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PHOSPHORITE DEPOSITION
(Australian Mineral Development Laboratory Report No. 593)

by

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CONTENTS

FOREWORD

This report gives the results of a survey of the literature on the deposition of phosphorites carried out by the Australian Mineral Development Laboratory at the request of the Bureau of Mineral Resources.

It is included in the Bureau's Record series so that it may have a wide distribution among workers in this field in Australia.

It has not been altered in any way.

SUMMARY

History

A literature survey on the deposition of sedimentary phosphates was requested by the Bureau of Mineral Resources.

Objectives

The aim of the literature review was not only to give a comprehensive account of the present state of the theories on the genesis of phosphorites, but also to reveal any aspects of the subject which could profitably be studied by further experimental work. It is not the object of this survey to provide a classification of the geology of phosphorite deposits.

Summary of Work Done

A systematic search of both Chemical Abstracts from Volume 1 (1907), to the present day, and Mineralogical Abstracts from 1960 to the present day, formed the basis of the search. Particular emphasis was laid on establishing some semblance of order to the physico-chemical aspects of the problem.

Personal correspondence with researchers in the USA, UK, and the USSR also provided a valuable source of some literature.

Conclusions and Recommendations

The vast phosphorite deposits of economic importance are restricted to a marine environment. Their origin is considered in terms of -

i. Accumulation
ii. Replacement
iii. Precipitation.

The "accumulation" theory; that is the simple accumulation of the phosphatic remains of dead organisms, is no longer considered a likely mode of formation, though it may contribute to a minor extent.

The "replacement" theory states that phosphorites are formed as a result of the replacement of calcareous and other rocks, by phosphatic solutions.

"Precipitation" either as a direct inorganic phenomenon, due to the super saturation of sea water, or controlled by organisms, is the third theory.

The feasibility of both replacement and inorganic precipitation as workable theories, has been extensively investigated and the experimental evidence is summarized.

It is generally concluded that the main mineral constituent of phosphorite deposits is a carbonate-fluorapatite, with the carbonate ion present as an integral part of the apatite structure. This mineral species has been formed synthetically, by the replacement of pre-existing carbonate material. Replacement has also been observed in natural occurrences.

Direct inorganic precipitation of carbonate-fluorapatite has been demonstrated in the laboratory, under conditions simulating a marine environment. There is little doubt that this process could be operative as a mechanism for phosphorite formation.

Precipitation controlled by organisms is also quite feasible but wanting in proof.

Most of the experimental evidence rests on the criteria of precipitates from solution being fundamentally different from those obtained by replacement and it is considered that the most serious deficiency in the understanding of mechanisms of phosphorite formation is the lack of data on the detailed mineralogy and petrography of the various varieties.

It is therefore recommended that as the next stage of this programme, these parameters should be properly documented. Some preliminary work of this type has already been carried out in these laboratories.

1. INTRODUCTION

Definition. The term phosphorite, though not rigorously defined, is generally accepted as a sedimentary deposit composed mainly of phosphate minerals. The deposits of economic importance are usually restricted to a marine environment, although some guano deposits and bone beds are also worked on a large scale.

Occurrence. The principal marine phosphorites of economic importance cover wide areas in North Africa, the USSR and the USA. The beds range in age from Cambrian to Pleistocene and extend with remarkable uniformity over thousands of square miles. The Permian Phosphoria formation of the western United States, alone, covers 135,000 square miles.

Classification. Penrose (1888) sub-divided all phosphorites into four groups:

a. amorphous nodular phosphorites
b. beds of phosphate limestones,
c. guanos,
d. bone beds.

The essential features of this classification still remain, except that the beds of phosphate limestones later become known as bedded phosphate rocks.

Engelhardt (1891) first classified the Russian phosphorites. The nodular phosphorites (bedded phosphate rock was not known at that time) were sub-divided into three types; the quartz-arenaceous, distinguished by their low P_2O_5 content and difficulty in grinding; the glauconite-arenaceous somewhat higher in phosphate and more readily ground but not suitable for chemical treatment owing to a higher content of sesquioxides; the dense phosphates (argillaceous) were the most high grade variety and could be used for the production of super-phosphate. This classification fully satisfied industrial requirements, as all Russian phosphorites could easily fit into any of these groups.

Bushinskii (1945) constructs a genetic classification defining:

i. Marine
ii. Continental
iii. Worked deposits.

Marine deposits are either chemically precipitated (the bedded and nodular varieties) or "organogeneous" (bone).

Continental types include organogeneous (bone), organogeneous-metosomatic (island and cave deposits), metasomatic, or hydro thermal; the worked deposits may be residual, redeposited, or metamorphic. Bushinskii uses only texture and structure in sub-dividing the chemical precipitates.

Significant mineralogical and petrological differences exist between the various types and Carozzi (1960) lists the following varieties:

Primary Origin:

Variety	Group
Arenaceous and Argillaceous phosphorites	Detrital varieties
Glauconitic phosphorites	
Ovulitic phosphorites	
Oolitic phosphorites	
Pebbly phosphorites	
Nodular phosphorites	
Ovulitic phosphatic chalks	
Phosphorites with sponge spicules	Organic varieties
Crinoidal phosphorites	
Phosphorites with radiolaria	
Bone phosphorites (bone-beds)	
Coprolitic and pellet phosphorites	
Guano	

Secondary Origin:

Phosphatic sands
Phosphatized rocks
Residual phosphorites
Transported residual phosphorites

Bateman (1959) distinguishes between the following occurrences:

i. Marine sedimentary phosphate beds
ii. Phosphatic marls and limestones
iii. Calcareous beds replaced by phosphates
iv. Land pebble
v. River pebble
vi. Residual concentrations.

Phosphatic marls and limestones are merely normal sedimentary beds with a high phosphate content. They are usually of too low grade to be of any use. Land pebble represents marine re-working of underlying phosphatic limestone, and deposition of hard, resistant pebbles of phosphate in a gravel bed, subsequently exposed by erosion. River pebble occurs as bars and banks in stream channels and consist of hard pieces of phosphate gathered by the streams, where they have crossed phosphatic beds. Residual concentrations are derived from the erosion of underlying phosphate beds and are accumulations of heterogeneous pieces of phosphate that have suffered some solution and redeposition.

A most recent classification of phosphorites is that given by Gimmelfarb et al (1959). They use a broad genetic basis which they sub-divide on petrographic features such as texture and structure. The two basic genetic groups they define are -

a. Marine
b. Continental

In a third special group they place the <u>metamorphosed phosphorites</u>, which can form from phosphorites of various genetic groups.

The group of marine phosphorites they divide into two sub-groups;

i. primary sedimentary deposits
ii. redeposited, (mechanically).

Sub-groups are distinguished in the continental phosphorites as well:

i. epigenetic phosphorites, caused by the process of continental chemical weathering and formed from phosphatized rocks and phosphorites by their chemical reprocessing.

ii. organic phosphorites (mainly guano).

Each genetic group has specific types of phosphorites which are distinguished mainly by their textural and structural characteristics.

The classification of Gimmelfarb et al is summarised in Table 1.

Mineralogy. The phosphate minerals of the sedimentary deposits are cryptocrystalline to amorphous, thoroughly mixed (often concretionary and virtually isotropic. The only ones abundant in the sedimentary environment are the calcium phosphates, i.e. the apatite group. The carbonate-fluorapatites (francolite)(Altschuler et al, 1952) and carbonate hydroxylapatite (dahllite) are quantitatively the most important. Where the fluorine content of a CO_2- bearing apatite is not known, the term carbonate-apatite is used.

Collophane, a non-definitive term is applied to many of these mineral complexes.

Most of the experimental work on the controversy of phosphorite deposition is concerned with establishing the exact nature of the phosphate minerals and preparing the phase synthetically. More precisely this is resolved to locating the position of the carbonate ion in the carbonate fluorapatite, i.e. is the carbonate ion present as an integral part of the structure, absorbed on the surface, or present as a fine, mechanical mixture of apatite and carbonate mineral. Having established the exact nature of the mineral species, the experimentalists have tried to find out if this phase can be prepared synthetically, by either replacement of pre-existing material, or as a direct inorganic precipitate due to supersaturation.

Associated with the phosphate minerals are the common minerals of sediments including calcite, dolomite, chalcedony, the clay minerals, pyrite and glauconite.

Phosphorites also contain abnormal concentrations of certain rare elements, but only a few are present in significant quantities (e.g. strontium, arsenic, uranium, the rare earths, lead, zirconium and possibly beryllium, and niobium). Undoubtedly phosphates owe some of their rare metals to co-existing organic matter and sulphides, rather than to the phosphates themselves. Phosphates also have a tendency to pick up some of their trace constituents long after burial.

Depositional Environment and Petrology. Phosphorites form mainly in the border zones between the shallow water platform sediments and the deep water geosynclinal accumulation i.e. on the shelf on one side of a large deep basin.

According to Carozzi (1960), two different types of deposits may be distinguished:

i. The platform phosphorites having a nodular, pebbly habit, low to moderate P_2O_5 and are associated with glauconite and arenaceous materials. (The coarse-grained, light coloured variety of Youssef, (1965)).

ii. The geosynclinal phosphorites are of a bedded, platy or flagstone type, high in P_2O_5 and associated with limestones, black shales and chert. (The fine-grained, dark coloured variety of Youssef (1965)).

According to McKelvey et al, (1953) the great bulk of phosphatic material of the Phosphoria formation is "conglomerated" into pellets and nodules. These are generally elliptical with the long axis parallel to the bedding. They range in diameter from 0.05 mm to more than 3 cm, and are generally well sorted. Most are structureless granules but some of the larger ones are concentrically laminated and others are compound. The phosphatic rocks are generally well cemented with carbonate, fluorapatite, argillaceous matter, chert, calcite and dolomite.

In the Phosphoria, the phosphatic layers range in thickness from a few millimetres to 2 metres. Most are only a few millimetres and are interbedded with phosphatic mudstone or carbonate rocks.

Phosphatic nodules or pebbles are also widely scattered in limestone and chalk. They also occur on the sea bottom of the present day and vary from granules to pebbles several centimetres in diameter. Typically irregular in shape, they are black in colour and have a dense, hard, shiny surface. The large ones contain much foreign matter, including sand grains, mica flakes, shell debris and sponge spicules.

Fossil Content. The only common fossil constituents of phosphorites are bones, shark's teeth, fish scales and the remains of Lingula and Trilobites, all of which are marine and highly phosphatic. Diminutive rolled and phosphatized casts of certain gastropods and other invertebrates also occur. There is a rarity of bottom living types.

Significant Associations. The phosphorite facies are associated with marine limestones often being interbedded with marine fossiliferous bands, with sandstones, carbonaceous shales and glauconites, but never associated with beds of lagoonal or freshwater origin.

There is also a noticeable lack of clastics within the phosphatic layers, a loose association with major and minor unconformities, a presence of much chert, plus a close association with calcareous sediments.

Glauconite and pyrite together with the presence of many trace elements complete the unique association of phosphorites.

Conditions of Formation. Any theory of phosphorite deposition must satisfy several well established geological facts. The fossils prove a marine environment, and the lack of clastics also requires a period of non-deposition of normal sediments.

Association with pyrite, black shales, hydrocarbons and glauconite point towards deposition under reducing conditions, i.e. negative Eh.

A comparison is often made between ironstones and phosphate deposits. The similarities of many microstructures, the lithologic associations, plus the co-occurrence of iron silicates (glauconite) with some phosphatic deposits, and the abnormal concentrations of P_2O_5 with some iron silicates and carbonates, suggest similar environment.

2. THE PROBLEM OF PHOSPHORITE DEPOSITION

2.1 General

Theories concerning the origin of phosphorites can be grouped under the following headings:

i. Accumulations a. Biological
  b. Others

ii. Replacements

iii. Precipitations a. Inorganic control
  b. Organic control

Early theories on phosphorite deposition, from the middle of the nineteenth century, ascribed them to simple biological accumulations of coprolites, plankton showers, fish remains, phosphatic hard parts of organisms and other remains.

The replacement of pre-existing calcareous material by alkaline phosphate solutions was also considered as a possible mechanism from the very earliest (Murray and Renard, 1891; Mansfield, 1921, 1931), and had been proved experimentally (Irvine and Anderson, 1891).

In 1937 a new approach to the problem of phosphorite deposition was introduced by Kazakov. Kazakov's theory stated that the sedimentary phosphates were a result of a direct inorganic chemical precipitation formed on supersaturation of sea-water. This won wide acceptance and has basically been changed little, except for modifications by McKelvey et al, 1953.

Accompanying the development of Kazakov's theory has been the accumulation of evidence supporting chemical replacement as the mechanism of formation.

Other theories fall within the same three groups, but invoke different controls.

Residual accumulation at unconformities rather than a primary biological accumulation is one variation (Grabau, 1919).

Some theories of precipitation require a biogeochemical control by micro-organisms, (Cayeux, 1936; McConnell, 1965; Bushinskii, 1966).

In Soviet geology some prominence is given to a volcanic-sedimentary hypothesis (Bushinskii, 1966), and Brodskaya (1966) identifies three types of phosphorite associated with volcanic manifestations in the zone of the Pacific belt. Replacement, however, although recognised as an active process, is not regarded as a mechanism likely to explain the origin of major phosphate deposits.

Mansfield (1940b) also recognised the association of phosphates and volcanism and proposed that fluorine from volcanic emanations was necessary in order to "fix" the phosphate and render it insoluble through the geologic periods.

2.2 General Chemical Considerations

It is considered relevant at this stage to quote from the absorbing paper of Krumbeing and Garrels (1952), on "the Origin and Classification of Chemical Sediments in Terms of pH and Oxidation-Reduction Potentials". These authors favour a low pH (7.0-7.5) and restricted basins for phosphorite deposition.

They divide chemical sediments of marine origin into three main classes, representing deposition in:

a. normal marine, open circulation environments;

b. restricted humid (euxinic) environments, and

c. arid (evaporite) environments.

The view is taken that the hydrogen ion concentration (pH) and the oxidation-reduction potential (Eh) afford two basic controls which largely determine the kinds of chemical end members produced by inorganic and biochemical reactions.

Certain of the end members depend mainly on one or other of the two controls and some depend on both.

Within the framework of these controls they consider the deposition of calcium carbonate, iron minerals, manganese minerals, phosphates, evaporites and organic matter.

Only calcium carbonate and phosphate need concern us in any detail:

a. Precipitation of Calcium Carbonate. The lack of dependence of calcium and carbonate ions on the Eh of the solution is one clue to its ubiquitous character. It is however strongly dependent on pH.
Krumbein and Garrels state that organisms act through processes that in many cases are extremely complex, but no organic mechanism can operate to produce calcium carbonate (or presumably other sediments) in an environment that is far out of equilibrium with inorganic calcium carbonate. Therefore pH is still a controlling factor. Effects of changes in salinity (at constant pH) and of pressure on solubility are slight even over extreme ranges, compared with the pH control.
Other controls are minor or act through a pH mechanism, e.g. an increase in temperature causes precipitation of calcite from a saturated solution of sea-water, but the effect is largely because of increase of pH through removal of CO_2 (c.f. Emery, 1946).

In summary, they state that the independence of calcium and carbonate ions on oxidation-reduction potentials explains calcite occurrence over the entire range, from well-oxygenated to stagnant water environments. The pH of carbonate ion suggests that most precipitation of calcium carbonate takes place because of increase in pH whether the mechanism be organic or inorganic, and that truly acid environments (pH 7. 0 or less), are unfavourable to limestone deposition.

b. Controls of Phosphate Deposition. The controlling factors in the deposition of phosphorite (which they qualify as tricalcium phosphate) are strikingly similar to calcium carbonate. Neither calcium nor phosphate ion is affected by Eh changes within the limits which occur in nature; phosphate ion however is strongly pH dependent. Consequently phosphorite solubility, in terms of sea water, decreases with increasing pH, and its solubility curve is essentially parallel to that of calcium carbonate although the absolute values are much less.

Dietz, Emery and Shepard (1942), say the open ocean is essentially saturated with phosphate, indicating that an amount equal to the increment is precipitated each year.

When calcite and phosphorite co-precipitate because of pH increase, the ratio is very high in favour of calcite. Both carbonate ion and phosphate ion are in equilibrium with the same calcium ion in sea water. Because the absolute solubility of calcium phosphate is so much less than that of calcite, and because the solubility-pH curves are nearly parallel, it follows that precipitation by pH increase of sea water, saturated with both compounds, will result in a sediment composed almost entirely of calcite and with only a trace of phosphorite, i.e. for phosphorites to form requires either higher concentrations than normal sea water or lower pH values than calcite deposition.

A sediment high in calcium phosphate and low in calcium carbonate can be formed only where conditions permit continuous removal of calcium as the phosphate, and in which the solubility product of the carbonate is not exceeded. They suggest that this might well occur in a restricted basin with a relatively low pH (7.0-7.5). In this environment calcium carbonate would not be expected to form. The carbonate ion remains low and constant because of its dependence on pH and the CO_2 partial pressure in the atmosphere. On the other hand, the phosphate ion might well be supplied as soluble phosphate in association with sodium or other cation, and the phosphate ion concentration could easily become sufficient to precipitate phosphorite, since it has no upper limit determined by formation of a gaseous phase, as does carbonate. In summary, the precipitation of phosphate is independent of Eh, but increases with increasing pH. Precipitation of phosphorite from normal sea water (saturated with both calcite and phosphorite) as a result of pH increase would be expected to yield a sediment with a very small proportion of phosphorite. They suggest that phosphorites may represent precipitation in restricted basins with relatively low pH.

Other observations connected with phosphorites include the formation of pyrite and organic matter. This implies reducing conditions with negative Eh values. Chert appears to be largely pH and Eh independent, as it occurs in a wide variety of sediments.

Further, they add, that both calcite and calcium phosphate may occur together in sediments but it is commonly true that phosphate rich sediments are not highly calcareous. This suggests lower pH values than are required for calcite precipitation, and these lower values favour higher concentrations of phosphate ion. Where calcite is present in abundance, the pH was probably not lower than 7.8; but where phosphate is abundant, the pH values may be as low as 7.0.

Throughout the literature many reviews of thought on the origin of phosphorite are given. Some, of necessity, are short, others are sadly incomplete, yet others are biased. Some approach the problem from one particular aspect.

The more notable reviews are to be found in Degens, 1965; Pevear, 1967; Ames, 1959; Bushinskii, 1966; Warin, 1967 and Jaffe, 1951.

It is perhaps elementary, but nevertheless necessary to emphasize here two dangers concerned with any attempt at deriving a petrogenetic theory.

Firstly, there is the danger of supporting one particular theory, to the exclusion of all other thought. This usually signifies a complete inability to think in terms of different processes as being simultaneously active.

Secondly, there is the danger of extrapolation from experimental systems of simplified chemistry, to the origin of the vast, complex, multicomponent systems of nature.

3. THE PROBLEM OF PHOSPHORITE MINERAL COMPOSITION

Most of the experimental work concerned with phosphorite deposition is directed towards establishing whether the synthetic products of inorganic precipitation or replacement are the same as the minerals composing phosphorites. Before this can be of value, of course, one has to establish the exact nature of the phosphate minerals (and likewise the synthetic products).

In this case the problem is resolved into:

1. Whether the CO_2 (of the carbonate fluorapatite) is an integral member of the structure; whether it is merely adsorbed on the surface; or, present as impurities of calcite or aragonite?

2. If the CO_2 is substituting in the structure, then what is its ionic position?

The first problem is the only one directly concerned with phosphorite genesis; since basically the Replacement proponents deny the existence of carbonate-apatite precipitated from aqueous solution, and advocate formation only as a replacement product (if one accepts the view of the CO_2 being located within the structure).

In order to establish whether the CO_2 is part of the apatite structure or not, many methods have been used. Gruner and McConnell (1937), presented optical and x-ray data to substantiate the location of CO_3 groups within the apatite lattice.

Silverman et al (1952), used differential thermal analysis methods capable of detecting 1.6% calcite, and also the much greater solubility of calcite compared with apatite in triammonium citrate solution, but found no calcite in carbonate-apatites.

Tuddenham and Lyon (1960), using infra-red studies, showed that the absorptions characteristic of the simple carbonate minerals were absent.

Refractive indices decrease and birefringence increases with increasing CO_2 content (thus supporting a structural CO_2) and McConnell (1952), in trying to explain such a trend, measured the form birefringence of a mixture of calcite and fluorapatite, in the volume ratio of 1:10. He showed that such a mixture would not yield a mean refractive index for francolite, which is lower than that for fluorapatite. McConnell also heated francolite at 1100°C for 45 minutes and still retained some CO_2 (see also McConnell, 1958).

The existence of carbonate-apatite as a distinct variety of apatite, rather than a mixture of a carbonate phase and fluorapatite has also been demonstrated by x-ray powder patterns. Altschuler et al (1952), have shown that carbon-fluorapatite has a characteristic x-ray pattern compared with those of fluorapatite and hydroxyapatite and has distinctly different, but related cell parameters, i.e. varying only in the "a" direction.

Veiderma (1964), studied various naturally occurring phosphorites by thermo-analytical methods. She confirms the view that carbonate is found within the phosphate structure.

Many physiological chemists and dental workers however, consider that the CO_2 is present as amorphous carbonate, mainly in the form of $CaCO_3$ (Thewlis et al, 1939; Carlstrom, 1955).

Posner and Duyckaerts (1954) reported that the CO_2 can be nearly completely removed by acid leaching, without affecting the x-ray pattern, and Posner (1954), has presented x-ray diffraction and infra-red spectroscopic data that show the carbonate to be present as a separate admixed phase.

Neuman and Neuman (1953), offered the alternative explanation that the carbonate (or bicarbonate) ions are adsorbed on the surface, primarily by exchange with phosphate.

To quote from Degens (1965), it is generally recognized that the carbonate ion enters the apatite structure of the phosphorite mineral, and must be considered as a distinct variety of apatite, rather than as a mixture of $CaCO_3$ (calcite or aragonite) and fluorapatite, i.e. CO_2 is truly present in the structure and does not occur as a coexisting carbonate, or in an adsorbed state. (McConnell, 1952a, and b, 1958, and Altschuler, 1953).

14

According to McConnell (1965), and Simpson (1965), it is impossible to detect the presence or amount of structural carbonate, present in apatite, by x-ray powder diffraction or optical data. The usual procedure is to measure the Ca/P ratio and if this exceeds 1.67 (the theoretical values for stoichiometric apatite) then it is assumed that the phosphate deficiency is due to substitution of carbonate for phosphate. However, excess calcium could also result from $CaCO_3$ adsorbed on the fine apatite crystallites or present as a separate phase.

McConnell (1966), can detect, by x-ray diffraction, carbonate in amounts as small as 2%, if present as calcite, and claims that some, if not all, precipitated apatites with carbonate in the analysis, or with Ca/P greater than 1.67 contain no separate $CaCO_3$ phase. He also examined such precipitates by optical microscopy and found no separate carbonate phase.

However Trautz (1955), has pointed out that if the carbonate phase is poorly crystallized or amorphous, it can be present in amounts up to 20% and still defy identification.

Lastly, the work of Termine (1967) and Termine and Posner (1966), based on infra-red studies, shows that carbonate-apatites formed by replacement are fundamentally different from those which are directly precipitated from solution. These authors believe that precipitated carbonate-apatite contains adsorbed rather than structurally bonded carbonate, but they are mainly concerned with the composition of bone apatite.

Winand (1963), investigated natural and synthetic calcium phosphates and carbonate-apatites by x-ray diffraction, infra-red spectrometry, thermogravimetric methods and differential thermal analysis. From their experimental results they concluded that most natural carbonate-apatites (including bone salts), have the CO_3'' ions present in the lattice, a PO_4'' group being substituted by $(CO_3'' + F')$ (or OH' partially) groups.

Smith and Lehr (1965), studied apatites from 47 different localities representing nearly all commercially exploited deposits. Having obtained refined lattice parameters they showed that dual substitution of carbonate and fluoride for phosphate takes place as this results in regular changes of the unit cell dimensions. These changes were also reflected in regular variations of optical properties and infra-red spectra, as well as in the chemical reactivity of the apatites.

Trueman (1965), examined numerous samples of apatite from Christmas Island and on the basis of chemical analysis also came to the conclusion that the carbonate ions, together with fluorine or hydroxyl ions substitute for PO_4 ions. These results are in accordance with the theory advanced by McConnell (1952a), Simpson (1964), and Winand (1963).

In summary, one can say that the weight of evidence lies in favour of carbonate fluorapatite being a definite mineral species with the CO_3 ion present as an integral part of the lattice.

If this is the case then the surmise that precipitates from solution are fundamentally different from those formed as a result of replacement is critical.

The Soviet experimentalists have confirmed the possibility of direct precipitation of carbonate-fluorapatite from aqueous solution, but give little information on the methods of identification of their products. There is also some doubt as to whether carbonate-apatite precipitates directly or whether the first precipitates are hydroxyl-apatite which later absorbs fluorine and carbonate ions to produce the carbonate-fluorapatite typical of marine phosphorites. Nevertheless, there seems little doubt that carbonate-fluorapatite can be precipitated directly from solution under conditions similar to a marine environment.

Klement et al (1942), however, state that precipitates from aqueous solution do not, and cannot, contain carbonate-apatite (only hydroxyl-apatite and calcite), but in the light of more recent work the author expresses some doubt as to the validity of their conclusions.

Ames (1959) has demonstrated the formation of carbonate-apatite synthetically by the replacement mechanism.

4. THEORIES ON PHOSPHORITE DEPOSITION

4.1 Accumulations

Bushinskii (1966) credits Kaizerling (1845) as being the first to publish the theory that phosphorites represent the bones of dead animals (thus he explained the formation of the Kursk deposit). Unfortunately no reference is given for Kaizerling's paper.

In the 1870's phosphate nodule beds and phosphorites in marine sequences were explained, as accumulations of coproliths. Sollas (1873) and Fischer (1873) explained the phosphate nodules of the Cretaceous of England as formed in this manner.

Murray and Renard, (1891), as a result of their oceanographic surveys on the "Challenger" expedition, suggested that phosphorite beds accumulated from the constant showering of the sea floor by dead plankton, whose death was the result of the mixing of a cold water mass with a warm water mass. Organic matter would be deposited in such abundance that special chemical conditions might operate so that phosphate would not be returned to the sea water but would rather be collected as nodules. Later Murray (1898), cited the case of the massive destruction of millions of tile fish along the east coast of the United States, presumably due to the shifting of currents.

Blackwelder (1915) has suggested a wholesale killing of fishes by changes of current or temperature in the ocean.

Grabau (1919) pointed out the association of phosphorites with unconformites and a calcareous bedrock, and suggested an origin by residual accumulation.

Pardee (1917) suggested that the deposition of the phosphoria was due to the cool climate of the Permian, which is known to have produced glacial periods. Carbon dioxide, supplied by the atmosphere and decaying organic matter, is more soluble in waters of low temperature. Under such conditions calcareous remains would tend to be dissolved and phosphatic substances would accumulate in relatively pure form. The carbon dioxide content and pressure in sea-water was therefore recognised as a possible control on phosphorite deposition.

Both Gibson (1967), and Rooney and Kerr (1967) attach great importance to the presence of clinoptilolite derived from volcanic ash, in the origin of the phosphorite of North Carolina. The latter authors suggested that widespread ash falls of long duration killed large numbers of marine organisms whose subsequent decay contributed phosphate.

Cathcart (1967), however, showed that over the whole deposit the amount of clinoptilolite ranges from nil to about 5% and is present only in the minus 200-mesh fraction.

Most theories of phosphorite deposition concerning an accumulative process involve a biological source of the phosphorous, i.e. bones, coprolites and others. These are usually based on the mass death of organisms.

Bushinskii (1966) states that there are two major objections to any biolithic hypothesis. Firstly, a study of the organic remains in phosphorites indicate that they reflect a normal assembly of fauna and not a mixture of two zoogeographic provinces. Secondly, phosphorites are not scattered randomly among different sediments but occupy a definite position in the facies profile.

4.2 Replacements

Murray and Renard (1891) suggested that ammonium phosphate liberated by organisms may replace calcium carbonate. Irvine and Anderson, 1891, gave experimental proof of the feasibility of this. They immersed a porous variety of coral in a solution of ammonium phosphate for 6 months. This resulted in a 60% replacement of the calcium carbonate by calcium phosphate.

Blackwelder (1916), also suggested that ammoniacal solutions, derived from the decay of marine organisms, dissolve phosphatic material from bones, teeth and shells. This phosphate may then locally replace carbonates and enrich the calcium phosphate in bones and phosphatic shells. He thought, however, that to a greater extent, it would be precipitated directly, forming nodules and bedded phosphorite.

Clark (1924), and also Hutchinson (1950), reported the replacement of rock by phosphatic solutions, in localities where the rock was overlain by guano.

Trueman (1965), in his investigations of the phosphate, volcanic and carbonate rocks of Christmas Island identifies phosphate deposits formed by the replacement of volcanic rocks.

Ames (1959, 1961), investigated a portion of the system Na_3PO_4-$CaCO_3$-H_2O at low temperature, and the mechanism of calcite-phosphate exchange was studied both under equilibrium and non-equilibrium conditions.

He showed that at room temperature alkaline phosphate solutions will cause rapid metasomatic replacement of calcite, resulting in a carbonate-apatite of variable composition.

A column containing 10 g of precipitated calcite was constructed and a 0.3 M Na_3PO_4 solution passed over the calcite at a flow rate of 7 ml per hour per cm^2 and a pH of 12.4. Care was taken that the system was Ca-saturated with respect to its HCO_3^1 content. Samples of the calcite were removed at intervals, washed with distilled water, air dried, and x-ray diffraction patterns obtained. These patterns showed the simultaneous

17

disappearance of calcite and appearance of an apatite corresponding to the idealized equation:

$$NaOH + 3Na_3PO_4 + 5CaCO_3 \longrightarrow Ca_5(PO_4)_3OH + 5Na_2CO_3$$

In the course of the experiments changes were made in the molar concentrations of the phosphate solutions, crystal size of the calcite minerals, pH, temperature and time of reaction.

The external morphology of the calcite was preserved in the resulting apatite.

Tracer techniques (radioactive isotopes) allowed the determination of the replacement rate as well as the mechanism of metasomatism.

With the replacement of a synthetic $Ca^{45}CO_3$, the quantitative retention of the Ca^{45} within the resulting apatite was confirmed.

The amount of Sr^{90} removed per unit time allowed a quantitative estimate of the effect of pH on the relative rate of replacement. A pH greater than 7 was found to be required to achieve substantial exchange rates.

To substantiate the assumption that CO_3'' was being replaced by PO_4''' during the calcite-phosphate reaction, a synthetic $CaC^{14}O_3$ was replaced under the conditions of the original calcite column. X-ray diffraction patterns were made from this calcite at intervals. Results showed that in the apatite lattice CO_3'' can be accommodated in amounts up to about 10% by weight and will co-exist as true carbonate in excess of this figure.

Relative replacement rates then were a function of solution pH, PO_4''' content in relation to HCO_3' concentration and calcite grain size (surface area).

In conclusion Ames postulated the following environmental conditions required for the formation of natural phosphates by the replacement of calcium carbonate:

a. a pH of 7 or greater,

b. presence of calcareous materials, and a system that is Ca saturated with respect to its HCO_3' content,

c. PO_4''' concentrations exceeding 0.1 ppm,

d. a non-depositional environment.

The replacement is little affected by large quantities of alkalis and the redox potential apparently does not control the exchange rate to a significant extent. An increase in grain size of the calcite precursor material will reduce the efficiency of phosphate metasomatism, while an increase in temperature will speed up the reaction.

Stability relations in the system $Na_3PO_4 - CaCO_3 - H_2O$ indicated, therefore, that the formation of carbonate-apatite can be a result of the incomplete replacement of CO_3'' by PO_4''' and extrapolating somewhat, Ames concludes that this is the most probable mode of origin of large marine phosphorite deposits. This is due to the operation of the replacement mechanism with PO_4''' and Ca^{++} concentrations far below those required for apatite formation by precipitation.

Simpson (1964) also prepared alkali carbonate-apatite in the laboratory by a replacement reaction of solid $CaCO_3$ with sodium and potassium phosphate solutions. He also found that the alkali content and to a lesser extent the carbon dioxide content of the apatite was dependent on the pH of the solution, from which it was formed. The highest contents were crystals formed in the most basic solutions.

The apatite had a continuous weight loss from room temperature to 900°C of more than 11%, of which less than half could be accounted for by carbon dioxide. The mean index of refraction, crystallinity and carbon dioxide content charged systematically with heat treatment. Water formed the other volatile when the apatite was heated, and was probably present as hydronium ions substituting for Ca^{++} and PO_4''' respectively.

Ames' minimal value of 0.1 ppm phosphate required for replacement to proceed, was considered by Pevear (1966). He compared this value to actual reported concentrations of phosphates in marine environments and found concentrations high enough to cause phosphatization only in estuaries and fjords. These large phosphorus values are due to the high productivity of organisms, especially plants.

Pevear also gives a comprehensive summary of the state of the controversy on phosphorite deposition, sections of which are quoted below.

Clark and Turner (1955) studied the reactions between solid $CaCO_3$ and orthophosphate solutions at low partial pressures of CO_2. Results indicated that the stable product was hydroxyapatite. Hydroxyapatite precipitated directly even though dicalcium phosphate formed initially under certain conditions.

Youseff (1965) and Bushinskii (1935) both suggest replacement as a very probable mechanism for the formation of economic phosphate deposits.

Aside from the development of extensive phosphorite deposits, phosphatization of all kinds of organic residue such as shell materials, wood, faecal pellets, teeth, etc. is common in marine environments (Goldberg and Parker, (1960), Adams et al (1961), Arrhenius (1963)).

Hamilton (1956) has described phosphatized globigorina ooze from the top of a Pacific guyot. Wilcox (1953) and Cayeux (1939) described phosphatization of fossils in English and French deposits respectively. Malde (1959) has shown that South Carolina deposits are derived from a phosphatized marl bed.

Dietz et al (1942) found phosphatized forms on the sea floor off California. Riggs (1965) has described replacement of dolomite rhombs in deposits off central Florida. Many similar reports have been published.

The work of Klement et al (1942) on the non-existence of carbonate apatite precipitated from aqueous solutions is relevant here. According to Klement et al the carbonate phosphates do not precipitate from aqueous solutions, in contrast to (F. OH, Cl) - apatites, which do. They precipitated calcium phosphate in the presence of sodium bicarbonate and analysed the results. From the lack of stoichiometric ratio of $CaCO_3$ to P_2O_5 and the direct correspondence of the amount of CO_2 in the precipitate, with the amount of $NaHCO_3$ added, they conclude that carbonate-apatite does not form in this manner.

They x-rayed the various precipitates and by comparison of the reflection angles of various lines, concluded that the apatite lattice had not changed and, therefore, that no carbonate had been added to the lattice.

Summarizing, they deduced that precipitates from phosphate and calcium solutions in the presence of carbonate contain only hydroxyapatite and $CaCO_3$ in various proportions and-no-carbonate-apatite.

It is obviously very important that any product of experimental work connected with the synthesis of phosphorite minerals should be checked by chemical and x-ray methods and, if possible, other supporting structural work.

On the other hand apatites precipitated directly from aqueous solution at room temperature may well contain $CaCO_3$ only as an amorphous or adsorbed phase, rather than as an integral part of the crystal structure - (Klement et al, (1942), Ames (1959), Arnold (1950), Trautz (1955), Termine and Posner (1966) and Pevear (1967).

Hayek (1955) in his experiments with synthetic calcium phosphates came to the consluion that adsorption is a feasible process and states that if $Ca^{++}$is precipitated at pH 6 or higher with phosphate, in the presence of carbonates, the hydroxyapatite could form carbonate-apatite by adsorption of HCO_3 followed by surface reaction. The carbonate content of bones and teeth, which have the hydroxyapatite lattice could be explained in this way.

The experiments of Riviere (1941), are relevant here. Riviere states that $(NH_4)_3 PO_4$ liberated from decayed organic matter can co-precipitate with carbonates as dicalcium phosphate and ammonium magnesium phosphates. This can only happen however, in concentrated solutions and with a pH of about 6. The first precipitate is rich in ammonium magnesium phosphate. In the presence of $CaCO_3$ this salt produced phospho-carbonates in equilibrium with mono- and di-phosphates in solution, the relative amounts depending on the pH. Precipitation is almost complete at pH 8, the normal alkalinity of sea-water. The solubility of $Ca_3(PO_4)_2$ is also linked to pH. This salt dissolves mostly as di-calcium phosphate.

Riviere carried out the following experiments:

1. Sea water was shaken for several hours with excess di-calcium phosphate, then filtered; the pH fell from 7.76 to 7.4 and P_2O_5in solution increased sharply. The di-calcium phosphate substitutes for the bi-carbonates normally present in sea-water, whereas the CO_2 thus liberated lowers the pH. No di-calcium phosphate can precipitate in sea-water unless more than 1000 times the normal concentration is present.

2. The above experiment was carried out with CO_2 bubbling through the solution; the amount of phosphate in solution increased as the pH fell to 5.8.

3. Some of the solution from (2) was filtered and freed of CO_2 by bubbling CO_2-free air through it. There was an abundant precipitate of calcium and magnesium di-phosphate plus a small amount of carbonate (probably as phosphocarbonate). The filtrate had a pH of 7.2. In such an environment, a rise of pH would cause precipititation of di-phosphates, which would then convert to tri-calcium phosphate by diagenesis.

4. Some part of the solution from (2) was filtered and left in contact with excess $CaCO_3$ in a closed system. The pH rose to 6.2 without any perceptible change in the amount of P_2O_5 in solution. CO_2 was then eliminated as in (3). After filtration, the solution had a pH of 7.32 and the phosphate in solution had diminished. The phosphate probably precipitated on the excess $CaCO_3$ as tri-calcium phosphocarbonate (dahllite). Thus phosphate solutions can phosphatize $CaCO_3$ if the pH rises because of algal activity or simple agitation. This replacement can take place with much less phosphate in solution than simple precipitation. Variations of total pressure seem to have little influence on the reaction described but variations in temperature affect the solubility of CO_2 and thus effect these reactions.

Summary. In reviewing the evidence for the replacement mechanism, one can confidently state that there is no doubt at all that phosphatization does take place and that this has been verified by synthetic work in the relevant systems. Whether this is the process responsible for the formation of the vast phosphorite deposits is still open to conjecture.

There is a certain element of doubt, however, when one considers the role of the carbonate ion, i.e. is the product formed by the replacement of carbonate fundamentally different from that formed on direct precipitation from aqueous solution? Further, how do these two products, if different, compare with the minerals found in some phosphorite deposits?

4.3 Precipitation by Inorganic Control

In 1937 (1939 and 1950) Kazakov proposed direct inorganic precipitation from sea-water, as the origin of marine phosphorite deposits. His conclusions were based on the observations, made by the "Meteor" expedition, of progressive changes in the physico-chemistry of sea water with depth. The P_2O_5 content of marine waters increases with depth from a minimum in the zone of photosynthesis to a maximum at about 500 metres depth as the pH and temperature decrease, and the partial pressure of CO_2 increases.

Kazakov's hypothesis states that phosphate is chemically precipitated on shelving bottoms between depths of 50 and 200 metres, where the pH of ascending cold waters rises as their temperature increases and the partial pressure of CO_2 decreases. The water first becomes saturated with calcium carbonate, which is immediately precipitated, and later with calcium phosphate. Phosphate cannot be precipitated, either in the zone of photosynthesis where available phosphorus is assimilated by the phytoplankton or at depths below 200 metres where the high content of CO_2 prevents conditions of supersaturation.

Emphasis is laid on the calcium carbonate precipitation, prior to calcium phosphate and allows the numerous replacement processes observed to take place.

McKelvey et al (1952) in their study of the Permian Phosphoria formation of the United States drew largely on the theory of Kazakov, but with an important modification, namely that the phosphate precipitation occurred before carbonate, and that the solubility curves of calcium carbonate and phosphate overlap in such a way that independent precipitation of phosphate is possible.

This phase of the problem, as well as the relation of MgO to the system, has been studied by Rubey (this is mentioned in the paper by McKelvey, but the author was unable to locate the published article). Rubey permitted McKelvey to say that the solubility-pH curves of apatite and carbonate in the sea are roughly similar, but do not coincide precisely. This lack of precise coincidence is, of course, most significant. Were it not true, carbonate-fluorapatite and calcite would be precipitated together and in about the same proportion as they are found in sea water (i.e. $CaCO_3 \gg PO_4'''$). Phosphate would be found only in slightly phosphatic limestones, and concentrations of phosphate could be formed only by weathering.

McKelvey also stated that phosphorites could be due in part to accumulation of organic remains, since if the environment allowed inorganic precipitation of phosphate then phosphate from dead organisms would not be reabsorbed in water already saturated with phosphate. Depth of deposition they suggested, was between 200 and 1000 metres.

Smirnov, Ivnitskaya and Zalavina (1958 and 1962), refined the experimental data of Kazakov on the solubility of phosphates in sea-water with the addition of CO_2, F, and SO_3 in the equilibrium system. The physicochemical parameters of calcium phosphate precipitation were determined by studying the equilibrium in the system $CaO-P_2O_5-H_2O$. A NaCl content of 3.5% and a CaO content of 560 mg per litre or multiple of it, assured a similar environment to natural sea-water. Hydroxylapatite precipitated first (not calcite), and the P_2O_5 content in the equilibrium liquid phase was 0.10-0.20 mg per litre at pH 8.1, i.e. that amount required to saturate the water.

The influence of the fluorine ion on the system was investigated fully by Kazakov who found that the solid phases in that case were isomorphic mixtures of hydroxylfluorapatite and the precipitation of fluorite started when concentrations of fluorine exceeded 10-15 mg per litre depending on the mean pH.

CO_2 was then introduced into the system and the P_2O_5 content in the equilibrium liquid phase sharply increased. The solid phases were hydroxyl-carbonate-apatite and calcite.

On alkalization of the liquid phase, hydroxylcarbonate-apatite precipitated first and then calcium carbonate. The pH remained constant during precipitation.

In addition to the $CaO-P_2O_5-NaCl-H_2O$ and $CaO-P_2O_5-CO_2-NaCl-H_2O$ systems investigated in detail, preliminary studies were conducted on the $CaO-P_2O_5-F-NaCl-H_2O$, $CaO-P_2C_5-CO_2-F-NaCl-H_2O$, and $CaO-P_2O_5-SO_3-F-NaCl-H_2O$ systems. The solid phases contained fluorapatite, fluorcarbonate apatite, and fluorsulphate apatite.

The precipitation of fluorsulphateapatite in combination with fluorcarbonate-apatite is possible only by an increase in the concentrations of CaO and SO_4 in ocean water (as for instance in a hot, arid climate).

Smirnov et al therefore conclude that sea-water, with a salinity of 3.5%, a CaO content of 560 mg per litre, 1 mg fluorine per litre, 2200 mg SO_4 per litre and a CO_2 content of 73 mg per litre can contain in solution P_2O_5 amounting to 0.1-0.2 mg per litre at pH 8.0-8.2 and 0.3-0.7 mg per litre at pH 7.6-7.8.

Ocean water at pH 8.1 which contains approximately 0.05 mg P per litre (i.e. 0.114 mg P_2O_5 per litre) is almost saturated with phosphates. Therefore the precipitation of phosphate from both sea and bottom (silt) waters is possible as a result of its alkalization by the removal of CO_2, or mixing with more alkaline waters.

Emery (1960) in his account of the sea-bottom waters off California, where recent or young phosphorite nodules and slabs are known to exist, states that the P_2O_5 concentration is 0.15-0.20 mg per litre and the pH values vary from 7.7 to 8.5.

Kramer (1964) states that the Pacific Ocean is slightly supersaturated with hydroxylapatite and carbonate-fluorapatite.

Additional, confirmatory work, on the possibility of precipitation of calcium phosphate from sea water was carried out by Rozhkova, Serebryakova and Makarova (1962). These authors considered Kazakov's conditions of artificial and natural precipitation too dissimilar to be meaningful. The pH values (of Kazakov) of 7.9-8.3 for the zone of photosynthesis and 6.97-9.02 and 9.24 in the equilibrium liquid phase (over the sediment) cannot be said to coincide. (Kazakov in his later study of 1939 gave a narrower interval of the latter values of 8.0 ± 0.5).

Rozhkova et al carried out experiments with the precipitation of calcium phosphate from a solution of salt water. They observed the precipitation of phosphate from a solution with a P_2O_5 content of 4.9 mg per litre, but at a concentration of 4.1 mg per litre precipitation did not occur even with a pH of 9.0.

They conclude that the reasoning of Kazakov on the possibility of the precipitation of calcium phosphate during the upwelling of deep waters, with a P_2O_5 content of 0.70 mg per litre (in the zone of the shelf) was formulated without taking into account the actual existing conditions.

Neither Kazakov nor Smirnov et al mention the size of the precipitated phosphate particles, but Rozhkova et al state that their precipitates were extremely fine and did not settle for several days.

Bushinskii (1966), points out that in the experimental work of Smirnov et al (1962), the CaO content in the initial solution was slightly exaggerated in comparison with normal sea water (560 instead of 420 mg per litre). Roxhkova et al (1962), however, used a greatly undersaturated (with respect to CaO) solution (180.6 and 89.6 mg per litre).

Therefore (concludes Bushinskii, 1966) the minimum P_2O_5 concentration of 4.1 mg per litre, which Rozhkova established, must be decreased by a factor of 2.5 in its application to natural sea water.

A recent development of the Kazakov hypothesis is that of Smirnov (1964), that phosphorite deposition is brought about by changes that occur as water masses from different sources meet and mix.

Sheldon (1964), also believes that the source of phosphates is deep waters carried by upwelling currents and that the phosphate is precipitated either chemically or biochemically and that silica is precipitated biochemically. From palaeogeographic studies of modern and ancient phosphorites bearing basins he found that phosphorites were deposited in warm seas in the latitude range 5 to 42°. These deposits correlate with the latitudinal distribution of divergent and dynamically caused ocean upwelling.

23

Gibson (1967), interpreted the palaeoenvironment of phosphorite deposition of North Carolina, mainly from the benthonic foraminifera. He concluded that deposition was in cool temperate waters ranging in depth from 100-200 metres in the phosphatic beds, to less than 70 metres in the upper calcareous beds where phosphate is scarce.

Since the main experimental evidence used by the proponents of the Replacement Theory is based on the non-existence of carbonate apatite precipitated from solution, it is important here to mention other recent work in which carbonate-apatite has been prepared synthetically by precipitation. Romo (1954), carried out a synthesis in the presence of an excess of alkali according to the following reaction:

$$10CaCO_3 + 6KH_2PO_4 + 12OH' \rightarrow Ca_{10}(PO_4)_6CO_3 + 6K^{+} + 9CO_3'' + 12H_2O$$

Legeros (1965), precipitated carbonate apatites by dropping $Ca(Ac)_2$ solution at 100°C, into phosphate-carbonate solutions, with carbonate to phosphate molar ratios, C/P from 0 to 50. Legeros et al (1967) used a similar preparation.

Simpson (1965) prepared carbonate apatite from reagent grade basic dicalcium phosphate having a Ca:P ratio of 1.03, and low alkali calcium carbonate.

4.4 Precipitation by Organic Control

Breger (1917), Cayeux (1936), Oppenheimer (1958), Brodskaya (1961), Bushinskii (1964), McConnell (1965) and Riggs (1965) all suggest that some organic process or organism provides the mechanism of phosphorite formation.

It is a well established fact that certain organic tissues can nucleate hydroxyapatite and that they do so even when reconstituted experimentally (see Glimcker, 1960).

Hydroxyapatite plays an important role in biological mineralization systems and according to McConnell (1965) the principles of inorganic chemistry seem to be inadequate to account for phosphorite formation. He points out that carbon dioxide is an essential component of the mineral complex of phosphorites, teeth and bones and states that cogent analogies exist between the processes that take place during precipitation of phosphorite and the biochemical processes of formation of bones, teeth and phosphatic shells of invertebrates. He suggests that a possible biochemical influence is exerted by the common enzyme, carbonic anhydrase, which may influence the precipitation of carbonate hydroxyapatite.

McConnell, et al (1961) reasoned that carbonic anhydrase, might play an active part in the precipitations of carbonate hydroxyapatite in the oral cavity. The correctness of this prediction was demonstrated not only for saliva "in vitrio" but for synthetic systems which simulated saliva with respect to salinity and concentrations of phosphate and calcium ions. Precipitates were also obtained in the absence of the enzyme, provided the solutions were brought near saturation by bubbling carbon dioxide through them. Thus it was inferred that in the absence of the enzyme, larger concentrations of carbonate and/or bicarbonate ions were essential to the precipitation process, with respect to the formation of carbonate hydroxyapatite, at the pH, temperature and ionic strength approximating that of saliva.

Corroborative evidence comes from Hammen (1965) who says that the mantle tissue of lingula reevi has a high activity of the enzyme carbonic anhydrase.

McConnell states, therefore, that nektonic, or possibly planktonic organisms of various kinds are quite important in the precipitation of carbonate fluorapatite from sea water, particularly in view of the fact that certain bacteria appear to be capable of initiating similar types of precipitation (Ennever, 1963; and Rizzo et al, 1963).

Ennever (1963 grew mineralized oral bacteria cultures in "calcifying solutions" not unlike sea water (or saliva) except that they contained more than 100 times as much phosphorus as is found even in high-phosphate sea water. Extracts from bacteria also seemed to initiate apatite-like precipitates.

Rizzo et al (1963) grew mineralized oral bacteria cultures in dialysis tubes implanted within the intestinal cavity of rats. Dead bacteria seemed more susceptible to mineralization than living species!

McConnell states further that in as much as the activities of the calcium and phosphate ions appear to be sufficiently great to cause precipitation spontaneously, it seems that natural inhibiting factors may exist that are necessarily overcome under conditions of actual precipitation. Some of the ways in which organisms could presumably alter the delicate conditions required for precipitation are implied by extensive studies on the mineralization of bone. He assumes they could produce localized changes in the pH, the activity of carbonate or bicarbonate ions, the ionic strength, or the pyrophosphate activity in terms of their metabolic processes.

He comes to six main conclusions:

1. Sea water is almost saturated, if not supersaturated, with carbonate fluorapatite, of somewhat variable composition.
2. That certain analogies are relevant with respect to the biologic processes of tooth, bone and shell formation.
3. Such biochemical systems can be influenced (in vitrio), by a common enzyme (carbonic anhydrase).
4. That the necessary conditions for precipitation probably cannot be evaluated solely by means of inorganic chemical theory.
5. Precipitation may be impeded in cases of apparent supersaturation by some inhibitor.
6. Greater understanding of the processes involved in the mineralization of bones and shells should furnish important clues to the precipitation of phosphorites and vice versa.

Pevear (1967) in summarizing McConnell's paper states that the fact is that dental calculus, i.e. deposits on the teeth, is a complex mass of living and dead bacteria with included food debris, saliva, enzymes, epithelial cells and so forth. Within such a mass (or within masses of dead cells in vitrio) solutions become trapped and phosphate concentration, resulting from decay and break down of organic materials can probably reach high enough values to bring about precipitation of a poorly crystallized hydroxy-apatite. He concludes that the extrapolation of this information to marine conditions is difficult, if not impossible, especially since the enzyme, carbonic anhydrase related to the formation of bone and dental calculus, is absent from sea water.

There can be little doubt that micro-organisms may be very influential in controlling the character of marine sediments, especially in near shore areas where nutrients are available (Oppenheimer, 1960). Present day calcium carbonate precipitating marine bacteria have been described (Greenfield, 1963), but none are presently known that will precipitate apatite from sea water.

Riggs (1965) proposes that phosphorite is deposited by organisms in areas of upwelling waters. Both he and McConnell (1965) therefore require an abnormally high concentration of phosphorus in sea water.

Pevear (1967) suggests this may not be necessary as many organisms are able to concentrate elements that are present in very low concentrations in sea water. Continuous extraction of phosphate from circulating, normal sea water is therefore a likely alternative.

Bushinskii (1964) agrees with Pevear (1966), Degens (1965) and Youssef (1965) that organisms can raise the concentration of dissolved phosphate in the sea, near productive areas, but does not specify an explicit mechanism for phosphorite formation.

Cayeux (1936) and Riggs (1966) both find what they interpret as fossil bacteria in some phosphorites. Cayeux suggests that these organisms have played an active role in its formation.

Youssef (1965) also suggests a biochemical mode of formation for bedded phosphorites, controlled by the configuration of the sea floor. He states that decaying organisms on the bottom of depressions of an otherwise open sea produce ammonium phosphate and ammonia. Nitration bacteria oxidize ammonia into nitrates that act as fertilizers for the phytoplanktons on which other nektons and planktons flourish. On death, the biota fall to the bottom of the sea floor depressions, where the amounts of soluble phosphates increase in due course beyond the needs of the animals and plants living above. The sheltered depressions preserve the solutions from dissipation in the open sea. The ammonium phosphate reacts with the Ca ions or with precipitating $CaCO_3$ to give calcium phosphate.

It is relevant at this point to consider the information available on the precipitation of calcium carbonate in sea water, that is particularly relevant to phosphorite deposition and its possible causes.

Precipitation of Calcium Carbonate. Observations of patches of milky water at sea were observed as long ago as 1836 by the British nautical survey and recently Wells and Illing (1964) reported the present day instantaneous precipitation of calcium carbonate in the Persian Gulf. This covers an area of tens of thousands of square kilometres in its shallow southern part. The average "whiting", as the turbid areas are called, is commonly about one kilometre across, occurs throughout the year, and produces about one gramme of microcrystalline aragonite for every 100 litres of water. The precipitate flocculates and settles out on the sea bed within a few hours of its formation. This is not accompanied by salinity or temperature variations, or by detectable changes in pH. Plankton analysis, however, shows a five to ten-fold increase in the siliceous diatompopulation in the "whiting". Wells and Illing consider

26

that this probably provides the mechanism needed for triggering the precipitation.

Further, the increase in phytoplankton would sharply increase the carbon dioxide consumption from the water. This would tend to raise the pH, but the change would be resisted by natural buffering. The water is generally saturated with respect to aragonite, so that the critical level is soon reached at which equilibrium can only be restored by precipitation.

Alekin and Moricheva (1961) agree that organisms play a large part in enriching and concentrating $CaCO_3$, which has precipitated from its supersaturated solution in sea water. Precipitation is a slow process and occurs only to form a highly dispersed suspension of carbonate particles.

Lalou (1957), in a study of the production of carbonate by marine bacteria states that the results indicate the production of carbonates is due mostly to the activity of sulphate-reducing bacteria.

Fischer and Garrison (1967) after examining samples from the sea floor of the Eastern Mediterranean and off Barbados came to the conclusion that calcite can be precipitated chemically in sea water.

E-an Zen (1960) on considering carbonate equilibria in the open sea from the point of view of phase equilibria, came to the conclusions that monomineralic carbonate deposits, calcite or dolomite, should result under equilibrium conditions. The contact between the dolomite and calcite beds should be sharp, although the two carbonates should be in mutual equilibrium.

At surface conditions, calcite is the equilibrium carbonate, whereas dolomite becomes relatively more stable at depth (i.e. greater pressure).

Upon evaporation, normal sea water should precipitate dolomite. In the sedimentary record, extensive two-carbonate rock systems are not uncommon, but these cannot be due to direct chemical precipitation.

In summarizing the evidence on precipitation of phosphates controlled by bacteria or other organisms, there seems little doubt that this can be operative as an effective mechanism. It is unfortunate however, that no evidence is presented as to the precise way in which this process takes place. It should also be pointed out that if the process is operative, the laws of inorganic chemistry must still apply.

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31

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36

TABLE 1 : THE CLASSIFICATION OF PHOSPHORITES DUE TO GIMMELFARB ET AL. (1959)

Genetic Group	Structure-texture Type	Varieties	Notes
Marine: Primary sediments	Stratified aphanitic		Most abundant
	Stratified, oolitic-granular	Carbonaceous, siliceous, monomineralic	
	Granular	Arenaceous-siltstones, marlaceous, monomineralic	
	Concretionary	Arenaceous, glauconitic, argillaceous, monomineralic	
	Coquina phosphorites	Quartzitic, quartzitic-carbonaceous	
Redeposited (mechanically)	Phosphorite gravel		
	Phosphorite pebbles		
	Phosphorite conglomerate	Carbonaceous, siliceous and others	
Continental: Epigenetic	Residual metasomatic	–	Developed during formation of residual soil.
	Sinter phosphorites		
Organic	–	–	Mainly guano
Metamorphosed:	Micrograined	Carbonaceous, siliceous	Formed by regional or contact metamorphism
	Crystalline-granular	Quartzitic-diopsidic	