

# PHOSPHORUS, A KEY TO LIFE ON THE PRIMITIVE EARTH

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**Abstract.** The phosphorus of the primitive Earth was present as phosphates. It is strongly probable that a portion of the phosphate was present as condensed phosphates. The primitive Earth was highly deficient in the total available phosphorus until a sufficient quantity of phosphorus weathered from the igneous rocks in which it was entrapped. Approximately three billion years were required for the seas to become saturated. Until this time passed the seas acted as a giant sink for phosphorus, diluting it to the extent that all forms of life were deprived of the vital nutrient. When the seas became saturated, the rate of turn over of the phosphorus increased rapidly. As the seas pulsated, they left the excess precipitate phosphorus as sedimentary rock in locally rich deposits on which life could thrive.

## 1. Introduction

The role of phosphorus on the primitive Earth and its availability to primitive life forms has been the subject of numerous scientific articles. The apparent enigma of the role of phosphorus in chemical evolution is a result of the element's indispensable function in living organisms in contrast to its limited availability for abiotic phosphorylation reactions. Living organisms are capable of collecting, storing and enzymatically utilizing phosphorus derived from very dilute solutions. On the other hand, if it was necessary for phosphorylated organic compounds to emerge on Earth before life became possible, the availability of a reactive primordial source of phosphorus was of paramount importance.

An adequate source of available phosphorus of the proper chemical form to permit spontaneous phosphorylation to occur is not easily envisioned. Orthophosphates are poorly soluble in natural water systems and no large natural bodies of water are known which contain more than parts per million of phosphorus. The stable form of phosphorus in aqueous systems is the orthophosphate molecule which does not spontaneously undergo phosphorylation reactions. Conversely, condensed phosphates are metastable in aqueous media but are capable of active phosphorylation reactions. Condensed phosphates could, therefore, independently participate in prebiotic phosphorylation reactions, while some special energy event would have been required to activate orthophosphates for phosphorylation.

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The phosphorus of the primitive Earth was initially locked in igneous rock, mostly as calcium orthophosphate. It was very slowly leached from the surface rocks as the rocks cracked, weathered, and decomposed, and the phosphorus was carried to the seas in run-off water. We have estimated that about three billion years were required before sufficient rock had decomposed to saturate the seas with respect to apatites. Once the seas were saturated, vast sedimentary deposits of phosphates began to form, and the quantity of phosphorus accessible to living organisms also increased rapidly as the phosphorus became localized in the rich deposits. In time the sea receded leaving the sedimentary deposits exposed to weathering and leaching. The sedimentary deposits were more porous and permeable and of much smaller particle size than the igneous rocks from which they were derived, and the total quantity of mobilized phosphorus continued to increase until today the turnover time of phosphorus in the seas is about fifty thousand years. The quantity of phosphorus contained in igneous rock continues to decrease as the quantity contained in sedimentary rock and the biosphere continues to increase. Phosphorus is probably the limiting nutrient for life on Earth.

### 1.1 THE PRIMITIVE EARTH

The primitive Earth is a poorly defined physicochemical system. Even the most general concepts of its origin and properties are vague and controversial. Since the properties of phosphorus are dependent upon its history, environment, and phase state, any discussion of the element in an undefinable system is unavoidably destined to be vague and controversial. Even if a consentaneous model is arbitrarily chosen, the limits are too broad to allow definitive generalization in most cases. Nevertheless, there are a few extrapolations which can be made from the contemporary Earth system which are germane to the primitive system.

In the following work we shall, as far as it is possible, resist the temptation to define systems of expediency. An attempt will be made to restrict the speculations about phosphorus to areas capable of proof, though admittedly the proofs may not yet exist, and the speculations may be based upon relatively crude measurements or estimates made by qualified authors. A limited number of assumptions will be made concerning the formation of the Earth. For the most part, the formation will be considered the dominion of astronomy, while we shall concentrate on the role and status of phosphorus from the time of an incipient hydrosphere.

Some authors have assumed that the early seas were acidic, while others have assumed that the seas were basic or near neutral. It will be seen that the pH of the early seas has little significance in considering the role or quantity of phosphorus in the seas, provided that the pH conditions are not considered to be extreme. Also, whether or not the atmosphere of the young planet is assumed to be oxidizing or reducing will be of secondary importance with respect to phosphorus. An atmosphere containing either water or carbon dioxide is an oxidizing atmosphere with respect to phosphorus. Even an

atmosphere composed of pure carbon monoxide is incapable of reducing phosphates. Consequently, the atmosphere of the primitive Earth was surely oxidizing to phosphorus.

## 1.2. THE STATUS OF PHOSPHORUS ON THE MATURING EARTH

It is well recognized that almost all of the mineral phosphorus of Earth is present as the very sparingly soluble apatites. Because the orthophosphates are so poorly soluble some authors have proposed that the phosphorus of the primitive Earth was present in a more soluble form, thus making it more available for both prebiotic phosphorylation reactions and primitive life. The calcium, magnesium, and heavy metal salts of hypophosphorous acid are highly soluble in water, thus causing hypophosphites to be an attractive potential source of phosphorus for a rich 'primordial broth'. It is improbable, however, that even a significant fraction of the Earth's phosphorus has existed as the salts of the lower oxides. It is believed that phosphates were the only natural mineral form of phosphorus on both the primitive and the current Earth systems.

There is no tangible evidence that the phosphorus of the lithosphere has ever existed in a reduced state during geological time. The one and only form of phosphorus which is thermodynamically stable in a hydrous atmosphere (gaseous or liquid) at temperatures between 0 °C and 100 °C is the simple orthophosphate. If the phosphorus of the lithosphere was at any time in a reduced state, no vestige of the reduced state remains. Unless igneous deposits of reduced phosphorus compounds can be found on the modern planet, the concept that high concentrations of hypophosphites and other soluble lower oxides of phosphorus permeated the primitive seas must be relegated to conjecture rather than science. The fact that meteorites contain phosphides and even elemental phosphorus can hardly be considered evidence of a reduced state of phosphorus on the primitive earth. One of the accepted indicators of the nonterrestrial origin of iron bodies is the presence of schreibersite  $(\text{Fe, Ni})_3\text{P}$ , barringerite  $(\text{Fe, Ni})_2\text{P}$  or similar phosphides [1]. Moreover, meteors also contain reduced silicon and silisides which are unknown in the existing lithosphere.

Arguments can be presented which severely limit the probability of phosphorus surviving in a reduced state on the primitive Earth long enough for even a simulance of a hydrosphere to have been formed. Although silicon is several hundred times more abundant than phosphorus in the lithosphere, silicon is found only as the oxidized silicate. The free energy of formation of  $\text{P}_2\text{O}_5$  ( $\Delta F^\circ = -327$  kcal) is approximately 85% of the free energy of formation of  $\text{Si}_2\text{O}_4$  ( $\Delta F^\circ = -384$  kcal). Kinetically, phosphorus is generally more readily oxidized than silicon at lower temperatures, and it is unlikely that 0.1% to 0.2% of the lithosphere could have survived in a reduced state while a component comprising about one-quarter of the lithosphere was completely oxidized.

Over 90% of the volume of the lithosphere is oxygen [2], leaving phosphorus with almost no chance of avoiding contact with oxygen. It is improbable that the silicon of the lithosphere was oxidized to silicate *after the lithosphere solidified*. That is to say, both the silicates and the phosphates had formed prior to the solidification of the lithosphere.

Only silicon is abundant enough in the lithosphere to combine with the oxygen in excess of the combining quantity of hydrogen. Most of the oxygen of the surface of the Earth is divided between hydrogen and silicon. The conditions which oxidized silicon to silicates also must have oxidized phosphorus to phosphates.

The foregoing arguments lead to only one conclusion. No matter how broad were the physicochemical limits of the primitive Earth, the chemistry of phosphorus is such that the phosphorus of the primitive Earth was present as a phosphate.

### 1.3. THE QUANTITY OF PHOSPHORUS IN THE PRIMITIVE SEAS

It is generally assumed that most of the early life forms were aquatic. If a mechanism can be envisioned by which the concentration of phosphorus in the seas became large, it is relatively simple to devise routes for massive, prebiotic phosphorylation reactions which are at least plausible. It is, however, improbable, if not impossible, that the seas of the Earth have ever been rich in phosphorus. It has been assumed by most authors that the phosphorus contained in the sedimentary deposits of the Earth was originally contained in igneous rock and that the phosphorus was removed from the rocks by weathering. If this was not the case, it is unlikely that a more plausible concept will be forthcoming.

Although the abiotic phosphorylation of organic compounds might have been induced under conditions where the concentration of orthophosphate was 0.1 M or less, phosphorylation chemistry *per se* is not within the scope of this analysis. However, it is generally conceded that condensed phosphates are superior phosphorylating compounds when compared to orthophosphates [3]. It will be seen that there has never been sufficient phosphorus available to raise the phosphate concentration of the seas to 0.1 M irrespective of the form of the phosphorus or the composition of the seas.

Horn and Adams [4] estimate that a total of  $22.4 \cdot 10^{20}$  g of phosphorus has been leached from the igneous rocks of the Earth since the beginning of geological time until today. Several investigators have estimated the total volume of the oceans at  $14 \cdot 10^{20}$  l [5, 6]. *If all of the phosphorus leached from the igneous rocks of the Earth had been transported to the oceans and had all remained dissolved, the concentration of the oceans would be only 0.05 M in phosphorus!*

Redfield estimates the total phosphorus of the crust as  $40 \cdot 10^{20}$  g [7]. If the total phosphorus of the crust were dissolved in the oceans, the concentration would still be less than 0.1 M. The oceans of the Earth have never contained high concentrations of phosphorus! Undoubtedly the concentration of phosphorus has never been much, if any, greater than it is today.

Even if one makes the assumption of Schwartz [8] that the hydrosphere has grown linearly during geological time or that the hydrosphere was formed in  $3 \cdot 10^8$  yr as suggested by Arrhenius [9], the above conclusions are unaltered. If the rate of release deviated as the hydrosphere grew, the rate would deviate in the direction of an increase in rate as the hydrosphere grew, making the primitive seas more deficient in phosphorus than the current seas, the phosphorus content of which is controlled by the solubility of

apatite. The primitive seas were probably severely deficient in phosphorus. Because of this deficiency, prebiotic phosphorylation reactions were of necessity confined to isolated, favorable locations in which the concentration of phosphorus was great enough for the rate of formation of the phosphorylated compounds to exceed the rate of decomposition of the compounds. Even if minute quantities of phosphorylated organic compounds were formed in the expanses of the seas, the same thermodynamic arguments which prohibit the utilization of forms of phosphorus other than phosphates must be applied. All known phosphorylated organic compounds are thermodynamically unstable in an aqueous environment.

#### 1.4. THE AVAILABILITY OF PHOSPHORUS ON THE PRIMITIVE EARTH

Despite the evidence that primitive life forms existed on Earth about three billion years ago there is no evidence of the development of a large biomass until the Cambrian Period. Physical conditions were either not conducive to larger populations or insufficient nutrients were available to allow for rapid growth rates. It is entirely possible that phosphorus has been a limiting nutrient throughout biotime. Phosphorus was at first inaccessible because it was locked in impervious igneous rock. As the rocks slowly weathered, the phosphorus was gradually released, but so slowly that a very long time was required before the hydrosphere became saturated with respect to calcium phosphate. Once the saturation had occurred, the phosphorus began to precipitate as enriched sedimentary deposits that were more easily weathered and upon which life could flourish.

An intriguing question arises. How much time was required for sufficient phosphorus to be leached from igneous rocks to saturate the seas with respect to calcium phosphate? Several observations suggest that the seas of the Earth did not become saturated with phosphorus for at least three billion years. The evidence for this belief is:

(1) About half of the phosphorus of the lithosphere is contained in sedimentary deposits, but the Precambrian deposits are insignificant in size when compared to the Cambrian and Postcambrian deposits [10]. This suggests that the seas did not contain sufficient phosphorus to exceed the solubility product of apatite until the Cambrian Period was approaching.

(2) "The Precambrian sedimentary iron ores are generally only weakly phosphatic." "Iron-rich sedimentary rocks of the post-Precambrian age are characteristically enriched in phosphate and this is true for all facies, including limonite, hematite, magnetite, chamosite, and siderite ores." [11]

(3) Precambrian fossils contain neither crustaceans nor vertebrates. Modern crustaceans and vertebrates utilize phosphorus in bone and calcitesticaceous shell formation. Because both calcium and carbon dioxide were probably abundant in the primitive seas the absence of vertebrates and crustaceans suggests that insufficient phosphorus was available to initiate nucleation of apatites and carbonates.

(4) It has been estimated by McKelvey [12] that today  $2 \cdot 10^6$  metric tons of phosphorus is delivered to the seas each year. The vast majority of this phosphorus is

derived from sources other than igneous rocks. It is doubtful that more than a few hundred tons are of igneous origin. The Horn and Adams estimate of  $22.4 \cdot 10^{14}$  tons of phosphorus liberated from igneous rock during geological time would have been liberated in only  $1.12 \cdot 10^9$  yr if phosphorus had leached from igneous rock at a rate which even approached current run-off values. The rate of leaching from igneous rock was surely very small compared to the rate of release of soil, sedimentary rock, and biological activity.

If one makes an assumption as to the mechanism of phosphorus release from igneous rock, an estimate can be made of the time required to first saturate the seas with respect to apatite. Igneous rock has low porosity and is almost impermeable to water. Any phosphorus leached from igneous rock by weathering was, therefore, of necessity removed from the surface of the rock and not dissolved from pores deep in the rock. It is, therefore, reasonable to assume that the rate of leaching of phosphorus from igneous rock is a function of the exposed surface of the rock, all other conditions being equal. The total surface area of the rocks of the crust of the Earth has increased continuously as they have been cracked, crushed, ground and dissolved into smaller and smaller particles.

Assume that the rate of removal of phosphorus P is a function of the surface area of the rocks containing the phosphorus

$$\frac{dP}{dt} = kS, \quad (1)$$

where  $t$  is time and  $k$  is a constant.

The rate of formation of new surface caused by crushing, grinding, dissolving, and weathering is a function of the exposed surface during the initial stages of degradation.

$$\frac{dS}{dt} = k'S. \quad (2)$$

If Equation (2) is integrated

$$S = S_0 e^{k't}. \quad (3)$$

Where  $S_0$  is unit surface area at zero time and is assigned a value of unity. Substituting for  $S$  in Equation (1) yields

$$\frac{dP}{dt} = kS_0 e^{k't} = k e^{k't}. \quad (4)$$

Integrating (4)

$$P = \frac{k}{k'} e^{k't} - \frac{k}{k'}, \quad (5)$$

and

$$\ln \left( P + \frac{k}{k'} \right) = \ln \frac{k}{k'} + k't. \quad (6)$$

If  $k$  is assumed to be of the same order of magnitude as  $k'$  then

$$\ln P \approx k't . \quad (7)$$

An estimate of  $k'$  may be obtained by utilizing the estimate of Horn and Adams and assuming that leaching was initiated  $4.3 \cdot 10^9$  yr ago.

$$k' = \frac{\ln 22.4 \cdot 10^{14} \text{ tons}}{4.3 \cdot 10^9 \text{ yrs}} = 8.2 \cdot 10^{-9} .$$

To obtain the time required to saturate the seas, the value  $9.8 \cdot 10^{10}$  tons estimated to be the current quantity of phosphorus in the seas is employed [4].

$$t = \frac{\ln 9.8 \cdot 10^{10}}{8.2 \cdot 10^{-9}} = 3 \cdot 10^9 \text{ yr.}$$

Once the seas became saturated with respect to apatite, the quantity of releasable phosphorus quickly moved from a deficit position to a surplus as the vast sedimentary deposits began to form. It is estimated that currently only  $4.9 \cdot 10^4$  yr are required to supply sufficient phosphorus to resaturate the seas [36].

Life became abundant only after sufficient phosphorus became available to nourish an abundant biomass during the late Proterozoic era, flourishing in the Cambrian period. "Ohne Phosphor Kein Leben." (*Amm.*)

#### 1.5. PHOSPHATE SOLUBILIZATION

There is an all but limitless number of ways that locally high concentrations of phosphates could have been generated during the Precambrian period. There are natural deposits of soluble phosphates which are probably abiotic. The phosphate deposits of the Eastern coast of the United States contain  $\text{NaBePO}_4$ , a highly soluble phosphate. Even deposits of  $\text{NaH}_2\text{PO}_4$  are known in the Western United States [13]. Either the monosodium phosphate was crystallized from an acidic mother liquor ( $\text{pH} \sim 4.5$ ) or it is the decomposition product of a condensed phosphate. When either long chain polyphosphates or the ring metaphosphates hydrolyze, the  $\text{H}_2\text{PO}_4^-$  ion is the end product of the reaction.

Both  $\text{SO}_2$  and  $\text{SO}_3$  are capable of solubilizing apatites [14]. Even on the contemporary Earth abundant supplies of both compounds occur naturally. Moreover, high concentrations of carbonation in spring waters contribute to high concentrations of phosphorus and calcium [15, 16]. Hydrogen sulfide, ammonium sulfide and the alkali metal sulfides are all excellent solubilizing agents for iron, nickel, lead, copper, and similar metal phosphates. Many of the standard laboratory preparations of soluble phosphates depend upon the precipitation of a metal sulfide.

It has been noted by several authors that sodium chloride, as found in evaporating seawater on the beaches of the Earth, is capable of increasing the solubility of

apatite [17]. Phosphate rock can also be solubilized with aqueous silicate solution. One hundred grams of phosphate rock containing 12.8% phosphorus was treated with 815 g of aqueous solution containing 150 g of 42° Be' sodium silicate (Fisher) and heated to boiling. Within eight hours the phosphorus content of the rock had fallen to 12.6% [18, 19].

The above observation is believed to be significant because it is probably the mechanism responsible for the phosphorus utilized by the primitive life forms found in chert deposits. The Gunflint Chert specimens discovered by Tyler are prime examples of the conditions under which silicates are capable of solubilizing apatites [20]. The Tyler organisms are over two billion years old, and it is clearly evident that the chert deposits were viscous silicious fluids at the time the organisms were encapsulated. The properties of soluble silicates would suggest that the organisms were probably in an aqueous solution of silicates and that the organisms became entrapped in the gelatinous silicates which settled as they polymerized.

A sample of the Gunflint Chert from the Schreiber Beach area was supplied by Dr. K. A. Kvenvolden of the U.S. Geological Survey, Menlo Park, California. The sample was analyzed for total phosphorus and found to contain 49 ppm phosphorus. Care was exercised to prevent contamination but it is unlikely that concentrations as high as 50 ppm would result from surface contamination. Aqueous solutions of silicates normally are composed of three degrees of molecular complexity. A part of silicate is in true solution as the simple 'monomeric' molecule, a part as macromolecules, and a part as a colloidal dispersion [21]. The relative quantities of each of the species depend upon the counter-ions and pH of the medium, as well as temperature, pressure, etc. As the pH is lowered or multivalent counter-ions are introduced, the silicates will form micells which will ultimately flocculate and coalesce to a gelatinous mass. The soluble fraction is the fraction capable of displacing phosphorus from apatite at temperatures less than 100°C.

#### 1.6. CONDENSED PHOSPHATE

Much misinformation appears in the literature of the primitive Earth concerning the properties of condensed phosphates. For example it has been suggested that trimetaphosphate is the only condensed phosphate soluble in water which contains as much calcium as seawater. This is not the case for a variety of reasons. Perhaps it would be helpful to review these reasons.

First, trimetaphosphate is only one member of a series of ring phosphates having similar properties. The tetra-, hexa-, and octametaphosphates can all be prepared as pure crystalline solids [22, 23, 24]. (The true ring hexametaphosphate is not to be confused with the amorphous hexametaphosphate of commerce which is truly a polyphosphate.) The solution properties of the other true metaphosphates are similar, though not identical to trimetaphosphate. Moreover, tetrametaphosphate is a prime candidate to have appeared on the primitive Earth because it is the hydrolysis product of  $P_4O_{10}$  (the correct formula for  $P_2O_5$ ) which is a highly symmetrical molecule, volatile at high



temperature. Lightning which struck outcroppings of apatite would have produced  $P_4O_{10}$  vapor and the  $P_4O_{10}$  surely would have hydrolyzed to tetrametaphosphate. The tetrametaphosphate will then, in turn, hydrolyze to tetrapolyphosphate, tripolyphosphate, pyro- and orthophosphates [25].

The second misconception is that the polyphosphates are insoluble in the presence of calcium under all conditions of basic pH. All soluble polyphosphate anions are soluble in the presence of calcium of the concentration of seawater, provided the molar concentration of the phosphate approaches the concentration of the calcium [26, 27]. (The formation of water soluble calcium complexes is one of the more important functions of condensed phosphates.) On the other hand, if the concentration of the calcium, magnesium, etc., is in excess of the condensed phosphate, then the phosphate becomes very slightly soluble. The point to be recognized is that conditions must be carefully defined before generalized statements can be made. Locally, it is entirely possible that a body of water could contain high concentrations of phosphates in the presence of calcium ions far in excess of that contained in modern seawater. Furthermore, brackish waters, depleted in calcium, can contain high concentrations of freshly weathered phosphates.

The long chain polyphosphates present yet another case to be considered because the salts do not crystallize even when salted from solution with calcium or magnesium. It is only when the long chains have degraded to smaller molecules that the salts crystallize. In the strictest thermodynamic sense, the solubility of the amorphous solids is undefinable, and these compounds have a pronounced tendency to resist crystallization. The precipitation is more nearly related to the flocculation of a colloid than the precipitation of an insoluble salt. Additionally, the same complexing conditions exist for the glassy polyphosphates as exist for the short chain crystalline polyphosphates mentioned above. It can further be expected that in primordial waters organic molecules of the immediate environment that could be electrostatically attracted or could coordinate with exterior metal cations would form a film or envelope around this macromolecular polyphosphate complex. Through this 'scavenging' effect, the organic molecules would be brought into contact with the phosphorylating reagent, and the phosphorylation reaction would not be subject to the kinetic control of random collisions in a dilute solution [26].

The condensed phosphates are thermodynamically unstable in aqueous media, but it is this instability which makes them indispensable to the life on Earth. In the fundamental sense, it is the condensed phosphates that are vital to life and not the simple orthophosphates. The tripolyphosphate moiety of adenosine triphosphate is identical to the tripolyphosphate of commerce and detergent formulations. Condensed phosphates are unique in their ability to resist rather drastic changes in their aqueous environment without sudden changes in form, although they may react very rapidly when subjected to the controlled action of an enzyme of a biological organism. Conversely, other oxo-anions capable of forming anhydride linkages are destroyed on contact with water or polymerize rapidly with relatively minor changes when acidified. Polysulfates are typical of this rapid decomposition when dissolved, while soluble silicates typify the rapidly reorganizing

species when the pH is lowered. Mere contact with atmosphere carbon dioxide is sufficient to cause the precipitation of silicates.

#### 1.7. POSSIBLE ROUTES TO THE FORMATION OF CONDENSED PHOSPHATES ON THE PRIMITIVE EARTH

The molecular complexity of a phosphate depends upon the  $M_2O/P_2O_5$  ratio of the molecules. The particular compound or compounds formed at any prescribed  $M_2O/P_2O_5$  ratio depends upon the thermal history of the phosphate and the specific counter-cations comprising the  $M_2O$  fraction. M is defined as one equivalent of metal,  $H^+$ ,  $NH_4^+$ , or R (organic radical).

The phosphates are named according to their structures rather than according to their compositions. Metaphosphates are ring compounds with an  $M_2O/P_2O_5$  ratio equal to unity. Long chain polyphosphates have compositions in which the  $M_2O/P_2O_5$  ratios are essentially unity, but they bear limited physical or chemical similarity to the rings. This point has created extensive confusion in the phosphorus literature. Moreover, the long chain phosphates are metastable with respect to the ring phosphates and can be easily converted to rings by tempering. In solution the long chain phosphates also degrade to rings, shorter chains and orthophosphate.

Ultraphosphates are crosslinked and branched structures containing triply linked phosphorus atoms. When a single phosphorus atom is linked to three other phosphorus atoms through POP bonds, the phosphates are highly reactive and are capable of reacting with alcohols, ether, etc. very rapidly at reduced temperatures [28]. Phosphorus pentoxide is the end member of the ultraphosphate series of compounds. As mentioned earlier, it is probably true that  $P_4O_{10}$  was formed by the impact of lightening on an outcropping of phosphate rock. Yet another source of vaporous ultraphosphoric acid could occur if sulfuric acid contacted magmas which contained phosphorus. Ultraphosphoric acid boils at  $864^\circ C$  and has a composition of 8%  $H_2O$  and 92%  $P_2O_5$ , and is, therefore, a highly crosslinked condensed phosphate. The primary reason for an interest in these compounds is their ability to phosphorylate. As noted, the P—O—P linkages of ultraphosphates are electron deficient when compared with poly- and metaphosphates [29].

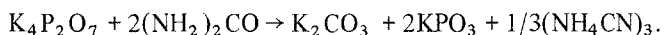
In order to convert orthophosphates into condensed phosphates, it is only necessary that a second substance has a greater affinity for the metal oxide associated with the phosphate than the phosphate itself. On the other hand, it is also possible that the effective  $M_2O/P_2O_5$  ratio can be lowered by reducing the metal oxide to a lower oxidation state. For example,  $2FePO_4 + CO \rightarrow Fe_2P_2O_7 + CO_2$  converts the  $M_2O/P_2O_5$  ratio from 3 to 2 without removing metal from the phosphate. The  $Fe_2P_2O_7$  is easily solubilized by allowing the  $Fe_2P_2O_7$  to react with an aqueous solution of  $H_2S$ , or other soluble sulfide.

In addition to the reducing power of CO, its ability to form metal carbonyls is also significant. If an iron, nickel, or cobalt phosphate is heated with CO, a part of the metal should be lost as the carbonyl which vaporizes.

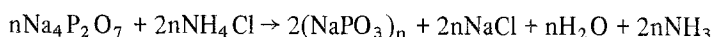


A reaction of this type was observed while heating metal phosphate under an atmosphere of CO, but the details of the reaction were not studied [30]. The reaction is potentially important enough to merit additional study.

Numerous authors have mentioned the influence of urea and cyanates upon the dehydration of acidic phosphates. It has also been demonstrated that urea has the ability not only to remove water from a phosphate but also metal oxides [31].



The exact chemical species to which the urea decomposes has not been established, but it is probably not ammonium cyanide. The reaction is similar to the well known reaction

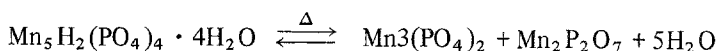


Despite the many possible routes to condensed phosphates on the primitive Earth, it is doubtful that the total quantity of condensed phosphates has ever been any greater than it is today. This is to say, the  $\text{M}_2\text{O}/\text{P}_2\text{O}_5$  ratio of the lithosphere has probably been more or less constant, but unquestionably varied from location to location as the Earth differentiated in composition. Deposits are known in which the nonvolatile  $\text{M}_2\text{O}/\text{P}_2\text{O}_5$  ratio is less than three. A few examples will be discussed, but it should be recognized that care must be exercised to be assured that the phosphates are not of biological origin. The deposits of  $\text{Na}_3\text{PO}_4$  and  $\text{NaH}_2\text{PO}_4$  in the salt lake deposits reported by McKelvey [13] are indicative that condensed sodium phosphates existed.  $\text{NaH}_2\text{PO}_4$  is a degradation product of all condensed sodium phosphates with the exception of  $\text{Na}_4\text{P}_2\text{O}_7$ . It is difficult to imagine any mechanism other than the hydrolytic degradation of a condensed phosphate which would yield an acidic phosphate ( $\text{pH} = 4.5$ ) near deposits of trona.

For any appreciable concentration of condensed phosphates to accumulate even locally, it is necessary that their rate of formation or leaching, as the case may be, exceed their rate of degradation. Even under the most pampered of conditions, the most unreactive of condensed phosphates have half-lives of no more than about 2000 years when dissolved [32].

It is possible that condensed phosphates could have formed locally while the lithosphere was still molten. No indisputable evidence has been reported that supports this concept, but it is doubtful that many studies have been directed toward this end. An indirect and certainly inconclusive fragment of evidence that condensed phosphates may have existed on the primitive Earth can be found in the granite pegmatites of Branchville, Connecticut [33].

#### 1.8. MINERAL DEPOSITS OF CONDENSED PHOSPHATES



This reaction suggests that hureaulite may have been formed from manganous pyrophosphate. The report by Shepard [34] in 1878 that a new mineral,  $\text{Ca}_2\text{P}_2\text{O}_7$ , had

been found in the West Indies is worthy of further investigation. Shepard suggests that the mineral is of igneous origin because it is anhydrous. Unfortunately, he did not disclose the exact location of the deposit. Much could be learned of the history of this phosphate by subjecting it to X-ray analyses.

Calcium pyrophosphate,  $\text{Ca}_2\text{P}_2\text{O}_7$ , exists in three well-known anhydrous crystalline forms. The  $\gamma\text{Ca}_2\text{P}_2\text{O}_7$  results from the thermal decomposition of  $\text{CaHPO}_4$  or  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . The  $\beta\text{Ca}_2\text{P}_2\text{O}_7$  may be obtained from  $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  by dehydration or by heating the  $\gamma\text{Ca}_2\text{P}_2\text{O}_7$  above  $700^\circ\text{C}$ . The  $\alpha\text{Ca}_2\text{P}_2\text{O}_7$  is obtained by heating  $\beta\text{Ca}_2\text{P}_2\text{O}_7$  to temperatures above  $1150^\circ\text{C}$ .

It is entirely possible that some of the hydroxyl apatite found in igneous rock formed from condensed phosphates [26]. Van Wazer [35] notes the significance of Tromel's report that the hydroxyl apatite could be formed at temperature as high as  $1050^\circ\text{C}$  [36]. Most deposits of  $\text{Ca}_2\text{P}_2\text{O}_7$  of igneous origin would probably have been converted to hydroxyl apatite in deposits rich in lime or to brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in deposits exposed to water only. Obviously, brushite and monelite ( $\text{CaHPO}_4$ ) are prime candidates to have been derived from condensed phosphate, provided they are associated with igneous rather than guano deposits. Even the acidic phosphates of guano deposits are at least partially derived from condensed phosphates, e.g., adenosine di- and tri-'poly'-phosphate, but these are of no significance to prebiotic phosphorylations.

It is reported that the minerals lomonosorite and metalomonosorite contain sodium metaphosphates [37, 38]. The compositions of the minerals are  $\text{X}(\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9)$   $[\text{NaPO}_3]_{1/x}$  and  $\text{X}(\text{Na}_3\text{H}_3\text{MnTi}_3\text{Si}_9\text{O}_{12})(2\text{NaPO}_3)_{2/x}$ , and they were found in pegmatites. It has been demonstrated that  $\text{P}_4\text{O}_{10}$  is vaporized from calcium orthophosphates above  $1350^\circ\text{C}$  [39].  $\text{SiO}_2$  aids in the process as would be expected from the electric furnace route to elemental phosphorus. Perhaps vaporous  $\text{P}_4\text{O}_{10}$  was a reactant in the formation of lomonosorites.

#### 1.9. APATITE AS A CATALYST IN POP FORMATION

It has been suggested that the apatite structure can be used as a catalyst for the formation of condensed phosphates [40]. Although the apatite route to condensed phosphates is convenient, it is by no means a requirement. Both calcite and apatite are capable of strongly absorbing polyphosphates. Their role as a scavenger and protector of P—O—P linkages to yield a surface rich in condensed phosphate should equal or surpass their importance in synthesis. The problems associated with an understanding of the function of condensed phosphates on the primitive Earth are of collection and storage, rather than synthesis.

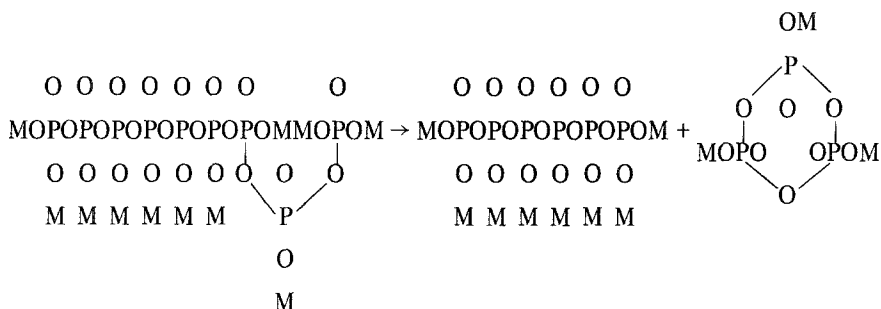
Once a POP linkage is formed it will remain indefinitely unless it encounters a second substance capable of reacting with the P—O—P bond. This is to say that the number of P—O—P bonds in a condensed phosphate is absolutely dependent upon the  $\text{M}_2\text{O}/\text{P}_2\text{O}_5$  ratio of the phosphate system [41]. It should be clearly understood that  $\text{M}_2\text{O}$  of the ratio refers to water, metal oxides, etc., of compositions and not solvates, complexes and

the like. Isolated P–O–P linkages are intrinsically thermodynamically stable. They are unstable only in systems containing a second reactive species.

### 1.10. HYDROLYTIC DEGRADATION

Two excellent reviews of the hydrolytic degradation of condensed phosphates have appeared in recent years [42, 43]. The reader is referred to these reviews for a detailed discussion of hydrolytic degradation. Only a few points relative to the published literature dealing with the primitive Earth will be mentioned.

Gabel cited [25] the fact that long chain condensed phosphates are highly soluble in media containing relatively high concentrations of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ . In this respect they approach or exceed trimetaphosphate. This is particularly true when considering long term availability of POP linkages. Long chain phosphates are a precursor of trimetaphosphate in an aqueous medium [29, 44, 45, 46].



This reaction continues until the long chain phosphate is degraded. A portion of the long chain phosphate is also sacrificed to orthophosphate by the loss of end groups.

The conversion of condensed phosphates to orthophosphates is controlled by kinetics rather than thermodynamics when the phosphates are dissolved in aqueous media. As previously mentioned, in a biologically sterile system pyrophosphate has a half-life in excess of 2000 yr [32]. Although a time span measured in thousands of years is insignificant in geological time, it is a highly significant period when judged either chemically or biologically and furnishes an adequate period for the initiation and propagation of a life-cycle. It has been repeatedly emphasized by those interested in the ecological behavior of phosphates that the rate of turn over of phosphorus is very rapid in microbiological systems and only a small quantity is required to sustain abundant life — a fact which makes it virtually impossible to prevent the ultimate eutrophication of lakes imbedded in ‘civilized’ eco-systems.

## 2. Conclusion

The so-called phosphorus enigma of chemical evolution is not well founded. Phosphorus on the primitive Earth, just as phosphorus on the contemporary Earth, existed as

phosphates. Although the concentration of orthophosphate and condensed phosphates was never very high throughout the expanse of the hydrosphere of the Earth, differentiation and weathering would have ultimately led to localized environments of relatively high concentrations of soluble orthophosphate and condensed phosphates. Condensed phosphates have a high negative free energy of hydrolysis and they are unique among oxo-anions in their ability to resist drastic changes in their aqueous environment. Furthermore, the ability of condensed phosphates to form water soluble calcium complexes which can further complex with dissolved organic molecules, and thereby scavenge their immediate environment, makes the condensed phosphates capable of acting as template and phosphorylating agent in a dilute aqueous solution. Since biological polymerizations proceed via phosphorylation reactions, it is inevitable that primordial biologically relevant organic monomers which became incorporated into metallic polyphosphate complexes would in time form oligomers of higher complexity. Indeed, the ability of condensed phosphates to effect the formation of peptides in dilute aqueous solutions of amino acids is well known [47].

Evolution proceeds in the direction of more highly structuralized matrices, but the organic monomers of the prebiotic milieu could not have given rise to functional biopolymers and emerging life forms without a pre-existing template and condensing agent. It was the unique physicochemical properties of condensed phosphates which have made phosphorus indispensable to the functioning of living organisms, and it was these same unique physicochemical properties of phosphorus to the exclusion of all other elements that cast it in the role of a key to life on the primitive Earth.

### References

- [1] Clarke, F. W.: 1924, *Data of Geochemistry*, United States Geological Survey Bulletin 770, Ed. 5, United States Printing Office, Washington, D.C., p. 332.
- [2] Rankama, K. and Sahama, T. H. G.: 1949, *Geochemistry*, The University of Chicago Press, Chicago, IL, p. 612.
- [3] Ponnampertuma, C. and Chang, S.: 1971, *Chemical Evolution and the Origin of Life*, North-Holland Publ. Co., p. 216.
- [4] Horn, M. K. and Adams, J. A. S.: 1966, *Geochim. Cosmochim. Acta* **30**, 279.
- [5] Mason, B.: 1966, *Principles of Geochemistry*, John Wiley and Sons, New York, p. 192.
- [6] Moore, C. B.: 1973, *Environmental Phosphorus Handbook*, John Wiley and Sons, New York, p. 8.
- [7] Redfield, A. C.: 1958, *Am. Scientist* **46**, 205.
- [8] Schwartz, A. W.: 1972, *Molecular Evolution*, Rohlfling and Oporin (eds.), Plenum Press, New York, p. 129.
- [9] Arrhenius, G., De, B. R. and Alfren, H.: 1974, *The Sea*, John Wiley and Sons, New York, p. 848.
- [10] Emigh, G. D., private communication.
- [11] McKelvey, V. E.: 1972, *Environmental Phosphorus Handbook*, John Wiley and Sons, New York, pp. 20–21.
- [12] McKelvey, V. E., Swanson, R. W., and Sheldon, R. P.: 1952, International Geological Congress 19th Algiers.
- [13] McKelvey, V. E.: 1973, *Environmental Phosphorus Handbook*, John Wiley and Sons, New York, p. 20.
- [14] Hughes, A. E. and Cameron, F. K.: 1931, *Ind. Eng. Chem.* **23**, 1262

- [15] Ref. [1], p. 198.
- [16] Neuberger, C., Grover, A., Kreidl, M., and Lowy, H.: 1957, *Arch. Biochem. Biophys.* **70**, 70.
- [17] Mellor, J. W.: 1923, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green and Co., London, Vol. 3, p. 876.
- [18] Griffith, E. J., unpublished work.
- [19] Isabe, T., Machida, K., and Miyoshi, S.: 1957, *J. Chem. Soc. Japan* **57**, 22.
- [20] Griffith, E. J., unpublished data.
- [21] Merrill, R. C.: 1947, *J. Chem. Ed.* **24**, 262.
- [22] Griffith, E. J.: 1956, *J. Am. Chem. Soc.* **78**, 3867.
- [23] Griffith, E. J. and Buxton, R. L.: 1965, *Inorg. Chem.* **4**, 549.
- [24] Schuelke, V.: 1965, *Angew. Chem.* **7**, 71. Thilo, E. and Schuelke, V.: 1965, *Z. anorg. Allgem. Chem.* **341**, 293.
- [25] Thilo, E. and Ratz, R.: 1949, *Z. anorg. Chem.* **260**, 255.
- [26] Gabel, N. W.: 1965, *Life Sci.* **4**, 2085
- [27] Griffith, E. J.: 1972, *Proc. 14th Water Quality Confer.*, University of Illinois, p. 115.
- [28] Thilo, E.: 1962, *Adv. Inorg. Chem.* **4**, Academic Press, New York, p. 58.
- [29] Griffith, E. J. and Buxton, R. L.: 1967, *J. Am. Chem. Soc.* **89**, 2884.
- [30] W. Lockhart: Monsanto, private Communication.
- [31] Griffith, E. J.: 1975, *J. Pure. App. Chem.*, in press.
- [32] Van Wazer, J. R., Griffith, E. J., and McCullough, J. F.: 1955, *J. Am. Chem. Soc.* **77**, 287.
- [33] Palache, C., Berman, H., and Frondel, C.: 1951, *Dana's System of Mineralogy*, John Wiley and Sons, New York, Vol. II, Ed. 7, p. 701.
- [34] Shepard, V.: 1878, *Am. Jour. Sci.* **15**, 49.
- [35] Van Wazer, J. R.: 1958, *Phosphorus and Its Compounds*, John Wiley and Sons, New York, p. 525.
- [37] Tromel, G.: 1932, *Mitt Kaiser-Wilhelm Inst. Eisenforsch.*, Dusseldorf **14**, 25.
- [37] Gerozemovskii, V. I. and Kazakova, M.: 1962, *Doklady* **142**, 670.
- [38] Semenev, E. I., Organova, N. I., and Kukhorchik, M. V.: 1961, *Kristallografiya* **6**, 925.
- [39] Aziev, R. G., Volkovich, S. N., and Mikhaieva, T. K.: 1972, *Russ. J. Phys. Chem.* **46**.
- [40] Newman, W. F. and Neuman, M. W.: 1973, *Biological Mineralization*, John Wiley and Sons, New York, p. 3.
- [41] Van Wazer, J. R. and Griffith, E. J.: 1955, *J. Am. Chem. Soc.* **77**, 6140.
- [42] Osterheld, R. K.: 1972, *Topics in Phosphorus Chemistry*, Vol. 7, John Wiley and Sons, New York, p. 103.
- [43] Shen, C. Y. and Morgan, F. W.: 1972, *Environmental Phosphorus Handbook*, John Wiley and Sons, New York, p. 241.
- [44] Bell, R. N.: 1947, *Ind. Eng. Chem.* **39**, 136.
- [45] McCullough, J. F., Van Wazer, J. R., and Griffith, E. J.: 1956, *J. Am. Chem. Soc.* **78**, 4528.
- [46] Wieker, W. and Thilo, E.: 1960, *Z. anorg. allgem. Chem.* **306**, 48.
- [47] Rabinowitz, T., Flores, J., Krebsbach, R., and Rogers, G.: 1969, *Nature* **224**, 795.
- [48] Zverbles, A. G.: 1975, *Rocks and Minerals*, Heldref Publications, Washington, D.C.