THE FORMATION OF STRENGITE FROM AMORPHOUS IRON OXIDE PRECIPITATES

FORMATION OF FERRIC PHOSPHATE MINERALS AND ADSORPTION OF PHOSPHATE ON AMORPHOUS IRON OXIDE

By

NORMAN DAVID WARRY, B.Sc.(Hons.)

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
September, 1972

MASTER OF SCIENCE (1972)
(Geology)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: Formation of Ferric Phosphate Minerals and Adsorption of Phosphate on Amorphous Iron Oxide

AUTHOR: Norman David Warry, B.Sc.(Hons.), McMaster University

SUPERVISOR: Professor J.R. Kramer

NUMBER OF PAGES: ix, 111.

ABSTRACT

A series of experiments was designed to investigate the reaction of orthophosphate with amorphous iron oxide under conditions approximating those encountered in lacustrine environments. A dynamic physical sorption reaction explained the uptake of the ion onto the solid. When total P was ≤ 200 µg/l and total Fe ≥ 2.5 mg/l, more than 95% of the dissolved orthophosphate was adsorbed onto the $Fe(OH)_3$ particles. When total Fe was = 0.25 mg/l or less, no phosphate was adsorbed. The sorption was a maximum in the pH range between 4 and 7.5, as long as particulate $Fe(OH)_3$ was present in the solution. Outside of this pH range, the sorption of phosphate by the solid decreased dramatically. The lower limit of Eh stability for the P-$Fe(OH)_3$ complex was found to be on the order of 200 mv, equivalent to 1 mg/l D.O. Below this Eh value, the complex dissolved. No upper limit of Eh stability was found.

The complex was capable of being altered to a crystalline mineralogical phase if total orthophosphate was increased to $> 10^{-4}$ M. The structure of this phase was quite similar to that expected for a mixture of the ferric phosphate minerals strengite and metastrengite.

Comparison of the conditions of formation ($\Sigma HPO_4^{-3} \gtrsim 1x10^{-3} M$, $Eh > 300$ mv, $pH \lesssim 7$) of this solid with those necessary for the formation of strengite (Nriagu, 1972b) show a good correlation. Formation of these mineral phases in lacustrine sediments is not likely, however, because the requisite conditions are rarely satisfied in natural lacustrine ~~sedimentary~~ environments.

ACKNOWLEDGEMENTS

I wish to thank the following people for their help and encouragement throughout this undertaking: Dr. J.R. Kramer, my research supervisor, for his knowledgeable direction of this project, and Dr. H.D. Grundy and Mr. L.J. Falkiner for their numerous helpful suggestions regarding the X-ray diffraction techniques employed in this study.

I also wish to thank Messrs. G. Eynon, T. Thomas, J. Garth and C. Turner for their valuable criticisms and aid in the preparation of the text. Mr. J.L. Griep helped in the translation of the German papers, and Mr. J. Whorwood provided the expertise necessary for the photographic work. Mrs. J. Allen kindly consented to type the manuscript.

This research was financed by the National Research Council of Canada.

TABLE OF CONTENTS

Page

CHAPTER I INTRODUCTION

CHAPTER II EXPERIMENTAL METHODS AND RESULTS

CHAPTER III INTERPRETATION AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

PAGE

I. 1 STATEMENT OF THE PROBLEM

Excess phosphate has been suggested as the main factor for nuisance algal blooms in lakes (Vollenweider, 1968; Burns & Ross, 1970). The exchange of phosphate between sediments and water has been recognized as an important control on phosphate availability in these waters (Einsele, 1938; Mortimer, 1941; Carritt and Goodgale, 1954; Burns & Ross, 1971). The chemical reactions between sediment and water involving P include adsorption, anion exchange, and dissolution and precipitation. The reactions are controlled principally by the Eh and pH of the environment, plus the ionic concentrations of the elements involved.

Investigations into sedimentary occurrences have shown correlations of P with fine-grain size, and with the presence of iron and manganese (Wentz & Lee, 1969; Williams et al. 1971a, b, c). To date, the investigations all seem to be limited by a lack of precise information regarding the surface reactions and the detailed mineralogy of the solid phases involved in the P reactions.

The purpose of this work is to:

1) Investigate the effects of master variables (pH, Eh, etc.) on the sorption of P with precipitated amorphous iron oxide, and

2) Define the diagenetic change of the sorbed P-iron oxide complex to a mineralogical phase.

I. 2 THE SYSTEM

A natural water system may be defined as a complex system consisting of four phases mixed in an inhomogeneous fashion. The four phases present in this system are a liquid phase, a gas phase, a solid phase, and a biological phase. An overall definition of a natural water system based on these four phases is usually impossible because of the large number of variables present in natural waters which affect the phase relations. However, there are situations where the water system is sufficiently homogeneous and well-characterized to produce a region which is uniquely identifiable. An example of such a unique region occurs in dimictic lakes where in summer a thermogradient prevents water circulation and the water column is divided into three distinct layers:

1) epilimnion - lighter, warmer water of relatively constant temperature or slightly decreasing temperature with depth;
2) thermocline - a thin (less than 2 ft.) layer of maximum temperature gradient;
3) hypolimnion - a layer of dense bottom water with a more or less constant temperature near 4°C.

These three regions are so different, in a chemical and physical sense, that, in a eutrophic lake, they can be identified easily by their distinct characteristics.

As no unique definition of the lake system as a whole exists, it will be discussed from the viewpoint of the four phases comprising it.

The Gaseous Phase

The presence of dissolved gases in the water column exerts a major controlling influence on the following master variables in nature waters: (1) the pH; and (2) the amount of dissolved oxygen present in the water whihh is reflected in the Eh of the water. In a water body isolated from reaction with the rocks and sediments, the pHis poorlybuffered and controlled at a near-neutral condition by the exchange of carbon dioxide between the water and the atmosphere.

The important variables affecting this exchange are the solubility and partial pressure of CO_2 at the gas-water interface, the resultant mixing of these saturated surface waters with the rest of the water column, and the temperature of the air and water. Many natural waters are not in equilibrium with the atmosphere, primarily because of the slowness of the gas transfer reaction between the gaseous and liquid phases compared to processes within the aqueous phase. As a result, pH values much different from the equilibrium value of 5.7 - due to CO_2 solution - have been obtained in areas of high photosynthetic or respiratory activity and smaller variations are usually found in areas of carbonate dissolution of precipitation.

The amount of dissolved oxygen in the water column is also dependent upon the exchange rate between the atmosphere and the water. However, in this case, the interphase transport process is quite rapid in comparison to the other transport processes and chemical reactions. Therefore, the main reason for oxygen depletion rests not with the dissolution kinetics of O_2, but with the unfavourable mixing processes between the surface and deeper waters. This lack of mixing is best exemplified during the summer periods of stratification in dimictic lakes, when there is no net transfer across the thermal boundary between the epilimnion and the hypolimnion. During these times, the bottom waters become significantly depleted in oxygen, a consequence of organic decay and respiration, coupled with a complete lack of oxygen transport in to the hypolimnetic water. This results in a lowering of the Eh in these bottom waters to levels of 200mv or less.

The Liquid Phase

The aqueous chemistry of natural waters is dominated by the chemical properties of water itself, notably its solvation ability and its highly electrostatic nature. It is the ability of water to solvate protons which permits the formation of hydrogen ions in solution, and it is this property which makes water a unique solvent. The solvation or hydrolysis property is the foremost consideration in the chemistry of elements dissolved in this liquid. For example, the most conspicuous feature of the aqueous chemistry of iron (III) is its tendency towards hydrolysis and/or the formation of complexes. Similarly, the aqueous chemistry of phosphorus is dominated by the dissociation products of phosphoric acid, the most common hydrolyzed form of phosphorus.

The electrostatic nature of water is demonstrated in the surface chemistry of solid matter and/or ions present in it. In aqueous solution, electrically charged particles are always surrounded by a diffuse layer of oppositely charged ions in the aqueous phase. The resultant electrical double layer exists at all solid-liquid interfaces in natural waters, and greatly effects the sorption-desorption characteristics of all solid particles present in the liquid domain. In natural waters, iron is always positively charged and phosphate always carries a negative charge.

The Solid Phase

The chemistry of a particular freshwater lake is largely influenced by the lithological characteristics of the lake basin. The reactions of water with lithological material have been shown by

Feth et al. (1964) and Garrels et al. (1967), to be important in determining the composition of surface water. A more emphatic statement was provided by Kramer (1964), when he wrote: "the ultimate source of all constituents in freshwater is either the lithosphere (sediment) or atmosphere".

The occurrence of any particular solid phase in a lake is dependent upon its solubility in freshwater. The solubility of a phase is dependent upon a large number of factors, such as: pH, temperature, degree of saturation of solution, the degree of hydration of the solid, its lattice energy, its surface free energy and its ability to form solid solutions. All of these factors must be considered when the precipitation and dissolution reactions of a solid are studied. Precipitation and dissolution reactions are paramount not only in determining which solid phases will be present, but also in modifying the pH and elemental concentrations found in the water.

For most solids, it is found that the first-formed solid phase is usually an amorphous precipitate with a disordered lattice structure. Such structurally disordered precipitates are referred to as the "active" form of the compound. Formation of a structurally ordered or "inactive" solid phase from this precipitate may take place in more than one way. In the case of iron hydroxide, the deactivation (i.e. structural ordering) of the amorphous solid occurs by the processes of condensation and dehydration. As Feitknecht & Schindler (1963) point out, these reactions lead to the formation of three difrerent solids from the amorphous $Fe(OH)_3$. The reactions involved may be summarized as:

$$\begin{tikzcd} & Fe_2O_3\ \text{(dehydration)} \\ \text{(amorph.)}\ Fe(OH)_3\ \text{(active)} \arrow[ur] \arrow[r] \arrow[dr] & FeO\,OH\ \text{(active)} \\ & \text{(amorph.)}\ FeO_{n/2}(OH)_{3-n}\ \text{(condensation)} \end{tikzcd}$$

The net result of these diagenetic changes is the formation of a thermodynamically stable but inhomogeneous mixture of iron oxide minerals in the sediment.

In addition to the solid phases present on the lake bottom, there is also a considerable amount of particulate solid material suspended throughout the water column. This material includes airborne dust, organic detritus, suspended sediment and colloid complexes formed by sorption of ionic species in the water onto suspended or dissolved organic and inorganic material. Not much information is available regarding these suspended particles. Recent evidence, however, (Shapiro, 1964) suggests that the amount of iron in the water column is related to the presence or absence of this suspended material, although the composition and identification of this suspended material has never been thoroughly investigated.

The Biological Phase

The biological population is the main cause of non-equilibrium conditions in a lake. This is a result of the continuous energy input by the sun, in order to maintain life. Consequently, the organisms produce a system whereby energy is conserved and entropy decreased, in direct opposition to the abiotic environment where energy is expended and entropy is increased. In a balanced ecological system, organic material is produced and destroyed at the same rate. The production and consumption of oxygen and carbon dioxide also take place at an identical rate.

The basis of the life-processes in the lentic environment is fundamentally the phytoplankton. They provide the first step in the ecological cycle and therefore control the productivity and composition of the other trophic levels in the biotic community. Stumm and Morgan (1970) list a typical plankton community as having the stoichiometry $C_{106}H_{263}O_{110}N_{16}P_1$ and an equation representing photosynthesis:

$$106\,CO_2 + 16\,NO_3^- + HPO_4^{-2} + 122\,H_2O + 18\,H^+ + \text{tr. elements} + \text{energy}$$

$$\mathrm{P}\Big\downarrow\Big\uparrow\mathrm{R}$$

$$(C_{106}\,H_{263}\,P_{110}\,N_{16}\,P) + 138\,O_2$$

in which P = photosynthesis and R = respiration.

From the above equation, it is obvious that phosphorus is an important element in phytoplankton metabolism. In fact, since it is required in the least quantity of the major elements, its presence or absence can be considered as the controlling factor in the metabolic reaction (Liebig's Law of The Minimum). For this reason, phosphorus has been often cited as the 'limiting' nutrient in phytoplankton production and hence increases in phosphorus concentrations in the lakes could result in an imbalance in the production-destruction equilibrium in the biotic environment.

Phytoplankton dependence on iron has not been as extensively studied as phosphorus, but Jeffries (1971) has pointed out that epilimnetic phytoplankton do concentrate iron in large amounts during bloom periods.

I. 3 AQUEOUS CHEMISTRY OF IRON

Though not normally present in concentrations greater than a few tenths of a milligram per litre, iron is nevertheless a ubiquitous constituent of natural waters. Its chemistry is dominated by the processes of oxidation and reduction, precipitation and dissolution, complex formation, and the metabolism of plants and animals.

Species in Natural Waters

Iron is present in natural surface waters in only the oxidation states of +2 and +3. Under reducing conditions and a pH of less than 11, ferrous iron is present as either the Fe^{+2} ion or as the hydrated $Fe(OH)^{+}$ ion, depending upon the concentration of the dissolved carbonate in the water. If the total C is less than 10^{-3}M and the pH is less than 8.5, then the $Fe(OH)^{+}$ ion dominates, but if the total C is greater than 10^{-2}M, then the Fe^{+2} ion is the major ionic species present. Above a pH of 11, the anion $HFeO_2^{-}$ can exist in appreciable quantities, but such a high pH is not often encountered in natural systems.

Ferric iron can occur in solution as Fe^{+3}, $Fe(OH)^{+2}$, or $Fe(OH)_2^{+}$; plus a number of polymeric species. The form of the ferric ion present is largely dependent upon the pH of the solution.

Recent reviews such as those of Shapiro (1964) and Stumm & Morgan (1970), indicate that dissolved iron species are not the major forms of this element in natural waters. Evans & Wang (1970) found that 90% of the total iron measured in Peoria Lake waters was present as particulate complexes rather than as a dissolved species. This particulate iron is usually considered to be present as either: 1) colloidal ferric hydroxide (hydrated iron oxide), or 2) a complex of unknown nature but probably associated with organic matter. An exact definition of these complexes has not been provided, although both ferrous and ferric iron are involved. One possible explanation put forward by Evans & Wang involves a sorbed complex species containing iron ions sorbed on the surfaces of clay particles.

Solubility Relations

Calculations involving the variables of principal importance in iron chemistry generally are not very useful in explaining the quantitative relationships between Eh, pH, dissolved carbon dioxide and dissolved iron in nature. From a qualitative viewpoint, the calculations do show the general effects of these variables on the activity of iron in

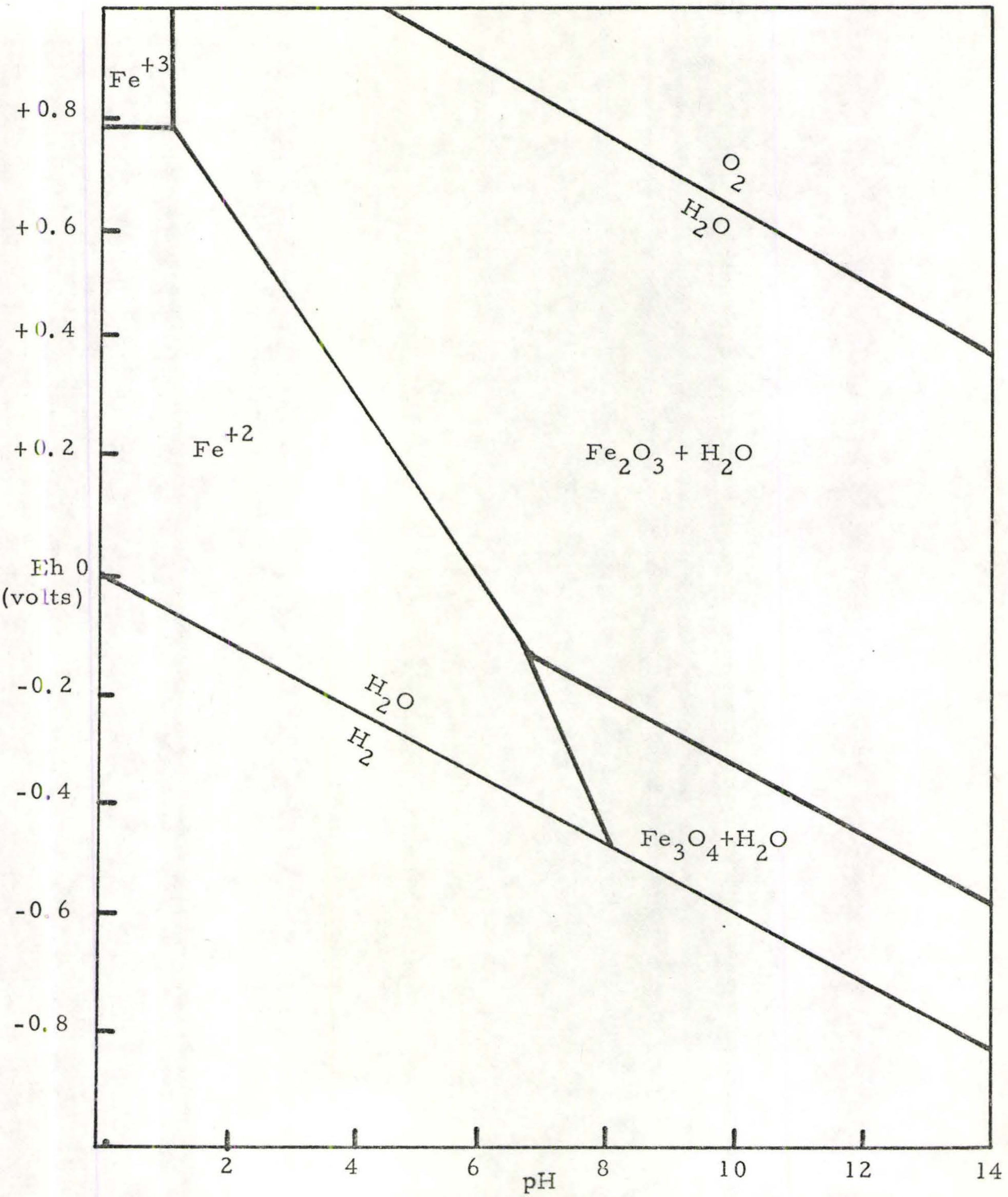


Fig. I. 3. 1. Phase diagram showing stable iron phases in natural waters.
Constructed using $\Sigma Fe=4.5\times10^{-5}M$
$\Sigma HCO_3^{-3}=1.0\times10^{-3}M$
$\Sigma SO_4^{-2}=1.0\times10^{-5}M$
$T = 25^oC$

natural systems. For instance, fig. I. 3. 1 shows the system $Fe\text{-}CO_2$ without any sulphur present. It can be seen that under the Eh-pH conditions of most natural surface waters ($5 < pH < 9$; $Eh > 250$ mv), $Fe(OH)_3$ should be the predominant form of iron, and measurements have shown this to be correct. The diagram also shows that a lowering of the Eh or pH should cause an increase in the amount of iron in solution. Such increases are observed in natural systems. If an amount of $S \approx 10^{-4}$ M is added to this system, the phase diagram would predict that under low Eh conditions, pyrite rather than siderite should form. This prediction also has been verified in nature. These diagrams, however, are useful only for qualitative predictions of stable phases. The real system is so complex that any quantitative extrapolations of the stability diagrams to the path of reaction is meaningless.

The effects of biological activity on the occurrence of iron and its forms have not been adequately investigated. Berner (1970) has shown that bacterial reduction of sulphate under anoxic conditions does provide sulphide ions which react with iron to form various insoluble iron sulphide minerals. Other mechanisms, such as incorporation of iron into phytoplankton, may remove iron from the water and store it in the living organisms or in the sediments.

Occurrence in Natural Waters

As previously mentioned, oxygenated waters at near-neutral pH's cannot contain significant amounts of uncomplexed dissolved iron. It is usually present as hydrated iron oxide or as some organic complex. In the sediments, iron is found in varied and complex mineralogical phases. The ferrous sulphide minerals such as pyrite and marcasite (FeS_2) comprise one such group. The ferrous carbonate mineral siderite ($FeCO_3$) is another. Ferric minerals include the oxides and hydroxides such as hematite (Fe_2O_3) ilmenite (amorph. FeO OH) and geothite (α-FeO OH). Other iron phosphate minerals of note include strengite ($FePO_4 . 2H_2O$) and its dimorph metastrengite (phosphosiderite). Finally, iron-bearing silicate minerals such as pyroxenes, amphiboles, micas, and olivines are usually found as allogenic detrital components in most lacustrine sediments.

I.4 AQUEOUS CHEMISTRY OF PHOSPHORUS

The stable and generally prevalent form of phosphorus in nature is some form of the oxyanion PO_4^{-3}. Its chemistry in the natural environment is influenced by precipitation and dissolution as well as complex formation, in much the same way as is iron. However, the importance of oxidation and reduction reactions in phosphorus chemistry is much less than in the case of iron, while the interactions with the biological systems are greatly increased. This increased activity in the biological sphere results in a much larger dynamic component in phosphorus distribution as compared to that of iron. Its temporal and spatial distributions are highly dependent upon biochemical influences, the extent of which are seen in the schematic representation of the P cycle in lakes, shown in fig. I.4.1.

Species in Natural Waters

Dissolved phosphorus may exist in aqueous solution as any one of a number of ionic species. These include orthophosphates, condensed phosphates, organic orthophosphates, inositol phosphates and a large number of other organic and inorganic forms. A complete list of these forms is found in table I.4.1.

TABLE I.4.1.

FORMS OF PHOSPHORUS OF POSSIBLE SIGNIFICANCE IN NATURAL WATERS

DISSOLVED FORMS	DISSOLVED SPECIES	SOLID FORMS	SOLID REPRESENTATIVE
Orthophosphate	$H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}, $FeHPO_4^+$	Mineral Phases	
Inorganic Condensed Phosphates	$H_2P_2O_7^{2-}$, $CaP_2O_7^{2-}$, $P_3O_{10}^{5-}$, $P_3O_9^{3-}$	hydroxylapatite	$Ca_{10}(OH)_2(PO_4)_6$
Organic Orthophosphates		brushite	$CaHPO_4 \cdot 2H_2O$
Sugars	Glucose-1-phosphate	carbonate fluorapatite	$(Ca)_{10}(F,OH)_2(PO_4,CO_3)_6$
Inositol phosphates	Inositol hexaphosphate	variscite, strengite	$AlPO_4 \cdot 2\,H_2O$; $FePO_4 \cdot 2\,H_2O$
Phospholipids	Glycerophosphate	wavellite	$Al_3(OH)_3(PO_4)_2$
Phosphoamides	Phosphocreatine	Mixed phases, Solid Solutions, Sorbed species, etc.	
Organic Condensed Phosphates		clay-phosphate	$Si_2O_5Al_2(OH)_4 \cdot PO_4$
		metal-hydroxide-phosphate	$Fe(OH)_x(PO_4)_{1-x/3}$
		Suspended or Insoluble Organic Phosphorus	
		bacterial cell material	Inositol hexaphosphate,
		plankton material	phospholipid, nucleic
		plant debris	acids, phosphoprotein,
		proteins	polysaccharide, phosphate

Table adapted from Stumm & Morgan (1970).

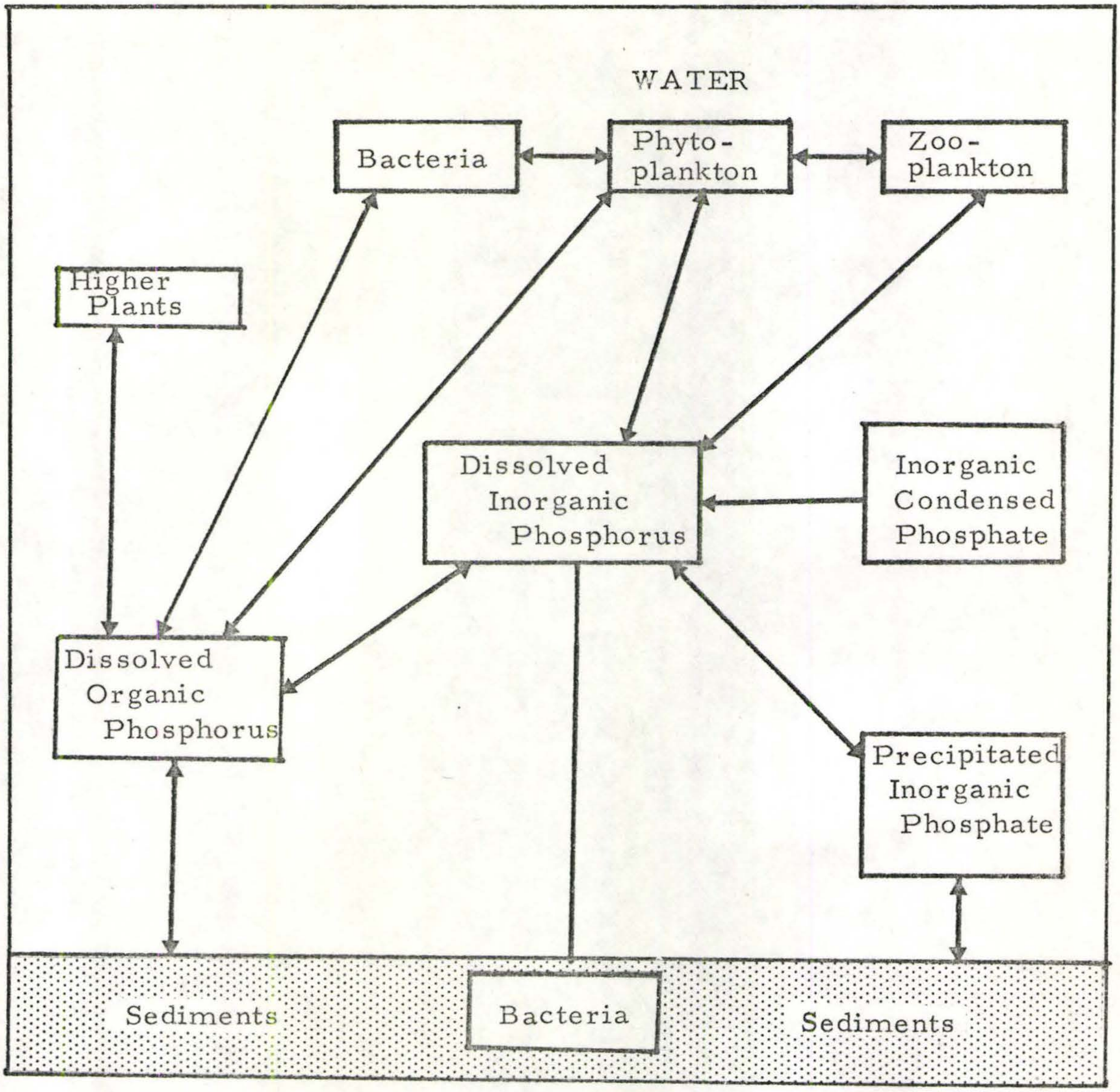


Fig. I.4.1. Phosphorus cycle in lake water, adapted from Stumm & Morgan. Schematic representation of major phosphorus locations and their interactions in a natural body of water.

Elucidation and identification of the various phosphate species present in natural waters has been a subject of considerable confusion in recent years. As Rigler (1968) pointed out, the amount of phosphorus found in any one form is often a function of the analytical technique employed in analysis, and therefore is not indicative of the true amounts in solution. If Rigler's earlier (1964) scheme is adopted, total phosphorus is divided into a suspended fraction, a dissolved-organic fraction and an inorganic fraction. Other authors, such as Hutchinson (1957), Strickland and Parsons (1966), and Minear (1972), have employed different classification schemes, but they all suffer from the same inherent difficulties mentioned above.

It is generally agreed, however, that the reactive phosphorus in the water column is present as inorganic orthophosphate, i.e. as one of the dissociation products of phosphoric acid. The relative abundances of these forms at different pH's is shown in fig. I. 4. 2.

Solubility Relations

As with the iron system, solubility relationships calculated for phosphate do not provide quantitative indications of what is actually observed. Qualitative extrapolations of phosphate equilibria are not

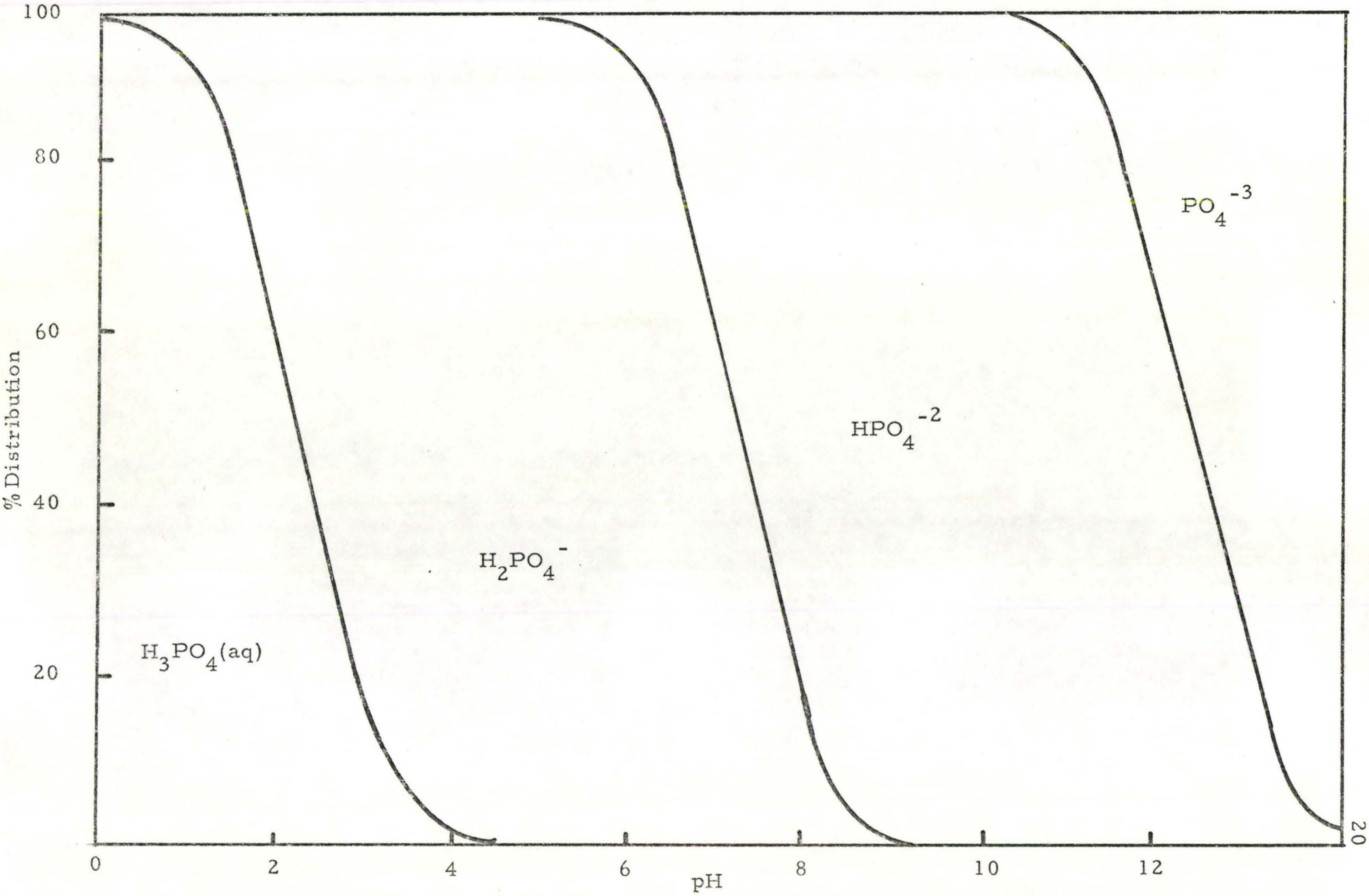


Fig. I.4.2. Percentage distribution of the dissociation products of phosphoric acid in solution as a function of pH at 25°C and 1 atmos. Adapted from Hem (1970).

always valid either, probably because of the large effect of the non-equilibrated biological systems on phosphate activity. General trends worthy of note include a lessening of phosphate solubility as pH is increased by precipitation as calcium phosphate, and removal of phosphate from solution as iron or aluminum phosphates as the pH is lowered. Both of these phenomena have been reported to occur by Stumm (1964). He has also shown that phosphate concentrations in water are greatly dependent upon the concentration of calcium in the water.

Unlike iron, phosphate solubility is greatly influenced by the formation of complexes. Phosphorus has a strong tendency to form polymeric complexes with itself and ionic complexes with many metals. As a result, much of the measured P in surface waters is very possibly complexed into one of these insoluble forms. The extent of the complexing will depend on the relative concentrations of the metal species involved, the pH and the presence of competing ligands such as sulphate, and organic molecules in the water. The metal ions most likely to affect the concentration of P in natural waters are those that are present in concentrations comparable to or less than those of phosphorus. These metal ions include iron, aluminum and manganese, and their interaction with phosphorus has been shown to be theoretically possible under conditions present in natural waters (Stumm & Morgan, 1970).

I.5 PREVIOUS WORK

Interaction with Sediments

The uptake or release of P with natural sediments has been found to depend upon the conditions of Eh, pH, calcium concentration and physical agitation processes operative in lacustrine systems. Experiments designed to study the effect of pH on inorganic phosphate removal from water by sediment have shown that phosphate removal is at a maximum between pH values of 5 and 7, Hayes, MacPherson & Sinclair (1958). Similar experiments by Stevenson (1949) have shown that P increases in overlying water with an increase in pH above 7.0. Carritt & Goodgale (1954) also suggest that "the return of phosphorus to solution ... is favoured by an increase in pH".

The effects of Eh, or more precisely, the amounts of dissolved oxygen present in the water, on phosphate availability in the aqueous phase have been investigated by Mortimer (1941, 1942). He measured large (2-3 orders of magnitude) increases in P concentration in the hypolimnetic waters of Lake Windermere. In a later (1971) paper, he concluded that the total oxygen concentration in the water drops to less than 2 mg/l, many elements including P, Fe, Mn and nitrogen are brought into solution from the sediments. At oxygen concentrations greater than this value, sediment release of nutrients is nil. Similarly, Burns & Ross (1971) demonstrated that when the sediment surface was under the influence of reducing rather than oxidizing conditions, P release to the water increased by a factor of ten.

Agitation of lake sediments has been shown to have a considerable effect on phosphate concentrations in overlying waters. Carritt & Goodgale (1954) agitated estuarine sediments and found that the failure to measure other important variables such as pH led to inconclusive results. Harter (1968), working with natural sediments in the pH range of 5-7 found that agitated sediment was capable of removing large quantities of P from solution. Shukla et al. (1971) found the same P removal capacity to be operative in Wisconsin lake sediments. Stevenson (1949) agitated ocean sediments and found variable results, P removal occurring in a pH range of 5-7 while P release was found at pH values outside this range.

Field observations support the hypothesis that large quantities of P are associated with fine-grained sediments. Kramer et al. (1970) recorded large increases in soluble orthophosphate in Western Lake Erie immediately following a stormy period of weather.

This increase in P was correlated with an increase in turbidity, and led to the conclusion that the P was associated with the fine-grained particulate matter thrown into suspension during the storm.

Exchange Mechanisms of P with Sediments

The relationship of P uptake and release by sediments has led to the conclusion that this phenomena is a result of a physico-chemical adsorption process. This exchange process between sediments and water has been investigated by Hayes & Phillips (1958) using radioactive P^{32}. It was discovered that the total amount of P available for exchange was large, and that this reaction occurred very quickly, with exchange times being of the order of a few minutes. The highly dependent nature of this exchange with respect to the prevailing Eh and pH conditions, also lends support to the idea of a physico-chemical sorption reaction being determinant in the exchange of P between sediment and water.

Einsele (1938) and Ohle (1938, 1954), both postulated adsorption as the mechanism of reaction between phosphate and ferric hydroxide gels. Mortimer (1941) attributed the large-scale release of P from lake muds to sorption processes, as did Carritt & Goodgale (1954), Harter (1968) and Williams *et al.* (1971b). Olsen (1964), showed that the exchange of P with sediment under aerobic and anaerobic conditions could be described mathematically. His equation consisted of an adsorption term and an exchange term, but the term revealing the most significant correlation with respect to P uptake under oxidizing and reducing conditions was the adsorption term.

An alternate explanation of the mechanism of phosphate exchange was provided by Swenson and his coworkers (1949). They proposed a mechanism of phosphate fixation by iron and aluminum as a chemical exchange between the hydroxyl groups of the amorphous hydroxides of these metals and the phosphate anions in solution. The reaction was represented by the equation:

$$Al(H_2O)_3\,(OH)_3 + H_2PO_4^- \rightleftharpoons Al(H_2O)_3(OH)_2\,H_2PO_4 + OH^-$$

Later work by Parks (1964) has shown that the most probable reaction of phosphate with the amorphous oxides of iron and aluminum is a physically controlled sorption reaction depending on electrostatic reactions between the solid and the phosphate ions.

Amounts and Forms of P in Sediments

Total P has often been measured in lake sediments. Thomas & Kemp (1971), provided an overall picture of P concentrations in Great Lake sediments when they measured total P in both coarse and fine sediments of Lakes Erie and Ontario. They found that the top three cm. of these sediments produced total P values of between 600 and 2500 ppm. These values are about 10^3 times higher than are normally found in the overlying water. Similar measurements have been recorded by Kuhn et al. (1970) for Lake Michigan sediments; by Williams et al. (1971a) for Lake Mendota sediments and by Edmundson et al. (1970) for Lake Washington. They all show the same 10^3 difference between sediments and water P concentrations, and all the measurements are in the range of 600 to 2500 ppm. for total P in the sediments.

Many attempts have been made to identify and characterize the forms of inorganic phosphorus in the sediments. It is found commonly in oceanic environments as apatite. Recently, however, it has been discovered that P can be found in the form of iron phosphate minerals as well. For example, Mackereth (1966) reported finding vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) in lacustrine sediments, as did Rosenqvist (1970). Shapiro and Edmundson (1971), reported the presence of the reduced iron phosphate mineral phosphoferrite in the sediments of Lake Washington, while Williams et al. (1971a, b, c) have proposed a hydrated iron oxide-orthophosphate complex to be prevalent in the sediments of Wisconsin lakes.

Other mineral phases which have been proposed as being of possible significance in lacustrine sediments include strengite

($FePO_4 . 2H_2 0$), its dimorph metastrengite and the aluminum phosphates metavariscite and wavellite. None of these phases has been reported to occur in natural sediments to date, however.

Wentz & Lee (1969), proposed a number of modes of P association in sediments. These included detrital minerals, P associated with organic minerals, carbonate P, P sorbed on particulate matter and P co-precipitated with Fe and Mn. Organically bound P is mostly present as inositol hexaphosphate or one of its derivatives. According to Hutchinson (1957), this type of P comprises up to 50% of the total organic P in sediments.

Phosphorus present in organic tissue as organically bound compounds does not remain in this form when the organism dies. Burns & Ross (1971), found that almost all organic material sedimented on the lake bottom was degraded within a few months and that 75% of the total P contained in this material was retained in the inorganic phase of the sediment. In addition, most organic phosphate is easily hydrolyzable and can therefore be changed to orthophosphate. As a result, the largest fraction of phosphate present in lake sediments can be considered as orthophosphate and therefore it is capable of being incorporated directly into the solid phase in the lake.

The distribution of phosphorus in the sediment has been considered as a possible clue to its association in the solid phase. Investigations by Williams et al. (1971c) and Shukla et al. (1971) have shown that the levels of inorganic P in the sediment are governed by the amounts of Fe in the sediments. They have shown that there is a statistically valid correlation between total P, Fe, and inorganic P. The correlation coefficients describing the relationships all exceeded 0.935. These correlations were reported for simple correlation analysis. In the same study, factor analysis also showed that Fe and inorganic P were closely related in the sediments, but that there was no significant correlation between Ca and P. Least squares analysis was applied to sediments gathered from Northern Ontario lakes by Brydges (1970) and showed a significant correlation between inorganic P and Fe. Statistical analysis applied to Lake Kinneret in Israel (Serruya, 1971) shows a good correlation between iron and inorganic P, but almost no correlation between carbonate and P. It appears that most of the phorphorus is associated with iron in freshwater systems.

I. 6 Fe - P SYSTEM

Adsorption

As indicated earlier, phosphate and iron distributions in natural waters are apparently related by the processes of adsorption. As indicated by Stumm & Morgan, the oxides and hydroxides of Fe and Al adsorb significant amounts of phosphorus. Swenson, Cole and Sieling (1949) summarized work dealing with the fixation of phosphate by iron and aluminum oxides. Their work indicated that concentrations of 9 millimoles of Fe or Al could adsorb up to 90% of the total phosphate in solutions containing 1 millimole/l of the anion. They also reported that this phenomenon was pH dependent with a pH increase above 6.5 causing a noticeable decrease in the amount of PO_4^{-3} adsorbed onto the amorphous precipitate of Fe and Al. It was also discovered that under these conditions, but at a pH of 8.5, no phosphate was adsorbed by $Fe(OH)_3$; yet 70% of the total phosphate in solution was still fixed by aluminum hydroxide at a pH of 9.0. More recent investigations into this sorption process indicate that it is a rapid phenomenon having a half-life of about ten minutes in the case of aluminum according to Kar (1958). This compares favourably with the reaction times of natural sediments for P adsorption as reported by Hayes & Phillips (1958). The removal capacity of aluminum hydroxide for phosphate in solution was found by Hsu & Rennie (1962) to be about 10^{-4} moles of P/gm of $Al(OH)_3$. Such experiments indicate that sorption of phosphate onto the surfaces of the oxides and hydroxides of iron and aluminum can account for the removal of large quantities of phosphate from aqueous solution in a short period of time.

Clay minerals are quite capable of sorbing phosphate and depsoting it on the lake bottom. Black (1950) has shown that kaolinite will adsorb up to 0.15 mgm of P/gm of clay in dilute solution of about 5 ppm. P, while Haseman and his coworkers (1951) found that more concentrated phosphate solutions of 0.1-1.0 M permitted phosphate adsorption with numerous clay minerals to a maximum value of 20 mgm PO_4^{-3} sorbed /gm of clay at a temperature of 26°C. These sorption reactions were found to follow a typical Freundlich adsorption curve, much like that found by Carritt & Goodgale (1954) for phosphate sorption by $Fe(OH)_3$.

Low & Black (1950) produced evidence to support the idea that in dilute solutions (1 ppm. total P or less) adsorption onto clay mineral surfaces resulted from chemical rather than physical interactions. A later paper by Muljadi, Posner & Quirk (1966), showed that these reactions involved the exchange of phosphate with the hydroxyl groups in the clays. Livingstone & Boykin (1965) have shown that natural sediments have an even greater tendency to sorb phosphate than the pure clay minerals, indicating that reaction with clays is not the only process in the sorption reactions of natural sediment with phosphate.

The reaction of phosphate with iron hydroxide has been shown to be extremely efficient in removing phosphate from solution. The results of Einsele (1938) and Ohle (1954) show that almost 100% of the phosphate in a relatively dilute (0.050 mg P/l) solution is removed by amorphous iron hydroxide in the pH range of 5 to 8. The iron was present in concentrations of about 0.3 g/l in these experiments.

I. 7 MINERALOGY

Mineralogical evidence is available which upholds the idea of the possible formation of iron phosphate minerals in lacustrine sediments.

The iron phosphate minerals most often referred to as being likely to form under the P, T conditions found at the earth's surface are the minerals strengite ($FePO_4, 2H_2O$), its monoclinic di morph metastrengite (phosphosiderite) ($FePO_4 . 2H_2O$), and the reduced iron phosphate vivianite ($Fe_3(PO_4)_2 . 8H_2O$). Neither strengite nor metastrengite have ever been identified in lake sediments, but their paragenetic relationships as reported by Moore (1970b),indicate that they are late-forming minerals in hydrothermally altered rocks and therefore do form under P, T conditions not too different from those encountered at the earth's surface. Using data from a large number of specimens, Moore (1970b) presented a strong argument in favour of the formation of these two highly hydrated iron phosphate minerals under conditions of low T and P.

Mackereth (1966) has suggested that vivianite nodules form under localized reducing conditions around a source of organic matter. Rosenqvist (1970) reported that this mineral formed in sediments only in regions where the Eh was measured around -390 mv and the pH around 7.4. He concluded that vivianite formed nodules in these discrete areas because of competing sulphide reactions for the iron.

Strengite and metastrengite are comprised of a three-dimensional network of PO_4^{-3} tetrahedra linked with four metal-oxygen $(H_2O)_2$ octahedra, fig. I. 7.1(a) and (b). The tilt between the PO_4^{-3} groups and the $Fe-O-H_2O$ octahedra provides the only difference between the orthorhombic strengite and the monoclinic metastrengite structures. This difference is illustrated in fig. I. 7.1. The vivianite structure, consisting of parallel slabs perpendicular to the b-axis of the insular octahedral singlets and doublets joined by PO_4^{-3} tetrahedra, is somewhat more closed than either the strengite or metastrengite structures and hence is stable under higher P, T conditions.

All of these minerals have been synthesized under relatively mild chemical conditions. Chang & Jackson (1957), first prepared a mixture of strengite and metastrengite by digesting ferric phosphate precipitates in solutions containing chloride and sodium as extraneous ions. Lehrecke (1947) digested an amorphous ferric phosphate precipitate, which formed when solutions of ferric chloride

Fig. I. 7. 1(a) Structure of strengite looking up the a-axis. One octahedron, the H_2O oxygen atoms (Oh) and the PO_4^{-3} tetrahedral environment about the octahedron are shown. (After Moore, 1966).

Fig. I. 7. 1(b) Metastrengite crystal structure viewed on the a-c plane. The elements of the unit cell are shown. In addition, the environment of the tetrahedra and the H_2O groups about the octahedron are shown. The H_2O oxygens are specified, the Fe atoms are represented by circles. (After Moore, 1966).

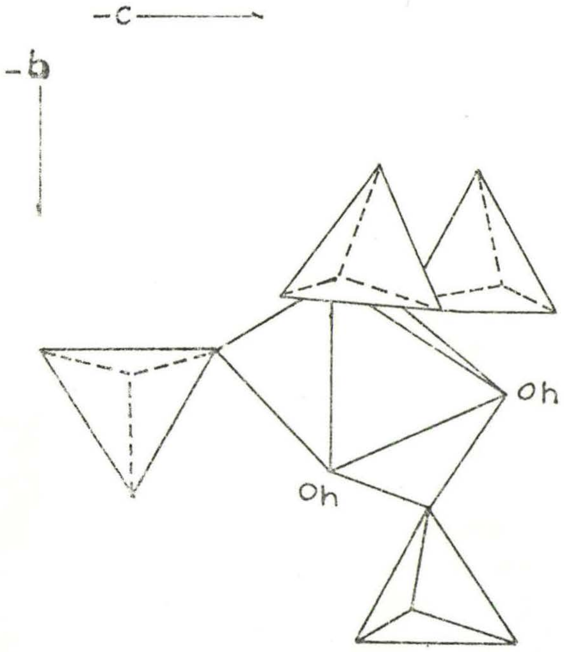


Fig. I.7.1(a)

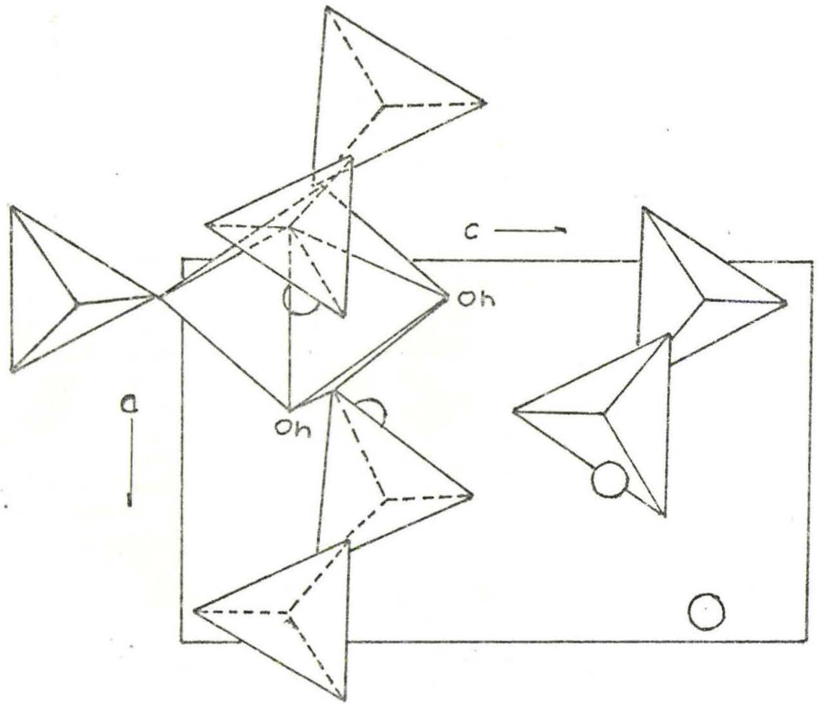


Fig. I.7.1(b)

and ammonium phosphate were mixed. Cate *et al.* (1959) crystallized strengite by mild (100°C) hydrothermal treatment of a suspension of amorphous ferric phosphate prepared by dissolving carbonyl iron powder in orthophosphoric acid. Nriagu (1972a) prepared the mineral by using Cate's method except that he substituted iron powder for the iron carbonyl. Nriagu (1972b) has also prepared vivianite synthetically.

II. 1 PLAN OF STUDY

In the previous chapter it was shown that the iron and phosphorus systems in lakes and other naturally occurring bodies of water are not easily characterized. The large number of physical-chemical variables are greatly modified by a host of biological variables, and neither of these systems is as yet adequately defined.

From the information available, however, we know that a large proportion of the phosphorus in lakes and rivers is in an insoluble form and becomes available to the dynamic system only through the slow processes of dissolution of insoluble mineral and organic species. The important missing link in the understanding of the phosphorus cycle in natural waters is to be found in the qualitative and quantitative definitions of the processes of fixation of this element and in the reverse processes of dissolution of these solid phases, whether these processes involved by physical or biological in origin.

This study attempts to isolate variables related to the inorganic fixation process between iron and phosphorus and to observe the effect of these variables on the inorganic precipitation mechanism of phosphorus with hydrated iron oxide, and on the subsequent process of mineralization of the complex.

Two series of experiments were undertaken:

(1) The first series of experiments was designed to determine the effects of iron concentration, Eh, pH, and agitation on the sorption process.

(2) The second series of experiments was designed to investigate the effects of pH, phosphate concentration and phosphate form, on the mineralization of the sorbed complex.

II. 2 METHODS

Each experiment was designed to investigate the effect of one variable on the sorption process, or on the mineralization process. All experiments were conducted using the simplest chemical systems so that extraneous chemical species would not interfere with the processes being investigated. As a result of this requirement, all experiments were conducted in distilled-deionized water and the only chemicals added to the solution were those required to produce the necessary chemical conditions of the experiments. In addition, the master variables of Eh, pH, temperature and ionic concentrations of the elements involved were set at values approximating as closely as possible those encountered in the natural environment.

Except where specified, the pH of all solutions was in the range of 6 to 8, and the Eh was of the order of 370 mv. The mineralization experiments were carried out at a temperature of 90°C, in order to increase kinetic rates to a value which would produce the reaction end-products in a time short enough to be useful in this study. The rest of the experiments were run at room temperature, which varied between 20-23°C.

Total phosphate was determined using the molybdenum blue method with extraction in isobutanol as given by Sutherland et al. (1966). In addition, all glassware was washed thoroughly in sulphuric acid and allowed to soak in 1.0 N acid for two days prior to analysis in order to remove any phosphate sorbed onto the glass surface.

Iron was measured spectrophotometrically as its ortho-phenanthroline complex, as given by Shapiro & Brannock (1962).

Mineralogical data were obtained using a Philips X-ray generator, employing a Guinier camera mount for most of the work. When pure crystalline phases were seen, a conventional diffraction pattern was obtained so that comparison could be made with the A.S.T.M. listing for the mineral. Optical observations were performed using a binocular microscope.

Standard Solutions

Two standard iron solutions were employed in the research. The first was prepared by dissolution of 1.2523 g of pure iron powder in 100 ml of 12N HCl and subsequent dilution with D.D. water to a final volume of 500 ml. 10.00 ml of this stock solution were pipetted into a 1000 ml volumetric flask and diulted to volume with D.D. water. The resultant iron concentration of this solution was 25 mg Fe^{+3}/l. It was labelled iron standard A.

The second solution was prepared by dissolving 1.4600 g of $FeCl_3 \cdot 6\ H_2O$ in 995 ml of D. D. H_2O. 5 ml of 12N HCl were added to keep the pH low. The final total iron concentration of this solution was 206 mg Fe^{+3}/l and the solution is referred to as iron standard B.

Three phosphate standards were prepared. The first was made by dissolving 0.01569 g of KH_2PO_4 in 1000.0 ml of D. D. H_2O. This solution contained about 12 mg PO_4^{-3}/l and is hereafter referred to as phosphate standard P-1. A second phosphate standard was prepared by diluting 40.0 ml of phosphate standard P-1 to 2000 ml with D. D. H_2O. This working standard contained about 240 µg PO_4^{-3}/l and is referred to as phosphate standard P-2. A third phosphate standard was prepared by dissolving 0.00160 g of KH_2PO_4 in 1000 ml of D. D. H_2O and diluting 150 ml of this solution to 1000 ml. This final standard contained 170 µg PO_4^{-3}/l and is referred to as phosphate standard P-3.

II. 3 EXPERIMENT NO. 1

Effect of Total Concentration on Phosphate Removal

Introduction

This experiment was undertaken to determine the effect of the concentration of iron on the removal of phosphate from aqueous solution. In this context, various concentrations of Fe and P in acid medium were mixed and the pH raised to 7. Total iron concentrations of 0.25 mg/l and 2.5 mg/l were used to approximate the average iron concentrations in freshwater lakes. The 250 mg/l of iron experiment gives an upper limit for phosphate removal by "iron hydroxide". The phosphate concentration employed was 240 μg PO_4^{-3}/l, a reasonable approximation of the total phosphate concentrations found in hypolimnetic lake waters.

Experimental

Three beakers, each containing a total volume of 100 ml. of solution were prepared in the following manner. In beaker A, 2.00 ml of phosphate standard P-1 were pipetted into and mixed thoroughly with 98.0 ml of Fe standard B, producing 100.0 ml. of a solution containing 250 mg Fe/l, and 240 μg PO_4^{-3}/l, having a pH of 2.1. Beaker B contained 10.00 ml. of iron standard B mixed thoroughly with 90.0 ml of phosphate standard P-2, to produce a solution of 2.5 mg Fe/l, and 216 μg PO_4^{-3}/l, having a pH of 2.08. The solution in Beaker C was prepared by mixing 1.00 ml of iron standard B with 99.0 ml of phosphate standard P-2, producing a solution which contained 0.25 mg Fe/l, 240 μg PO_4^{-3}/l and having a pH of 2.8.

To each beaker was added an amount of 0.1N NaOH necessary to raise the pH to about 7 (4-5 drops). The solutions were stirred for about 5 minutes after the addition of the NaOH. Upon standing at room temperature for three hours, the top 20 ml of solution were decanted and analyzed for phosphate. Subsequent batches of three flasks were prepared in an identical manner, except that the phosphate analyses were carried out after time periods of 15 hrs., 24 hrs., and 48 hrs. An additional run was made with the beaker B solution to determine a value for this solution after six hours of settling.

TABLE II. 3. 1 SUMMARY OF EXPERIMENT NO. 1

Beaker	Fe (mg/l)	P (µg/l)	Initial pH	Approximate pH*	% P REMAINING IN SOLUTION AFTER:				
					3 hrs.	6 hrs.	15 hrs.	24 hrs.	48 hrs.
A	250	240	2.1	7.1	10.0	-	2.0	0.0	0.0
B	2.5	216	2.1	7.2	91.5	66.7	37.4	30.0	3.8
C	0.25	240	3.1	7.2	100.0	-	100.0	100.0	100.0

* The pH values are not exact. Since any pH value between 6.6 and 7.5 would produce the desired precipitate, an exact measurement of the pH in these solutions was not required. The pH value in each set of beakers was always within 0.2 pH units of the values reported above.

Results

A plot of phosphate concentration in the top 40 ml (28 mm) of solution vs. settling time is shown in fig. II. 3. 1. The three different iron concentrations of 250 mg/l, 2.5 mg/l and 0.25 mg/l produce three quite different curves on the graph.

A straight line plot was obtained from the results with beaker A. This indicated that there was no decrease in the total phosphate concentration in the top 28 mm of the liquid during the 48 hr. period of the experiment. No visible change was detected either, the solution remaining clear and colorless throughout the duration of the experiment.

The two curves constructed from the measurements with beakers B and C both showed significant decreases in the total phosphate concentration with time. Beaker C did show a much faster rate of phosphate removal than beaker B. No measurable phosphate remained in beaker C after 24 hrs., while phosphate was still detectable in beaker B after 48 hrs. of settling. Visually, beaker B turned a light orange-yellow colour when the pH was raised, while beaker C became opaque, with the formation of many small (0.1-0.5 mm in diameter) particles of a deep red-brown gelatinous precipitate. Beaker C cleared fairly quickly, with most of this red-brown material having accumulated on the bottom after three hours. A considerable volume of yellow-orange material persisted in suspension for upwards of 10 hrs. in beaker C, but most of this had disappeared after 15 hrs. and the solution was completely clear and colourless after 24 hrs.

Beaker B became clear and colourless after 24 hrs., but no precipitate was seen on the bottom of the beaker until 48 hrs. had passed, at which time a very small amount of the yellow-orange gelatinous material was visible.

The above description of activity is indicative of the phosphate being present entirely as a sorbed species on the surface of the amorphous iron oxide particles. Such an association would explain the observed correlation between the presence or absence of the iron oxide precipitate and the accompanying absence or presence of phosphate in the top 28 mm of solution. If the phosphate is present only as a sorbed species on the surface of a solid, it should exhibit settling characteristics analogous to those of a solid material.

This prediction is verified by the results obtained from beakers B and C. For beaker B, a comparison of the rate of phosphate removal from solution with that of settling velocity vs. particle size is shown in fig. II. 3. 2. For the standard curve, the graph was constructed using Stoke's Law and a density of 3.5 for the iron oxide particles. From fig. II. 3. 2, it can be seen that the rate of phosphate

Fig. II. 3. 1. Effect of total iron concentration on removal of phosphate from solution by $Fe(OH)_3$. Initial concentrations were: ΣP = 216-240 μg PO_4^{-3}/l; ΣFe 0.25 mg/l, 2.5 mg/l and 250 mg/l.

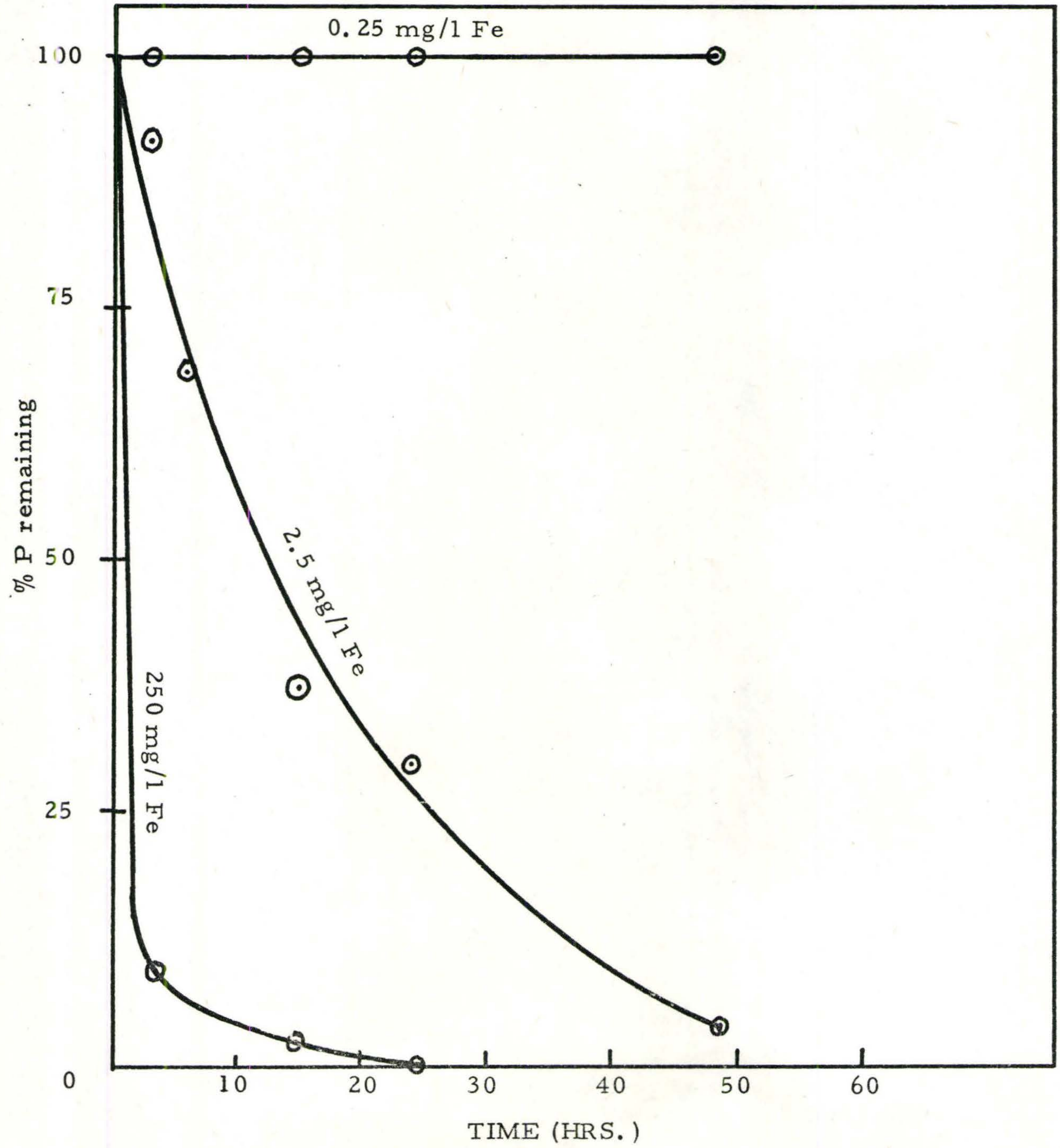
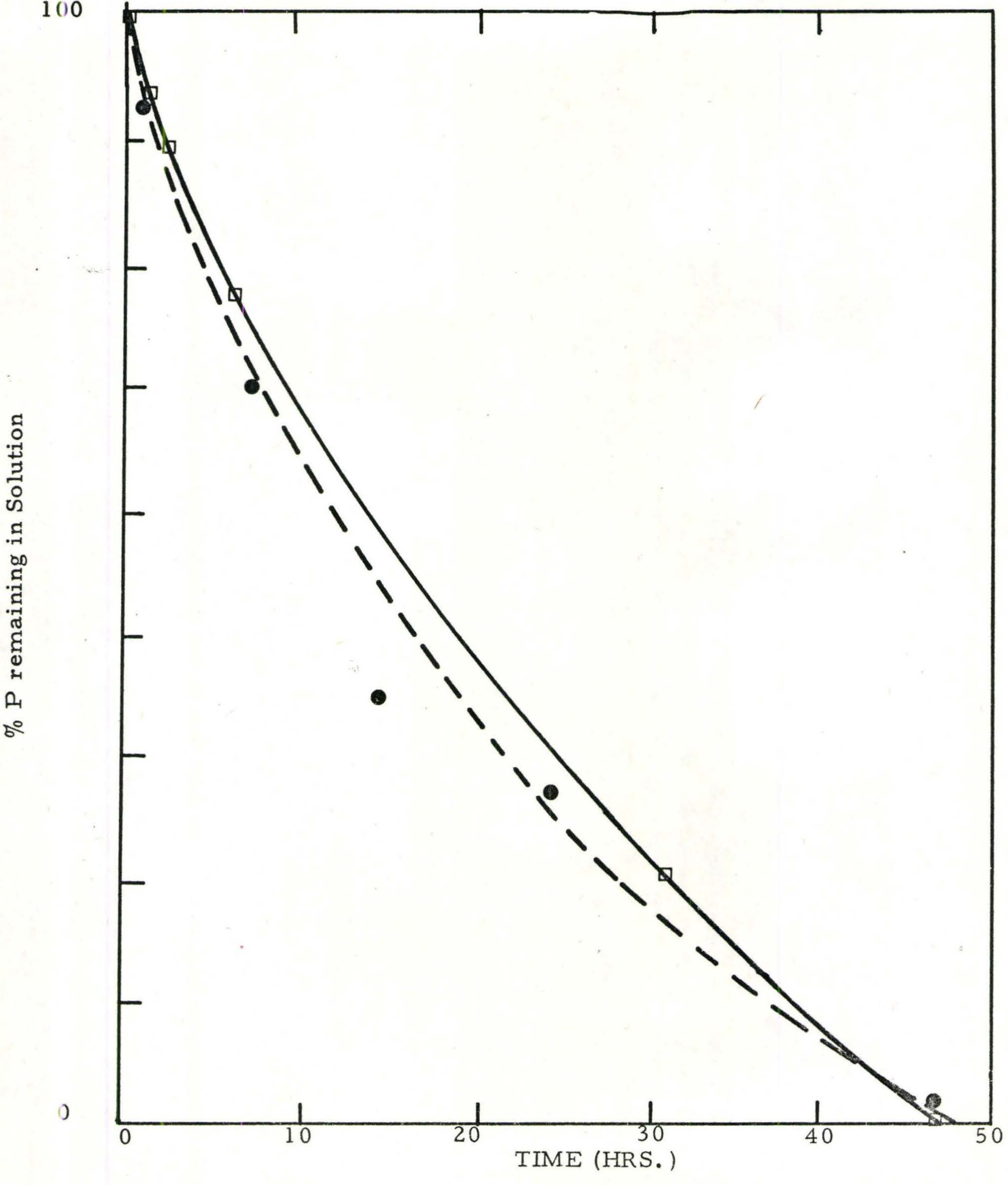


Fig. II. 3. 2. Comparison of Experimentally Determined Phosphate Removal vs. Time (---) with Stoke's Law Plot of V vs. r^2 (—).



V vs. R^2 curve was constructed using P = 3.65, d = 2.8 cm.; 3.1×10^{-5} cm $< r < 6.9 \times 10^{-4}$ cm. % P vs. time curve was constructed from data in Table II. 3. 1.

removal from the top 28 mm of solution coincides almost exactly with the theoretical removal rate of iron oxide particles of radius between $3.1\text{x}10^{-5}$ cm and $6.9\ 10^{-4}$ cm by gravity settling.

Further support for phosphate removal by gravity settling is provided by the particles of beaker C. If the experimentally determined settling time of 3 hrs., the measured settling distance of 2.8 cm and a particle density of 3.5 are employed, Stoke's Law predicts a radius of 0.4 mm as being the necessary particle size to fit these conditions. The measured particle sizes in beaker C are between 0.1 and 0.5 mm, well in agreement with the mathematical predictions.

No amorphous precipitate formed in beaker A and thus the phosphate remained in solution as a dissolved ionic species.

II.4 EXPERIMENT NO. 2

The Effect of Agitation on the Release of Phosphate From $Fe(OH)_3$

Introduction

Large phosphate concentrations have been measured in surface waters immediately following periods of stormy weather, Kramer *et al.* (1969). He felt that the phosphate was associated with particulate matter, but confirmation of this idea has never been provided. Therefore, this experiment was undertaken to determine whether the phosphate associated with particulate matter could be measured when it was in suspension, or alternatively, whether the phosphate measured in suspension was physically separated from the solid. In this experiment, two groups of flasks were agitated for various lengths of time, then the solid was removed, either by gravity settling or by centrifuging. Total phosphate was measured before and after the removal of the solid.

Experimental

Two groups of three 1000 ml flasks were utilized in this experiment. Group A was used in a 24-hour experiment and group B in a 72-hour experiment. All six flasks contained 225 ml of phosphate standard P-2 mixed thoroughly with 25 ml of iron standard A. The pH in each was adjusted to about seven with 0.1 N NaOH.

The first three flasks were shaken mechanically for 24 hrs., then the uppermost 25 mls were removed and analyzed for phosphate. These flasks were then sealed and allowed to settle for two days after which time the next 40 mls were removed and analyzed for phosphate. The second group of three flasks was shaken for 72 hrs., after which time 25 ml aliquots were decanted and analyzed for phosphate. The remainder of group B was centrifuged at 2740 r.p.m. for 15 minutes, after which time the aqueous portion was analyzed for phosphate.

Agitation

From the results presented in Table II.4.1, agitation does not seem to be significant in releasing particulate-bound phosphate to the aqueous phase. The large concentrations of phosphate obtained while the particulate matter is in suspension and the complete lack of any phosphate in solution after settling are indicative of its being present only as a sorbed ionic species on the surface of the amorphous iron oxide precipitate. Even more convincing evidence of this association is provided by the results of the section involving centrifuging, which show that the reaction between phosphate and the solid is complete in a few minutes and involves all of the measurable phosphate in solution.

TABLE II.4.1 SUMMARY OF EXPERIMENT NUMBER 2

	Total Fe mg/l	Total P as PO_4^{-3} μg/l	pH	Eh	% P in Solution
GROUP A					
24 hr. dispersed					
FLASK 1	2.5	216	7.5	310	100
FLASK 2	2.5	216	7.5	280	98
FLASK 3	2.5	216	7.5	280	100
SETTLED					
FLASK 1	2.5	216	6.9	335	0
FLASK 2	2.5	216	7.5	310	0
FLASK 3	2.5	216	6.2	320	0
GROUP B					
72 hr. dispersed					
FLASK 4	2.5	216	7.5	310	100
FLASK 5	2.5	216	7.5	307	99
FLASK 6	2.5	216	7.5	317	99
AFTER CENTRIFUGING					
FLASK 4	2.5	216	7.5	310	0
FLASK 5	2.5	216	7.5	307	0

Comparison of Table II.4.1 with the results of Experiment No. I show a striking similarity. If the solid particles are permitted to settle slowly as in Experiment No. I, or are centrifuged and settle many times faster as in this experiment, the amount of orthophosphate removed from the solution is the same. In both cases, the removal of phosphate by particulate $Fe(OH)_3$ is essentially complete.

This experiment also indicated that phosphate is securely bound to the solid. No amount of physical agitation was capable of releasing the phosphate from the solid, even though this agitation was applied continuously for up to 72 hours. Finally, it was confirmed that the technique employed to measure total phosphate in solution included the phosphate bound to particulate iron hydroxide as well as that present solely as a dissolved ionic species.

II. 5 EXPERIMENT NO. 3

Effect of pH on Phosphate Removal by Amorphous Iron Oxide

Introduction

In this experiment, identical concentrations of Fe and P were mixed and brought up to various pH to ascertain the percentage of P removed. It has been shown (Einsele, 1938; Ohle, 1954) that the uptake of phosphate by amorphous iron oxide is highly pH dependent. Results have indicated that this uptake is greatest at pH values between 5.5 and 7.0 (Macpherson, 1958; Stephenson, 1949), but no one has attempted these experiments with the reactant concentration levels being those found in hypolimnetic lake waters. In addition, these experiments were designed to provide some insight into the reaction times involved in the uptake mechanism, and thereby identify the reaction mechanism.

Experimental

The experiments in this section were divided into two sections: the first measured the pH dependency, the second provided some indication of the reactions involved in this dependency. Sixteen identical solutions were prepared by mixing together 10.00 mls of iron standard (B) with 90.0 mls of phosphate standard (C) in 250 ml beakers. The pH's of the first set of seven beakers, Table II.5.1, were raised individually to values of 3.0, 4.0, 5.0, ... 10.0, by the addition of up to seven drops of 1.0N NaOH. Once a steady pH value was obtained, the beakers were removed and allowed to settle for 24 hours. After this time, 25 ml samples were withdrawn from the top and analyzed for phosphate. The pH never exceeded the final value in this first series of experiments.

A similar addition of 1.0N NaOH was made to each of the second set of seven beakers, Table II.5.1, except that this time the pH's were first raised to a value between 7 and 8 for a few seconds before being quickly adjusted and then stabilized at final values of 3.0, 4.0, 5.0, ... 10.0. At the final pH value, the solutions were stirred for twenty minutes before being allowed to settle for 24 hrs. After this time, 25 ml portions were decanted off and analyzed for phosphate.

The two final beakers, Table II.5.1, had their pH raised to a value of 7 or 8 for about ten seconds, then had it lowered to about 1.5 with dilute HCl and finally raised carefully to a final value of 4.0 and 5.0 respectively.The solutions were immediately transferred to centrifuge tubes and were spun at 2680 r.p.m. for 15 minutes, after which time 50 ml samples were withdrawn for a phosphate analysis.

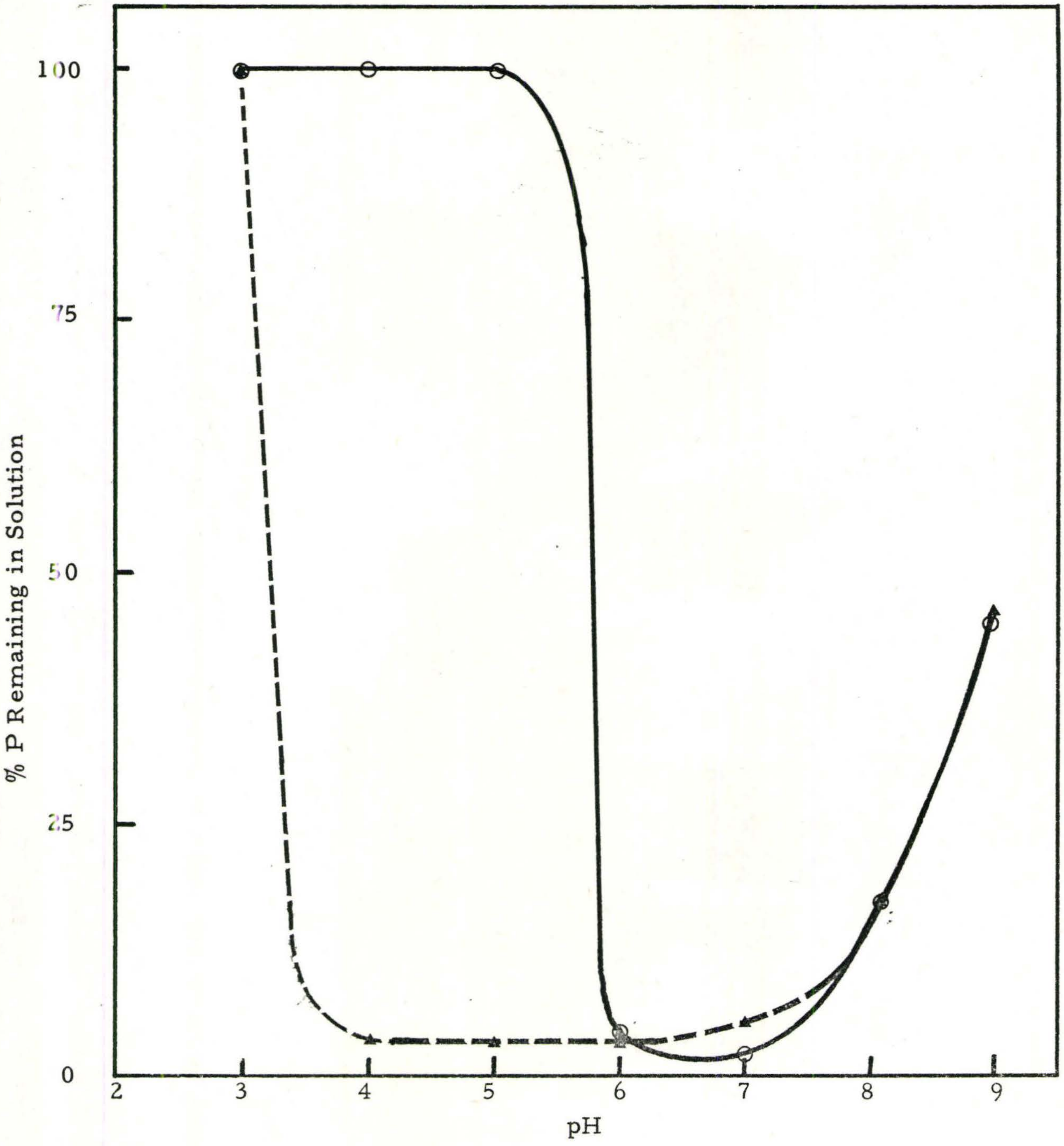
TABLE II.5.1 SUMMARY OF EXPERIMENT NO. 3

Beaker No.	Initial pH	Final pH	Total Fe (mg/l)	Total P (μg/l)	Eh (mv)	% P Remaining
A	2.17	2.99	2.5	216	362	100.0
B	2.13	4.05	2.5	216	357	100.0
C	2.20	4.97	2.5	216	368	100.0
D	2.04	5.97	2.5	216	366	4.4
E	2.07	6.99	2.5	216	373	2.2
F	2.11	7.99	2.5	216	367	14.0
G	2.15	9.02	2.5	216	374	46.5
A	2.1-2.2	3.00	2.5	216	360-370	100.0
B	"	3.99	2.5	216	"	4.2
C	"	5.01	2.5	216	"	3.8
D	"	6.03	2.5	216	"	4.4
E	"	6.98	2.5	216	"	4.5
F	"	8.00	2.5	216	"	14.0
G	"	9.01	2.5	216	"	47.0
C-1	2.11	4.01	2.5	216	365	1.5
C-2	2.09	5.00	2.5	216	361	1.0

Fig. II. 5. 1. % P Remaining in Solution vs. pH

— With no precipitate below pH 6

-- With precipitate below pH 6



Σ Initial Fe = 25 mg/l.

Σ Initial PO_4^{-3} = 170 µg/l.

Effect of presence of amorphous iron oxide on phosphate in solution. Note that when precipitate is present, sorption of phosphate onto the solid is occurring down to pH 4, whereas solid does not form initially until a pH of almost 6 is reached.

Results

Fig. II.5.1 shows the percentage of phosphate remaining in solution vs. the pH for both sets of beakers measuring the pH dependency of the reaction. Between the pH values of 5.5 and 8.5, (solid line) almost all the phosphate is removed from solution by the amorphous precipitate. Outside this range, it is seen that phosphate remains in appreciable quantities in the solution. Once again, the appearance/disappearance of the precipitate can be correlated with the absence/presence of phosphate in solution. Also in accord with the previous experiment, a pH of 5.5, coupled with the Eh conditions and the total iron concentrations employed, produced the necessary conditions for "iron hydroxide" stability, as predicted by theoretical calculations.

The results from the second set of beakers are also shown in fig. II.5.1. The percentage phosphate remaining in solution vs. the pH curve (dotted line) for this set of beakers is quite different from the previous curve (solid line) in the pH region between 3 and 6. The much larger removal of phosphate in this pH range (dotted line) is easily explained by the presence of the iron hydroxide precipitate in the pH range of 4 to 6. Once again, the presence of the precipitate was a sufficient condition to remove over 95% of the phosphate from solution.

Obviously, the presence of particulate iron hydroxide is all that is needed to efficiently scavenge phosphate from aqueous solution in the pH region between 4 and 7.5. Since no release of phosphate from the solid is ever observed, it must be concluded that once formed, the phosphate-iron hydroxide complex is irreversibly bound in this pH range. In addition, both curves show much greater removal of phosphate by the precipitate when the solution pH is below 8 rather than above it, even though the solid is equally abundant in all cases. Obviously, the mechanism of phosphate uptake onto the amorphous iron oxide precipitate does not proceed very efficiently above a pH of 8.

The results tabulated at the bottom of Table II.5.1 (C-1, C-2) provide some indication of the reaction time necessary for the uptake of orthophosphate on amorphous iron oxide. Since the amount of phosphate measured in the solution after centrifuging is not greater than the amount remaining in solution after gravity settling of the precipitate, the uptake of orthophosphate by the solid must have been completed in the 90 second timespan between the first formation of the solid and the 30 seconds after the commencement of centrifuging. If this reaction were not completed in this time, any unreacted phosphate would have remained in the upper levels of the solution, and a significant increase in phosphate in the solution would have been observed. The speed and efficiency of the anion-solid reaction points to its being of a physical rather than of a chemical nature.

II. 6 EXPERIMENT NO. 4

Effect of Eh on Phosphate Removal by $Fe(OH)_3$

Introduction

The release of phosphate from the sediments has been found to depend on the amount of oxygen present in the mud. Mortimer (1941) and Burns & Ross (1971) have both presented convincing arguments based on field measurements to support this hypothesis. It is the purpose of this experiment to determine whether the release of phosphate from amorphous iron oxide is consistent with the measured values of Eh requisite for phosphate release from natural sediments. These experiments consisted of mixing Fe and P, forming a precipitate, and bubbling N_2 gas through to scavenge oxygen.

Experimental

Three flasks, each containing 250 ml of solution prepared by mixing 225 ml of phosphate standard P-2 with 25 ml of iron standard A, were employed in this experiment. The pH of each was raised to about seven by the addition of up to 4 drops of 0. 1N NaOH and then the flasks were left covered and undisturbed for 24 hrs. After this time, the top 20 mls were decanted and analyzed for phosphate. The Eh and pH of the remaining solution were measured. The flasks were made airtight with 2-holed rubber stoppers and pure nitrogen was bubbled through them for 24 hrs, at which time the stoppers were removed and the solutions were immediately measured for Eh. A 40.0 ml aliquot was decanted and analyzed for phosphate. Finally, the remainder of the solution was measured for its pH.

Another group of three flasks underwent identical treatment, but this time an additional 48 hours of contact with the air was permitted after the nitrogen bubbling. Throughout the length of this contact, the stoppers were in place and only two 4 mm passageways were open for diffusion of air. The Eh and pH of the solution were then measured and a 40 ml sample was decanted and analyzed for phosphate.

Results

Table II.6.1 is a summary of the results of this experiment. It can be seen that the Eh of the water has a significant effect on the amount of phosphate present in solution. As in the previous experiments, the presence of phosphate in the water was correlated with the absence of the orange-brown precipitate in the flasks. It was also found that when the Eh was lowered to between 192 and 200 mv from the original

TABLE II. 6. 1 SUMMARY OF EXPERIMENT NO. 4

	TOTAL Fe (mg/l)	TOTAL PO_4^{-3} (µg/l)	Eh	pH	PO_4^{-3} REMAINING IN WATER (%)
BATCH A	2.5	216	390	6.3	0
	2.5	216	390	6.3	0
	2.5	216	370	6.9	0
	2.5	216	192	8.6	95
	2.5	216	195	8.7	97
	2.5	216	190	9.0	96
BATCH B	2.5	216	270	7.5	0
	2.5	216	272	7.3	0
	2.5	216	273	7.1	0
	2.5	216	192	7.4	98
	2.5	216	198	7.7	97
	2.5	216	200	7.5	97
	2.5	216	257	7.1	0
	2.5	216	254	7.5	0
	2.5	216	249	7.8	0

370 mv, the precipitate had disappeared even though the pH was maintained between 7.1 and 7.8. The Eh was raised again, this time to a value between 249 and 257 mv. It was then found that the precipitate had reappeared. If a plot of Eh vs. pO_2 is constructed, it is found that the equivalent D.O. concentrate for disappearance and reappearance of precipitate fall between 0.18 and 1.2mg/l O_2. The dissolved oxygen values measured by Mortimer (1972) as being necessary for release of phosphate and iron into the water from lacustrine sediments range between 1-2 mg/l O_2. Comparison of this range of D.O. values with those presented in this study (0.18 - 1/2 mg/l O_2) for a similar dissolution process operative in laboratory systems provides excellent agreement between laboratory and field studies.

The disappearance of the precipitate is a result of the reduction of Fe^{+3} to Fe^{+2}, and the concurrent large increase in solubility. This results in the dissolution of the ferric-phosphate complex and the mobilization of the associated ions into the aqueous phase. Upon the return of oxidizing conditions, the complex reforms, and the ions are once again incorporated into a solid phase and removed from solution. The sudden and dramatic increases and decreases in phosphate observed in the experiment are indicative of this phenomenon.

II. 7 EXPERIMENT NO. 5

Preparation of Pure Mineralogical Phases

Introduction

These experiments were carried out to define the mineralogical significance of the observed association of iron and phosphate in lake sediments (Serruya, 1971; Williams et al., 1971 a, b, c). Therefore, it is important to know if the insoluble mineral phases can form from the P-iron oxide utilized in experiments 1 through 4.

Since the phases to be worked with would not be well crystallized, it was necessary to use a rather sensitive X-ray technique in order to identify them. As a result, the Guinier camera attachment designed for this purpose was employed in the research. In order to calibrate this camera, pure phases of the minerals strengite and metastrengite were required.

Experimental

Pure samples of strengite and metastrengite were crystallized from colloidal suspensions of precipitated iron phosphate by digestion of this material at 90°C for periods of up to two weeks.

The colloidal suspensions were prepared by the method of Cate et al. (1959) using the modifications of Nriagu (1972a). After digestion, a 0.1 g sample was analyzed for Fe and PO_4^{-3}, by first dissolving the sample in 10.0 ml of 10 N HCl, diluting it to 100 ml with D. D. H_20 and measuring for total iron and total phosphate colorimetrically. Another 0.10 g sample was analyzed for its total water content employing D. T. A. analysis.

After analysis, another sample from the same digest was taken and X-rayed conventionally and its diffraction trace was indexed and compared to the A. S. T. M. listing for these minerals. This same powder was then X-rayed using the Guinier camera and the pattern obtained was employed as a comparative standard in future investigations.

Results

The crystalline mineralogical phases were identified by a number of tests. First, chemical analysis showed that the synthetic iron phosphate mineral was of the chemical composition to be expected for strengite and metastrengite. A comparison of the theoretical composition and that obtained in this study is shown in the following table:

	Fe	PO_4	H_2O
Found	28.9%	52.9%	18.1%
Theoretical	29.10	52.50	18.34

These results are within the errors of the determinations because of the methods employed and the dilutions required to prepare the sample. In addition, the stoichiometric formula indicates a molar ratio of 1:1 for iron and phosphate. Using the above figures, a molar ratio of 1.01:1.00 is found for P:Fe.

Comparison of the experimentally determined d spacings and intensities of this mineral phase with A.S.T.M. file cards (Table II. 7.1) for strengite and metastrengite showed that these minerals had been synthesized. However, the monoclinic metastrengite was never pure and was always minor relative to orthorhombic strengite.

Viewed under a binocular microscope, the pure mineral phases were seen to have crystallized as clear colourless spheres averaging about 50 μ in diameter. Seen with the naked eye, the material looked like the light pink described by Nriagu (1972a). If allowed to crystallize for three weeks instead of the normal 10 days, the spheres were larger, averaging about 70 μ in diameter, and they were often found agglomerated into chains ranging from 2 to upwards of 10 spheres in length.

TABLE II. 7. 1

METASTRENGITE				STRENGITE			
Theor.		Measured		Theor.		Measured	
I	dA^{o}	I	dA^{o}	I	dA^{o}	I	dA^{o}
40	6.48			80	5.50	80	5.50
60	4.90	50	4.93	60	4.95	60	4.95
80	4.69	80	4.68	100	4.38	100	4.38
80	4.37	75	4.38	60	3.98	50	3.99
40	4.12	75	3.62	40	3.72		
80	3.61	100	2.80	80	3.11	60	3.11
100	2.78	40	2.54	60	3.00	50	3.00
60	2.57	40	2.010	60	2.95	50	2.96
20	2.342			80	2.54	60	2.54
20	2.258			40	2.445	40	2.446
20	2.122			40	2.180		
60	2.010			40	2.101		
				40	2.001		

Comparison of Experimentally determined d-spacings and intensities with those of A.S.T.M. listings for the minerals strengite and metastrengite.

II.8 EXPERIMENT NO. 6

Diagenetic Changes of the P-Iron Oxide Precipitate

Introduction

It was necessary to discover whether or not the crystalline iron phosphate mineral could form at near-neutral pH conditions. Thermodynamic calculations by Nriagu (1972b) indicated that strengite formation is possible under these pH conditions, but previous authors (Cate *et al.*, 1959; Williams *et al.*, 1971c) had suggested that strengite formation under these conditions is not very likely.

Experimental

This experiment was designed to follow the course of crystallization of the pure iron phosphate colloid at neutral conditions. About 1.0 g of this amorphous material was placed in a glass bottle which was filled with 250 ml of D. D. water having an Eh of about 350 mv. The pH was carefully raised to 6.5 and the material was digested for periods up to 22 days. After each 24 - hour period, a sample of the white colloid was removed and X-rayed using the Guinier camera. A separate sample was permitted to digest, uninterrupted, for the full 10 day period before it too was removed and X-rayed.

The rest of the amorphous white colloid was placed in two 1000 ml containers and stored at room temperature for a year in order to discover whether crystallization could occur at this temperature in this length of time.

Results

Table II.8.2 produces a comparison of the experimentally determined d-spacings and intensities with those of the pure mineral species. The table indicates that at a pH of about seven, digestion of the colloidal iron phosphate will produce a crystalline material which is a composite of both the pure minerals. Much more of the orthorhombic strengite is present than the monoclinic metastrengite (phosphosiderite) as is indicated by the lack of prominent phosphosiderite peaks. The broadening of some of the other peaks, noticeably those at 2.54°A, 2.80°A, and 2.44°A, is also an indication of the presence of two phases rather than one.

The absence of the very distinctive peak for metastrengite at 6.51°A is explainable if the cell dimensions of the minerals are considered. Coupled with the small quantities of phosphosiderite present, the similarity of the cell parameters of the two structures (Table II.8.1) could produce insufficiently large resolution to be de-

TABLE II. 8. 1 CELL PARAMETERS OF STRENGITE and METASTRENGITE

DATA OBTAINED FROM MOORE (1966)

Name	Formula	Density	Space Group	a	b	c	β
Strengite	$FePO_4.2H_2 0$	2.87	Pbca	10.05	9.80	8.73	-
Metastrengite	$FePO_4.2H_2 0$	2.76	$P2_{1/n}$	5.32	9.75	8.65	$90^\circ 36'$

TABLE II. 8. 2. Comparison of d-Spacings measured for crystalline product digested at pH 7 with A. S. T. M. d-spacings listed for strengite and metastrengite.

pH 7 DIGEST dA°	STRENGITE dA°	METASTRENGITE dA°
5.50	5.50	6.48
4.90-4.95	4.95	4.90
4.69		4.69
4.37-4.38	4.38	4.37
4.12		4.12
3.99	3.98	
3.62		3.61
3.11	3.11	
3.00	3.00	
2.96	2.95	
2.76-2.80		2.78
2.54-2.57	2.54	2.57
2.43-2.45	2.445	
2.101	2.101	
2.010		2.010
2.001	2.001	

tectable with the diffraction trace when the phases are mixed.

Once it had been established that a crystalline phase did form at a pH of about seven, it was decided to investigate the crystallization process of this mineral. Figure II. 8. 1 showsthe changes in the crystalline structure of the colloidal precipitate in daily intervals. It can be seen that after two days, the digestion process had suddenly produced a crystalline structure which did not change, even after prolonged digestion periods of up to three weeks. Therefore, it can be concluded that the crystalline material described above and heretofore referred to as material S, is a stable crystalline phase. From a comparison of the Guinier photograph of the 3-week run and the newly crystallized material (fig. II. 8. 2), it can be seen that no structural changes have taken place in the mineral. The only observable difference is in the intensity of the reflections. The 3-week digest produces a much higher intensity from peak reflections, and weaker reflections are visible as well. However, the major reflections in all three photographs are identical, indicating identical crystal structures in all three solids.

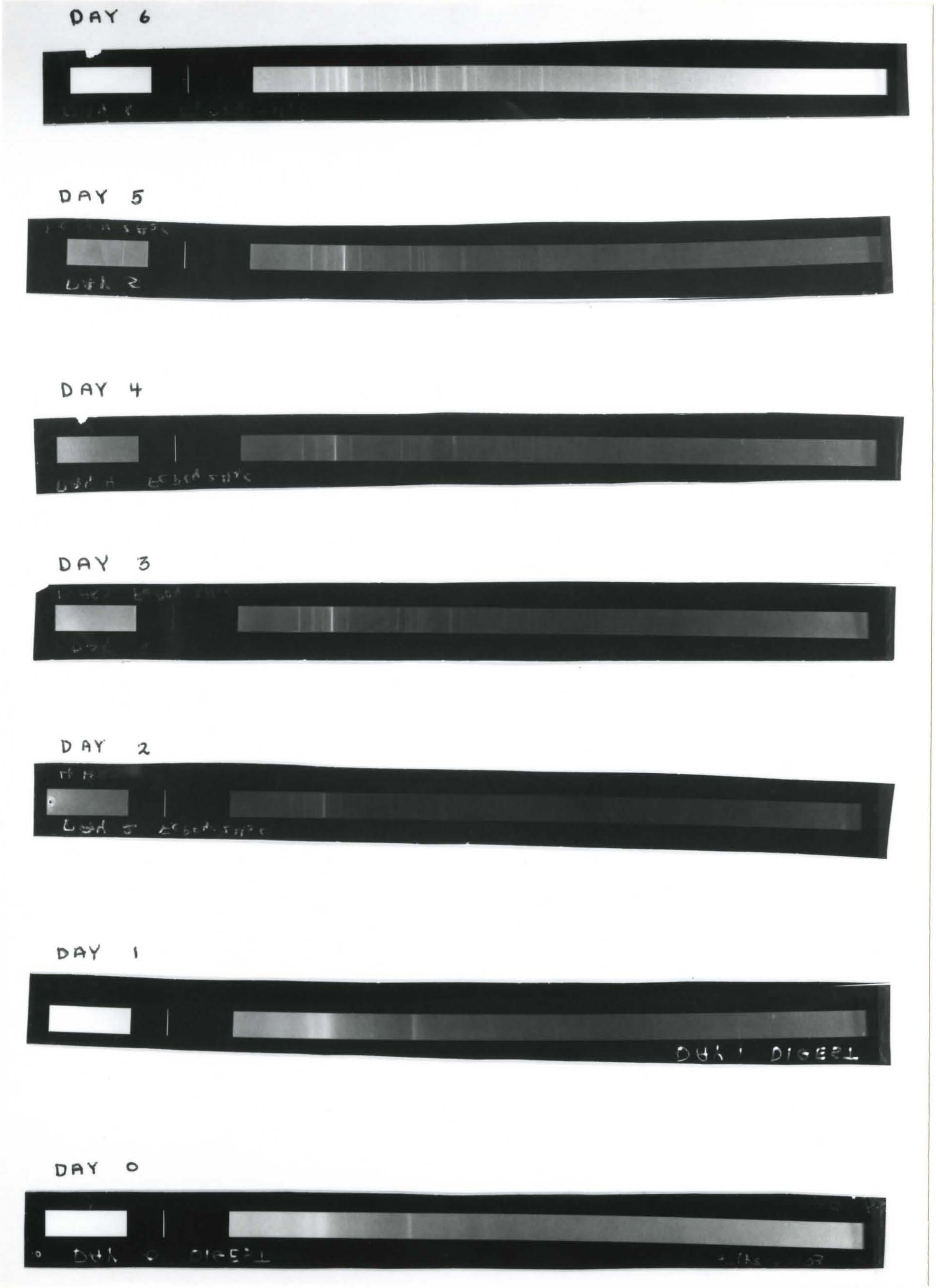
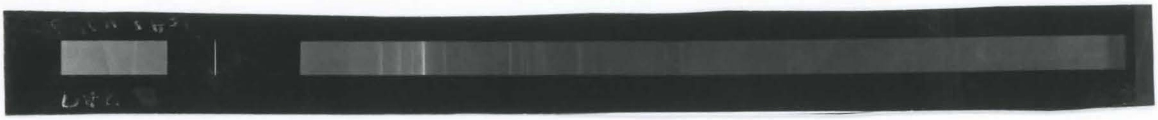


Fig. II.8.1. The course of crystallization of the ferric phosphate precipitate from Experiment No. 6. The sharp line on the left side of each film is a reference line. Major identifying reflections at 2 θ values of 20.20° (strongest), 16.05°, 17.90°, 19.75° and 22.25°.

DAY 2



PRODUCT S

3 WEEK DIGEST

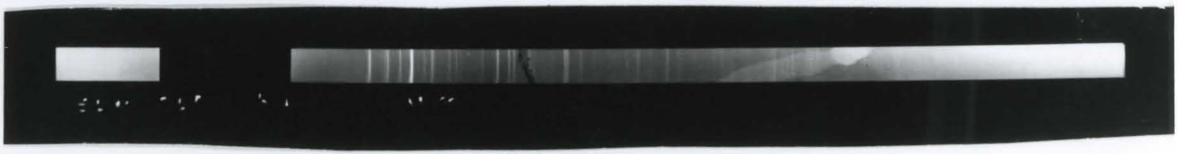


Fig. II. 8. 2. Comparison of Guinier photographs of product S with the pure ferric phosphate precipitate after (i) a 2-day and (ii) a 3-week digestion period. Relative intensities and 2 θ values of the reflections in all three photographs are identical.

II. 9 EXPERIMENT NO. 7

Effect of Phosphate Addition on $Fe(OH)_3$ Diagenesis

Introduction

Strengite or metastrengite possibly forms from amorphous iron oxide if the phosphate concentration is sufficiently high (Nriagu, 1972b). Therefore, a synthesis of one or more of these minerals from the "iron hydroxide" under neutral pH and oxidizing Eh conditions was attempted. In addition, the concentrations of iron and phosphate were about the same order of magnitude as lacustrine sediments. In this experiment, a predetermined amount of amorphous iron oxide was digested with various concentrations of HPO_4^{-2} in aqueous solution for periods of up to 2 weeks. The HPO_4^{-2} was added as either a solid or as a dissolved species.

Experimental

About 0.4 g of amorphous iron oxide was placed in a glass bottle and then 250 ml of D. D. water was added. The final pH of this mixture was adjusted with NaOH to be between 6.0 and 7.3 in all experiments. The bottle was then placed in a constant temperature bath and its contents digested at 90°C for a period of eight days.

TABLE II.9.1 EXPERIMENT NO. 7 - EXPERIMENTAL CONDITIONS

FLASK NO.	Final pH	Eh	KH_2PO_4 as Solid	KH_2PO_4 as Liquid	Final PO_4 Concentration moles/l.
1	6.8	367	Yes	No	3.9×10^{-5}
2	7.3	372	Yes	No	3.9×10^{-4}
3	6.5	368	No	Yes	3.9×10^{-5}
4	6.9	363	No	Yes	3.9×10^{-4}
5	7.0	359	No	Yes	3.9×10^{-3}

TABLE II.9.2 EXPERIMENT NO. 7 - DIGESTION PRODUCTS

Digestion Product	Digestion Time	Solid KH_2PO_4 Added	Dissolved KH_2PO_4 Added	Final P Conc. (m/l)
Amorphous	2 weeks	x		3.9×10^{-5}
? Product S?	2 weeks	x		3.9×10^{-4}
Amorphous	2 weeks		x	3.9×10^{-5}
Amorphous	2 weeks		x	3.9×10^{-4}
Product S	2 weeks		x	3.9×10^{-3}

Five separate bottles were utilized, and phosphate was added as either a dissolved or solid form (Table II. 9. 1). The dissolved phosphate was added as a 5 ml solution of KH_2PO_4, the solid as crystals of this salt. The concentrations of added phosphate ranged from 0. 01 g to 0. 1 g (. 04 g /l - . 4 g /l).

After digestion, the solid material was filtered on a Millipore 0. 45 μ filter and then it was dried, examined microscopically and X-rayed with the Guinier camera. Before being X-rayed, the precipitates were photographed.

Results

The results of this experiment are listed in Table II. 9. 1. It is seen that only one set of conditions produced an identifiable crystalline product. The phosphate concentration which produced this product was 0. 1g PO_4^{-3}/250 ml solution or 3.9×10^{-3} mPO_4^{-3}/l. The crystalline product was identified as being identical to product S of experiment 6. A comparison of the Guinier photograph of product S and this product is found in fig. II. 9. 1.

A product of one other set of conditions gave a Guinier photograph whose identifiable reflections indicated a similarity to product S. Unfortunately, the lines on the photograph are so faint that they cannot be positively identified. The photograph is shown in fig. II. 9. 1. None of the other sets of conditions gave products which could be positively identified utilizing X-ray diffraction.

Colour photographs of the products do show other evidence of the presence of the minerals strengite and/or metastrengite. Fig. II. 9. 2 is a photograph of the precipitate from flask 5, the material which gave the identifiable X-ray plates. It can be seen that much of the brown amorphous iron oxide is ringed with spherical white crystals. These are the crystals of product S. In addition, this photograph shows a few discreet areas of accumulations of white spheres which are very reminiscent of pure products S, seen in Fig. II. 9. 3. The position and formation of the white crystalline material on the outside of the "iron hydroxide" is indicative of a replacement growth of the crystals from the $Fe(OH)_3$ rather than direct precipitation of the crystalline ferric phosphate mineral from solution.

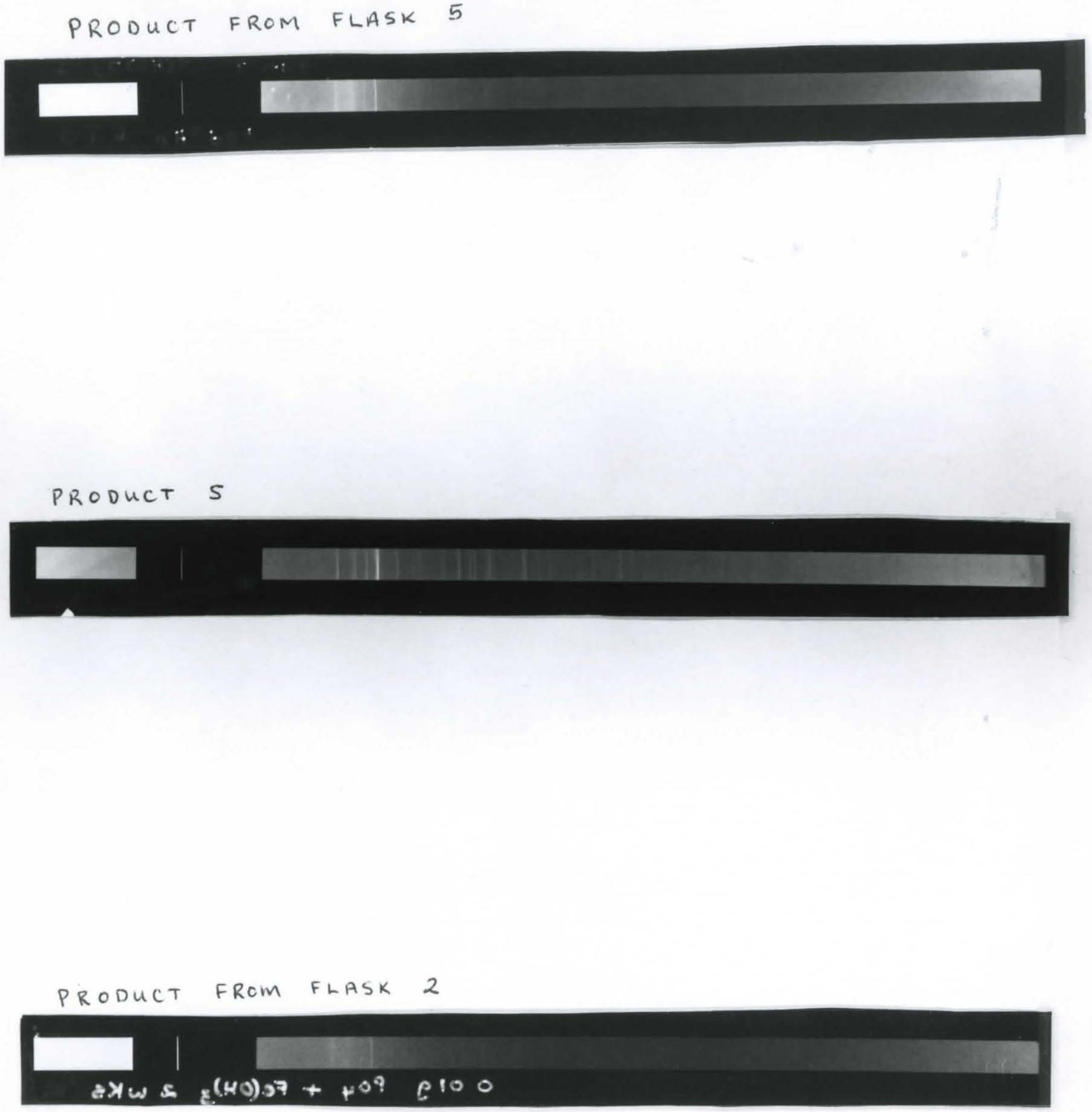


Fig. II. 9. 1. Comparison of Guinier photograph of product S with two products of Experiment No. 7. Product from flask 5 exhibited enough reflections to prove it was the same crystalline material as product S. Product from flask 2 gave less intense reflections, and no positive identification of this product was possible. The reflections obtained, however, do look similar to those of product S and those from the product in flask 5.

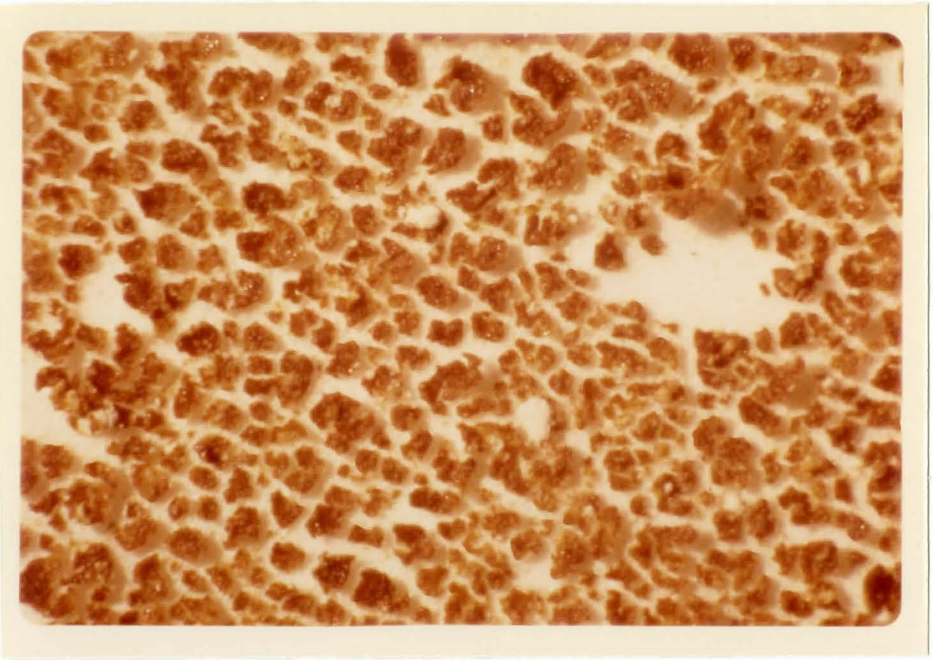


Fig. II.9.2. Precipitate from flask 5. Lighter, spherical areas on surface of red-brown material is product S, as are the two distinct white regions near the centre of the photograph. 1" = 0.535 mm.

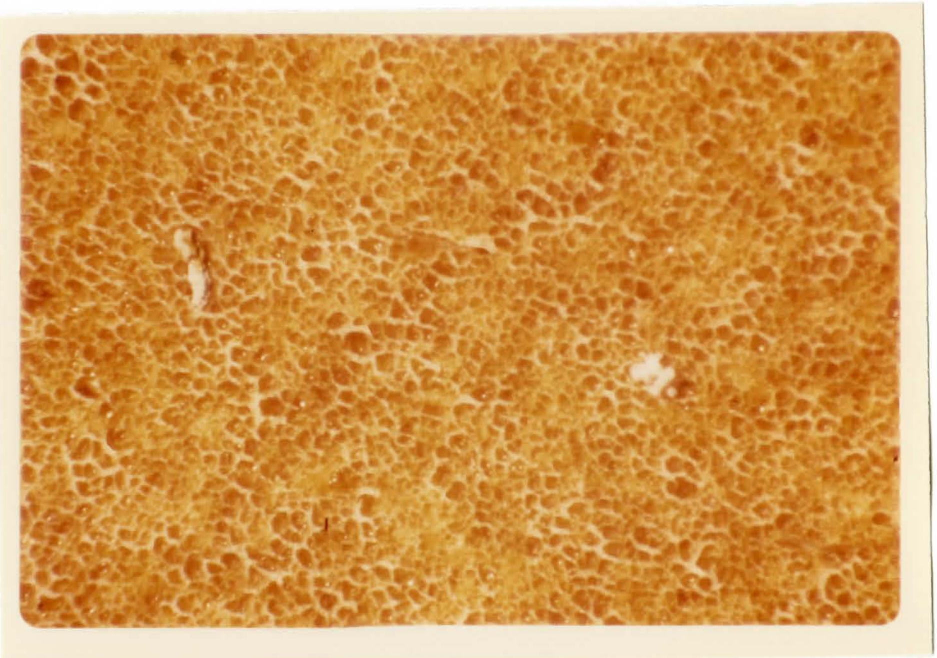


Fig. II.9.3. Precipitate from flask 4. Two discreet areas of product S accumulation. Typical of low phosphate precipitates in this study. 1" = 0.535 mm.

Figure II. 9. 3 shows the effect of a smaller concentration of dissolved phosphate on the formation of the crystalline iron phosphate mineral. No crystalline phase could be positively identified from this precipitate, but the discreet areas of accumulation of the white crystalline material are very similar to those found at higher phosphate concentrations and seen in fig. II. 9. 2.

The solid potassium phosphate salt also produced crystalline material which is very similar in appearance to the pure product S. Comparison of fig. II. 9. 4 and II. 9. 5 verify this observation. Additional support comes from the faint lines observed on the Guinier photograph of this precipitate. Proof of the formation of this product from the KH_2PO_4 crystals is provided in the last set of colour photographs, figs. II. 9. 7 and II. 9. 6. The formation of white spheres is seen on the edge of the KH_2PO_4 crystal in fig. II. 9. 6. Also, the formation of a lighter area of yellow-orange colour as opposed to the darker red-brown colour of the "iron hydroxide" is seen around the edges of this crystal and is immediately obvious in fig. II. 9. 7. Here the potassium phosphate crystal has been removed and the area which was underneath the crystal is visible.

This experiment confirms that the crystalline ferric phosphate minerals strengite and/or metastrengite are able to form from a precipitated amorphous iron oxide-phosphate complex; provided that the

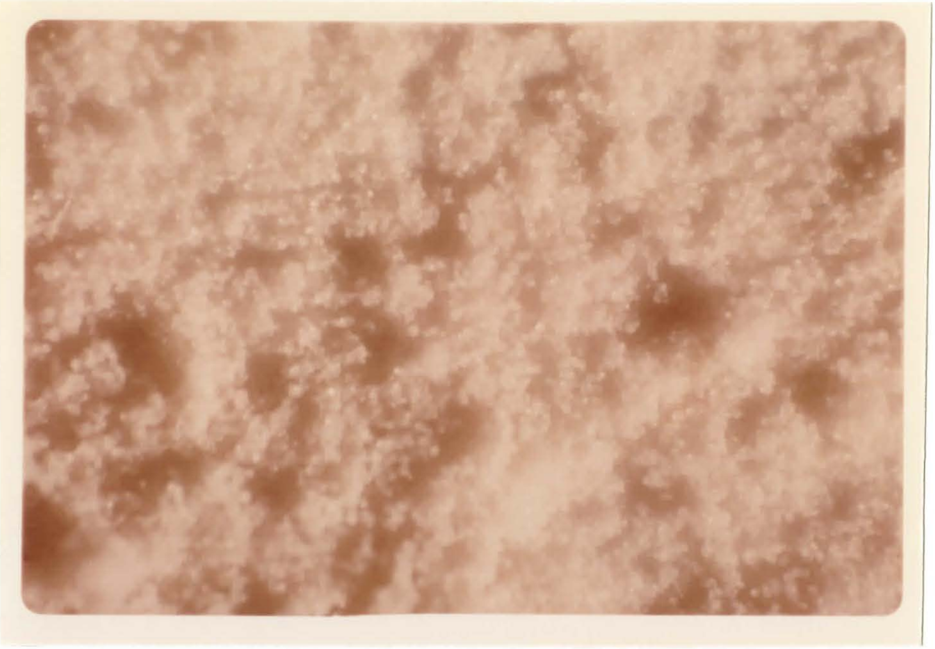


Fig. II.9.4. Pure product S. Crystals are spherical and somewhat transparent. They appear white when a number are present together. 1" = 0.535 mm.

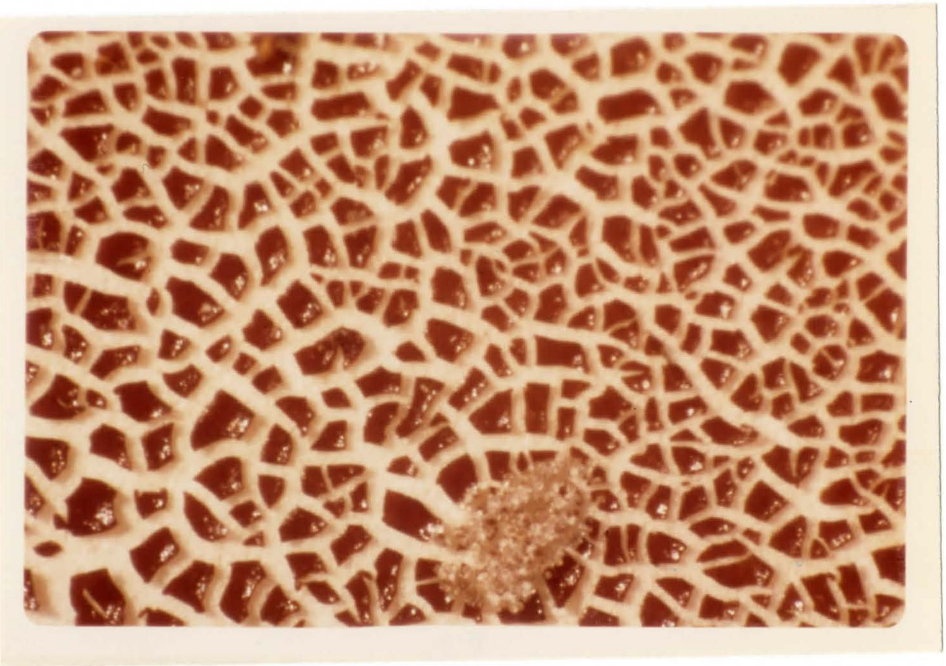


Fig. II.9.5. Precipitate from flask 1. Notice how much darker $Fe(OH)_3$ is compared to that in Fig. II.9.3. Obvious formation of spherical crystals at bottom. Compare to product S, above. 1" = 0.535 mm.

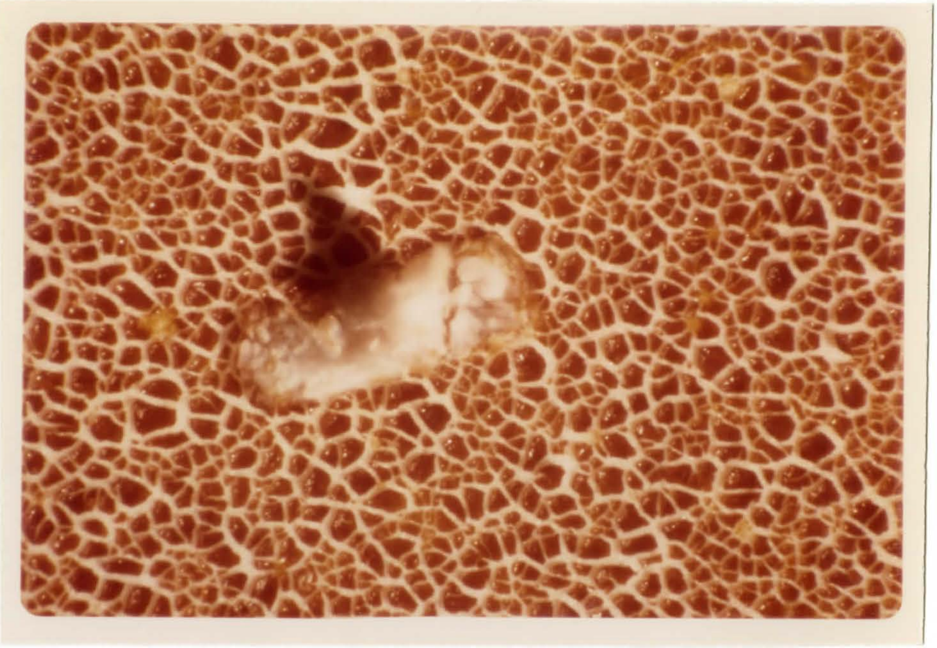


Fig. II.9.6. Precipitate from flask 2. Undissolved crystal of KH_2PO_4 has discoloured $Fe(OH)_3$ around crystal edges. Spherical particles are forming on the left side of the crystal. 1" = 0.535 mm.

Fig. II.9.7. Precipitate from flask 1. KH_2PO_4 crystal has been removed and underside is seen to be an area much lighter in colour than the surrounding precipitate. Definite proof of reaction between PO_4^{-3} and solid $Fe(OH)_3$. 1" = 0.535 mm.

total phosphate concentration is greater than 10^{-4} M at a pH of 7. It also provides speculative evidence that under neutral pH conditions and lower total phosphate concentrations, migration of the anion takes place and discreet nodules of these minerals are capable of forming (see fig. II. 9. 3). Finally, localized areas of high phosphate concentration are seen to be capable of providing sites for the formation of these minerals (figs. II. 9. 5 and II. 9. 6).

III. 1 THE MODEL

Introduction

The interaction of iron and phosphorus in dilute aqueous systems has been shown to be dependent largely upon the Eh, pH, and activities of HPO_4^{-2} and Fe. The results presented in the previous section indicate that the initial reaction of phosphate with amorphous iron oxide is not at equilibrium and also that this reaction is a physical rather than a chemical exchange reaction. Furthermore, it has been shown that once this reaction is completed and the solid complex is formed, marked changes in the chemical environment are required to dissolve the complex. In addition, it has been demonstrated that this complex is capable of diagenetic alteration to an insoluble crystalline form. The significance of the results will be discussed with reference to the variables investigated, but prior to this discussion, a model consistent with the observed phenomena is presented.

The Form of the Model

For the purposes of this model, it is postulated that the amorphous iron oxide exists in dilute aqueous solution as a hydrated polymeric complex having the stoichiometry $Fe_n(OH)_{3n}.3nH_2O$, where n is much greater than 1. This arrangement was formulated on the basis of known facts about the form of hydrated ferric oxide in dilute aqueous solutions.

Corsini (1972) has indicated that three OH^- ions are associated with each ferric ion under the chemical conditions present in such solutions. Cotton and Wilkinson (1970) stated that ferric hydroxide is best described as hydrous ferric oxide, $Fe_2O_3.nH_2O$. They also confirmed that iron (III) is octahedrally co-ordinated in most of its complexes. Combination of these three ideas lead to the stoichiometric arrangement $Fe_n(OH)_{3n}.3nH_2O$ described above.

A series of three reactions is proposed to describe the alteration of this structureless complex to a crystalline ferric phosphate mineral. The three reactions are listed below:

i) A chemisorption reaction. This reaction involves electrostatic forces, having its basis in the charge difference between the positively charged solid and the negatively charged phosphate anion. It also involves the interaction of the amorphous iron oxide complex with a specific anion, in this case, orthophosphate. Consequently, it is a very rapid and extremely efficient reaction. It has the form:

$$Fe_n(OH)_{3n}.3nH_2O + HPO_4^{-2} = (Fe_n(OH)_{3n}.3nH_2O.HPO_4)^{2-}$$

ii) A chemical exchange reaction. This reaction is a simple chemical exchange of orthophosphate for hydroxyl on the particle surface. As such, it is governed by chemical kinetics and by equilibrium processes. It has the form:

$$(Fe_n(OH)_{3n} \cdot 3nH_2O. HPO_4)^{2-} = Fe(OH)(HPO_4) \cdot 2\ H_2O + 2OH^- +$$

$$Fe_{n-1}(OH)_{n-1} \cdot 3(n-1)H_2O$$

iii) A dehydration reaction. It involves not only a loss of water, but also a deactivation of the solid into a more orderly and structured form than its previously amorphous state. The time for this reaction to reach completion in experiment number 7 (90°C) was about two weeks. A first order extrapolation of this rate of reaction necessitates a reaction time for the dehydration and structural ordering to take place at ambient temperatures of 0-20°C of between 20 and 100 years. This reaction has the form:

$$Fe(OH). (HPO_4). 2\ H_2O = FePO_4. 2\ H_2O + H_2O.$$

III. 2 DISCUSSION

The reaction between particulate iron hydroxide and orthophosphate embodies two significant characteristics: first, their initial reaction is not in chemical equilibrium; and second, the behaviour of the solid product of this reaction is as inert particulate material rather than as a chemically active colloidal solid.

Evidence for the non-equilibrium condition of the reaction is provided by fig. II. 5. 1. In this diagram, the solid is seen to exist outside its pH conditions of formation. Such behaviour is characteristic of a solid not in equilibrium with its surroundings, i. e. this solid is in metastable equilibrium with its surroundings. It should not be expected, therefore, to conform to the solubility relations predicted for it by equilibrium concepts. An example of this anomalous behaviour is described below.

Using the most recently determined K_{sp} for crystalline $FePO_4 \cdot 2H_2O$($10^{-34.88}$) as determined by Nriagu (1972a) and the experimental conditions of this study, ($\Sigma Fe = 4.5 \times 10^{-5}$M and $\Sigma PO_4 = 2.3 \times 10^{-6}$M) it is found that any pH value greater than 1.5 should be sufficient to induce precipitation of the solid. However, in none of the experiments conducted during this study was precipitation of any solid initiated until a pH of at least 5 had been reached. The solid most likely to precipitate at this pH under the Eh and ionic concentrations used in this study was amorphous iron oxide, represented as $Fe(OH)_3$. This, in fact, was the only solid initially identifiable in the solution.

An equilibrium interpretation of the reaction also provides no explanation for the obvious increase in phosphate activity observed in experiment No. 3 at pH's greater than 8. If equilibrium solubility calculations are employed, any pH above a value of 1.5 should result in the greater stability of the solid and therefore in a resultant low and constant value of total phosphate and total iron in the solution. From the experiments it is seen that phosphate activity in solution remains low and constant throughout the pH range of 4 to 8. Outside this range, a considerable increase in phosphate activity is observed, a phenomenon irreconcilable with an equilibrium interpretation of the precipitation-dissolution reaction taking place.

The model presented in this study circumvents these difficulties by providing a dynamic non-equilibrated chemisorption reaction as being primarily responsible for the uptake of phosphate on the amorphous iron oxide. This type of reaction and its component parts (reaction (i), section III.1) not only explain the observed phenomena, but are also consistent with the chemical solubility relations described above for $Fe(OH)_3$, and with the physical properties exhibited by this solid phase. One such physical property can be demonstrated by reference to the work of Parks (1969). He measured the surface charge of water-saturated iron hydroxide as being positive for all pH values less than 8.5. Therefore, the uptake of phosphate onto these particles should be highly efficient and proceed at a constant rate for all pH values up to 8.5. Once this pH value is approached, the decreasingly positive surface charge should not be as efficient in adsorbing phosphate and the amount of the uptake should be reduced. This theoretically predicted behaviour for amorphous iron oxide coincides exactly with the experimentally observed behaviour of the solid in experiment No. 3.

The particulate nature of the reaction product is demonstrated by its behaviour after the reaction between the phosphate and the iron hydroxide has been completed. Under all pH conditions the precipitate settled out of solution, and at none of the pH values investigated was a colloidal suspension produced. The settling of these particles took place in a manner almost identical with that expected for inert spherical particles (fig. II.3.2). Results of the gravity settling experiments indicated that the solid size was equivalent to spherical particles with an average radius of 1×10^{-4} cm, while the centrifuging experiment confirmed that the phosphate was bound completely with the solid particles of the precipitate.

Other properties of the phosphate-iron hydroxide complex were examined. It was found that the complex would dissolve if the total dissolved oxygen concentration (reflected in the Eh) of the water was decreased to a level of between 0.8 and 1.2 mg/l O_2. It was also found that the solid could reform when the Eh of the solution was raised sufficiently. This behaviour is indicative of a redox reaction, whereby the iron is present either as Fe^{+2} or Fe^{+3}, depending on the concentration of dissolved oxygen in the water. When the iron is reduced, the solid particles are dissolved and the component ions of this material are released into the aqueous phase. This accounts for the large increases in phosphate concentration when the Eh was sufficiently low ($\approx$ 200 mv).

Subsequently, the phosphate-iron-hydroxide complex was found to be capable of diagenetic alteration to a crystalline mineralogical phase. From the X-ray data obtained for this mineral, it was identified as a mixture of the ferric phosphate minerals strengite and metastrengite. The positive identification of the phase confirms the theoretical predictions of Nriagu (1972b) regarding the stability of strengite. He defined the conditions for stability of this mineral in the near-neutral pH range as being high Eh and a total orthophosphate concentration of greater than 10^{-3}M. The experimental results of this study

(Tables II. 9.1 and II. 9. 2) confirm the validity of this hypothesis.

There is evidence also that strengite is capable of forming at lower total orthophosphate concentrations. Figs. II. 9. 3 and II. 9. 5 show that areas of material which resemble strengite in appearance do form in discreet locations, even at total orthophosphate conditions much less than those predicted. This would indicate that the phosphate is highly mobile and is capable of producing local concentrations great enough to exceed the phosphate concentrations necessary for strengite and/or metastrengite stability at these sites. It would therefore be possible for nodules of these minerals to form in localized regions.

The failure of the room temperature digestion of the precipitate to produce an identifiable crystalline material cannot be explained by reference to the stability diagrams of Nriagu (1972b). Evidently, there is some kinetic inhibition of the reaction at room temperature, but this inhibition is overcome if the temperature of the digestion medium is maintained in the region of 90°C for a few days. Unfortunately, the results of this study do not permit an accurate estimation of the time of crystallization at 0°C, if such a crystallization process does occur at this temperature. As mentioned earlier, if it is assumed that crystallization does take place at 0°C, the reaction time can be estimated as being of the order of 100 years.

On the basis of the model and the experimental evidence discussed above, it may be stated that the initial reaction of phosphate with iron hydroxide cannot be correlated with the equilibrium concepts of solubility regarding strengite or metastrengite in dilute aqueous environments. Furthermore, the formation of one or both of these solid phases is not likely in natural lacustrine sediments. Their formation in certain environments is, however, possible.

III. 3 APPLICATION TO NATURAL WATER SYSTEMS

The results of this study have widespread application to the lentic environment. A better understanding of natural water systems id facilitated by knowledge of the non-equilibrium precipitation-dissolution relationship between iron and phosphate in these systems.

Since the stability of the iron-phosphate complex is largely dependent upon variations in Eh and pH, factors which change the pH of water to values greater than 8 or less than 5; or decrease the Eh to less than 200 mv will affect the reactions of Fe^{+3} with orthophosphate to a marked degree. The extent to which external factors are able to affect the variables Eh and pH can be demonstrated for a shallow monomictic lake. In this case, the formation of the phosphate-amorphous iron oxide complex may be dependent upon the trophic state of the lake. In an area of eutrophic conditions, and therefore of high photosynthetic activity, the pH of the surface waters may reach values of 9 to 10. Any Fe-oxide bound phosphate in suspension in this water would become immediately available to the biosphere, as it would be instantly released from the complex in a usable form upon contact with the high pH water.

In a water body whose pH does not rise above 8, suspension of the ferric-oxide-phosphate complex would not result in the release of phosphate and therefore, no blooms would be expected in these waters. Such is the case in shallow, oligotrophic lakes.

The behaviour of phosphate and iron in the most common type of lake encountered in temperate climates - a dimictic, temperate lake - can also be explained from the results of this study. As long as conditions remain relatively oxidizing (D.O. $>$ 1 mg/l) fixation of phosphate as a complex with particulate amorphous iron oxide will take place. However, if the biological growth rate is sufficiently high, the necessarily equivalent decay rate of organic detritus will consume most of the oxygen in the hypolimnion during times of thermal stratification and reducing conditions will result in this region. These conditions will be manifested by mobilization of phosphate in the hypolimnetic lake waters, thereby causing the large-scale phosphate increases observed (Mortimer, 1941-42; Burns & Ross, 1970) in these waters. Formation of the ferric phosphate minerals strengite and/or metastrengite is not likely to occur under these conditions.

Conversely, if the trophic state of the lake is such that the production of organic detritus is small, or if conditions are such that oxygen depletion is minimal, then the possibility of strengite and/or metastrengite formation in the sediments will exist, provided that total phosphate concentrations are $> 10^{-4}$ M. A combination of both of these requirements is not normally found in lake systems, but a nearshore environment having constant inputs of iron and orthophosphate (such as Lake Ontario near the entrance of the Burlington Beach Canal) would satisfy the requisite conditions. In an area such as this, the formation of one or both of these mineralogical phases is possible.

The existence of these high pH conditions would explain the sudden large increases in phosphate measured in the surface waters of Lake Erie (Kramer et al. 1970) following a storm. The turbulence created by the storm carried a large volume of sediment into suspension and the high pH conditions instantly released the phosphate as HPO_4^{-2} into the water. This large influx of biologically useful orthophosphate resulted in the reported (Kramer et al. 1970) algal bloom which took place the following day.

To date, studies of the authigenic constituents of recent sediments and soils have not led to identification of these minerals. Since their formation is possibly related to the problem of eutrophication in that the formation of these minerals would fix the reactive orthophosphate in an insoluble mineralogical phase, more detailed mineralogical investigations of soils and recent sediments need to be carried out in order to confirm or reject this hypothesis.

III. 4 FUTURE WORK

To verify whether the diagenetic alteration of an amorphous P-iron oxide complex to a crystalline ferric phosphate mineral actually takes place in lacustrine sediments, work is being initiated by means of a detailed investigation of Hamilton Bay and the near-shore sediments of Lake Ontario. In this regard, it is hoped to determine whether the abnormally high concentrations of iron and phosphorus in these bodies of water are capable of supporting strengite mineralization in their oxidized portion and/or vivianite formation in areas subject to reducing conditions.

In addition, it has been proposed to commence electrophoretic investigation into the adsorption reaction of phosphate with ferric hydroxide, thereby determining whether there is an electrokinetic basis for the seemingly significant Fe to P ratio of 10:1 found in experimental and naturally occurring conditions.

Finally, careful kinetic investigations need to be carried out in order to determine the time required for mineralization of the P-iron oxide complex, and to define exactly the steps in its formation.

REFERENCES

Abbott, W. (1969). High Levels of Nitrate and Phosphate in Carboy Microcosm Studies. J. W.P.C.F., V. 41, No. 10, pp. 1748-1758.

Bache, D.W. (1964). Aluminum and Iron Phosphate Studies Relating to Soils. I. Solution and Hydrolysis of Variscite and Strengite. J. Soil Sci., V. 15, pp. 113-123.

Berner, R.A. (1970). An Idealized Model of Dissolved Sulphate Distribution in Recent Sediments. Geochim. et Cosmochim. Acta, V. 36, pp. 1497-1503.

Borensztajm, J. (1966). Structures Cristallines de la metavariscite et de la metastrengite. Bull. Soc. Franc. Miner. Crist. LXXXIX, pp. 428-438.

Brunskill, G.J., D. Povoledo, B.W. Graham and M.P. Stainton (1971). Chemistry of Surface Sediments of Sixteen Lakes in the Experimental Lakes Area, Northwestern Ontario. J. Fish Res. Bd. Can., V. 28, No. 2, pp. 277-294.

Brydges, T. (1970). Sediment Analysis. Ontario Water Resources Comm. Publ. at 14th Conf. Great Lakes Res., Toronto.

Burns, H. M. and C. Ross (1971). Nutrient Relationships in a Stratified Eutrophic Lake. Proc. 14th Conf. Great Lakes Res., Toronto.

Campbell, N. J. ed. (1969). Pollution of Lake Erie. V. 2. Report to the International Joint Commission by the International Lake Erie and Lake Ontario Water Pollution Boards.

Carritt, D. E. and S. Goodgale (1954). Sorption Reactions and some Ecological Implications. Deep-sea Res., V. 1, pp. 224-243.

Cate, W. E., E. O. Huffman and M. E. Denning (1959). Preparation of Crystalline Ferric Phosphates. Soil Sci., V. 88, pp. 130-131.

Chang, S. C. and M. L. Jackson (1957). Solubility Product of Iron Phosphate. Soil Sci. Soc. Amer. Proc., V. 23, pp. 265-268.

Cole, C. V. and M. L. Jackson (1950). Colloidal Phosphates of Aluminium and Iron. J. Phys. Chem., V. 54, pp. 128-142.

________ and ________ (1951). Solubility Equilibrium Constant of Dihydroxyaluminum Dihydrogen Phosphate Relating to a Mechanism of Phosphate Fixation in Soils. Soil Sci. Soc., Amer. Proc., V. 15, pp. 84-89.

Corsini, A. (1972). Personal Communication.

Cotton, F. A. and G. Wilkinson (1966). Advanced Inorganic Chemistry. John Wiley and Sons Inc., New York.

Degens, E. T. (1965). Geochemistry of Sediments: A Brief Survey. Prentice Hall, 1965.

Egan, E. T., Z. T. Wakefield and B. B. Luff (1961). Low Temperature Heat Capacity, Entropy and Heat of Formation of Crystalline and Colloidal Ferric Phosphate Dihydrate. J. Phys. Chem., V. 65, pp. 1265-1270.

Einsele, W. (1938). Die Bildung und die Umbildungen von Eisenphosphat und Ihre Dynamischen Beziehungen zum Sediment und zum Freien Wasser. Arch. Hydrobiol., V. 33, pp. 364-387.

Evans, L. T. and E. W. Russell (1959). The Adsorption of Humic and Fulvic Acids by Clays. J. Soil Sci., V. 10, pp. 119-132.

________ and W. C. Wang (1970). The Behaviour of Iron in Peoria Lake. 63rd Annual Meeting of the Illinois State Academy of Sci., Chicago.

Feitknecht, W. and P. Shindler (1963). Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution. Butterworths, London.

Feth, J. H., C. E. Robertson and W. L. Polzer (1964). Sources of Mineral Constituents in Water from Granitic Rocks in Sierra Nevada. U.S.G.S. Water Supply Paper 1535-I.

Fitzgerald, G.P. (1970). Aerobic Lake Muds for Removal of Phosphorus from Lake Waters. Limnol. and Oceanog., V.15, No. 4, pp. 550-556.

Frink, C.R. (1969). Chemical and Mineralogical Characteristics of Eutrophic Lake Sediments. Soil Sci. Soc. Amer. Proc. V.33, No. 3, pp. 369-372.

Garrels, R.M. and C.L. Christ (1965). Solutions, Minerals and Equilibria. Harper and Row, New York.

________ and F.T. Mackenzie (1967). Origin of the Chemical Composition of some Springs and Lakes _in_ Equilibrium Concepts in Natural Water Chemistry. Am. Chem. Soc. Advances in Chem., Ser. V.67, pp. 222-242.

Harter, R.D. (1968). Adsorption of Phosphorus by Lake Sediment. Soil Sci. Soc. Amer. Proc., V. 32, pp. 514-518.

Haseman, J.F., J.R. Lehr and J.P. Smith (1951). Mineralogical Character of Some Iron and Aluminum Phosphates Containing Potassium and Aluminum. Proc. Soil Sci. Amer., V. 15, pp. 257-272.

Hayes, F.R. (1964). The Mud-water Interface. Oceanog. Mar. Biol. Ann. Rev., V. 2, pp. 121-145.

________, J.A. McCarter, M.L. Cameron and D.A. Livingstone (1952). On the Kinetics of phosphorus Exchange in Lakes. J. Ecol., V. 40, pp. 202-216.

Hayes, F.R., L.B. MacPherson and N.R. Sinclair (1958). Lake Water and Sediment, III. The Effect of pH on the Partition of Inorganic Phosphate between Water and Oxidized Mud or its Ash. Limnol. and Oceanog., V. 3, pp. 318-326.

________ and J.E. Phillips (1958). Lake Water and Sediment. IV. Radiophosphorus Equilibrium with Mud, Plants and Bacteria under Oxidized and Reduced Conditions. Limnol. and Oceanog., V. 3, pp. 459-475.

________, B.L. Reid and M.L. Cameron (1950). Lake Water and Sediment Oxidation - Reduction Relations at the Mud-Water Interface. Limnol. Oceanog., V. 3, pp. 308-317.

Hem, J.D. (1970). Study and interpretation of the Chemical Characteristics of Natural Water. U.S.G.S. Water-Supply Paper No. 1473.

Holden, A.V. (1961). The Removal of Dissolved Phosphate from Lake Waters by Bottom Deposits. Verh. Int. Ver. Theor. Agnew. Limnol., V. 14, pp. 247-251.

Hsu, P.H. and D.A. Rennie (1962). Reactions of Phosphate in Aluminum Systems. I & II. Can. J. Soil Sci., V. 42, pp. 197-221.

Hutchinson, G.E. (1957). A Treatise on Limnology, V. 1, 1915 p., John Wiley and Sons Inc., New York.

Hynes, H.B.N. and B.J. Grieb (1970). Movement of Phosphate and Other Ions From and Through Lake Muds. J. Fish. Res. Bd. Can., V. 27, pp. 653-668.

Jeffries, D. (1971). The Time-Concentration Relationship of Trace Metals in the Growth of Algae. Unpublished Bachelor's Thesis, McMaster University.

Kar, K.R. (1958). Radioactive Tracer Study of the Absorption of Phosphate Ions by Aluminum Oxide. J. Sci. Industr. Res., No. 17B, pp. 175-178.

Kramer, J.R. (1964). Theoretical Model for the Chemical Composition of Freshwater with Application to the Great Lakes. Great Lakes Res. Div., U. of Michigan, V. 11, pp. 147—160.

________, H. E. Allen, G.W. Baulne and N.M. Burns (1970). Lake Erie Time Study (LETS).Canada Centre for Inland Waters, Burlington, Ontario.

Kuhn, J.K. and J.A. Schleicher (1970). Phosphorus Content in Unconsolidated Sediments from Southern Lake Michigan. Illinois Geol. Survey, Environ. Geology Note No. 39.

Latterel, J.D., R.E. Holt and D.R. Timmons (1971). Phosphate Availability in Lake Sediments. J. Soil and Water Conserv., V. 26, pp. 21-24.

Lehrecke, H.W. (1947). Iron compounds and Phosphatic Fertilizers, Tests with X-ray Powder Diagrams. Chem. Age (London), V. 57, pp. 672-674.

Livingston, D.A. and J.C. Boykin (1962). Vertical Distribution of Phosphorus in Linsley Pond Mud. Limnol. & Oceanog., V. 7, No. 5, pp. 57-62.

Low, P.F. and C.A. Black (1950). Reactions of Phosphate with Kaolinite. Proc. Soil Sci. Amer., V. 15, pp. 273-290.

Mackereth, F.J.H. (1966). Some chemical observations on Post-Glacial Lake Sediments. Phil. Trans. Roy. Soc. London, Ser. B., V. 250, pp. 165-213.

McCarty, P.L. (1970). Chemistry of Nitrogen and Phosphorus in Water. J. Amer. Water Works Assoc., V. 62, pp. 127-140.

Minear, R.A. (1972). Characterization of Naturally Occurring Dissolved Organophosphorus Compounds. Environ. Sci. and Tech., V. 6, No. 5, pp. 431-437.

Moore, P.B. (1965). A Structural Classification of Fe-Mn Orthophosphate Hydrates. Amer. Mineral., V. 50, pp. 2052-2062.

________ (1966). The Crystal Structure of Metastrengite. Amer. Mineral., V. 51, pp. 168-176.

________ (1970a). Crystal Chemistry of the Basic Iron Phosphates. Amer. Mineral., V. 55, pp. 135-170.

________ (1970b). A Crystal-chemical Basis for Short Transition Series Orthophosphate and Orthoarsenate Parageneses. Neues Jahrb. Mineral. Manatsh. Jg., H. 1, pp. 39-44.

Moore, P.B. (1971). The $Fe_3(H_2O)_n(PO_4)_2$ Homologous Series. Crystal Chemical Relationships and Oxidized Equivalents. Amer. Mineral., V. 56, pp. 1-7.

Mori, H. and T. Ito (1950). The Crystal Structures of Vivianite and Symplesite. Acta Crystallogr., V. 3, pp. 1-6.

Mortimer, C.H. (1941). The Exchange of Dissolved Substances Between Mud and Water in Lakes. I. J. Ecol., V. 29, pp. 280-329.

________ (1942). The Exchange of Dissolved Substances Between Mud and Water in Lakes. II. J. Ecol., V. 30, pp. 147-201.

________ (1971). Chemical Exchanges between Sediments and Water in The Great Lakes - Speculations on Probable Regulatory Mechanisms. Limnol. and Oceanog., V. 15, No. 2, pp. 387-404.

Muljadi, D., A.M. Posner and J.P. Quirk (1966). The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite and Pseudoboemite; Part I. The Isotherms and the Factor of pH on Adsorption; Part II. The Location of the Adsorption Sites; Part III, The Effect of Temperature on Adsorption. J. Soil Sci., V. 17, No. 2.

Nriagu, J.O. (1972a). Stability of Strengite. Amer. J. Sci (in press).

________ (1972b). Stability of Vivianite and Ion-Pair Formation in the System $Fe_3(PO_4)$ - H_3PO_4 - H_2O. Geochim. et Cosmochim. Acta, V. 36, pp. 459-470.

Ohle, W. (1938). Die Bedeutung der Austauschvorgänge Zwischen Schlamm und Wasser für den Stoffkreislauf der Gewässer. Vom Wasser XIII, pp. 87-97.

________ (1954). Phosphor als Initialfacktor der Gewässereutrophierung. Naturwissenschaften, V. 41, pp. 11-23.

Olsen, S. (1964). Phosphate Equilibrium Between Reduced Sediments and Water. Laboratory Experiments with Radioactive Phosphorus. Verh. Int. Ver. Limnol., V. 15, pp. 333-341.

Palache, C., H. Berman and C. Frondel (1951). Dana's System of Mineralogy, V. 2. John Wiley & Sons Inc., New York.

Parks, G.A. (1964). Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals <u>in</u> Equilibrium Concepts in Natural Water Systems (W. Stumm, Ed.). Amer. Chem. Soc. Spec. Publ., V. 67, pp. 121-160.

Pomery, L.R., E.E. Smith and C.M. Grant (1965). The Exchange of Phosphate between Estuarine Water and Sediments. Limnol. and Oceanog., V. 10, pp. 167-172.

Porcella, D.B., E.J. Middlebrooks and J.S. Kumagi (1969). Biological Effects on Sediment-water Nutrient Interchange. Amer. Chem. Soc. Div. of Water, Air and Waste Chemistry, V.9, No. 2, pp. 152-157.

Rigler, F.H. (1964). The Phosphorus Fractions and Turnover Time of Inorganic Phosphorus in Different types of Lakes. Limnol. and Oceanog., V. 9, pp. 511-518.

________ (1968). Further Observations Inconsistent with the Hypothesis that the Molybdenum Blue Method Measures Orthophosphate in Lake Water. Limnol. and Oceanogr., V. 13, pp. 7-13.

Rosenqvist, I.Th. (1970). Formation of Vivianite in Holocene clay Sediments. Lithos, V. 3, pp. 327-334.

Schofield, C.L. (1971). Mineralization of Organic Phosphorus in Oligotrophic Lake Sediments. Water Resources Research; U.S. Dept. of Inter. Tech. Report No. 29, April, 1971.

Serruya, C. (1971). Lake Kinneret: The Nutrient Chemistry of the Sediments. Limnol. and Oceanog., V. 16, No. 3, pp. 510-521.

Shapiro, L. and W.W. Brannock (1962). Rapid Changes of Silicate, Carbonate and Phosphate Rocks. Geol. Survey Bull. 1144-A.

________ (1964). Effect of Yellow Organic acids on Iron and other Metals in Water. J. of Water Works Assoc., V. 56, pp. 1062-1082.

Shapiro, J.W., W.T. Edmundson and D.E. Allison (1971). Changes in Chemical Composition of Sediments in Lake Washington. Limnol. and Oceanog., V. 16, pp. 437-452.

Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong and R.F. Harris (1971). Sorption of Inorganic Phosphate by Lake Sediments. Soil Sci. Soc. Amer. Proc. V. 35, pp. 244-249.

Stevenson, W. (1949). Certain Effects of Agitation Upon the Release of Phosphate from Mud. J. Mar. Biol. Assoc., V. 28, pp. 371-380.

Stumm, W. (1964). Chemistry of Natural Waters in Relation to Water Quality Environment Measurements. U.S.P.H.S. Report 999 - WP - 15.

________ and J.J. Morgan (1970). Aquatic Chemistry. John Wiley & Sons, Inc., New York.

Sutherland, J.C., J.R. Kramer, L. Nichos and T.D. Kuntz (1966). Mineral-water Equilibria. Great Lakes: Silica and Phosphorus. Univ. Mich. Great Lakes Div. Pub. No. 15, pp. 439-445.

Swenson, R.M., C.V. Cole and D.H. Seiling (1949). Fixation of Phosphate by Iron and Aluminum and Replacement by Organic and Inorganic Ions. Soil Sci., V. 67, pp. 3-22.

Thomas, R.L. and A.L.W. Kemp, Unpublished data, Canada Centre for Inland Waters, Burlington, Ontario.

Van Wazer, J.R. Ed. (1961). Phosphorus and its Compounds, V.II. Interscience, New York.

Vollenweider, R.A. (1968). Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication. Organization for Economic Co-operation and Development DAS/CSI, V. 68, p. 159.

Wentz, D.A. and F.G. Lee (1969). Sedimentary Phosphorus in Lake Cores - Observations and Depositional Pattern in Lake Mendota. Environ. Sci. and Tech., V.3., pp. 750-754.

Williams, J.D.H., J.K. Syers and R.F. Harris (1970). Adsorption and Desorption of Inorganic Phosphorus in a 0.1 M NaCl System. Environ. Sci. and Tech., V. 4, pp. 517-519.

________, ________, ________ and D.E. Armstrong (1971a). Fractionation of Inorganic Phosphate in Calcareous Lake Sediments. Soil Sci. Soc. Amer. Proc., Vol. 35, pp. 250-255.

________, ________, D.E. Armstrong and R.F. Harris (1971b). Characterization of Inorganic Phosphate in Noncalcareous Lake Sediments. Soil Sci. Soc. Amer. Proc., Vol. 35, pp. 556-561.

________, ________, ________ and ________ (1971c). Levels of Native Inorganic and Total Phosphorus in Lake Sediments as Related to Other Sediment Parameters. Environ. Sci. and Tech., V.5,

Williams, J. D. H. and T. Mayer (1971). Effect of Diagenetic Formation of Apatite on Regeneration of Phosphorus from Sediments of Lakes Erie and Ontario. Proc. 14th Conf. Great Lakes Res., Toronto.

Zicker, E. L., K. C. Berger and A. D. Hasler (1956). Phosphorus Release from Bog Lake Muds. Limnol. and Oceanog., V. 1, pp. 296-303.