effects are known for temperature, concentration of reactants, method of combining reactants (48, 144, 174, 175), and for impurities, particularly those which form insoluble precipitates such as carbonates and sulfates (11, 93) or which chelate the cations, as do certain organic acids and phosphates (104, 153, 212). Hence any variables that influence the rate and extent of ionization of phosphoric acid or the bonding of the alkaline earth cation may alter the nature of the orthophosphates obtained from solution.

2. *Preparation from solution*

(a) Conventional methods

A compilation of references to selected methods for

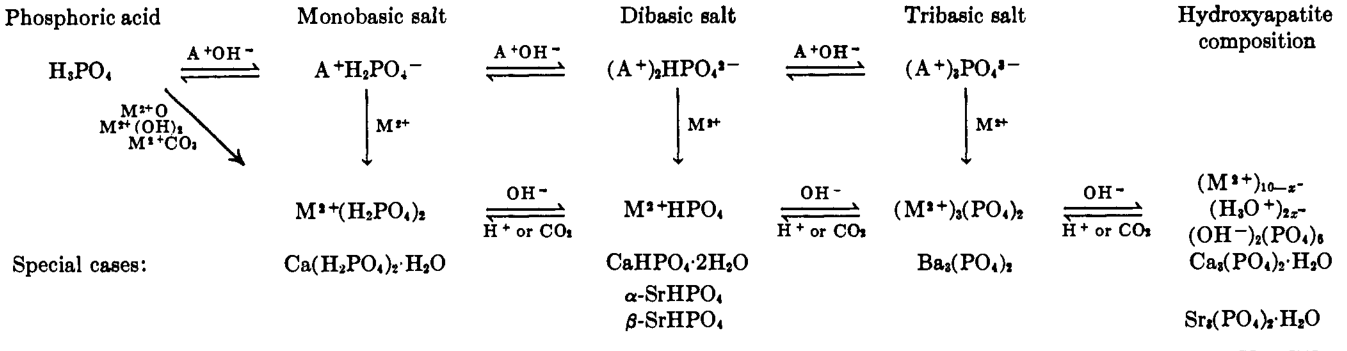


FIG. 4. Generalized scheme for precipitation of alkaline earth orthophosphates from aqueous solutions. $A^+ = NH_4^+, Na^+, K^+, CH_3$. or C_2H_5; $M^{2+} = Ca^{2+}, Sr^{2+}$, or Ba^{2+}.

preparing specific alkaline earth orthophosphates from solution is given in table 3. The selections are based on simplicity and reliability. Posner and Perloff (168) describe precipitation methods for various hydroxyapatites of calcium, and Hayek and Petter (87) give similar data for preparing the hydroxyapatites of strontium and barium by hydrothermal synthesis. Mellor (136) and Gmelin (78, 79) list additional methods for preparing alkaline earth orthophosphates of strontium and barium, but the compilations are not critical and the identifications not entirely reliable.

TABLE 3

Summary of selected methods for preparing alkaline earth orthophosphates from aqueous solution

(Both the oxide and the carbonate can be used where only the oxide is indicated)

Compound		General Method of Preparation	References
$Ca(H_2PO_4)_2$		CaO in excess H_3PO_4 evaporated at 125–130°C.	(93, 187)
$Ca(H_2PO_4)_2 \cdot H_2O$		CaO in excess H_3PO_4 evaporated at 35–40°C.	(120)
$CaHPO_4$		CaO in excess H_3PO_4 heated at 100–110°C.	(93)
		$Ca(NO_3)_2$ and $NH_4H_2PO_4$ at pH 3 and 83°C.	(187)
$CaHPO_4 \cdot 2H_2O$		Slow ammoniation of CaO in excess H_3PO_4 below 25°C.	(15)
		Ammoniacal $CaCl_2$ added to $NH_4H_2PO_4$ below pH 5 and 30°C.	(2)
$Ca_4H(PO_4)_3 \cdot 3H_2O$		$CaHPO_4 \cdot 2H_2O$ and 0.5 *M* sodium acetate at 40°C.	(39)
β-$Ca_3(PO_4)_2$		$Ca(NO_3)_2$ plus Na_2HPO_4 and Mg^{2+} or Mn^{2+} (about 1%) at 70°C.	(86)
Calcium Hydroxyapatites	Mole Ratio Ca/P*		
(a)	1.41	Dilute $CaCl_2$ plus excess of dilute Na_2HPO_4 at 25°C.	(10)
(b)	1.50	$Ca(OH)_2$ added to dilute H_3PO_4 to phenolphthalein end point	(53)
		Slow hydrolysis of $CaHPO_4 \cdot 2H_2O$ (good crystals obtained)	(141)
(c)	1.61	$Ca(OH)_2$ added to dilute H_3PO_4 as in (b), then boiled	(217)
(d)	1.67	$Ca(OH)_2$ added to dilute H_3PO_4, then neutralized at boiling	(217)
(e)	1.75	Freshly precipitated "tricalcium phosphate" plus lime	(68)
Compound			
$Sr(H_2PO_4)_2$		SrO in excess H_3PO_4 evaporated below 60°C.	(194)
$Sr(H_2PO_4)_2 \cdot H_2O$		SrO in excess H_3PO_4 evaporated under vacuum	(136, 198)
β-$SrHPO_4$		$(NH_4)_2HPO_4$ added to Sr^{2+} below 25°C.	(143)
α-$SrHPO_4$		$(NH_4)_2HPO_4$ added to Sr^{2+} above 50°C.	(143)
$Sr_3(PO_4)_2$ (large single crystals)		Slow hydrolysis of $SrHPO_4$ in Soxhlet	(143)
Strontium Hydroxyapatites			
(a) $Sr_3(PO_4)_2 \cdot xH_2O$		Ammoniated $SrCl_2$ and Na_2HPO_4	(5)
		SrO added to H_3PO_4	(183, 217)
(b) $Sr_{10}(OH)_2(PO_4)_6$		$(NH_4)_2HPO_4$ and $Sr(NO_3)_2$ brought to pH 12 with ethylenediamine; precipitate fired at 950°C.	(47)
(c) Others		$SrHPO_4$ in basic solution at 100°C.	(5, 110, 117, 174, 183, 194)
Compound			
$Ba(H_2PO_4)_2$		BaO in excess H_3PO_4 evaporated at low temperature	(159, 181, 194)
$BaHPO_4$		BaO added to excess H_3PO_4	(194)
		$(NH_4)_2HPO_4$ added to Ba^{2+}	(194)
$Ba_3(PO_4)_2$		$BaCl_2$ and KH_2PO_4 with NaOH to maintain neutrality	(174)
		Excess $Ba(OH)_2$ added to H_3PO_4 at 100°C.	(183)
Barium Hydroxyapatite			
(a) Nonstoichiometric		$BaCl_2$, Na_2HPO_4, and NaOH at 100°C.	(111)
(b) $Ba_{10}(OH)_2(PO_4)_6$		See solid-state methods, table 4	

* Weight ratio Ca/P = mole ratio Ca/P × 1.291.

(b) Novel methods

The technique of homogeneous precipitation recently summarized by Gordon, Salutsky, and Willard (80) has been applied to the preparation of dibasic phosphates ($MHPO_4$) from aqueous solution in extremely well-crystallized form (1). Briefly, a large excess of urea is added to an acid solution of the alkaline earth carbonate, hydroxide, or oxide, in at least 100 per cent excess H_3PO_4, and the quiescent solution is hydrolyzed above 60°C. The pH of the system slowly rises as the urea decomposes in effect to ammonia and carbon dioxide, forcing the neutralization of the phosphoric acid.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O \tag{5}$$

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O \tag{6}$$

Precipitation of the dibasic orthophosphates results. In the strongly acid region the alkaline earth carbonates are not precipitated, since excess carbon dioxide is evolved as a gas. Large crystals of $BaHPO_4$, α- and β-$SrHPO_4$, $CaHPO_4$, and even $CaHPO_4 \cdot 2H_2O$ (up to 1 cm.) have been obtained at 65°C., using 0.1 to 0.2 *M* alkaline earth oxide dissolved in 0.5 to 2.0 *M* H_3PO_4 and 0.5 to 2.0 *M* urea, and then hydrolyzed, without stirring, to a pH between 2.5 and 6.0 for periods up to twelve days. In general, the rate of precipitation increases with the temperature and the concentration of urea and the alkaline earth ion and decreases with the concentration of phosphoric acid.

Other interesting methods for obtaining crystalline phosphates from solution are: (*1*) homogeneous liberation of ammonia from the reaction of ammonium chloride with aqueous methanolamine (182) and (*2*) the diffusion of a buffered solution of suitable cation into a solution of Na_2HPO_4 in a special glass tube (100).

3. Preparation by solid-state reaction

The basic phosphates, $M_3(PO_4)_2$, and the frequently cation-deficient $M_{10}(OH)_2(PO_4)_6$ are stoichiometrically prepared by solid-state reaction at elevated temperatures, as shown in table 4. Other than the many studies of the competition of calcium and strontium in the deposition of bone mineral (153), surprisingly little study of the mixed alkaline earth orthophosphates has been reported. Collin (47) devised a method for preparing solid solutions of strontium calcium hydroxyapatite covering the range 0 to 100 atom per cent strontium, which superseded an earlier method in which solid solutions were not observed (117). A study of the neutralization of phosphoric acid by various BaO–SrO mixtures led to the conclusion that a homogeneous series of barium strontium apatites does not precipitate from solution, whereas prolonged calcination of precipitated strontium hydroxyapatite and tribasic barium orthophosphate leads to a series of solid solutions of $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ (162).

TABLE 4

Solid-state methods for preparing basic alkaline earth orthophosphates

Compound	General Method of Preparation	Reference
β-$Ca_3(PO_4)_2$......	$Ca_2P_2O_7 + CaCO_3$ at 1000°C.	(109)
$Ca_{10}(OH)_2(PO_4)_6$..	$CaHPO_4 + H_2O$ at 300°C. and 1250 lb./in.^{2}	(160)
$Sr_3(PO_4)_2$........	$Sr_2P_2O_7 + SrCO_3$ at 1000°C.	(110)
$Sr_{10}(OH)_2(PO_4)_6$...	$6SrHPO_4 + 4SrCO_3$, or	(178)
	$3Sr_3(PO_4)_2 + SrCO_3 + H_2O$ at 1150°C.	(110)
$Ba_3(PO_4)_2$........	$2BaHPO_4 + BaCO_3$ at 1000–1100°C.	(111)
$Ba_{10}(OH)_2(PO_4)_6$..	$3Ba_3(PO_4)_2 + BaO_2 + H_2O$ at 1000°C.	(111)

Work is needed on the mixed alkaline earth orthophosphates similar to that on the mixed alkaline earth carbonates. However, the chemistry of the mixed orthophosphates is much more complex than that of the mixed carbonates, where only calcite and aragonite structures are formed (230). Since reliable x-ray data on nearly all known alkaline earth orthophosphates are now available, studies of this nature should proceed with greater ease in the future.

4. Derivatives by solid-state reaction

(a) Monobasic orthophosphates

The reactions of orthophosphates of the type $M(H_2PO_4)_2$ are very complicated, owing to the formation of chains made up of large numbers of phosphorus atoms per molecule. Further complication arises from the indiscriminate use of the term "metaphosphate," since in many cases polyphosphate is the substance actually present. In this section, the reactions at high temperatures of the monobasic alkaline earth orthophosphates are summarized, and an attempt to clarify the nomenclature of some known condensed phosphates is made so that summarized x-ray data (84, 92, 118, 133, 178) may be correctly applied in the identification of these compounds.

Preparation and x-ray data for the fired products of the monobasic calcium orthophosphates have been most recently summarized by McIntosh and Jablonski (133), their summary being based partially upon the data of previous authors (14, 30, 92, 94, 95). In table 5 the nomenclature given in these sources is correlated with more precise and definitive notations evolved from studies using paper chromatography (156, 198). An obvious conclusion to be drawn from table 5 is that most well-known calcium "metaphosphates" are long-chain polyphosphates and contain no ring metaphosphate structures (156). Thilo and Grunze (198) found trimetaphosphate by heating $Ca(H_2PO_4)_2$ at 300°C. and tetrametaphosphate by heating at 500°C.; however, at 600°C. only the high-molecular-weight polyphosphate known as β-calcium metaphosphate was found. The anhydrous $CaSO_4$-type (orthorhombic) structure suggested for δ-calcium metaphosphate by Ohashi and Van Wazer (156) is difficult to explain and may result from contamination by $CaHPO_4$, since McIntosh and Jablonski (133) could prepare δ-calcium metaphosphate (at 400°C.) only with $CaHPO_4$ present as an impurity in the starting monobasic calcium orthophosphate. Ohashi and Van Wazer obtained their sample from Hill (94), whose x-ray data correspond to those listed for "$Ca(PO_3)_n$" in an earlier paper (14).

The thermal degradation of $Sr(H_2PO_4)_2$ as recently reported (178) is given in table 6. According to Thilo and Grunze (198) the dehydration of $Sr(H_2PO_4)_2 \cdot H_2O$ is similar to that of $Ca(H_2PO_4)_2 \cdot H_2O$ except that the trimetaphosphate, $Sr_3(P_3O_9)_2$, appears only between 400° and 500°C. and accounts for only a maximum 9.8 per cent of the phosphate content. The strontium tetrametaphosphate is not observed at all, and of the intermediate products, only $Sr(H_2PO_4)_2$ and $Sr(H_2P_2O_7)$ are crystalline (198). It is probable that Thilo and Grunze used static methods to ascertain the 400–500°C. region of stability of trimetaphosphate. Hence the endothermic transition at 320–330°C. of $Sr(H_2P_2O_7)$ to "γ-$Sr(PO_3)_2$," using continuous heating (178), may mark the formation of the trimetaphosphate. McKeag and Steward (134) report x-ray data for a strontium tetrapolyphosphate, $Sr_3P_4O_{13}$, which appears to be similar in structure to a low-temperature form of $Ba_3P_4O_{13}$ discussed in the next section. The strontium tetrapolyphosphate was formed by combining $SrHPO_4$ with about 20 per cent excess $(NH_4)_2HPO_4$ and firing at 700–800°C.

There is considerable disagreement on the condensed phosphates derived from $Ba(H_2PO_4)_2$. The firing progression summarized from the literature (11, 157, 198)

TABLE 5

Derivatives of monobasic calcium orthophosphates, $Ca(H_2PO_4)_2 \cdot H_2O$ *and* $Ca(H_2PO_4)_2$*, by air or steam firing with definitive notations as determined by paper chromatography*

Temperature	Reference	Descriptive Notations	References	Definitive Notations	References
°C.					
240	(148)	One amorphous phase plus two crystalline diphosphate phases	(148)	Long-chain polyphosphates plus $Ca(H_2P_2O_7)$ and $Ca_{1.5}HP_2O_7$ (β-diphosphate)	(148)
250	(133)	Calcium metaphosphate (amorphous)	(133)	Polyphosphates of low and high molecular weight	(198)
270–280 (steam)	(133)	Calcium acid pyrophosphate	(13, 94, 133)	Acid dipolyphosphate, $Ca(H_2P_2O_7)$	(198)
280	(148)	Amorphous phase plus calcium triphosphate and diphosphate	(148)	Long-chain polyphosphates plus tripolyphosphate, $Ca_2(HP_3O_{10})$, $Ca(H_2P_2O_7)$, and $Ca_{1.5}HP_2O_7$.	(148)
300	(198)	Calcium trimetaphosphate	(198)	Trimetaphosphate, $Ca_3(P_3O_9)_2$	(198)
310	(148)	Calcium tripolyphosphate plus γ-metaphosphate	(148)	Tripolyphosphate, $Ca_2(HP_3O_{10})$, plus polyphosphates of higher molecular weight	(148)
300–330 (steam)	(133)	Tetracalcium dihydrogen hexaphosphate	(94,133)	82–88% tripolyphosphate; remainder dipoly- and orthophosphates	(156)
				Tripolyphosphate and smaller amounts of other polyphosphates	(148, 198)
340–360	(133)	γ-Calcium metaphosphate*	(30, 94, 133)	59% "nonmoving" polyphosphate*; 30% tripolyphosphate; remainder ortho- and dipolyphosphates	(156)
400	(133)	δ-Calcium metaphosphate*	(13, 94, 133)	68% "nonmoving" polyphosphate*; 15% orthophosphate; remainder di- and tripolyphosphates	(156)
500	(198)	Calcium tetrametaphosphate	(133)	Tetrametaphosphate, $Ca_2(P_4O_{12})$	(198)
450–970	(133)	β-Calcium metaphosphate	(92, 94, 133)	100% "nonmoving" polyphosphate†	(156)
				High-molecular-weight polyphosphate, m.p. 960–970°C.	(198)
920	(92)	Trömelite‡	(92, 215)	83% pentapolyphosphate, $Ca_7(P_5O_{16})_2$: remainder dipoly-, tripoly-, and orthophosphates	(156) (215)
970	(95)	α-Calcium metaphosphate	(92, 94, 95)	98.5% "nonmoving" polyphosphate†; m.p. 984°C.	(156)
				Polyphosphates of unresolved composition	(198)

* Both γ- and δ-calcium metaphosphate modifications contain small amounts of water, $\gamma = 1.45$ per cent and $\delta = 1.00$ per cent H_2O (94). There are approximately 200–600 phosphorus atoms per chain in these compounds. The δ-metaphosphate is said to have a crystal structure similar to that of anhydrous $CaSO_4$ (156).

† The "nonmoving" polyphosphate of β- and α-calcium metaphosphates contains approximately 10,000 phosphorus atoms per chain.

‡ Trömelite has never been reported as a derivative of $Ca(H_2PO_4)_2$; it is tabulated since it is a polyphosphate and appears on the $CaO-P_2O_5$ phase diagram both alone and in solid solutions with α- and β-calcium metaphosphates (92).

is shown in table 7. The barium tetrametaphosphate, $Ba_2(PO_3)_4$, of Osterheld and Langguth (157), produced by heating $Ba(H_2PO_4)_2$ at 245°C., is not included in table 7, since its occurrence is denied by the chromatographic analyses of Thilo and Grunze (198), who could not find evidence of tetrametaphosphate as a decomposition product of $Ba(H_2PO_4)_2$ unless the resultant polyphosphate was allowed to hydrolyze by long-term standing in acid solution. An investigation in this laboratory (1) showed that when $Ba(H_2PO_4)_2$ was heated for 3 hr. at 245°C., the results of Thilo and Grunze (198) were reproduced in that large amounts of ortho- and dipolyphosphates were found together with tripoly-, tetrapoly-, and pentapolyphosphates, as well as nonmoving polyphosphate, while there was no evidence for ring metaphosphates. However, the weight loss corresponded exactly to that calculated for the formation of $Ba_2(PO_3)_4$, in agreement with Osterheld and Langguth (157).

It has also been shown by chromatographic analysis (118) that when mixtures of $BaHPO_4$ and $Ba(H_2PO_4)_2$ are heated to constant weight at 550°C., tetrapolyphosphate, $Ba_3P_4O_{13}$, is the principal polyphosphate formed between $Ba_2P_2O_7$ and the composition known as $Ba_2(PO_3)_4$. X-ray data for the $Ba_2(PO_3)_4$ composition (118, 157) show it to be clearly different from the dimorphous barium tetrapolyphosphates, $Ba_3P_4O_{13}$ (84, 134). Chro-

TABLE 6

Derivatives of monobasic strontium orthophosphate

Firing Progression by Differential Thermal Analysis (178)	Probable Correspondence to Findings of Thilo and Grunze (198)
$Sr(H_2PO_4)_2 \cdot H_2O$	
$\downarrow$ 100°C.	
$Sr(H_2PO_4)_2$	Crystalline orthophosphate
$\downarrow$ 190–250°C.	
$Sr(H_2P_2O_7)$	Crystalline dipolyphosphate
$\downarrow$ 320–330°C.	
γ-$Sr(PO_3)_2$	Trimetaphosphate + polyphosphates of low molecular weight
$\downarrow$ 420°C.	
β-$Sr(PO_3)_2$	Polyphosphates of intermediate molecular weight
$\downarrow$ 850°C.	
α-$Sr(PO_3)_2$	Polyphosphates of high molecular weight melting at 980°C.

TABLE 7

Derivatives of monobasic barium orthophosphate

Firing Progression	Chromatographic Analysis	Reference
$Ba(H_2PO_4)_2$		
$\downarrow$ 180–220°C. $-1.85\ H_2O$		
$Ba_{n/2}(H_2P_nO_{3n+1})$	Polyphosphates of low and high molecular weight ($n = 1$ to 10): no ring metaphosphates	(198)
$\downarrow$ 400°C.		
$Ba_{n/2}(H_2P_nO_{3n+1})$	Only polyphosphates of high molecular weight:	(198)
	m.p. 845 ± 5°C.	(11)
vacuum $\downarrow$ 1275°C.	875°C.	(157)
	860°C.	(198)
$Ba_2P_2O_7 + P_2O_5$		(11)

matographic analysis of the low-temperature (or β) form of $Ba_3P_4O_{13}$ shows that it consists largely of tetrapolyphosphate and dipolyphosphate (118). The high-temperature (or α) form of $Ba_3P_4O_{13}$ has not been chromatographed. The firing progressions leading to the dimorphous barium tetrapolyphosphates (84, 118, 134) are given below.

$$3BaHPO_4 + 1.2(NH_4)_2HPO_4 \xrightarrow{550\text{–}800°C.} \beta\text{-}Ba_3P_4O_{13} \xrightarrow{870 \pm 10°C.} \alpha\text{-}Ba_3P_4O_{13} \tag{7}$$

The high-temperature form of barium tetrapolyphosphate melts at 990°C. (84).

(b) Dibasic orthophosphates

Calcium is the only one of the alkaline earths that forms a hydrated dibasic orthophosphate. The dehydration of $CaHPO_4 \cdot 2H_2O$ to $CaHPO_4$ is a complex process, especially in the absence of air or moisture, and several dehydration studies have been made (121, 172, 211, 216) to define compounds intermediate between the dihydrate and the anhydrous salt. By analogy with $CaSO_4 \cdot 2H_2O$, which is isostructural with $CaHPO_4 \cdot 2H_2O$, one could propose at least one intermediate hydrate, $CaHPO_4 \cdot 0.5H_2O$, the existence of which is supported by recent findings (121) as well as by results given by Mellor (136). Optical crystallographic study of $CaSO_4 \cdot 2H_2O$ (235) has shown that crystals of compounds formed with the loss of water are preferentially oriented along specific planes of the mother crystals. Such a study of $CaHPO_4 \cdot 2H_2O$ has not yet been reported and would be of interest.

The general idealized reaction for the formation of alkaline earth pyrophosphate from a dibasic phosphate is shown in equation 8.

$$2MHPO_4 \xrightarrow{\text{heat}} M_2P_2O_7 + H_2O \tag{8}$$

A summary of known data on the formation of pyrophosphates by the heating of $MHPO_4$ is given in table 8. Approximate phase diagrams for mixtures of alkaline earth pyrophosphates have been reported (173) in connection with phosphor studies, since the pyrophosphates form efficient phosphors when suitable activator metals are added (134, 173, 179).

(c) Tribasic orthophosphates

The general behavior seems to be simple for the calcium and strontium "tribasic hydrates," which are apatitic (5, 14, 32, 96, 153, 162, 220).

$$M_3(PO_4)_2 \cdot xH_2O \xrightarrow{700\text{–}900°C.} M_3(PO_4)_2 + xH_2O \tag{9}$$

Only one anhydrous $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ structure has been discovered (232), but for calcium the progression shown in equation 10 has been found (34, 35, 155, 208).

$$\beta\text{-}Ca_3(PO_4)_2 \xrightarrow{1180°C.} \alpha\text{-}Ca_3(PO_4)_2 \xrightarrow{1430°C.} \alpha'\text{-}Ca_3(PO_4)_2 \tag{10}$$

The stabilization of whitlockite [β-$Ca_3(PO_4)_2$] by magnesium, iron, and aluminum in the solid state is demonstrated in Ando's recent studies of $Ca_3(PO_4)_2$ (7, 8). On the other hand, barium favors the formation of α-$Ca_3(PO_4)_2$ (7). Hence, the situation is similar to that prevailing in solution, as discussed earlier in Section III,A, in that only cations smaller than Ca^{2+} favor the whitlockite structure.

The normal structure of $Sr_3(PO_4)_2$ can be modified to the structure of whitlockite by substituting aluminum, zinc, magnesium, calcium, or cadmium for strontium (113, 223). This strontium whitlockite structure is strongly luminescent in the visible range when activated by Sn^{2+} (42, 113, 199) or Cu^+ (223), whereas the normal $Sr_3(PO_4)_2$ produces only weak ultraviolet fluorescence. The minimum atomic ratios of foreign cation required to produce the whitlockite structure in $Sr_3(PO_4)_2$ have been reported (113). Ba^{2+}, a cation larger than Sr^{2+}, does not induce the formation of $Sr_3(PO_4)_2$ with the β-$Ca_3(PO_4)_2$ structure.

The whitlockite structure is unusual in several respects, as evidenced from its crystallography (described in Section VI,C). In addition, tin-activated β-$Ca_3(PO_4)_2$ phosphors cooled to minus 190°C. and reheated show anomalous jumps in fluorescent intensity at temperatures around $-40°$ and $+35°$C., indicating phase transitions at remarkably low temperatures (114). Calorimetric measurements confirmed the two phase transitions and showed that they were not connected with the presence of tin.

TABLE 8

Alkaline earth pyrophosphates derived from monetites, $MHPO_4$, *and their temperatures of formation in air*

Calcium			Strontium			Barium		
Salt	Temperature	Reference	Salt	Temperature	Reference	Salt	Temperature	Reference
	°C.			°C.			°C.	
γ-$Ca_2P_2O_7$	320–400	(133)	$Sr_2P_2O_7 \cdot 0.5H_2O$*	300	(178)			
β-$Ca_2P_2O_7$	700–750	(133)	β-$Sr_2P_2O_7$	400	(178)			
				575*				
α-$Ca_2P_2O_7$	1140	(133)	α-$Sr_2P_2O_7$	760–800	(178)	α-$Ba_2P_2O_7$	385	(57)
						δ-$Ba_2P_2O_7$	790	(173)

* Only when β-$SrHPO_4$ is starting material.

(d) Apatites and octacalcium phosphate

Data for the stoichiometric hydroxyapatite, chloroapatite, and fluoroapatite of calcium (211) indicate these to be stable to about 1400°, 1500°, and 1650°C., respectively, when ignited in the presence of moisture. No complete study of the SrO–P_2O_5 and BaO–P_2O_5 systems has been made, but methods of preparation given for $Sr_{10}(OH)_2(PO_4)_6$ and $Ba_{10}(OH)_2(PO_4)_6$ indicate that these are stable at 1150°C. Halogenated apatites of barium and strontium are well known (3, 4, 6, 103) and are normally synthesized by firing in air a suitable mixture of solids around 1150°C., as is done to produce calcium halophosphate phosphors (103).

The thermal degradation of octacalcium phosphate (39), for which no strontium or barium analogs have been discovered, is given in equation 11.

$$2Ca_4H(PO_4)_3 \cdot 3H_2O \xrightarrow{220°C.} (Ca^{2+}_{10-x})(H_3O^+)_{2x}(OH^-)_2(PO_4{}^{3-})_6 + CaHPO_4 \xrightarrow{1000°C.} \beta\text{-}Ca_3(PO_4)_2 + \text{trace } \beta\text{-}Ca_2P_2O_7 \quad (11)$$

The general formula for calcium hydroxyapatite is used in equation 11, since the exact composition of the apatite formed is not known.

B. SOLUTION CHEMISTRY OF THE CONDENSED PHOSPHATES

The inorganic polyphosphates, especially the Group I polyphosphates, have been reviewed by Van Wazer and Callis (43, 212). Methods of measurement were described and the complexing action of the alkaline earth phosphates among others was discussed (212). In general, the chain polyphosphates or ring metaphosphates form much stronger complexes than do the orthophosphates; hence the orthophosphates will be omitted from the following presentation.

1. Polyphosphates

Quantitative data on the dissociation constants of various calcium and barium polyphosphate complexes are summarized in table 9. "Heterometric," pH, and conductometric titrations of the pyrophosphates and tripolyphosphates of calcium, strontium, and barium show that the tendency to complex-ion formation decreases with increasing size of the cation (26). Calcium forms an insoluble tripolyphosphate, $Ca_5(P_3O_{10})_2$, which redissolves in excess tripolyphosphate, forming the stable complex $(CaP_3O_{10})^{3-}$. The corresponding strontium salt, $Sr_5(P_3O_{10})_2$, is less soluble (26–28), but will form the complex $(SrP_3O_{10})^{3-}$ with a large excess of tripolyphosphate. Barium readily forms the insoluble salt $Ba_5(P_3O_{10})_2$ (26, 28, 44), which is almost completely insoluble in excess polyphosphate. Temperature has a negligible effect on the stability of the calcium tripolyphosphate complexes (56, 171). The stability of polyphosphates toward hydrolysis decreases in the order pyrophosphate to tripolyphosphate to tetrapolyphosphate (171).

TABLE 9

Negative logarithm of dissociation constants at 25°C. of various calcium and barium polyphosphates

Complex	pK_D	Method	Comments
$(CaP_2O_7)^{2-}$	4.95	Acid–base titration (225)	In good agreement with "guesstimated" value given by Van Wazer and Callis (212)
	5.00	Colorimetric determination of pH (231)	
$(CaHP_2O_7)^-$	2.30	Acid–base titration (225)	
$(CaP_3O_{10})^{3-}$	5.44	Acid–base titration (225)	
	4.95	Acid–base titration (131); temperature 20°C.	In 0.1 *M* KCl
	6.5	Solubility oxalate (81); temperature 30°C.	
$(CaHP_3O_{10})^{2-}$	3.01	Acid–base titration (225)	
	3.1	Acid–base titration (131); temperature 20°C.	
$(BaP_2O_7)^{2-}$	4.5	Polarography (213)	
$(BaP_3O_{10})^{3-}$	4.5	Polarography (213)	

Recently the calcium pyrophosphates have been carefully reinvestigated, resulting in the isolation of several new compounds (37, 38). It is expected that further work will result in a clearer understanding of the chemistry of pyrophosphates. Substitution of the water of crystallization in alkaline earth pyrophosphates by H_2O_2 is known, and equilibria in the system $Ba_2P_2O_7$–H_2O–H_2O_2 have been studied (149).

2. Ring metaphosphates

The dissociation constants for the trimetaphosphate and tetrametaphosphate complexes of the alkaline earth metals taken from the work of Monk and associates (55, 105, 106, 140) are listed by Van Wazer and Callis (212). The dissociation constants for the tetrametaphosphates are approximately two orders of magnitude lower than those of the trimetaphosphates (10^{-6} vs. 10^{-4}), and a gradual increase in magnitude with increase in size of the cation is noted for both the trimetaphosphate and the tetrametaphosphate.

The hydrolysis of trimetaphosphate ions to tripolyphosphate ions depends on the pH of the solution, the charge on the ions, and the presence of other ions. In a study of the hydrolysis of sodium phosphate (22), the hydrolysis of trimetaphosphate ($P_3O_9{}^{3-}$) to acid tripolyphosphate ($H_2P_3O_{10}{}^{3-}$) in the presence of hydroxyl ions was established. The rate of hydrolysis in dilute solution is slow, requiring several days for completion at ordinary temperatures. Calcium or barium ions strongly catalyze the reaction in basic solution but produce a slight decrease in rate in acid solution (101). In general, the rates of reaction of the trimetaphosphate species are in the inverse order of their charge (88), i.e., $M^{II}P_3O_9{}^- > M^IP_3O_9{}^{2-} > P_3O_9{}^{3-}$. Another study of the trimetaphosphates confirms earlier work and provides kinetic data on the

Ca^{2+}- and Ba^{2+}-catalyzed hydrolysis (102). The product of the reaction between $Na_3P_3O_9$ and $BaCl_2$ is $Ba_5(P_3O_{10})_2$, the tripolyphosphate, in agreement with the mechanism proposed for the hydrolysis.

The hexametaphosphate $Ba_3(PO_3)_6$ has been reported (44, 176), but in view of the tendency of metaphosphates to undergo hydrolysis, the possibility of polyphosphate formation should not be ignored.

V. THERMODYNAMIC PROPERTIES OF ALKALINE EARTH PHOSPHATES

A. SOLUBILITY PRODUCTS

The recent monograph by Neuman and Neuman (153) emphasizes the necessity of taking into account ionic strength and activity to avoid larger errors in calculating solubility products. When activities are ignored, the error is about 1200 per cent for dibasic calcium orthophosphate at the concentrations found in biological serums. Hence, emphasis is placed on thermodynamic solubility products, that is, those corrected for activity to minimize effects due to pH, ionic strength, and M/P ratio in solution, all of which strongly influence the apparent solubility.

1. Calcium orthophosphates

The solubilities of calcium phosphates in water, acids, bases, salt solutions, etc., are given in Linke's recent revision of Seidell's compilation of solubilities (123). Specific treatment of bone mineral, which does not exhibit a fixed solubility product, is given by Neuman and Neuman (153). The formation constants of various organic and phosphorus-containing chelates of calcium are also known (104, 153, 212). In general, acids that contain two or three carboxyl groups and a hydroxyl group sterically available for bonding form the more stable organic chelates of calcium. The citrate ion is by far the most effective calcium-complexing organic acid known, although polymeric phosphates match or exceed citrate in their ability to complex calcium (153). On the other hand, collagen, a protein found in the body, has a unique ability to induce crystallization of $CaHPO_4 \cdot 2H_2O$ under physiological conditions, with normal solubility decreased by 60 per cent in collagen-seeded solutions at 37°C. (73).

Table 10 lists thermodynamic solubility products for the calcium orthophosphates. The familiar decrease in solubility with increasing Ca/P mole ratio and temperature is evident. The maximum pH at which $CaHPO_4 \cdot 2H_2O$ is stable at 38°C. has been shown to be 6.93 at infinitely low Ca/P ratio, with $CaHPO_4 \cdot 2H_2O$ being converted to hydroxyapatite at lower pH as the Ca/P ratio of the solution is increased (66). The solubility product of $CaHPO_4$ is decreased by only one order of magnitude as the equilibrium temperature is increased from 25° to 90°C. (145), but obviously much more as the equilibrium pH or Ca/P ratio is increased to favor formation of hydroxyapatite.

TABLE 10

Negative logarithm of the thermodynamic solubility products of calcium orthophosphates at infinite dilution and 25°C.

Compound	pK_{sp}	Reference
$Ca(H_2PO_4)_2$ and $Ca(H_2PO_4)_2 \cdot H_2O$	1.14	(69)
$CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$	6.66	(69)
	6.57	(192)
	6.56	(146)
	7.91 at 90°C.	(145)
$Ca_3(PO_4)_2$*, tribasic calcium phosphate	26	(107)
	32.5 at 38°C.	(98)
$Ca_4H(PO_4)_3 \cdot 3H_2O$, octacalcium phosphate	46.9	(147)
$Ca_{10}(OH)_2(PO_4)_6$, calcium hydroxyapatite	115	(46)

* Present knowledge indicates that calcium hydroxyapatite, approaching the composition $Ca_3(PO_4)_2 \cdot xH_2O$, was the actual saturating solid.

Ando (7, 8) has studied the effect of magnesium oxide and sodium oxide on the solubilities of calcium phosphate fertilizers in citric acid and ammonium citrate and found that the solubility is decreased so much by the presence of large amounts of magnesia that only citric acid or acidic citrate is suitable for testing such fertilizers. This effect is caused by the ability of Mg^{2+} to stabilize the β-$Ca_3(PO_4)_2$ structure, which is much less soluble in citrate solutions than is α-$Ca_3(PO_4)_2$. Sodium ion induces the formation of $CaNaPO_4$, rhenanite, which is dimorphous. The high-temperature form, termed α-rhenanite by Ando (8), is highly soluble in citrate and is stable over the range 0.2–0.6 mole Na_2O per mole P_2O_5.

2. Strontium and barium orthophosphates

The solubility data of Tartar and Lorah (194) and of Holt, Pierce, and Kajdi (99) are available for strontium orthophosphates. For barium orthophosphates the data of these authors plus those of Artur (11) have been compiled by Linke (123). The solubility products, at infinite dilution, for $SrHPO_4$, $Sr_3(PO_4)_2$, $BaHPO_4$, $Ba_3(PO_4)_2$, and $Mg_3(PO_4)_2$ are given in table 11.

TABLE 11

Negative logarithm of the thermodynamic solubility products of some strontium and barium orthophosphates at infinite dilution and 38°C. (99)

Compound	pK_{sp}	Compound	pK_{sp}
$SrHPO_4$	7.06	$Ba_3(PO_4)_2$	29.34†
$Sr_3(PO_4)_2$*	27.8	$Mg_3(PO_4)_2$	27.2
$BaHPO_4$	7.56		

* Present knowledge indicates that strontium hydroxyapatite, approaching the composition $Sr_3(PO_4)_2 \cdot xH_2O$, was the actual saturating solid.

† At ionic strength of 0.0008, not at infinite dilution where solubility would be slightly lower.

3. Comparison of solubility products

Comparing the results in tables 10 and 11, and ignoring the 13° temperature difference, the solubility products are $CaHPO_4 > SrHPO_4 > BaHPO_4 \gg Sr_3$-

$(PO_4)_2$, $Mg_3(PO_4)_2 > Ba_3(PO_4)_2 > Ca_3(PO_4)_2 > Ca_4H(PO_4)_3 \gg Ca_{10}(OH)_2(PO_4)_6$. The adverse effects of magnesium and strontium on calcification probably cannot be rationalized on the basis that $Mg_3(PO_4)_2$ and $SrHPO_4$ are less soluble than $CaHPO_4 \cdot 2H_2O$, which is believed to occur as an initial phase in the deposition of calcium (112, 152, 153), but some enlightenment is gained by the fact that strontium and calcium combine to form a homogeneous series of hydroxyapatites (47). In addition, it has been established that $Sr_3(PO_4)_2$ can be made to crystallize in the whitlockite [β-$Ca_3(PO_4)_2$] structure in the presence of certain cations, including Mg^{2+}. This may cause an interaction with calcium whitlockite which is known to occur in some calcification processes of the body. Of course, it would be extremely naive to think that such complex systems as are found in nature could be explained solely by the available data on solubility and crystal structure. However, the data give direction to research and to further understanding of these systems.

B. THERMOCHEMICAL DATA

Selected values of thermodynamic properties of the alkaline earth phosphates are given in Circular 500 of the National Bureau of Standards (180). The data on the strontium and barium phosphates are limited almost entirely to heats of formation determined prior to 1900. The available values are tabulated in table 12 and compared with corresponding values for the calcium phosphates, which have been more thoroughly studied. In addition, table 13 lists values of $H^0 - H^0_0$ and S^0 at 298.16°K. for several calcium phosphates. Comparable data on strontium or barium phosphates do not exist.

1. *Monobasic orthophosphates*

Measurements of the low-temperature heat capacity of $Ca(H_2PO_4)_2 \cdot H_2O$ (64) yield the values of entropy and heat content listed in table 13. The entropy value of 62.10 cal. mole^{-1} degree^{-1} is much larger than the earlier value of 49.7 cal. mole^{-1} degree^{-1} (69), but is preferred in view of the straightforward manner of its determination.

TABLE 13

Heat contents and entropies at 298.16°K. for various calcium phosphates

	$H^0 - H^0_0$	S^0	References
	cal. mole^{-1}	*cal. mole^{-1} degree^{-1}*	
$Ca(H_2PO_4)_2 \cdot H_2O(c)$	9,950	62.10	(64)
	—	49.7	(69)
$CaHPO_4(c)$	—	21.0	(180)
	—	28.0	(69)
	—	19.2	(234)
$CaHPO_4 \cdot 2H_2O(c)$	—	40.0	(180)
	—	46.7	(69)
β-$Ca_3(PO_4)_2(c)$	9,143	56.40	(69, 180)
α-$Ca_3(PO_4)_2(c)$	9,282	57.58	(69, 180)
β-$Ca_2P_2O_7(c)$	7,430	45.25	(60)
β-$Ca(PO_3)_2(c)$	5,715	35.12	(59)
$Ca_{10}F_2(PO_4)_4(c)$	30,340	185.5	(63)
$Ca_{10}(OH)_2(PO_4)_6(c)$	30,710	186.6	(62)

The most recent value of the heat of formation of $Ca(H_2PO_4)_2$ (64) was calculated from equation 12.

$$2(H_3PO_4 \cdot 1.0055H_2O)(l) + Ca(OH)_2(c) = Ca(H_2PO_4)_2(c) + 2H_2O(l) + aq \quad (12)$$

Standard values of heats of formation at 25°C. (180) were used, and the heat of reaction (−35,770 cal.) was obtained by measuring the difference between the sum of the heats of solution of products and reactants in 4 molal hydrochloric acid. The resultant heat of formation at 25°C. for $Ca(H_2PO_4)_2(c)$ is −746,040 cal. mole^{-1} (table 12).

The most reliable value for the heat of formation of $Ca(H_2PO_4)_2 \cdot H_2O$ (64) listed in table 12 was calculated from equation 13.

$$2(H_3PO_4 \cdot 1.0055H_2O)\ (l) + Ca(OH)_2(c) = Ca(H_2PO_4)_2 \cdot H_2O(c) + H_2O(l) + aq \quad (13)$$

Standard values of heats of formation at 25°C. were used, and the heat of reaction of −38,228 cal. was determined in the same manner as above for $Ca(H_2PO_4)_2$.

TABLE 12

Heats of formation at 298.16°K. of the alkaline earth orthophosphates

Orthophosphate	ΔH^0			Reference
	M = Ca	M = Sr	M = Ba	
	cal. mole^{-1}	*cal. mole^{-1}*	*cal. mole^{-1}*	
$M(H_2PO_4)_2(c)$	−744,400	—	−749,600	(180)
	−746,040	—	—	(64)
$M(H_2PO_4)_2 \cdot H_2O(c)$	−818,000	−819.400	−492,000 (?)	(180)
	−821.490	—	—	(69)
(69) recalculated A	−817,860	—	—	—
(69) recalculated B	−816,830	—	—	—
	−816,820	—	—	(64)
$MHPO_4(c)$	−435,200	−431.300	−465,800	(180)
	−434,700	—	—	(69)
$MHPO_4 \cdot 2H_2O(c)$	−576.000	Not applicable	Not applicable	(180)
	−575.720	Not applicable	Not applicable	(69)
$M_3(PO_4)_2(c)$	−986.200 (β)	−987,300	−998,000	(180)
	−988.900 (α)			(180)

Farr's value (69) is based upon an estimated value of the heat of formation of $Ca(H_2PO_4)_2 \cdot H_2O(aq)$ of −820,660 cal. mole^{-1} calculated from the heats of formation of $H_2PO_4^-(aq)$, $Ca^{2+}(aq)$, and $H_2O(l)$. The heat of formation of crystalline $Ca(H_2PO_4)_2 \cdot H_2O$ was calculated from equation 14.

$$Ca(H_2PO_4)_2 \cdot H_2O(c) + aq = Ca(H_2PO_4)_2 \cdot H_2O(aq) \quad (14)$$

A value of 830 cal. mole^{-1} for the heat of solution at 25°C. in infinitely dilute solution was used. This value was determined graphically from data on the system $CaO–P_2O_5–H_2O$ (67), but more recent work discussed below indicates that it is probably in error by several kilocalories, leading to an error in ΔH_f^0 for $Ca(H_2PO_4)_2 \cdot H_2O(c)$ calculated by Farr (69). The derivation of the recalculated values shown in table 12 is discussed below.

The heat of solution at 25°C. of $Ca(H_2PO_4)_2 \cdot H_2O$ in hydrochloric and phosphoric acids was measured as a function of the concentration of solvent (58), giving the results shown in figure 5. A linear extrapolation of the ΔH values to infinite dilution gives a heat of solution of −2850 cal. mole^{-1} when plotted against $m^{1/3}$ or −2750 cal. mole^{-1} by extrapolating ΔH as a function of $m^{1/2}$ (figure 5). The average observed heat of solution at infinite dilution is −2800 cal. mole^{-1}.

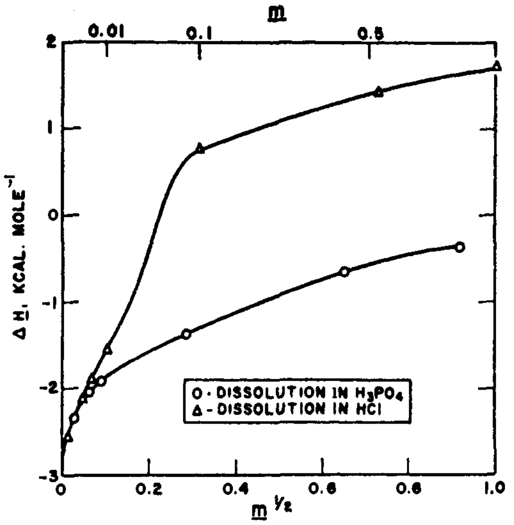


FIG. 5. Heat of solution of $Ca(H_2PO_4)_2 \cdot H_2O$ at 25°C. in phosphoric and hydrochloric acids. From Egan, Luff, and Wakefield (58); reproduced by permission of the American Chemical Society and the authors.

A heat of solution at infinite dilution can also be calculated from the heats of formation of the constituents in equation 15.

$$Ca(H_2PO_4)_2 \cdot H_2O(c) + aq = Ca^{2+}(aq) + 2H_2PO_4^-(aq) + H_2O(l) \quad (15)$$

The heats of formation used were −816,820 cal. mole^{-1} for $Ca(H_2PO_4)_2 \cdot H_2O(c)$ (64); −129,770 cal. mole^{-1} for $Ca^{2+}(aq)$ (180); −68,317 cal. mole^{-1} for $H_2O(l)$ (180); and −311,280 cal. mole^{-1} for $H_2PO_4^-(aq)$. The last value was derived from the heat of formation of $H_3PO_4(aq)$, −309,440 cal. mole^{-1} (69), and the heat of the first ionization of H_3PO_4, −1843 cal. mole^{-1}, this value being the average of three determinations (18, 154, 161). The calculated value of the heat of solution, −3830 cal. mole^{-1}, is still about 1 kcal. greater in magnitude than the observed value.

If the average observed value of −2800 cal. mole^{-1} for the heat of solution is used to calculate ΔH_f^0 of $Ca(H_2PO_4)_2 \cdot H_2O(c)$, Farr's recalculated value A (table 12) is obtained. If the computed heat of solution of −3830 cal. mole^{-1} is used, Farr's recalculated value B is obtained. Both are in substantial agreement with the experimentally determined value of −816,820 cal. mole^{-1} (64).

The heat of hydration of $Ca(H_2PO_4)_2(c)$ was calculated from equation 16.

$$Ca(H_2PO_4)_2(c) + H_2O(l) = Ca(H_2PO_4)_2 \cdot H_2O(c) \quad (16)$$

Egan's values for the heats of formation gave a value of −2460 cal. mole^{-1} at 25°C. (64), which is equivalent in sign but not in magnitude to the older, less reliable value of −4950 cal. mole^{-1} (132).

The value of the heat of formation of $Ba(H_2PO_4)_2$ given in table 12 is only slightly different (5200 cal. mole^{-1}) from the value for $Ca(H_2PO_4)_2$, as would be expected for similar compounds. The monohydrate, $Sr(H_2PO_4)_2 \cdot H_2O$, has a heat of formation of −819,400 cal. mole^{-1}, which is very close to the value for $Ca(H_2PO_4)_2 \cdot H_2O$. The heat of formation of $Ba(H_2PO_4)_2 \cdot H_2O$ is given as −492,000 cal. mole^{-1}, but the value is undoubtedly incorrect, since the compound $Ba(H_2PO_4)_2 \cdot H_2O$ is not found under ordinary conditions and the value is not in line with the values for the calcium and strontium monohydrates.

2. Dibasic orthophosphates

Farr's value of the heat of formation of $CaHPO_4$ listed in table 12 (69) was estimated from the heats of formation of $Ca(NO_3)_2(c)$, H_3PO_4, and HNO_3 and the heats of solution of H_3PO_4 and $CaHPO_4$ in 20 per cent HNO_3. It is in good agreement with the accepted value (180). On the other hand, the entropy value in table 13 is considerably higher than either the value of Circular 500 (180) or a recent value calculated by Zhuk (234). Other thermodynamic values are listed by Farr (69), including a heat of hydration for $CaHPO_4(c)$ at 25°C. of −4380 cal. mole^{-1} taken from unpublished data of the Tennessee Valley Authority.

The heats of formation of $SrHPO_4$ and $BaHPO_4$ are reasonably close in value to that of $CaHPO_4$. It would be interesting to know whether the value listed for $SrHPO_4$ refers to the alpha or the beta modification, but since the determinations were made prior to 1900, the sample was not identified by x-ray diffraction techniques.

Values of the heat of formation and the entropy of $CaHPO_4 \cdot 2H_2O(c)$ given by Farr (69) are in good agreement for the former and fair for the latter (tables 12 and 13). The value of the heat of formation was estimated from the heats of formation of $CaHPO_4(c)$ (69) and $H_2O(l)$ (180), together with the heat of hydration of $CaHPO_4$ at 25°C. The good agreement between the resulting heats of formation lends credence to the heat of hydration value cited above.

3. Tribasic orthophosphates

The heats of formation, heat contents, and entropies of α- and β-$Ca_3(PO_4)_2$ at 298.16°K. are given in tables 12 and 13. A calculated value of S^0 for $Ca_3(PO_4)_2$ of 36.9 cal. mole^{-1} degree^{-1} (234) is in poor agreement with the tabulated values, although the method developed by Zhuk (233) has given good results for other compounds (234).

The heats of formation of $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ listed in table 12 are in line with the values listed for $Ca_3(PO_4)_2$. The magnitude of the heat of formation increases in going from $Ca_3(PO_4)_2$ to $Sr_3(PO_4)_2$ to $Ba_3(PO_4)_2$. A similar trend exists with the other values of heats of formation, especially between the values for the calcium and the barium orthophosphate compounds.

In distinguishing between the polymorphic modifications of $Ca_3(PO_4)_2$, the convention has been adopted that the higher-temperature modification is designated by α, while the lower is designated β. This convention is in common use by mineralogists, although in some thermodynamic treatments the designations are reversed.

The heat content and heat capacity of β-$Ca_3(PO_4)_2$ over the temperature range 298–1373°K. (36, 108) are given in equations 17 and 18.

$$H_T - H_{298.16} = 48.24T + 19.84 \times 10^{-3}T^2 + 5.00 \times 10^5T^{-1} - 17{,}824 \ (\pm 1.5\%,\ 298\text{–}1373\text{°K.}) \quad (17)$$

$$C_p = 48.24 + 39.68 \times 10^{-3}T - 5.00 \times 10^5T^{-2} \quad (18)$$

Evidence for two low-temperature phase transitions in β-$Ca_3(PO_4)_2$ at −40° and +35°C. has recently been obtained from measurements of the temperature dependence of luminescence of β-$Ca_3(PO_4)_2$ activated by Sn^{2+} (114). Calorimetric measurements of the combined effects of both transitions gave a $\Delta H_{\text{trans.}}$ = 1700 cal. mole^{-1} and a $\Delta S_{\text{trans.}}$ = 9.2 cal. mole^{-1} degree^{-1}. It was suggested that these transitions might be attributed to an ordering of the statistically distributed atoms in the β-$Ca_3(PO_4)_2$ structure (see Section VI,C).

At 1373°K. the low-temperature β-$Ca_3(PO_4)_2$ undergoes a transition to the high-temperature α-$Ca_3(PO_4)_2$ with a $\Delta H_{\text{trans.}}$ = 3700 cal. mole^{-1} and a $\Delta S_{\text{trans.}}$ = 2700 cal. mole^{-1} degree^{-1} (36, 108, 180). Corresponding thermodynamic data on α-$Ca_3(PO_4)_2$ (36, 108) are given in equations 19 and 20.

$$H_T - H_{298.16} = 79.00T - 18{,}600 \ (\pm 1.5\%,\ 1373\text{–}1600\text{°K.}) \quad (19)$$

$$C_p = 79.00 \quad (20)$$

The free energies of formation of tribasic calcium and tetracalcium orthophosphates have also been determined (29) in connection with phosphorus–oxygen equilibria in liquid iron by studying the reduction equilibria involving these phosphates.

4. Apatites of calcium

Measurements of the low-temperature heat capacities of calcium hydroxyapatite (62) from 13.18° to 300°K. and calcium fluoroapatite (63) from 13.32° to 300°K. give the values listed in table 13 for the entropy and heat content at 298.16°K. derived by the usual graphical integration methods. The observed heat contents in calories gram^{-1} were converted to calories mole^{-1} on the basis of a gram-formula weight of 1008.68 for $Ca_{10}F_2(PO_4)_6$ and 1004.70 for $Ca_{10}(OH)_2(PO_4)_6$. The hydroxyapatite was as close to the theoretical composition $Ca_{10}(OH)_2(PO_4)_6$ as could be expected. The heat capacity of fluoroapatite parallels that of hydroxyapatite, owing to their closely related nature (see Section VI,D), and therefore the entropies and heat contents at 298.16°K. are almost identical.

The heat contents for calcium hydroxyapatite were measured up to 1600°K. (61) and for calcium fluoroapatite up to 1500°K. (63). The following equations for heat content, heat capacity, and entropy per mole were derived from the observed heat contents. For calcium hydroxyapatite the equations are applicable over the range 298.16–1475°K. with an average deviation of 0.3 per cent between the derived and the observed heat contents.

$$H_T - H_{298.16} = 228.52T + 19.81 \times 10^{-3}T^2 + 50.00 \times 10^5T^{-1} - 86{,}670 \quad (21)$$

$$C_p = 228.52 + 39.62 \times 10^{-3}T - 50.00 \times 10^5T^{-2} \quad (22)$$

$$S_T - S_{293.16} = 526.19 \log T + 39.62 \times 10^{-3}T + 25.00 \times 10^5T^{-2} - 1342 \quad (23)$$

Similar equations for calcium fluoroapatite over the range 298.16–1580°K., with an average deviation of 0.4 per cent between derived and observed heat contents, are listed in equations 24–26.

$$H_T - H_{298.16} = 226.04T + 14.44 \times 10^{-3}T^2 + 48.82 \times 10^{-5}T^{-1} - 85{,}050 \quad (24)$$

$$C_p = 226.04 + 28.88 \times 10^{-3}T - 48.82 \times 10^6T^{-2} \quad (25)$$

$$S_T - S_{298.16} = 520.48 \log T + 28.88 \times 10^{-3}T + 24.41 \times 10^5T^{-2} - 1324 \quad (26)$$

X-ray examination of the fluoroapatite after measurements at the high temperatures showed no significant change in structure. Similar examinations of the calcium hydroxyapatite samples after runs at 1000° and 1200°C. also showed no change, with the exception of one sample which after a run at 1200°C. showed 10–15 per cent of what was probably $Ca_2P_2O_7$. No correction was made for this amount of pyrophosphate, owing to the similarities in its heat content to that of hydroxyapatite.

5. Condensed phosphates of calcium

The low-temperature heat capacity of β-calcium pyrophosphate was measured over the range 9.97–305°K. (60) and that of β-calcium metaphosphate over the range 10.26–306°K. (59) to give values of entropy and heat content at 298.16°K. (table 13) calculated by standard graphical integration techniques.

The heat contents of β-$Ca_2P_2O_7$ above 298.16°K. were determined up to 1473°K. (60), even though the $\beta \rightarrow \alpha$ transition temperature is reported as 1413°K. (91). Obviously the transition is sluggish. Above the melting point of 1626° ± 3°K. (91, 191) thirteen of fifteen liquid samples quenched to α-$Ca_2P_2O_7$ with their heat contents falling on a straight line. The remaining two samples quenched to β-$Ca_2P_2O_7$. The heat contents of those samples below 1626°K. which quenched to α-$Ca_2P_2O_7$ also fell on a straight line, and extrapolation of the two lines to the melting point gave a heat of fusion of 24,104 cal. mole^{-1}. The heat of the $\beta \rightarrow \alpha$ transition at 1413°K. was determined indirectly to be 1622 cal. mole^{-1} by an analogous extrapolation. A complete plot of heat content vs. temperature is shown in figure 6, taking the transition and melting-point temperatures from a previous study (91). The heat contents of γ-$Ca_2P_2O_7$ were found to be the same as those of β-$Ca_2P_2O_7$ at three different temperatures; and in the absence of knowledge of the range of existence of the γ-$Ca_2P_2O_7$ species, the data of figure 6 and equations 27–33 listed below were based upon the assumption that the relative heat content of β-$Ca_2P_2O_7$ at 298.16°K. is zero (60).

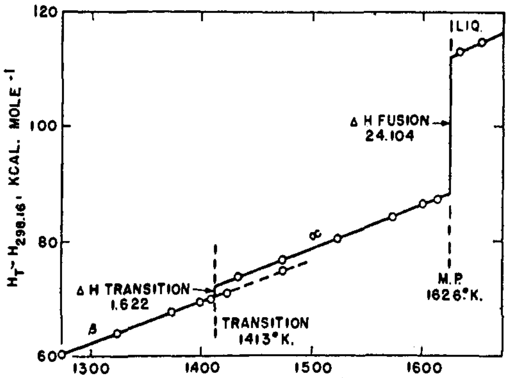


FIG. 6. Heat content above 298.16°K. vs. temperature for the calcium pyrophosphates. From Egan and Wakefield (60); reproduced by permission of the American Chemical Society and the authors.

$H_T - H_{298.16}$

β: $54.90T + 6.452 \times 10^{-3}T^2 + 12.73 \times 10^5T^{-1} - 21{,}210$ (±0.2%; 298.16–1413.16°K.) (27)

α: $76.111T - 35{,}700$ (±0.1%; 1413.16–1626.16°K.) (28)

Liquid: $96.854T - 45{,}330$ (±0.1%; 1626.16–1700°K.) (29)

$S_T - S_{298.16}$

β: $126.412 \log T + 12.904 \times 10^{-3}T + 6.365 \times 10^5T^{-2} - 323.808$ (298.16–1413.16°K.) (30)

α: $175.25 \log T - 457.97$ (1413.16–1626.16°K.) (31)

Liquid: $223.02 \log T - 596.52$ (1626.16–1700°K.) (32)

C_p

β: $54.90 + 12.904 \times 10^{-3}T - 12.73 \times 10^5T^{-2}$ (298.16–1413.16°K.) (33)

For the calcium metaphosphate, β-$Ca(PO_3)_2$, the heat contents above 298.16°K. were measured on both crystalline and vitreous samples (59) up to 1370°K., where the observed heat content of the melt was independent of the nature of the original material. However, the thermal behavior of calcium metaphosphate above 1220°K. is somewhat in question, owing to the close proximity of transition and melting temperatures, i.e., the $\beta \rightarrow \alpha$ transition temperature of calcium metaphosphate is 1239°K., while the melting points are 1233–1243°K. (198) or 1250°K. (91, 92) for the β-form and 1257°K. (91, 92) for the α-form. For obvious reasons there have been no measurements of the heat of transition of β- to α-calcium metaphosphate. The heat of fusion of calcium metaphosphate is 19,820 cal. mole^{-1}, the average of two values obtained from a study of the system $CaO–Al_2O_3–P_2O_5$ (191). Using these data, equations 34–43 for the molal thermodynamic functions were derived (59).

Crystals:

$$H_T - H_{298.16} = 46.4756T + 3.847 \times 10^{-3}T^2 + 13.029 \times 10^5T^{-1} - 18{,}572 \quad (\pm 0.4\%;\ 298.16\text{–}1250°\text{K.}) \qquad (34)$$

$$C_p = 46.48 + 7.694 \times 10^{-3}T - 13.029 \times 10^5T^{-2} \qquad (35)$$

$$S_T - S_{298.16} = 107.014 \log T + 7.694 \times 10^{-3}T + 6.515 \times 10^5T^{-2} - 274.42 \qquad (36)$$

Glass (not including heat of fusion):

$$H_T - H_{298.16} = 46.9233T + 3.527 \times 10^{-3}T^2 + 13.257 \times 10^5T^{-1} - 18{,}750 \quad (\pm 0.4\%;\ 298.16\text{–}1250°\text{K.}) \qquad (37)$$

$$C_p = 46.92 + 7.054 \times 10^{-3}T - 13.257 \times 10^5T^{-2} \qquad (38)$$

$$S_T - S_{298.16} = 108.045 \log T + 7.054 \times 10^{-3}T + 6.628 \times 10^5T^{-2} - 276.91 \qquad (39)$$

Fusion:

$$H_T - H_{298.16} = 0.448T - 0.32 \times 10^{-3}T^2 + 0.228 \times 10^5T^{-1} + 19{,}745 \qquad (40)$$

$$S_T - S_{298.16} = 1.0309 \log T - 0.64 \times 10^{-3}T + 0.114 \times 10^5T^{-2} + 13.46 \qquad (41)$$

Glass (including heat of fusion):

$$H_T - H_{298.16} = 46.923T + 3.527 \times 10^{-3}T^2 + 13.257 \times 10^5T^{-1} + 1170 \quad (42)$$

$$S_T - S_{298.16} = 108.045 \log T + 7.054 \times 10^{-6}T + 6.628 \times 10^6T^{-2} - 260.96 \quad (43)$$

VI. Crystal Structures of Alkaline Earth Phosphates

There are many compilations of x-ray powder diffraction patterns of precipitated and fired calcium phosphates (14, 93, 94, 96, 133). A similar compilation of diffraction patterns of strontium phosphates has also been recently published (178). However, comparable data on the barium phosphates are scattered throughout the literature. Thus, x-ray powder diffraction patterns suitable for identification purposes are given for dibasic barium orthophosphate, $BaHPO_4$ (41); tribasic barium orthophosphate, $Ba_3(PO_4)_2$ (232); barium hydroxyapatite (87, 111); and barium tetrametaphosphate, $Ba_2(PO_3)_4$ (118, 157); as well as for dimorphic modifications of both barium pyrophosphate, $Ba_2P_2O_7$ (118, 134, 173), and barium tetrapolyphosphate, $Ba_3P_4O_{13}$ (84, 118, 134).

Is on cell dimensions, space groups, and detailed atomic configurations derived from more detailed crystal structure studies is given under the specific compounds. Ångström units are used throughout. In those cases where dimensions were originally given in kX units, they were converted to Ångström units by multiplying by 1.00202.

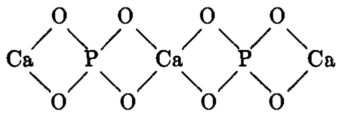
A. MONOBASIC ORTHOPHOSPHATES

1. $Ca(H_2PO_4)_2$ *and* $Ca(H_2PO_4)_2{\cdot}H_2O$

Both $Ca(H_2PO_4)_2$ and its monohydrate have long been known to be triclinic (85), but only recently were unit-cell dimensions determined (129, 187) by the use of single-crystal rotation and Weissenberg photographs (table 14). In the case of $Ca(H_2PO_4)_2{\cdot}H_2O$ the interaxial angles are in remarkably good agreement with the set determined much earlier (85), while recent determinations of unit-cell lengths (129, 187) also agree.

There is a marked similarity between the morphological elements of $Ca(H_2PO_4)_2{\cdot}H_2O$, $CaHPO_4{\cdot}2H_2O$ (brushite), and $CaSO_4{\cdot}2H_2O$ (gypsum) (85, 187). Since the gypsum structure was known to have alternate layers of $CaSO_4$ and H_2O (228), it was assumed (187) that the $Ca(H_2PO_4)_2{\cdot}H_2O$ structure was comprised of similar alternate layers of $CaHPO_4$ and $H_3PO_4{\cdot}H_2O$. Indeed, a complete structure analysis confirmed the presence of a morphological center of symmetry, thus establishing space group $P\bar{1}$, and revealed that the structure of $Ca(H_2PO_4)_2{\cdot}H_2O$ consists of parallel sheets of $CaPO_4$, separated by water molecules and phosphate ions (129).

The $CaPO_4$ sheets consist of discrete PO_4 tetrahedra and Ca^{2+} ions in parallel chains of the form:



Adjoining chains lying in $CaPO_4$ sheets in the (010) plane are separated by 2.3 A. to give a corrugated effect to the sheets. Water molecules lie between the sheets, as do the remaining PO_4 groups which occur in pairs across a center of symmetry. Calcium is coordinated to a total of eight oxygens: four in its own chain, two in neighboring chains, and one each to the oxygen of an intersheet H_2O and PO_4 group. The average bond lengths are:

Ca—O	2.52 ± 0.037 A.
P—O	1.52 ± 0.039 A.
O—O (within a PO_4 group)	2.48 ± 0.050 A.

The hydrogen positions have not been located exactly, but it is likely that they lie between oxygen atoms of neighboring PO_4 tetrahedra near a molecule of H_2O, thus forming hydrogen bonds which link the neighboring sheets of the structure together.

2. Similar orthophosphates

In phase studies (71, 72) of the system Ca^{2+}–NH_4^+–PO_4^{3-}–H_2O, a double salt of the composition $Ca_9(NH_4)_4H_{32}(PO_4)_{18}{\cdot}10H_2O$ was prepared. More recent work (40) has given the composition as $Ca_2NH_4H_7(PO_4)_4{\cdot}2H_2O$, and petrographic examination of this hydrated calcium phosphate containing ammonium ions shows a marked resemblance to monobasic calcium orthophosphate monohydrate in habit, form, and twinning. Unit-cell

TABLE 14

Unit-cell dimensions and space groups of the monobasic calcium orthophosphates

Calcium Orthophosphate	*a*	*b*	*c*	α	β	γ	*Z*	Space Group	Reference
	A.	*A.*	*A.*						
$Ca(H_2PO_4)_2$	5.55	7.60	9.07	121°54′	108°48′	87°28′	2	$P1$ or $P\bar{1}$	(187)
$Ca(H_2PO_4)_2{\cdot}H_2O$	—	—	—	98°40′	118°21′	83°16′	—	—	(85)
	5.67	11.92	6.51	98°11′*	118°31′	83°9′	2	$P1$ or $P\bar{1}$	(187)
	5.61	11.89	6.46	98°36′	118°0′	83°23′	2	$P\bar{1}$	(129)
$Ca_2(NH_4)H_7(PO_4)_4{\cdot}2H_2O$	5.79	12.52	6.50	97°57′	117°45′	98°0′	1	$P\bar{1}$ (assumed)	(40)
$CaCl(H_2PO_4){\cdot}H_2O$	5.76†	17.14	6.41†	90°	119°0′	90°	4	$C2/c$	(222)

* Reference 40.

† *a*- and *c*-axes reported by Walter-Levy, de Wolff, and Vincent (222) are interchanged.

dimensions also resemble those of $Ca(H_2PO_4)_2 \cdot H_2O$ (table 14) especially the *a* and *c* unit-cell lengths and angle *β*, which in $Ca(H_2PO_4)_2 \cdot H_2O$ lie in the plane of the $CaPO_4$ sheets. It is therefore hypothesized (40) that these $CaPO_4$ sheets also occur in $Ca_2NH_4H_7(PO_4)_4 \cdot 2H_2O$, as well as in an isomorph in which NH_4^+ is replaced by K^+. The ammonium or potassium ions are probably located between the $CaPO_4$ sheets where, owing to low atomic density, they could fit without greatly distorting the lattice. The unit-cell dimensions support the formula $Ca_2NH_4H_7(PO_4)_4 \cdot 2H_2O$.

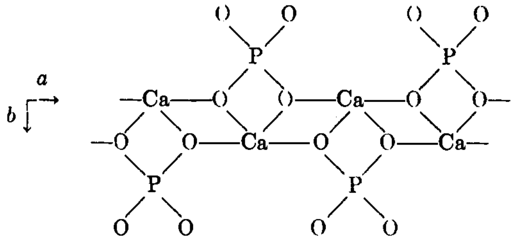
Another related compound which has *a*, *c*, and *β* values close to those of $Ca(H_2PO_4)_2 \cdot H_2O$ and $Ca_2NH_4H_7(PO_4)_4 \cdot 2H_2O$ is $CaClH_2PO_4 \cdot H_2O$ (222) (table 14). It also has a platelike habit characteristic of the $CaPO_4$ sheet structures; therefore it has been assumed (40) that it too is built up of such sheets. It is hypothesized (40) that $CaBrH_2PO_4 \cdot H_2O$ (221) and chlorospodiosite, Ca_2PO_4Cl (127), possess similar layer structures.

There are no structural data on the monobasic orthophosphates of strontium or barium.

B. DIBASIC ORTHOPHOSPHATES

1. *Monetites*, $MHPO_4$

Groth (82) reported that $CaHPO_4$ was triclinic pinacoidal, and recent work (128, 187), using single-crystal techniques, confirmed this assignment. The unit-cell dimensions reported (table 15) are in substantial agreement. Although Smith, Lehr, and Brown (187) could not discriminate between space groups $P1$ and $P\bar{1}$, later work by MacLennan and Beevers (128) showed the presence of a morphological center of symmetry and established the validity of space group $P\bar{1}$. Detailed structure analysis revealed that the $CaHPO_4$ structure consists of a three-dimensional network of PO_4^{3-} tetrahedra held together by Ca^{2+} ions in the interstices. Projection of the structure down the *c*-axis shows a double chain of Ca–PO_4–Ca extending along the *a*-axis and linked traversely in the *b* direction by Ca—O bonds forming a distorted sheet of atoms lying approximately in the (001) plane, thus:



The Ca–O coördination number varies from 7 to 8. The average bond lengths are:

Ca—O	2.46 ± 0.039 A.
P—O	1.54 ± 0.040 A.
O—O (within a PO_4 group)	2.51 ± 0.055 A., or 2.51 ± 0.078 A. (if related by a center of symmetry)

The positions of the hydrogen atoms could not be determined with any appreciable degree of accuracy, owing to the swamping effects of the heavy atoms, but it is likely that they are located between the oxygen atoms of neighboring PO_4 groups (128).

Anhydrous $BaHPO_4$ was reported to be orthorhombic by de Schulten (186); Bengtsson (24) confirmed this assignment and gave unit-cell dimensions (table 15). In the latter work, only the positions of the heavy barium atoms were determined and the space group was extremely doubtful. More recently, a complete structural analysis was presented on the basis of powder diffraction and qualitative single-crystal intensity data (142). This work was based upon the pseudo-cell noted previously by Bengtsson (24), having dimensions *a*/2, *b*/3, and *c* (axes oriented as in table 15). A more detailed study by Burley (41), using quantitative intensity data and based on three Fourier projections, showed that the original unit cell proposed by Bengtsson (24) was correct. The positions of the barium atoms are in excellent agreement with those found by Mooney (142), but the positions of the oxygen atoms are different. A projection of the structure on the *hk*0 plane (figure 7) illustrates the M—PO_4—M chain structure as was found also in $CaHPO_4$ (128). The discrete PO_4 tetrahedra are undistorted and held together by ionic bonding with Ba^{2+} ions and hydrogen bonding between

TABLE 15

Unit-cell dimensions and space groups of the dibasic alkaline earth orthophosphates

Orthophosphate	*a*	*b*	*c*	*α*	*β*	*γ*	*Z*	Space Group	Reference
	A.	*A.*	*A.*						
$CaHPO_4$	6.91	6.66	7.02	96°7′	103°53′	89°11′	4	$P\bar{1}$ or $P1$	(187)
	6.90 ± 0.01	6.65 ± 0.01	7.00 ± 0.01	96°21′	103°54′	88°44′	4	$P\bar{1}$	(128)
$BaHPO_4$	14.08*	17.10*	4.61*	—	—	—	12	*Pccn*	(24)
	7.05 ± 0.01†	5.71 ± 0.01†	4.61 ± 0.01†	—	—	—	2	*Pmn*	(142)
	14.12 ± 0.03	17.15 ± 0.03	4.59 ± 0.02	—	—	—	12	$Pn2_1a$	(41)
$CaHPO_4 \cdot 2H_2O$	5.812 ± 0.002	15.18 ± 0.003	6.239 ± 0.002	90°	116°25′ ± 2′	90°	4	*I* 2/*a*‡	(21)

* *a*-, *b*-, and *c*-axes reported by Bengtsson (24) are interchanged.
† *a*- and *b*-axes reported by Mooney (142) are interchanged.
‡ Standard international symbol is *C* 2/*c*.

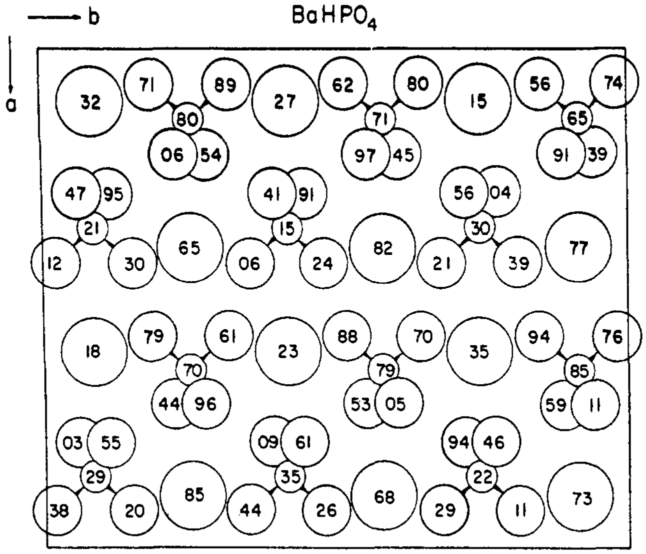


FIG. 7. Projection of the structure of BaHPO$_4$ on the $hk0$ plane. Circles in decreasing order of size represent Ba, O, and P, respectively. The numbers shown indicate the height in the c direction in units of $\frac{1}{100}$ of the c dimension of the unit cell. In a private communication Burley stated that the oxygen labeled 91 on the phosphorus at a height of 15, should be corrected to 89. From Burley (41); reproduced by permission of the National Bureau of Standards and the author.

neighboring tetrahedra. The positions of the hydrogen atoms were not determined uniquely. The barium atoms are coördinated with ten oxygen atoms, with seven of the ten more strongly bonded than the others. Average bond distances based on Burley's structure are:

Ba—O (seven nearest)	2.80 ± 0.067 A.
(three others)	3.43 ± 0.067 A.
P—O	1.56 ± 0.085 A.
O—O (within a PO$_4$ group)	2.55 ± 0.091 A.

There have been no detailed studies of the crystal structure of SrHPO$_4$, although some assignments of crystal systems have been suggested. Thus, de Schulten (186) thought that SrHPO$_4$ was orthorhombic, while Bengtsson (24) found a lower order of symmetry. The discovery that SrHPO$_4$ occurs in dimorphic modifications (143) helps to explain some of the past discrepancies. On the basis of marked similarities between the powder patterns of CaHPO$_4$ and α-SrHPO$_4$ it was postulated that these compounds are isostructural and therefore that α-SrHPO$_4$ is triclinic with space group $P\bar{1}$ (143). A microscopic examination of transparent prismatic to acicular crystals of SrHPO$_4$ indicated that the crystals were triclinic or possibly monoclinic, qualitatively supporting that postulate (99). More recent work (1) has shed further light on the subject. Single crystals of SrHPO$_4$ of prismatic or acicular habit and belonging to the triclinic system by microscopic analysis have been identified as α-SrHPO$_4$ by x-ray diffraction. In an analogous manner, rhombic plates of SrHPO$_4$ belonging to the orthorhombic system have been identified as β-SrHPO$_4$. Measurement of the refractive indices of the dimorphs (Section VII,A) leaves little doubt that the orthorhombic SrHPO$_4$ of de Schulten is β-SrHPO$_4$. Hence, with the strontium monetites there is demonstrated the interesting probability that β-SrHPO$_4$ (the low-temperature form) is isomorphous with BaHPO$_4$, while α-SrHPO$_4$ (the high-temperature form) is isomorphous with CaHPO$_4$.

2. Brushite, CaHPO$_4$·2H$_2$O

Early predictions (93, 195) that brushite (CaHPO$_4$·2H$_2$O) and gypsum (CaSO$_4$·2H$_2$O) are isomorphous were confirmed by single-crystal x-ray methods (21), giving the unit-cell dimensions and space groups listed in table 15. Detailed structural analysis (19) reveals that CaHPO$_4$·2H$_2$O is made up of discrete PO$_4$ groups with calcium atoms sharing the oxygen atoms to give a continuous chain of calcium and phosphorus atoms linked by oxygen atoms, as already shown for Ca(H$_2$PO$_4$)$_2$·H$_2$O. In addition, each calcium atom is bonded to two additional oxygen atoms in neighboring chains, resulting in the formation of the familiar corrugated sheets of composition CaPO$_4$. The sheets are linked by water molecules by means of two oxygen bonds to each calcium atom. The Ca—O, P—O, and O—O bond distances with subscripts denoting oxygen atoms in nonequivalent positions are:

Ca—O$_1$ (within chain)	2.82 A.
Ca—O$_2$ (within chain)	2.44 A.
Ca—O$_2$ (linking chains)	2.35 A.
Ca—O$_3$ (water molecules)	2.54 A.
P—O$_1$	1.53 A.
P—O$_2$	1.54 A.
O—O (within PO$_4$ group)	2.50–2.52 A.
O$_3$—O$_1$ (within same sheet)	2.62 A.
O$_3$—O$_1$ (between neighboring sheets)	2.82 A.
O$_3$—O$_3'$	2.63 A.

Again the hydrogen atoms are presumed to lie on a short O—O distance, the final choice in this instance being made on the basis of symmetry: namely, between the O$_3$—O$_3'$ bond. The P—O and O—O bonds within the PO$_4$ group form a regular tetrahedron within the limits of error. The Ca—O and P—O bond distances are much the same as those found for CaHPO$_4$ (128) with the exception of the Ca—O$_1$ bond distance, which is considerably longer than the usual Ca—O bond.

C. TRIBASIC ORTHOPHOSPHATES

The simplest structure in the M$_3$(PO$_4$)$_2$ group is that of the rhombohedral isostructural compounds, Sr$_3$(PO$_4$)$_2$ and Ba$_3$(PO$_4$)$_2$ (232). The unit cells, containing one molecule each, have the dimensions given in table 16. The two phosphate groups per unit cell are assumed to have the usual tetrahedral configuration with a P—O distance of 1.56 A. (227), with both phosphorus atoms and two of the oxygen atoms lying on the threefold axis. The coördination number of barium

TABLE 16

Unit-cell dimensions and space groups of the tribasic alkaline earth orthophosphates

	Rhombohedral Cell		Hexagonal Cell		Z	Space Group	Reference
	μ	α	a	c			
	A.		A.	A.			
β-Ca$_3$(PO$_4$)$_2$	13.65	44°06′	10.25 ± 0.03	36.9 ± 0.1	7	$R\bar{3}c$	(74)
	13.70	44°16′	10.32 ± 0.02	37.0 ± 0.05	7	$R\bar{3}c$	(125)
Sr$_3$(PO$_4$)$_2$	7.295	43°21′ ± 02′	5.389	19.79	1	$R\bar{3}m$	(232)
Ba$_3$(PO$_4$)$_2$	7.712	42°35′ ± 02′	5.601	21.00	1	$R\bar{3}m$	(232)
	Monoclinic Cell						
	a	b	c	β			
	A.	A.	A.				
γ-Ca$_3$(PO$_4$)$_2$	12.86 ± 0.02	9.11 ± 0.01	15.23 ± 0.02	125°20′ ± 12′	8	$P2_1/a$	(126)

and strontium is 12 for atoms of the first kind, in positions (0,0,0), and 10 for atoms of the second kind, in positions $\pm(u_1,u_1,u_1)$. The mean bond distances are:

Sr$_1$—O	2.86 A.	Ba$_1$—O	3.01 A.
Sr$_2$—O	2.67 A.	Ba$_2$—O	2.81 A.
Sr—O (mean)	2.73 A.	Ba—O (mean)	2.88 A.

The structures of the corresponding Ca$_3$(PO$_4$)$_2$ compounds are much more complicated. The mineral whitlockite, β-Ca$_3$(PO$_4$)$_2$, was first studied in 1941 and found to be rhombohedral with space group $R\bar{3}c$ (74, 75). However, the unit-cell dimensions (table 16) and the observed density demand seven Ca$_3$(PO$_4$)$_2$ per unit cell; this is not consistent with space group $R\bar{3}c$, which requires even numbers of atoms. It was suggested (193) that whitlockite was isotypic with palmierite, PbK$_2$(SO$_4$)$_2$ (23), which has a unit cell of the same size as Ba$_3$(PO$_4$)$_2$, but is not isostructural. However, comparison of the observed structure factors of β-Ca$_3$(PO$_4$)$_2$ with those calculated on the basis of a PbK$_2$(SO$_4$)$_2$-type and a Ba$_3$(PO$_4$)$_2$-type lattice, respectively, shows that the very strong reflections cannot be accounted for by a palmierite-type structure, but can be reasonably accounted for by a Ba$_3$(PO$_4$)$_2$-type structure (125). Evidence for pyroelectric and piezoelectric effects preclude space group $R\bar{3}c$, which has a center of symmetry, and indicate instead space group $R3c$. From the unit-cell dimensions and space group, the unit cell should contain eight Ca$_3$(PO$_4$)$_2$, but MacKay's values of cell dimensions and observed density (125) gave a value of 6.91 ± 0.06, indicating seven Ca$_3$(PO$_4$)$_2$ per unit cell in agreement with Frondel's earlier results (74). The explanation offered for the contradiction between the number of molecules per unit cell and the space group is that some type of statistical distribution of atoms takes place.

Figure 8 shows a projection of the Ba$_3$(PO$_4$)$_2$-type structure on the (0001) plane. In the β-Ca$_3$(PO$_4$)$_2$ cell are twelve columns (spaced 3.7 A. apart) of calcium, phosphorus, and oxygen atoms denoted by the large circles. Three of the columns coincide with triad axes (A columns), while the remaining nine lie halfway between the triads (B columns). The designations are those of MacKay (125). From comparison of intensities and Patterson sections, it has been shown that the statistical absences occur among atoms lying on the triad axes; therefore to account for seven Ca$_3$(PO$_4$)$_2$ per cell, each B column contains six Ca and four PO$_4$, while each A column contains three Ca and two PO$_4$. Two Ca and two PO$_4$ groups in the B columns are displaced from their normal triad positions in the Ba$_3$(PO$_4$)$_2$ cell in the direction of the glide planes toward each triad or A column. However, two Ca atoms on each B column remain undisplaced. A slight displacement perpendicular to the glide planes also occurs. The magnitude of the total displacement is approximately 0.36 A., but it was not possible to select unique directions for these displacements on the basis of MacKay's work (125), although possible directional displacements were suggested (see figure 8). It has been definitely established, however, that β-Ca$_3$(PO$_4$)$_2$ is structurally similar to Ba$_3$(PO$_4$)$_2$ with statistical absences accounting for the anomaly between the space group and the cell content. Precedent for such a statistical distribution of atoms is found in the Pb$_3$(PO$_4$)$_2$ defect apatite structure (70, 177).

The Debye–Scherrer patterns of mixed crystals of (Ca,Sr)$_3$(PO$_4$)$_2$ display a series of lines common with β-Ca$_3$(PO$_4$)$_2$ from 0 to 79 atomic per cent calcium. On the basis of such fragmentary evidence, it was suggested (31) that β-Ca$_3$(PO$_4$)$_2$ is isomorphous with Sr$_3$(PO$_4$)$_2$. In view of the detailed quantitative data of MacKay (125), that seems highly unlikely. Furthermore, Koelmans and Cox (113) have shown that the composition of Sr$_3$(PO$_4$)$_2$ must be modified to produce the whitlockite structure, as evidenced by x-ray diagrams and luminescence measurements. When part of the strontium of Sr$_3$(PO$_4$)$_2$ is substituted by smaller cations such as aluminum, magnesium, zinc, cadmium, or calcium, the structure and luminescent

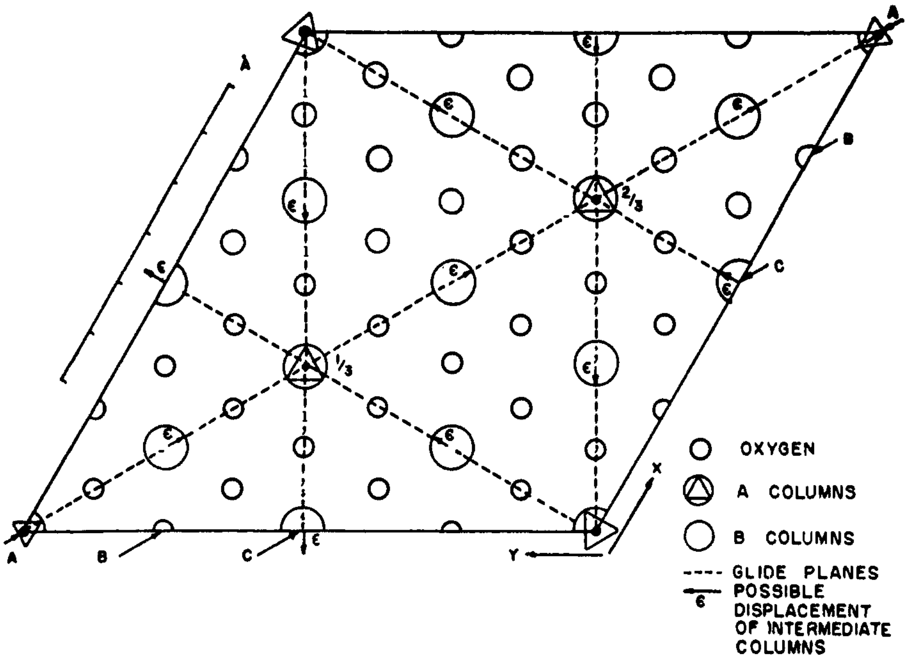


FIG. 8. Projection of the $Ba_3(PO_4)_2$-type structure on the (0001) plane, illustrating the displacements of the B columns in the β-$Ca_3(PO_4)_2$ structure. From MacKay (125); reproduced by permission of the University of London and the author.

properties change to those associated with β-$Ca_3(PO_4)_2$. When Ca^{2+} is the modifying cation, the changes occur when the Ca/Sr atom ratio of about 0.2 (about 17 atomic per cent calcium) is reached. Beyond that point, calcium and strontium appear to be isomorphous in the whitlockite structure. The fact remains that there is a fundamental difference between the structures of pure $Sr_3(PO_4)_2$ and β-$Ca_3(PO_4)_2$.

It has been noted that certain ions smaller than calcium ion stabilize or favor the formation of the whitlockite structure. The effect is particularly pronounced with Mg^{2+}, which may replace up to two of the twenty-one calcium atoms in the whitlockite unit cell accompanied by a regular decrease in the lattice dimensions. The unit-cell dimensions and magnesium contents of synthetic preparations, naturally occurring minerals, and pathological calcifications of whitlockite have been compared and show the contraction due to Mg^{2+} or Fe^{2+} substitution in all of the naturally occurring systems (203, 204).

Above 1180°C. β-$Ca_3(PO_4)_2$ undergoes a phase transition to the α-$Ca_3(PO_4)_2$ form, which is metastable at room temperature (34, 35, 208). A preliminary examination (125, 126) of the structure of α-$Ca_3(PO_4)_2$ showed that it was monoclinic (table 16). MacKay (126) points out that there are resemblances between the α- and β-polymorphs: namely, that both structures appear to be built up of columns parallel to their c-axes and spaced approximately 3.0 A. apart. However, there are also definite differences, as is obvious from the differences in space groups, $P2_1/a$ vs. $R3c$; and α-$Ca_3(PO_4)_2$ appears to have a structure unlike any other of the $M_3(PO_4)_2$-type compounds. In conclusion, neither the α-$Ca_3(PO_4)_2$ nor the β-$Ca_3(PO_4)_2$ structure has been completely worked out, and a lucid picture of the relationships of these compounds to each other and to the $Sr_3(PO_4)_2$ or $Ba_3(PO_4)_2$ structure remains to be drawn. A further complication has been introduced with the discovery of a new structure termed α'-$Ca_3(PO_4)_2$, which occurs with the inversion of α-$Ca_3(PO_4)_2$ at 1430°C. (155).

D. APATITES AND RELATED STRUCTURES

1. *Simple apatites*

The first apatite structure completely worked out was that of the mineral calcium fluoroapatite (135, 151). Several redeterminations of this structure (13, 20) and the structure of calcium hydroxyapatite (169), which is isomorphous, have confirmed, with only minor modifications, the Naray-Szabo hexagonal structure (151), having space group $P6_3/m$. Unit-cell dimensions given in table 17 for calcium fluoroapatite (20, 45, 151, 206, 217) and calcium hydroxyapatite (20, 45, 169, 206, 217) are in excellent agreement.

The apatite structure contains two types of positions for calcium. The atoms designated as Ca_I lie on the threefold axes and are coördinated to three oxygen atoms above and below the Ca_I sites in the c-axis direction, forming an irregular triangular prism. They are also bonded to three O_3 atoms on the same plane at somewhat longer interatomic spacings, giving

TABLE 17

Unit-cell dimensions of apatites

Apatite	a	c	c/a
	A.	A.	
$Ca_{10}F_2(PO_4)_6$			
Naray-Szabo (151)	9.37	6.88	0.734
Beevers and McIntyre (20)	9.37	6.88	0.734
Wallaeys (217)	9.37_1	6.88_7	0.735
Trautz (206)	9.37_7	6.88_2	0.734
Carlström (45)	9.37_0	6.88_4	0.735
Average of last three	9.37_1	6.88_4	0.735
$Ca_{10}(OH)_2(PO_4)_6$			
Beevers and McIntyre (20)	9.41	6.88	0.731
Wallaeys (217)	9.42_2	6.88_2	0.730
Posner, Perloff, and Diorio (169)	9.43_2	6.88_1	0.730
Trautz (206)	9.42_1	6.88_1	0.730
Carlström (45)	9.42_1	6.88_2	0.730
Average of last four	9.42_4	6.88_2	0.730
$Ca_{10}Cl_2(PO_4)_6$			
Hendricks, Jefferson, and Mosley (90)	9.52	6.85	0.720
$Sr_{10}F_2(PO_4)_6$			
Akhavan-Niaki and Wallaeys (6)	9.72_0	7.27_7	0.749
$Sr_{10}(OH)_2(PO_4)_6$			
Klement (110)	9.74	7.20	0.739
Akhavan-Niaki and Wallaeys (5)	9.76_3	7.27_7	0.745
Lagergren and Carlström (117)	9.76_1	7.27_7	0.746
Collin (47)	9.76_0	7.28_4	0.746
Average of last three	9.76_1	7.27_9	0.746
$Ba_{10}F_2(PO_4)_6$			
Akhavan-Niaki (6)	10.22	7.67	0.750
$Ba_{10}(OH)_2(PO_4)_6$			
Klement and Dihn (111)	10.19	7.70	0.756

a total oxygen coördination number of 9. Three Ca_2 atoms surround each fluorine atom in fluoroapatite or OH group in hydroxyapatite in a triangular planar arrangement. Each Ca_2 atom is therefore situated around a hexagonal screw axis with F at the center and is coördinated irregularly to six oxygen atoms in addition to the fluorine atom or hydroxyl group.

The latest refinement of the hydroxyapatite structure, using the least-squares method, has given interatomic distances which are more in accord with other calcium phosphate structures. The P—O and Ca—O bond lengths resulting from this work by Posner, Perloff, and Diorio (169) are listed below:

P—O Bond Lengths		Ca—O Bond Lengths	
	A.		A.
$P—O_1$	1.533	$Ca_1—O_1$	2.416
$P—O_2$	1.544	$Ca_1—O_2$	2.449
$P—O_3$	1.514	$Ca_1—O_3$	2.802
		$Ca_2—OH$	2.354
		$Ca_2—O_1$	2.712
		$Ca_2—O_2$	2.356
		$Ca_2—O_3$	2.367
		$Ca_2—O_3'$	2.511

The resulting PO_4 tetrahedron is relatively undistorted in contrast to the PO_4 tetrahedron of Naray-Szabo (151).

If the discussion of apatite structures could stop here, the subject would be most straightforward. Unfortunately, a whole series of calcium orthophosphates exhibit apatite x-ray diffraction patterns while at the same time varying in composition from a molar Ca/P ratio of 1.3 to over 2. This important and very interesting subject has been summarized in detail by Van Wazer (211) and the Neumans (153); therefore only the barest essentials are given here.

The lack of stoichiometry in the apatites may be explained by (*1*) surface adsorption or substitution, (*2*) isomorphous substitution of ions or groups for others within the lattice, and (*3*) the occurrence of defects or holes in normally occupied lattice positions. In view of the enormous amount of conflicting data, it is safest to agree that "all three explanations seem reasonable" (153).

The observance of apatite-like materials having a specific Ca/P ratio has led to the postulation of several "specific" compounds. Thus, hydroxyapatite having a Ca/P ratio of 1.50 has been called "tricalcium phosphate hydrate" (34, 90, 209) or even "α-tricalcium phosphate," a misnomer (54), because it is converted to β-$Ca_3(PO_4)_2$ on heating, whereas the stoichiometric hydroxyapatite is unaffected. However, it has been pointed out that such behavior is to be expected and that the results are dependent only on the Ca/P ratio, rather than on the initial atomic arrangement (65, 153, 211).

Similarly, the term "pseudoapatite" has been applied to a series of calcium hydroxyapatites whose variable Ca/P ratios have been explained by postulating the random absence of Ca^{2+} ions from certain positions in the hydroxyapatite lattice (165, 167). Electrical neutrality must be maintained by the substitution of H^+ for Ca^{2+} ions similar to the structure proposed for the apatite known as tricalcium phosphate hydrate (90). This approach has been expanded to include the lead apatites (168), for which the best match of calculated and observed intensity data is obtained when one of the four Pb_1 atoms is presumed missing per unit cell. Unfortunately, a similar calculation cannot be applied to the nonstoichiometric calcium hydroxyapatite structure, owing to the negligible effect on the x-ray intensities of removing a calcium ion from the lattice. However, since the observed index of refraction changes with the Ca/P ratio, it is likely that certain positions normally occupied by calcium atoms are empty (168). The possibility of vacancies is intriguing to those working in the field of solid-state defect structures and has support from the fact that other phosphates with defect structures have been observed (70, 125, 177).

A recent paper (39) describing the crystallography of octacalcium phosphate confirms the existence of a discrete compound having the formula $Ca_4H(PO_4)_3 \cdot 3H_2O$. Single crystals were obtained and measured by Weissenberg techniques, giving the triclinic lattice constants $a = 19.7$ A., $b = 9.59$ A., $c = 6.87$ A., $\alpha \cong \beta = 90.7°$, and $\gamma = 71.8°$. A layer-type structure was proposed (39) similar to, but not isostructural with, hydroxyapatite, having $CaPO_4$ sheets of the type found in $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4 \cdot 2H_2O$. The preparation and study of single crystals of octacalcium phosphate dispute previous conclusions (153, 211) that the compound was merely a form of calcium hydroxyapatite.

Calcium chloroapatite crystallizes in a Mehmel-type (135) structure with chlorine atoms in the $(0,0,0)$ and $(0,0,\frac{1}{2})$ positions (90) instead of the $(0,0,\frac{1}{4})$ and $(0,0,\frac{3}{4})$ positions occupied by fluorine atoms or hydroxyl groups in the Naray-Szabo type (151) of structure for fluoroapatite and hydroxyapatite. Calcium chloroapatite is, therefore, one of the pyromorphite $[Pb_{10}Cl_2(PO_4)_6]$ series (158). In spite of the difference in structure, a continuous series of solid solutions exist between fluoroapatite and chloroapatite (150, 218, 219).

Strontium fluoroapatite (6) and strontium hydroxyapatite (5, 47, 110, 117) also crystallize in hexagonal lattices with the unit-cell dimensions given in table 17. Presumably both have the calcium fluoroapatite or hydroxyapatite structure. A "tristrontium phosphate hydrate" compound analogous to the cation-deficient hydroxyapatite, $Ca_3(PO_4)_2 \cdot H_2O$, has been proposed and unit-cell dimensions of $a = 9.792$ and $c = 7.241$ A. have been determined (33). A similar compound, $Sr_3(PO_4)_2 \cdot 0.5H_2O$, with the apatite x-ray pattern has also been proposed (5). However, the existence of discrete compounds of this type is open to the same criticism as that already put forth for "tricalcium phosphate hydrate" (206, 211).

The dimensions of the hexagonal unit cell of barium fluoroapatite (6) and barium hydroxyapatite (111) are also given in table 17. Because of the significantly larger size of Ba^{2+} compared to Ca^{2+}, the barium apatites are presumably members of the pyromorphite series, crystallizing in the Mehmel-type (135) structure.

Scrutiny of the unit-cell dimensions in table 17 reveals some interesting facts. In cases where more than one precise determination of lattice constants has been made, there is good agreement between results. An increasing trend in the c/a ratio is noted in passing from the calcium to the barium apatites. This trend is readily explained by the fact that there are a greater number of cations having positions one above another in columns parallel to the c-axis than are adjacent to each other parallel to the a-axis. Therefore, an increase in cationic size is reflected more in an increase in the c dimension than in the a dimension. Comparing hydroxyapatite dimensions with fluoroapatite dimensions, the c dimension is unaffected by replacement of a fluorine atom by a hydroxyl group in the calcium and strontium apatites, whereas the a dimension is increased in both cases. This results in a decrease in the c/a ratio in going from fluoroapatite to the hydroxyapatite. Comparable precise data on barium hydroxyapatite are not available, but using the a and c dimensions listed, the c dimension increases and the a dimension decreases slightly in going from barium fluoroapatite to barium hydroxyapatite. This results in an increase in the c/a ratio which is opposite to that observed for the calcium and strontium apatites. The difference may reflect the basic differences in structure between the apatite (calcium and strontium) and the pyromorphite (barium) lattices.

The subject of the carbonate apatites is not considered to fall within the scope of this review, but has been reviewed by Carlström (45). A strontium carbonate apatite has been prepared with 0.9 mole CO_2 and lattice dimensions $a = 9.887$ A. and $c = 7.245$ A. (4). When strontium carbonate apatite is fused with SrF_2 at 1100°C., strontium fluoroapatite is formed.

2. Mixed-cation apatites

(a) Calcium strontium apatites

Mixtures of calcium fluoroapatite and strontium fluoroapatite heated to 950°C. form a continuous series of solid solutions whose a and c dimensions vary linearly between the dimensions of the two pure components (6). However, a study in which precipitated mixtures of calcium and strontium hydroxyapatite were heated at 1300°C. did not exhibit solid-solution behavior, and a special intermediate apatite of composition $Ca_5Sr_5(OH)_2(PO_4)_6$ was postulated (117). In a more recent study (47) solid solutions were prepared by precipitation from aqueous solution followed by heating to 950°C., a technique of the same general type used unsuccessfully by Lagergren and Carlström (117). Because the Ca/Sr ratio in the precipitated solid was always higher than in the initial solution, resulting in a continuously changing composition of solution and precipitate, homogeneous solid solutions were formed only after firing. The lattice dimensions of the fired apatites were linear functions of the atomic per cent of strontium in the final solid, thus proving the existence of solid solutions of calcium and strontium hydroxyapatites with no special status for the 50 atomic per cent phase.

(b) Strontium barium apatites

Akhavan-Niaki and Wallaeys (6) showed that strontium fluoroapatite and barium fluoroapatite heated to 950°C. also form solid solutions whose lattice dimensions follow Végard's law. However, since barium hydroxyapatite is not ordinarily precipitated from aqueous solution, the usual basic phosphates of strontium and barium—namely, strontium hydroxyapatite and tribasic barium orthophosphate—are of different structure (162). The hydroxyapatite $3Sr_3(PO_4)_2 \cdot Ba(OH)_2$ is claimed (32) to be isomorphous with "tristrontium phosphate hydrate," which Brasseur and Plumier (33) believe to be distinct from strontium hydroxyapatite. If "tristrontium phosphate hydrate" and strontium hydroxyapatite are identical, as proposed earlier, it is not surprising that $Sr_{10}(OH)_2(PO_4)_6$ and $Sr_9Ba(OH)_2(PO_4)_6$ are isomorphous.

(c) Calcium barium apatites

Contrary to the calcium strontium fluoroapatites and the strontium barium fluoroapatites, which form continuous series of solid solutions, the calcium fluoroapatite–barium fluoroapatite system has a zone of immiscibility between 6 and 64 atomic per cent barium (3). In the miscible regions, the lattice dimensions vary linearly with atomic per cent barium, but while the *a* dimension follows the same linear law in both miscible regions, the *c* dimension does not. No comparable study of the calcium barium hydroxyapatites has been made.

E. CONDENSED PHOSPHATES

The only detailed structural analyses of inorganic pyrophosphates are those of the $M^{IV}P_2O_7$ compounds (122); however, the unit-cell dimensions of several $M_2^{II}P_2O_7$ compounds are known (table 18). The high-temperature (or α) modifications of the alkaline earth pyrophosphates are isomorphous (163, 173), and single-crystal measurements on the α-modifications of calcium and strontium pyrophosphates show them to be orthorhombic. The α-$Ba_2P_2O_7$ structure was indexed from powder patterns by analogy (173). Weissenberg photographs show that β-$Ca_2P_2O_7$ is tetrahedral with space group $P4_1$ (50); and, since β-$Sr_2P_2O_7$ is isomorphous with β-$Ca_2P_2O_7$ (173), it probably crystallizes in space group $P4_1$. Recently determined unit-cell dimensions for β-$Sr_2P_2O_7$ (97) given in table 18 confirm its tetrahedral symmetry. There are no structures reported for γ-$Ca_2P_2O_7$ and δ-$Ba_2P_2O_7$.

The compound $Ca_2P_2O_7 \cdot 2H_2O$ has been isolated as a crystalline intermediate in the hydrolytic degradation of calcium polymetaphosphate (38). The triclinic lattice constants determined by single-crystal x-ray techniques were $a = 6.70$ A., $b = 7.38$ A., $c = 8.31$ A., $\alpha = 85°2'$, $\beta = 102°48'$, and $\gamma = 107°23'$, with two molecules per unit cell.

Unit-cell dimensions of a calcium metaphosphate have shown it to be orthorhombic with $a = 16.95$ A., $b = 7.66$ A., $c = 7.04$ A., and space group $P2_1/a$, and to have eight molecules per unit cell (49). This metaphosphate is probably the β-modification, which is stable over a wide temperature range, although it might also be δ-calcium metaphosphate, which exhibits structural similarities to anhydrous $CaSO_4$ (156), which is orthorhombic. No other structures of condensed phosphates have been reported.

VII. OPTICAL PROPERTIES OF ALKALINE EARTH PHOSPHATES

A. PETROGRAPHIC STUDIES

The value of optical methods in the rapid detection of impurities in supposedly pure samples has been known for many years. Petrographic determinations are particularly valuable, since they can be made upon crushed or ground fragments almost as well as upon well-developed crystals, and optical properties can usually be observed and accurately measured in a matter of minutes. Certain of the optical properties such as isotropy, anisotropy, uniaxiality, biaxiality, and optical character are qualitative and serve to place a substance in a particular group. The other properties are quantitative and specific and serve to identify a substance once it has been placed in its proper group. The quantitative properties reported in this review are refractive indices, birefringence, and optical axial angle.

1. *Calcium phosphates*

Because of their frequent occurrence in nature, the calcium orthophosphates have received considerable attention from mineralogists and others trained in the use of the polarizing microscope. Many available references have been critically compared and a summary of what appear to be the most accurate optical properties is given in table 19, although other reliable data are omitted in the interests of space. Refractive indices for several other apatites have been compiled by Larsen and Berman (119). It has also been shown that the average refractive index of synthetic calcium hydroxyapatite can be used to measure cation deficiency in terms of the Ca/P ratio (168).

TABLE 18

Unit-cell dimensions and space groups of alkaline earth pyrophosphates

	a	*b*	*c*	*Z*	Space Group	Reference
	A.	*A.*	*A.*			
α-Polymorphs (orthorhombic):						
$Ca_2P_2O_7$	8.44	12.52	5.26	4	—	(173)
$Sr_2P_2O_7$	8.87	13.27	5.39	4	—	(173)
$Ba_2P_2O_7$	9.35	13.87	5.61	4	—	(173)
β-Polymorphs (tetragonal):						
$Ca_2P_2O_7$	6.66	—	23.86	8	$P4_1$	(50)
$Sr_2P_2O_7$	6.92	—	24.79	8	$P4_1$	(97)

TABLE 19

Optical properties of the calcium orthophosphates

Compound	Mineralogical Name	Refractive Indices (Sodium D Light Unless Otherwise Noted)			Birefringence	Optical Angle	References
		n_γ	n_β	n_α			
Biaxial group							
$Ca(H_2PO_4)_2 \cdot H_2O$	None	1.5292	1.5176	1.4932	0.036 (−)	70°	(120)
		(425 mμ) 1.526	1.512	1.492	0.034 (−)	—	(187)
		(610 mμ) 1.529	1.515	1.496	0.033 (−)	81°30′	(187)
$Ca(H_2PO_4)_2$	None	1.601	1.580	1.547	0.054 (−)	—	(93)
		(425 mμ) 1.596	1.567	1.543	0.053 (+)	—	(187)
		(610 mμ) 1.602	1.572	1.548	0.054	85°14′	(187)
$CaHPO_4 \cdot 2H_2O$	Brushite	1.551	1.545	1.539	0.012	86°	(119)
		1.5516	1.5457	1.5394	0.0122 (−)	83°	(120)
		1.551	1.545	1.540	0.011 (+)	—	(14)
$CaHPO_4$	Monetite	1.640	1.615	1.587	0.053 (−)	—	(93)
		(425 mμ) 1.635	1.613	1.586	0.049 (−)	—	(187)
		(610 mμ) 1.640	1.616	1.588	0.052 (−)	84° 4′	(187)
α-$Ca_3(PO_4)_2$	None	1.591	—	1.588	0.003 (+)	—	(184)*
$Ca_4P_2O_9$	Hilgenstockite	1.647	—	1.643	0.004 (−)	80°	(184)*
Ca_2PO_4Cl	Chlorospodiosite	1.670	1.663	1.650	0.020 (−)	—	(127)
Uniaxial group							
		n_ω	n_ϵ				
β-$Ca_3(PO_4)_2$	Whitlockite	1.629	1.626 (mineral)		0.003 (−)	—	(74, 75)
		1.622	1.620 (synthetic)		0.002 (−)	—	(75)
$Ca_{10}F_2(PO_4)_6$	Fluoroapatite	1.633	1.630		0.003 (−)	—	(119)
		1.633	1.629		0.004 (−)	—	(139)
$Ca_{10}(OH)_2(PO_4)_6$	Hydroxyapatite	1.649	1.642		0.007 (−)	—	(160)
		1.651	1.644		0.007 (−)	—	(139)
$Ca_{10}Cl_2(PO_4)_6$	Chloroapatite	1.667	1.664		0.003 (−)	—	(119)
		1.6667	—		—	—	(136)
		1.666	—		—	—	(136)

* Cited by Farr (69).

All the calcium orthophosphates are optically negative [$n_\omega > n_\epsilon$ or $(n_\beta - n_\alpha) > (n_\gamma - n_\beta)$] except $Ca(H_2PO_4)_2$ and α-$Ca_3(PO_4)_2$. Since optically negative compounds normally crystallize in flat plates or tablets, while optically positive crystals take the habit of needles or prisms, this property is related to crystal structure (discussed in Section VI). The monobasic and dibasic orthophosphates are strongly birefringent, whereas the tribasic orthophosphates and the apatites are weakly birefringent, indicating that the general orientation of structural elements is similar among the acid orthophosphates and among the basic orthophosphates, and that the two groups are different from each other. Only $CaHPO_4 \cdot 2H_2O$ shows perfect cleavage (119) with cleavage planes of (010) and (301). The strong birefringence of chlorospodiosite (127) is unusual for a compound with such a high Ca/P mole ratio and probably occurs because it possesses the layer structure of $Ca(H_2PO_4)_2 \cdot H_2O$ (127).

The higher refractive indices for the mineral whitlockite vs. the synthetic β-$Ca_3(PO_4)_2$ are undoubtedly due to the presence of magnesium (2.53 per cent MgO) in the mineral, which causes a contraction of the lattice parameters (75). The refractive index progression in the apatites is Cl > OH > F, which is the same as the lattice parameter progression given in table 17.

Optical properties of many condensed phosphates of calcium are conveniently available in the literature (14, 69, 94, 115) and are not reviewed here.

2. Strontium and barium phosphates

Since none of the strontium and barium phosphates occur in nature, except perhaps strontium hydroxyapatite, only a few fragmentary studies of optical properties have been reported. The results are given in table 20. The recent optical study of $SrHPO_4$ (1) helps to clarify the confusion existing in this area, since it appears that de Schulten's orthorhombic $SrHPO_4$ (185) is actually the low-temperature (or β) form, and that the triclinic form reported by Holt, Pierce, and Kajdi (99) is the high-temperature (or α) form. Recently determined values for the refractive indices of $BaHPO_4$ (1) are considerably higher than Gaubert's values (76). Birefringence among the monetites is $CaHPO_4 > SrHPO_4 > BaHPO_4$. It is interesting that strontium chloroapatite is optically positive (76), since all the calcium apatites are negative. Optical data for barium phosphate glasses have been published (115), but are not pertinent to this review.

B. INFRARED SPECTRA

In recent years the use of infrared spectra to study

TABLE 20

Optical properties of some strontium and barium phosphates

Compound	Symmetry	Refractive Indices at 25°C. (Sodium D Light)	Birefringence	Reference
$SrHPO_4$	Orthorhombic	$n\gamma = 1.625$ $n\alpha = 1.608$	0.017	(76)
β-$SrHPO_4$	Orthorhombic	$n\gamma = 1.628$ $n\alpha = 1.607$	0.021	(1)
α-$SrHPO_4$	Triclinic	$n\gamma = 1.624$ $n\beta = 1.608$ $n\alpha = 1.593$	0.031(+)	(1)
$Sr_{10}Cl_2(PO_4)_6$	Hexagonal	$n\omega = 1.658$ $n\epsilon = 1.664$	0.006(+)	(76)
$BaHPO_4$	Orthorhombic	$n\gamma = 1.635$ $n\alpha = 1.617$	0.018	(76)
	Orthorhombic	$n\gamma = 1.647$ $n\alpha = 1.633$	0.014	(1)
β-$Ba_3P_4O_{13}$*		*Highest* = 1.628 Lowest = 1.618	0.010	(84)
α-$Ba_3P_4O_{13}$†		$n = 1.626$ (nearly isotropic)	—	(84)

* Low-temperature modification.

† High-temperature modification.

structure has been extended to inorganic and, more specifically, to phosphate compounds (52, 170, 188, 189), but in only a few instances have the alkaline earth phosphates been studied (51, 137, 138). To date, the most complete work on the infrared spectra of alkaline earth phosphates has been that of Corbridge and Lowe (51), and the condensed results given herein are taken largely from their work.

Infrared spectra of $Ca(H_2PO_4)_2$ (51) and $Ca(H_2PO_4)_2 \cdot H_2O$ (51, 137, 138) have been determined, but there are no data on the monobasic strontium or barium phosphates. Results on $Ca(H_2PO_4)_2 \cdot H_2O$ are in good agreement.

Of the dibasic phosphates, spectra have been determined on $CaHPO_4$ (51), $CaHPO_4 \cdot 2H_2O$ (137, 138), and $BaHPO_4$ (137, 138) but not on the dibasic strontium orthophosphates. In a study of the dehydration and rehydration of dibasic calcium phosphate (121), two species of water have been proposed: one characterized by a band at 663 cm.$^{-1}$ and a doublet at 3488–3522 cm.$^{-1}$, both associated with constitutional water; and a second with a doublet at 3158–3268 cm.$^{-1}$ but lacking the band at 663 cm.$^{-1}$, associated with water of rehydration.

Corbridge and Lowe (51) give spectra for all of the tribasic alkaline earth orthophosphates, with that for $Ca_3(PO_4)_2$ being in fair agreement with earlier results (138). However, it is probable that both reports (51, 138) incorporate the common mistake of confusing $Ca_3(PO_4)_2$ with calcium hydroxyapatite, since the broad band at about 1050 cm.$^{-1}$ has been definitely attributed to the latter compound (166). In a similar manner, the spectrum given for $Sr_3(PO_4)_2$ may also be that of the hydroxyapatite.

Data on three alkaline earth pyrophosphates are given (51), but with no indication of which polymorphic modification was measured. The spectrum of $CaH_2P_2O_7$ is also listed, but probably should be checked in view of the ambiguous results on the condensed phosphates in general. Other spectra given are those for strontium and barium trimetaphosphates and tetrametaphosphates of all of the alkaline earths.

The PO_4^{3-} ion has been assigned two fundamental vibrational frequencies in the infrared spectral region occurring at about 1082 and 980 cm.$^{-1}$ The multiple peaks observed in the tribasic orthophosphates in the region 1170–1000 cm.$^{-1}$ are probably associated with some kind of P—O *ionic* stretching. The condensed phosphates, containing P—O—P links, exhibit characteristic absorptions near 900 and 700 cm.$^{-1}$, the former shifting toward lower frequencies with increasing chain length and the latter consisting of one peak in the pyrophosphates, which contain a single P—O—P linkage, and two peaks in the tripolyphosphate and metaphosphates. The acid orthophosphates and pyrophosphates show a broad absorption at 2700 cm.$^{-1}$ characteristic of the P—O—H stretching frequency. In general, the cations have little effect on the spectra except to cause certain peaks to shift to lower frequencies with increasing mass of the cation.

Detailed spectra and interpretation can be found in the original literature, but owing to the newness of the application of infrared to inorganic solids and the questionable identification of many of the compounds, the present data in the literature, especially the assignments of frequencies to specific phosphate species, should be applied with caution.

VIII. SUMMARY

It is fortunate that the calcium phosphates have received concentrated study, since the behavior of the strontium and barium compounds may often be estimated from the behavior of their calcium counterparts. This is because the tendency toward complex behavior, hydrate formation, and hydrolysis normally decreases steadily in progressing from the calcium to the barium phosphates. As examples, calcium hydroxyapatite is easily precipitated from aqueous solution, whereas barium hydroxyapatite is precipitated only with great difficulty. $Ca_3(PO_4)_2$ can occur in three different crystal modifications, $Sr_3(PO_4)_2$ in two (with suitable modifiers present), and $Ba_3(PO_4)_2$ in only one form. Furthermore, the tendency to form ring metaphosphates decreases sharply with increasing ionic radius of the cation.

The use of chromatographic analysis is beginning to bring order to the study of the condensed phosphates, and it is expected that its continued application in the next ten years will result in further clarification of the polyphosphates and metaphosphates. An analogous situation exists in the solubility of the alkaline earth phosphates, where there is a wealth of data, yet there remains the need for solubility studies utilizing thermodynamic activity coefficients which make the results independent of the kind and number of ionic species in solution. Additional thermodynamic studies are also needed to gain a better understanding of the effect of temperature on the properties of the strontium and barium phosphates.

Considerable strides have been made in the determination of the crystal structures of the alkaline earth phosphates, especially those of calcium. Many of the crystals possess M—PO_4—M chains, resulting in certain similarities in structure, habit, and optical properties. Structures still unresolved include the monobasic orthophosphates of strontium and barium, the dimorphic modifications of $SrHPO_4$, the anomalous β-$Ca_3(PO_4)_2$, and the two high-temperature modifications of $Ca_3(PO_4)_2$. In addition, there is an almost total lack of definitive structure work on the many condensed phosphates of the alkaline earths. Infrared techniques are just beginning to be applied to the study of bonding in solid inorganic compounds and it is expected that more phosphates will be studied in detail. Work reported to date has been fragmentary and not completely reliable, owing to errors in identification of the compounds investigated.

In general, a systematic pattern of behavior of the alkaline earth phosphates is discernible from the results gathered to date. Future studies will undoubtedly result in a further improvement of our knowledge of these phosphates.

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