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Diagenetic Formation of Iron Phosphates in Recent Lake Sediments

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Abstract

Thermochemical data for many basic iron phosphates have been estimated by a method which regards these compounds as components on joins between the simple phosphates and hydroxides. The data so derived have been used to develop models depicting the phase compatibilities and the general diagenetic behavior of iron phosphates in subaqueous freshwater environments. The models are combined with measurements on the interstitial waters of Lake Erie to define the chemical requirements for the formation of vivianite and other iron phosphates in the Great Lakes sediments. In aerobic lake sediments, ferrosoferric (and manganousferric) hydroxyphosphates are the stable minerals which may be derived by phosphating ferromanganese oxides or by the oxidation of ferrous phosphates. Strengite and simple ferric phosphates are unlikely to be important diagenetic constituents of freshwater sediments. The stable and most probable phosphate minerals in reducing environments are vivianite, reddingite, and anapaite. The precipitation and dissolution of these iron phosphates (particularly vivianite and ludlamite, the dominant phases) in the Great Lakes sediments are considered an important buffer mechanism which regulates both the levels of phosphorus in the interstitial waters and the release of phosphorus to the overlying lake waters.

Introduction

Many investigators have made valuable contributions to the understanding of the mineralogical and petrological properties of the basic iron phosphates. However, the chemical constraints which predicate the environments of formation of these minerals have as yet received little attention. An understanding of the geochemical processes involved in the formation of iron phosphates in freshwater environments is of considerable interest in eutrophication abatement programs. Thus, their precipitation and dissolution may be an important buffer mechanism regulating the levels of phosphorus in freshwater water systems. Iron has been widely recognized to control the geochemical migration of phosphorus within and through aquatic ecosystems (Einselle, 1938; Mortimer, 1941); the mechanisms and products of iron-phosphorus interaction, however, remain obscure.

In this paper a method is described for making preliminary estimates of the thermochemical data for low temperature, basic iron phosphates. The data so derived have been used to develop models describing (a) the solubilities and stabilities of these phosphates in aqueous systems, and (b) the general geochemical behavior of these minerals in subaqueous freshwater environments. The models are combined with measurements on the interstitial waters of Lake Erie in an effort to define the chemical requirements in the formation of vivianite and other iron phosphates in Great Lakes sediments.

The need for experimental studies of iron-phosphate systems cannot be over-emphasized considering the potential use of iron phosphate mineral associations as geopotentiometers. In this connection, the work of Moore (1965, 1970, 1971) deserves special mention as it sheds considerable light on the crystal chemistry of these compounds.

Approximation of Thermochemical Constants

Except for vivianite and strengite, thermochemical data for the basic iron phosphates are not yet available. However, various models have recently come into the literature (Fyfe, Turner, and Verhoogen, 1958; Helgeson, 1969; Zen, 1972; Craig and Barton, 1973) for predicting and interpolating thermochemical constants with an accuracy adequate for assessing the geochemical behavior of mineral phases at near-surface environments. One of these, the ideal mixing model, has been employed in this report to approximate the free energies of formation (ΔG°_f) for the low temperature, basic iron, and manganese phosphates.

Most basic iron and manganese phosphates may be regarded as mixtures of simple metal phosphates and hydroxides. These phosphates are characterized by a general structural principle based on a stable polyatomic complex involving ferrosoferric oxy-hydroxy octahedral face-sharing trimers (Moore, 1970). Furthermore, we can show (see below) that the free energy of reaction, ΔG°_r, of simple metal hydroxides with metal phosphates to form hydroxyphosphates is generally small. It is therefore possible to use a mixing model to estimate the ΔG°_f for the basic iron phosphates. The mechanics of a predicted method which is based on reactions involving iron and manganese hydroxides and phosphates has been described in Nriagu (1974).

Table 2 gives the formation reactions for the basic Fe/Mn phosphates and the ΔG°_f for each mineral phase calculated using the thermochemical data in Table 1. To illustrate the method used to derive the ΔG°_f values in Table 2, consider the following reaction for formation of a typical ferrosoferric hydroxyphosphate:

$$n_1\mathrm{Fe(OH)_2} + n_2\mathrm{Fe(OH)_3} + n_3\mathrm{FePO_4\cdot 2H_2O} \rightarrow \mathrm{Fe^{2+}}_{n_1}\mathrm{Fe^{3+}}_{n_2}(\mathrm{PO_4})_{n_3}(\mathrm{OH})_{2n_1+3n_2}(\mathrm{H_2O})_{n_4} + (2n_3 - n_4)\mathrm{H_2O}$$

According to the mixing model, the free energy for the resultant hydroxyphosphate is given by

$$\Delta G^\circ_f(\text{hydroxyphosphate}) = n_i\Sigma\Delta G^\circ_f(\mathrm{r}_i) - (2n_3 - n_4)\Delta G^\circ_f(\mathrm{H_2O}) - 2.303RT\Sigma n_i \log(n_i)$$

TABLE 1. Thermodynamic Constants for Solid Phases and Aqueous Species Relevant to the Iron-Phosphate Systems at 25°C

Ion, compound	ΔG°_f (kcal.mol^{-1})	Source	Ion, compound	ΔG°_f (kcal.mol^{-1})	Source
Fe^{2+}	- 18.85	a	$Ca(OH)_2$	-229.0	i
Mn^{2+}	- 54.5	a	$Mg(OH)_2$	-204.6	i
Ca^{2+}	-132.2	b	MnO_2	-111.2	c
$H_2PO_4^-$	-270.17	c	Mn_2O_3	-210.6	c
HPO_4^{2-}	-260.34	c	$FePO_4\cdot 2H_2O$	-394.6	d
H_2O	- 56.69	c	$Ca_3(PO_4)_2$	-929.8	i
H_2O(bound)	- 56.5	i	$Fe_3(PO_4)_2\cdot 8H_2O$	-1046.2	f
$Fe(OH)_2$	-118.5	i	$Mn_3(PO_4)_2\cdot 3H_2O$	-854.8	g
$Fe(OH)_3$	-166.5	a	$Mn_3(PO_4)_2\cdot 3H_2O$	-870.9	h
$Mn(OH)_2$	-151.5	i	$Fe_5(PO_4)_3OH$	-1510.2	i

a: Wagman et al, 1968; b: Garrels and Christ, 1965; c: Wagman et al, 1969; d: Nriagu, 1972b; e: Duff, 1971a; f: Nriagu, 1972b; g: Latimer, 1952; h: this report; i: see Nriagu, 1974.

where r_i is the *i*-th solid phase and T is temperature.

The model subsumes that the addition (or removal) of water during the reaction does not entail a large configurational entropy contribution (see *e.g.* Moore, 1965; 1971). The calculations involve the use of constant ΔG°_f values for hydroxides components within the phosphate mineral lattice which may differ from the ΔG°_f values assigned to the components as separate phases. The derivation of such ΔG°_f data for water and the hydroxide components (Table 1) is described elsewhere (Nriagu, 1974;) the same principle has recently been used by Tardy and Garrels (1974) to estimate the free energies of formation of layer silicates. It should be emphasized that the calculative strategy

TABLE 2. Formation Reactions Used to Calculate the Thermochemical Data for Basic Iron Phosphates

Mineral Phase	Formation Reaction	ΔG°_f (k cal.mol^{-1})
Lipscombite	$Fe(OH)_2 + 2FePO_4.2H_2O \rightarrow Fe_3(PO_4)_2(OH)_2 + 4H_2O$	- 682.5
Tinticite	$Fe(OH)_3 + 2FePO_4.2H_2O \rightarrow Fe_3(PO_4)_2(OH)_3.3H_2O + H_2O$	- 900.1
Cacoxenite	$Fe(OH)_3 + 3FePO_4.2H_2O + 6H_2O \rightarrow Fe_4(PO_4)_3(OH)_3.12H_2O$	-1691.2
Rockbridgite	$Fe(OH)_2 + Fe(OH)_3 + 3FePO_4.2H_2O \rightarrow Fe_5(PO_4)_3(OH)_5 + 6H_2O$	-1131.8
Beraunite	$Fe(OH)_2 + Fe(OH)_3 + 4FePO_4.2H_2O \rightarrow Fe_6(PO_4)_4(OH)_5.6H_2O + 2H_2O$	-1753.7
Laueite/Strunzite	$Mn(OH)_2 + 2FePO_4.2H_2O + 4H_2O \rightarrow MnFe_2(OH)_2(PO_4)_2.8H_2O$	-1167.5
Mitridatite	$Ca(OH)_2 + 2FePO_4.2H_2O + 4H_2O \rightarrow CaFe_2(PO_4)_2(OH)_2.8H_2O$	-1245.0
Foucherite	$Ca(OH)_2 + 2Fe(OH)_3 + 2FePO_4.2H_2O + 3H_2O \rightarrow CaFe_4(OH)_8(PO_4)_2.7H_2O$	-1522.3
Anapaite	$Fe_3(PO_4)_2.8H_2O + 2Ca_3(PO_4)_2 + 4H_2O \rightarrow 3Ca_2Fe(PO_4)_2.4H_2O$	-1043.6

is empirical; its use is based on the good agreement of the predicted data with the experimental results (see Table 1 in Nriagu, 1974). The method is strictly valid when the stoichiometric coefficients for the reactants and products are integers.

The thermochemical data reported here are intended as first approximations to be corrected as additional experimental data become available. The error bounds for these data cannot be readily evaluated in the absence of control data. However, where accurate experimental data are available for comparison (notably for lead, calcium, and magnesium) the ΔG°_f values calculated by the present model are in very close agreement ($\pm$ 0.3 percent) with the experimental results (Nriagu, 1974). Furthermore, the stability fields defined with the present data fit quite well with the natural chemical environments of formation for the various phosphate phases (see below).

The present data are not precise enough to define the fine structures of complex diagrams or to delimit the chemical factors involved in the interconversions of the polymorphic forms of a given compound. They should, however, be adequate: (a) for predicting the relative stabilities and solubilities of these phosphates in aqueous systems and for assessing the behavior of these phosphates in near-surface environments such as are found in soils, sediments, and halos of ore bodies; and (b) as a basis for defining the chemical conditions for experimental investigation of individual mineral phases. There is of course the potential capability of supplying quantitative information on the amount of phosphorus which can be regenerated from a given body of sediment, a question of considerable interest in water resource management.

Models for Diagenetic Formation of Iron Phosphates in Recent Freshwater Environments

On the basis of the thermochemical data in Table 2, an equilibrium framework can be constructed to illustrate the chemical conditions favoring the formation of the various basic Fe/Mn phosphates. The models are particularly applicable to subaqueous, freshwater environments where total iron is in large excess over sulfur, as is true in many lake and river systems. In an earlier report Nriagu (1972a) showed that iron phosphates are unlikely to form in an anaerobic sulfuretum which contains large amounts of dissolved sulfides.

In formulating the chemical reactions and phase compatibilities for the phosphate minerals, the procedure given in Stumm and Morgan (1970) was followed very closely; reference to this text is recommended for a complete discussion. Table 3 gives the relevant reactions relating the mineral phases with the aqueous species. These reactions are valid in the pH range of 2–7, where $H_2PO_4^-$ is the dominant phosphate species. Where a phase boundary falls in a more alkaline region, the pertinent reactions have been rewritten with HPO_4^{2-} as the dominant phosphate species. To obtain an equation for a boundary between any two or more solid phases, the appropriate reactions in Table 3 are merely added in such a way that the oxidized state represents the product of the reactions (see Stumm and Morgan, 1970). It is worth remembering that

$$p\epsilon = \frac{-\Delta G^\circ_r}{2.303nRT} = \left(\frac{F}{2.303RT}\right)\mathrm{Eh}$$

where F is the Faraday constant.

In the diagrams below, $p\epsilon$/Eh and pH are used only as convenient variables, more so because these two are the environmental parameters most often measured. The use of any other pair of variables will result in different topological projections; the essential inferences will, however, remain the same.

In the discussions that follow, vivianite has been used to represent the ferrous phosphates, notably ludlamite $Fe_3(PO_4)_2\cdot 4H_2O$ and phosphoferrite, $Fe_3(PO_4)_2\cdot 3H_2O$. In a recent study of the topological and geochemical relationships among the three minerals, Moore (1971) showed that the partial dehydration of vivianite (or ludlamite) to another member in the $Fe^{2+}{}_3(PO_4)_2\cdot nH_2O$ homologous series involved mostly a denser condensation of the octahedral clusters in the crystal framework. Moore (1971) also showed that the activity of water was the major factor in the paragenetic relationships exhibited by these minerals and that the hydration/dehydration process was readily reversible. In subaqueous environments, it is therefore reasonable to expect that the Eh, pH, and ionic activities involved in vivianite formation will also be conducive to the formation of the other ferrous phosphates.

Figure 1 shows the phase compatibilities for end-member ferric and ferrous phosphates. As expected, vivianite is the stable mineral in reducing environments while tinticite and/or cacoxenite (stability field not shown as it coincides rather closely with that of tinticite) are stable under oxi-

TABLE 3. Solubility Expressions for Low Temperature Iron Phosphates

Mineral Phase	Dissolution Reaction	logK, $p\varepsilon^{o}$
Vivianite	$3Fe^{2+} + 2H_2PO_4^- + 8H_2O = Fe_3(PO_4)_2 \cdot 8H_2O + 4H^+$	- 3.1
Reddingite	$3Mn^{2+} + 2H_2PO_4^- + 3H_2O = Mn_3(PO_4)_2 \cdot 3H_2O + 4H^+$	- 2.2
Anapaite	$2Ca^{2+} + Fe^{2+} + 2H_2PO_4^- + 4H_2O = Ca_2Fe(PO_4)_2 \cdot 4H_2O + 4H^+$	- 4.9
Tinticite	$3Fe^{2+} + 2H_2PO_4^- + 6H_2O = Fe_3(PO_4)_2(OH)_3 \cdot 3H_2O + 7H^+ + 3e$	- 9.0
Cacoxenite	$4Fe^{2+} + 3H_2PO_4^- + 15H_2O = Fe_4(PO_4)_3(OH)_3 \cdot 12H_2O + 9H^+ + 4e$	- 8.2
Lipscombite	$3Fe^{2+} + 2H_2PO_4^- + 2H_2O = Fe_3(PO_4)_2(OH)_2 + 7H^+ + 3e$	- 6.8
Rockbridgite	$5Fe^{2+} + 3H_2PO_4^- + 5H_2O = Fe_5(PO_4)_3(OH)_5 + 11H^+ + 4e$	-10.3
Beraunite	$6Fe^{2+} + 4H_2PO_4^- + 11H_2O = Fe_6(PO_4)_4(OH)_5 \cdot 6H_2O + 13H^+ + 5e$	- 9.3
Laueite/Strunzite	$Mn^{2+} + 2Fe^{2+} + 2H_2PO_4^- + 10H_2O = MnFe_2(OH)_2(PO_4)_2 \cdot 8H_2O + 6H^+ + 2e$	-11.7
Mitridatite	$Ca^{2+} + 2Fe^{2+} + 2H_2PO_4^- + 10H_2O = CaFe_2(PO_4)_2(OH)_2 \cdot 8H_2O + 6H^+ + 2e$	-11.8
Foucherite	$Ca^{2+} + 4Fe^{2+} + 2H_2PO_4^- + 15H_2O = CaFe_4(OH)_8(PO_4)_2 \cdot 7H_2O + 12H^+ + 4e$	-13.9
Hydroxyapatite	$5Ca^{2+} + 3H_2PO_4^- + H_2O = Ca_5(PO_4)_3OH + H^+$	-13.2
Strengite	$Fe^{2+} + H_2PO_4^- + 2H_2O = FePO_4 \cdot 2H_2O + e$	- 5.7
Ferromanganese oxides	$Fe^{2+} + 3Mn^{2+} + 8H_2O = Fe(OH)_3 + MnO_2 + Mn_2O_3 + 13H^+ + 5e$	-21.5

dizing conditions. Notice that the dissolution of basic ferric phosphates in response to changes in the chemical environment will likely be incongruent, resulting in the formation of vivianite and ferrosoferric hydroxides. It is surprising that strengite is unstable (relative to tinticite/cacoxenite) considering its relative widespread occurrence (Palache, Berman, and Frondel, 1951). Strengite does not precipitate directly from aqueous solutions but once formed (by recrystallization of amorphous ferric phosphate) is remarkably stable (Nriagu, 1972b); changes in pH and Eh lead mainly to the substitution of OH^- for phosphate ions with the crystal configuration remaining intact. Crystalline strengite therefore is unlikely to be an important constituent in freshwater sediments.

Figure 2 shows the stability fields for the ferrosoferric hydroxyphosphates. For the range in pH of 6.5–9 and Eh $\leq$ 0, vivianite is the most stable mineral. Tinticite and cacoxenite are stable relative to lipscombite, beraunite, and rockbridgite only in highly restricted environments. Clearly vivianite, lipscombite, beraunite, and rockbridgite should constitute the stable mineral suite in most natural geo-

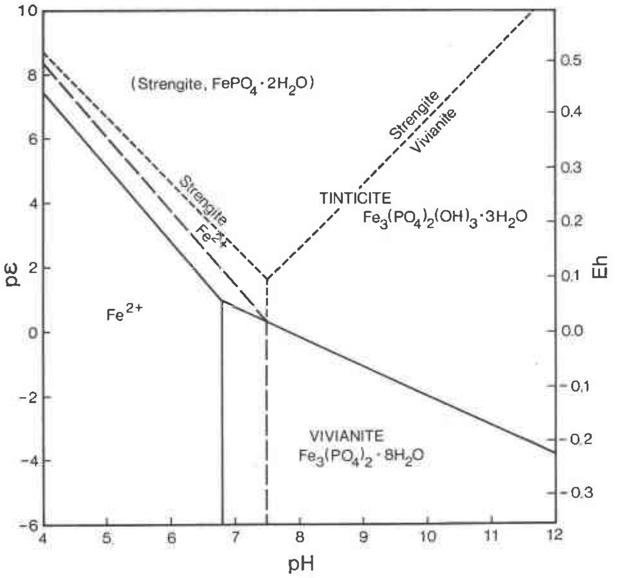

FIG. 1. Stability relationships among ferric and ferrous phosphates at an activity of dissolved phosphate of 10^{-6}. Solid and broken lines are the field boundaries at activities of dissolved iron species of 10^{-4} and 10^{-5}, respectively. The stability field for strengite is shown in dotted lines.

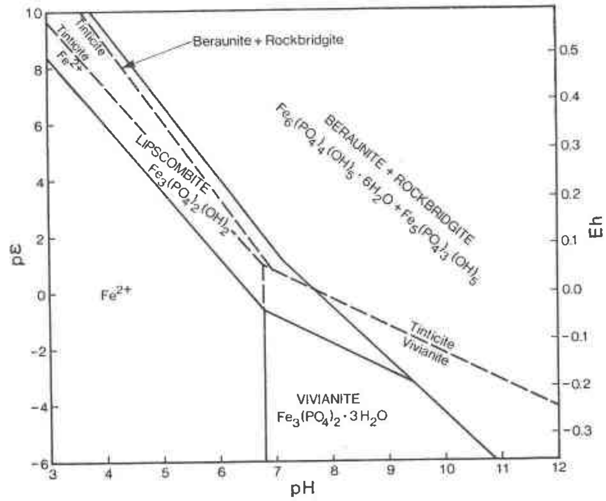

FIG. 2. Phase compatibilities for ferrosoferric hydroxyphosphates at phosphate and dissolved iron activities of 10^{-6} and 10^{-4}, respectively. The field boundaries for tinticite or cacoxenite are shown as dotted lines.

chemical environments. An important consequence of this observation is that lipscombite, beraunite, and rockbridgite are the stable and most likely products that can be derived from the oxidation of vivianite. Leavens (1972) has shown that rockbridgite, lipscombite, strengite, strunzite, laueite, and cacoxenite are the byproducts in the breakdown of vivianite at Mullica Hill and Hornerstown, New Jersey (USA). The present data suggest that lipscombite and rockbridgite are the primary oxidation products from vivianite and that the other associated minerals have been formed from collateral interaction of phosphate ions with the Fe/Mn oxides and hydroxides.

The phase relationships for manganese phosphates are shown in Figure 3. Notice that reddingite is slightly more stable than vivianite (or phosphoferrite). The formation of laueite/strunzite is favored by low Fe concentration and low pH; the predicted field of stability is consistent with the rare occurrences of these two minerals. On the basis of this figure, we infer that the phosphate mineral formed in most reducing natural environments will consist of solid solutions of vivianite (or phosphoferrite) with reddingite rather than pure vivianite or pure reddingite. The field boundary between lipscombite and the ferromanganese oxides ($Fe(OH)_3 + MnO_2 + Mn_2O_3$) is particularly noteworthy as it suggests that the basic Fe/Mn phosphates are stable relative to these metal oxides in a wide variety of natural geochemical environments. Consequently, the formation of ferromanganese concretions may be inhibited by large phosphate concentrations. This observation may be one of the reasons why ferromanganese concretions have not been found in many lake sediments even though the physico-chemical environments are conducive to their formation. Figure 4 compares the stability fields for iron phosphates with those for manganese phosphates. The notable features in this figure are the greater stability of Ca/Fe phosphates relative to Mn/Fe phosphates at earth-surface environments and the fact that both oxidized Mn/Fe and Ca/Fe phosphates are unstable relative to lipscombite.

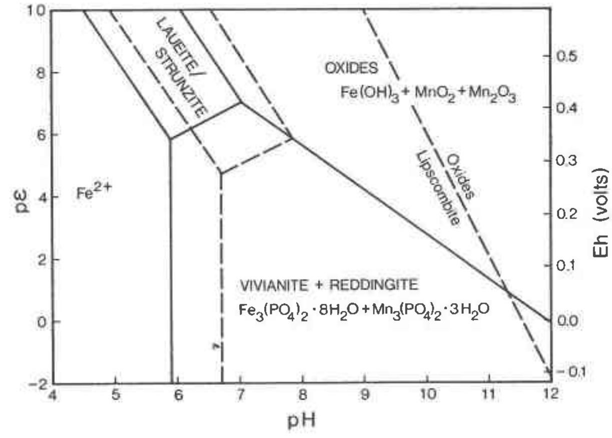

FIG. 3. Phase compatibilities for ferromanganese phosphates at dissolved phosphate and iron activities of 10^{-6} and 10^{-4}. Dissolved manganese activities are 10^{-2} (solid lines) and 10^{-4} (broken lines).

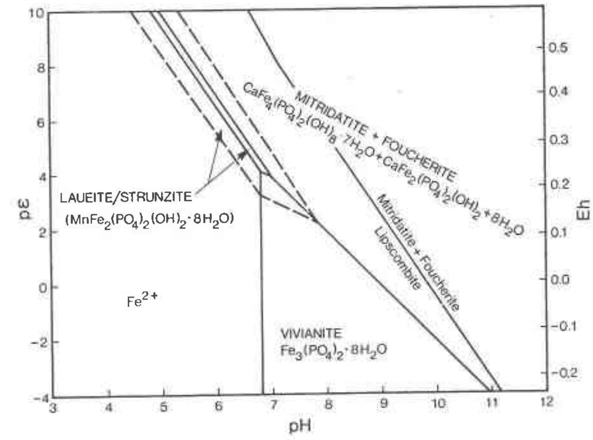

FIG. 4. Stability relations for ferromanganese and calcitic-iron phosphates at dissolved phosphate, iron, and calcium activities of 10^{-6}, 10^{-4}, and 10^{-3}, respectively. Dissolved Mn activities are 10^{-4} (solid lines) and 10^{-2} (broken lines).

The phase compatibilities for calcitic iron phosphates and hydroxyapatite are shown in Figure 5. The stability field for vivianite lies completely within that of apatite and has not been shown. For the pH, Ca and P concentrations likely to be encountered in many freshwater sediments, anapaite rather than hydroxyapatite would be the stable, Ca-bearing phosphate mineral. This observation conflicts with the suggestion by Sutherland *et al* (1966) that hydroxyapatite is the most stable diagenetic calcium phosphate. Notice also that lowering the Ca concentration will induce the conversion of hydroxyapatite to anapaite. Under oxidizing conditions, anapaite will be transformed to foucherite and mitridatite.

To understand the mechanisms of formation of the basic iron phosphates and their mineralogical associations, it is instructive to examine their natural modes of occurrence. In nature, these phosphates occur as weathering products of pegmatitic phosphate minerals; in gossans and halos around ore bodies; in ferromanganese oxide and bog ore beds; and as replacements and cements in clays, sands, and bone material. It is also generally true that particular mineral assemblages tend to be associated with certain source material. Thus tinticite, cacoxenite, and strengite are commonly associated with "limonite" beds; laueite, strunzite, and frondellite [$MnFe_5(PO_4)_3(OH)_5$] with ferromanganese oxides; anapaite, foucherite, and mitridatite with bone material and iron-rich carbonate beds. Lipscombite, beraunite, and rockbridgite are often found in association with vivianite, indicating the generic relationship. Apparently both the chemical characteristics of the aqueous system and the nature of the source material play important parts in determining the type of basic iron phosphate to be formed in a given environment.

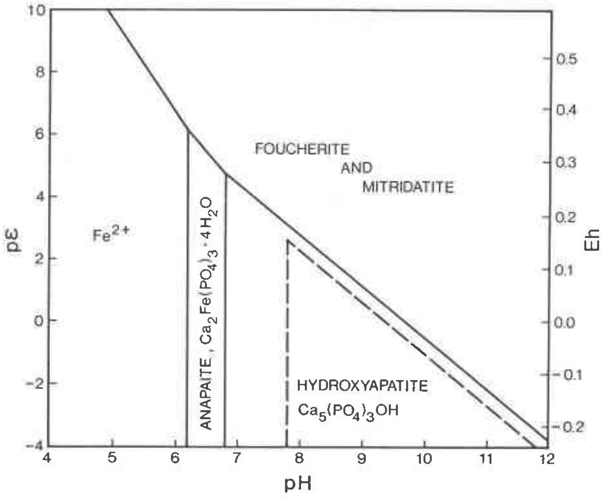

FIG. 5. Stability relations for calcium and iron phosphates at dissolved phosphate, iron and calcium activities of 10^{-6}, 10^{-4} and 10^{-3}. The broken lines show the stability field for hydroxyapatite when $A_{Ca^{2+}} = 10^{-4}$.

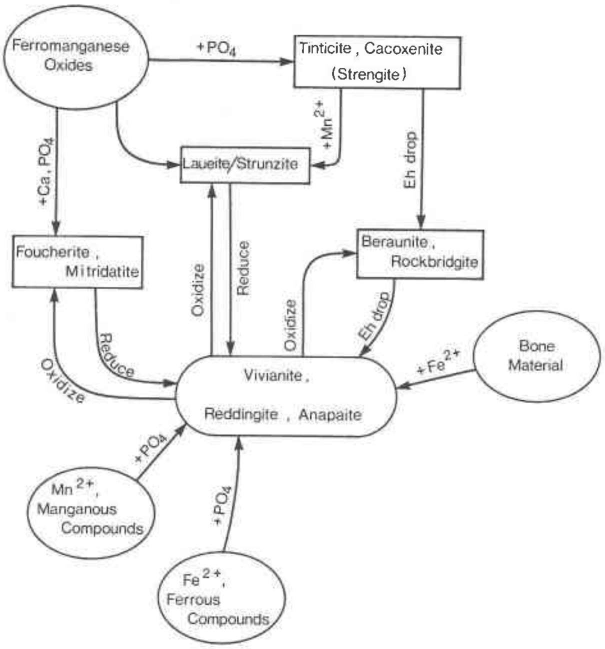

FIG. 6. The source material and the associated phosphate minerals likely to be encountered in recent lake and river systems.

In many lake sediments, the chemical conditions favor the formation of a wide variety of phosphate minerals. Figure 6 shows the source materials in a typical sedimentary setting and the basic iron phosphates that may be derived from them. Clearly the precursor materials essential for the formation of a large variety of iron phosphates occur in one form or another in many freshwater sediments. Thus the formation of ferric hydroxides in the oxidized microzones at the mud-water interface may lead to the formation of cacoxenite, tinticite, or cryptocrystalline strengite. Ferromanganese sands and concretions are abundant in many sediments; phosphating these under appropriate Eh conditions may lead to the formation of laueite, strunzite, cacoxenite, or anapaite. In sediments devoid of authigenic calcites, the alteration of bone material will invariably lead to the formation of anapaite, foucherite, or mitridatite; bones do not preserve well in such sediments. Subsequent reduction of most of the ferric minerals

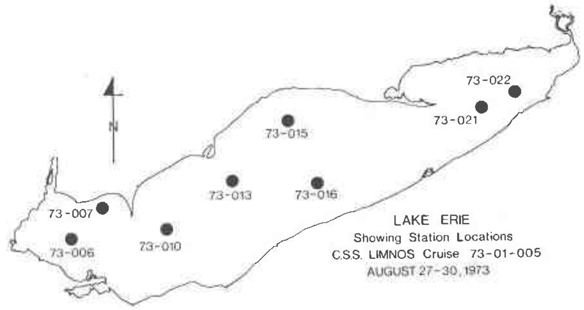

FIG. 7. Lake Erie showing location of sample stations.

may lead to the formation of vivianite, anapaite, and reddingite, or solid solutions involving these three minerals. Thus, analysis of vivianite particles from Lake Erie (see below) shows high Mn content, a feature which may be related to the fact that the core station was in an area where ferromanganese oxides are known to occur (R. L. Thomas, 1972, personal communication). On the other hand, calcium phosphates containing up to 5 percent Fe have also been reported in Lake Erie Sediments (Kingston and Williams, in preparation).

In lake sediments and river beds, vivianite is a primary mineral precipitated directly from the pore fluids (Mackareth, 1965; Kjensmo, 1968; Rosenquist, 1972; Leavens, 1972). In every case, the chemical environment of vivianite precipitation matches its stability field as defined in the present and previous (Nriagu, 1972a) reports. In response to changes in Eh, authigenic vivianite may be extensively oxidized to lipscombite, beraunite, and rockbridgeite (Leavens, 1972). The phosphate-rich grains reported in Lake Washington (Shapiro, Edmonton, and Allison, 1971) are believed to be extensively oxidized vivianite. Most often though, the vivianite grains in freshwater sediments show only surficial oxidation, possibly to (amorphous) lipscombite, beraunite, and rockbridgeite (Dell, 1973).

Diagenetic Formation of Iron Phosphates in Great Lakes Sediments

Several references have been made to authigenic vivianite in the postglacial clays of Lakes Superior, Erie, and Ontario (see Dell, 1973). In the following section, the theoretical models developed above will be combined with measurements on the interstitial waters to determine the chemical conditions responsible for the formation of vivianite and other iron phosphates in sediments of the Great Lakes. The chemical data for the interstitial waters of Lake Erie have been determined during the course of this study (see Appendix); the interstitial water compositions for the other lakes particularly with respect to Fe, Mn, P, and Ca concentrations are similar (see, *e.g.*, Weiler, 1974). In this regard, it would be expected that vivianite should be an important constituent of the sediments in Lakes Huron and Michigan.

Examination of Lake Erie Core Samples

Sediment samples were obtained from the stations in Figure 7 by means of a benthos corer. Upon retrieval, the cores were immediately extruded and the pore fluids in the appropriate interval extracted using the squeezer described by Kalil and Goldhaber (1973). Direct Eh and pH measurements on the pore waters were made in a flow-through cell connected to the outlet of the squeezer assembly. Following the conductivity measurements, the samples were acidified with nitric acid and stored. Subsequent determinations of the chemical parameters for the interstitial waters were made in the laboratory according to the methods described in Traversy (1971).

The vivianite nodules in the core samples were identified first by extracting the sand fraction ($>53\ \mu$) by sieving, examining this fraction under reflected light, and then examining both whole nodules and crushed specimens under the petrographic microscope. The vivianite occurred as small (averaging about 60 μ) subrounded nodules with a slightly rough surface. Occurrences of vivianite quoted in the literature are often characterized by the presence of bone, pieces of wood, or other organic material. The vivianite found in the cores from Lake Erie was not associated with any obvious microscopic organic remains although these materials were rather abundant.

The nodules from core 73-013 were rather small; however, another core collected at the same locality contained nodular aggregates up to 1 cm in diameter which displayed the same physical and optical characteristics as vivianite from core 73-013. These larger nodules were used in the chemical analyses (Table 4).

Results

The following is a brief description of the physical characteristics of a typical core (from Station 73-013) where vivianite was encountered:

Depth below mud-water interface (cm)	Description
0–10	very dark gray (5Y 3/1)[1], very soft, watery, silty clay with pronounced black laminations
10–29	very dark gray (5Y 3/1) silty clay with pronounced black laminations. Sediment is less soft than top 10 cms and becomes firmer with depth
29–180	dark gray (5Y 4/1), firm silty clay with thin black laminations throughout.

Vivianite nodules occurred throughout this core and were especially abundant in samples from the top 12 cm, with the exception of the top 2 cm in which only a few nodules were present. A sample taken at 18–20 cm contained very minor vivianite, and other samples taken at intervals down to 180 cm contained very few or no nodules.

Vivianite has been identified previously in similar sediments from Lakes Superior, Erie, and Ontario (Dell, 1973). It occurs in small sand size nodules, crystal clusters, and irregular masses. The vivianite is typically blue in color (colors range from pale blue, or greenish blue to bluish black), although when the material is in a reduced state it is white or colorless. Some specimens have well developed crystals, whereas others appear under the petrographic microscope to be rather poorly crystallized. The occurrence of vivianite in postglacial clays of the Great Lakes is not confined to any one depth in the sediment or to any one locality in the lakes.

Table 4 gives the chemical composition of the vivianite nodules. The data may be compared with the theoretical amounts of Fe, PO_4 and H_2O in vivianite of 33.4, 37.9, and 28.7 wt percent respectively. Apparently divalent cations substitute appreciably for iron in the vivianite lattice. In fact, these nodules consist of a mixture of vivianite and ludlamite, $(Fe,Mn,Mg)_3(PO_4)_2 \cdot 4H_2O$. Both the greenish tint and the low water contents (relative to the expected value for vivianite) of the samples reflect the partial dehydration of vivianite to ludlamite. Relative to the host sediments, the vivianite nodules are depleted in trace metals.

TABLE 4. Chemical Composition of Vivianite Grains from Station 73-013

Element, ion	Sample 13194-13*	Sample 13194-18*
Fe	29.2%	32.4%
PO_4	36.5%	36.2%
Mn	2%	2.2%
Ca	0.1%	405 μg/gm
Mg	3.3%	3.6%
K	436 μg/gm	711 μg/gm
Zn	115 μg/gm	137 μg/gm
Cu	40 μg/gm	44 μg/gm
Sr	6 μg/gm	0 μg/gm
Cd	6 μg/gm	6 μg/gm
Pb	6 μg/gm	12 μg/gm
Co	0	12 μg/gm
H_2O**	28.9%	25.5%
Insoluble residue***	2.1%	13.6%

*Samples 13194-13 and 13194-18 were recovered from depths of 120-130 cm and 170-180 cm below the mud-water interface respectively. The data are given relative to one gram of the soluble fraction. The following elements: Ni, Co, Cr, V, and Be were not detected.

**Calculated as percentage of the soluble fraction which cannot be accounted for in terms of elemental and ionic concentrations.

***Insoluble residue refers to the fraction insoluble in concentrated nitric acid.

Some chemical parameters for the interstitial waters from core 73-013 are shown in Table 5. Similar data have also been obtained for all the stations in Figure 7, and are presented in the Appendix. Lake Erie sediments contain 2–4 percent total iron, 0.05–0.5 percent total sulfur, and 0.04–0.3 percent total phosphorus. There is therefore a large excess of iron over total sulfur, and the formation of iron phosphates should be expected. To determine whether the pore fluids are saturated with respect to any of the iron phosphates, it was necessary to use the data in Table 5 to calculate ionic activities as defined by

$$A_i = M_i \gamma_i$$

$$-\log \gamma_i = K z_i^2 \sqrt{I}$$

In the above expressions, A_i, M_i, γ_i and Z_i are respectively the activity, molar concentration, activity coefficient, and charge of the i-th ion and K is an empirical constant. The ionic strength, I, was estimated from the specific conductance (μ) by means of the relation

$$I = 1.5 \times 10^{-5} \mu$$

The calculated ionic strengths were in reasonable agreement with the average I value of 0.0045 obtained using more complete chemical analyses (Weiler, personal communication).

In calculating the ionic activities, the formation of ion-pairs in the interstitial waters was ignored. It was further assumed that the dissolved Fe and Mn were mostly in the divalent form, a reasonable assumption considering the Eh data for the inter-

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[1] Color notation from Munsell Color Charts.

TABLE 5. Partial Analysis of Pore Fluids in Contact with Sediments from Station 73-013

Depth, below mud-water interface(cm)	pH	Eh(mv)	Cond. (μmhos)	Na*	K*	Mg*	Ca*	Mn*	Fe*	P*
0- 2	7.23	+20	330	17.4	2.5	7.4	36.3	1.3	0.5	36
2- 4	7.14	+21	355	16.8	2.9	8.2	38.9	1.9	2.7	44
4- 6	7.07	+25	370	18.8	3.4	7.8	38.4	1.5	2.8	39
6- 8	7.04	+23	375	18.4	3.8	7.8	38.6	1.5	3.7	50
8- 10	6.97	- 5	385	21.2	4.8	7.8	36.5	1.4	2.7	59
10- 12	7.09	-	347	18.8	3.1	7.5	36.0	1.5	2.3	55
18- 20	7.10	-	360	17.6	3.5	8.0	36.3	2.3	1.7	67
28- 30	6.98	+53	380	20.8	3.3	8.2	37.0	2.5	1.8	64
38- 40	7.14	+75	362	22.0	3.7	8.2	37.4	1.8	2.1	52
48- 50	7.20	+59	415	19.6	3.5	9.5	39.3	2.8	3.8	75
58- 60	6.90	+57	406	20.0	3.3	9.2	41.0	2.3	2.8	60
68- 70	6.93	+43	390	17.4	3.2	9.2	37.5	2.6	3.2	43
78- 80	6.97	+45	368	21.2	3.9	9.2	37.5	2.0	2.2	40
108-110	7.18	+49	356	19.8	3.8	8.0	-	1.8	4.5	76
148-150	7.29	+56	340	19.6	4.4	10.8	41.5	2.8	6.5	115
178-180	7.07	+46	422	20.0	4.4	9.8	43.1	1.5	2.8	54

* (in ppm)

stitial waters. The activity of HPO_4^{2-} ion was calculated from ΣP, the measured total P concentration by means of the equation,

$$A_{HPO_4^{2-}} = \Sigma P/\phi$$

where

$$\phi = \frac{1}{\gamma_{HPO_4^{2-}}} + \frac{A_{H^+}}{k_2 \gamma_{H_2PO_4^-}}$$

and k_2 is the second dissociation constant for phosphoric acid.

The calculated activities for HPO_4^{2-}, Fe^{2+}, Ca^{2+}, and Mn^{2+} ions for the pore fluids from Station 73-013 are shown in Table 6, along with ion activity products (IAP) for the formation reactions

$$\underset{\text{vivianite}}{Fe_3(PO_4)_2 \cdot 8H_2O} + 2H^+ \rightarrow 3Fe^{2+} + 2HPO^{2-}_4 + 8H_2O$$

TABLE 6. Ion Activities and Ion Activity Products Derived from Lake Erie (Station 73-013) Pore Fluid Data Given in Table 5

Depth (cm)	pH	$\log A_{HPO_4^{2-}}$	$\log A_{Fe^{2+}}$	$\log A_{Ca^{2+}}$	$\log A_{Mn^{2+}}$	IAP (Vivianite)	IAP (Reddingite)	IAP (Anapaite)	Vivianite observed
0- 2	7.23	-6.29	-5.18	-3.17	-4.77	-13.7	-12.4	-9.64	Yes
2- 4	7.14	-6.23	-4.45	-3.14	-4.60	-11.5	-12.0	-8.91	"
4- 6	7.07	-6.32	-4.43	-3.15	-4.71	-11.8	-12.6	-9.23	"
6- 8	7.04	-6.23	-4.32	-3.15	-4.71	-11.3	-12.5	-9.18	"
8- 10	6.97	-6.19	-4.46	-3.17	-4.74	-11.8	-12.7	-9.24	"
10- 12	7.09	-6.16	-4.53	-3.18	-4.71	-11.7	-12.3	-9.03	"
18- 20	7.10	-6.07	-4.65	-3.17	-4.52	-11.9	-11.5	-8.93	"
28- 30	6.98	-6.15	-4.62	-3.17	-4.48	-12.1	-11.8	-9.30	"
38- 40	7.14	-6.17	-4.56	-3.16	-4.63	-11.7	-12.0	-8.94	"
48- 50	6.98	-6.09	-4.30	-3.14	-4.44	-11.2	-11.6	-8.90	No
58- 60	6.90	-6.22	-4.43	-3.12	-4.52	-11.9	-12.2	-9.31	Yes
68- 70	7.09	-6.27	-4.37	-3.16	-4.47	-11.5	-11.8	-9.05	"
78- 80	6.97	-6.36	-4.53	-3.16	-4.58	-12.4	-12.5	-9.63	No
108-110	7.18	-5.99	-4.22	-	-4.63	-10.3	-11.5	-	"
148-150	7.29	-5.77	-4.06	-3.12	-4.44	- 9.2	-10.3	-7.26	"
178-180	7.07	-6.18	-4.45	-3.10	-4.71	-11.6	-12.4	-8.87	Yes

$$\underset{\text{reddingite}}{M_3(PO_4)_2 \cdot 3H_2O} + 2H^+ \rightarrow 3Mn^{2+} + 2HPO^{2-}_4 + 3H_2O$$

$$\underset{\text{anapaite}}{Ca_2Fe(PO_4)_2 \cdot 4H_2O} + 2H^+ \rightarrow 2Ca^{2+} + Fe^{2+} + 2HPO^{2-}_4 + 4H_2O$$

The average IAP value for vivianite calculated for the core intervals where this mineral was observed is −11.7. This figure is in good agreement with the equilibrium activity product of −11.3, considering that the measurements pertain to the temperature of the sediments of 2–5°C. The IAP (vivianite) of −9.2 at depth of about 110 cm below the mud-water interface suggests that the preformed vivianite is being diagenetically re-mobilized. The average IAP value of −9.1 for anapaite in the vivianite-bearing intervals may be compared with the equilibrium value of −9.4. It would therefore appear that the pore fluids are saturated with respect to anapaite. In support of such an inference are the data of Kingston and Williams (personal communication) which show phosphate grains with high Ca concentrations.

The enrichment of Mn in the vivianite from around Station 73-013 has been noted (Table 4). The large disparity between the IAP (reddingite) of −12.2 for the pore fluids and the corresponding equilibrium value of −0.4 as derived from Latimer's (1952) ΔG°_f value for $Mn_3(PO_4)_2$ suggests that Latimer's constant is probably too high. In view of the extensive co-precipitation of Fe and Mn in the vivianite nodules (Table 4), the IAP value can be used to estimate the ΔG°_f for reddingite. The value so derived is −870.9 kcal mol^{-1}. This represents the limiting upper value although the off-setting effects of temperature differences and solid solution formation on the derived ΔG°_f should be noted.

Figure 8 gives the calculated total Fe and P to be expected in the interstitial waters of sediments which are saturated with respect to vivianite. A comparison of these data with the measurements for all the stations in Figure 7 indicates that vivianite should occur extensively in both the western and central basins of Lake Erie.

Finally, several green, greenish-brown, orange, and greenish-yellow phosphatic grains have also been observed in the sediments of the Great Lakes, and would indicate the formation of several other ferrosoferric hydroxyphosphates in the lake environments. (Work is now in progress to try to characterize these mineral phases). Thermodynamic calculations using the data in Table 3 suggest that lipscombite, beraunite, and rockbridgite should in fact be stable in these lake sediments.

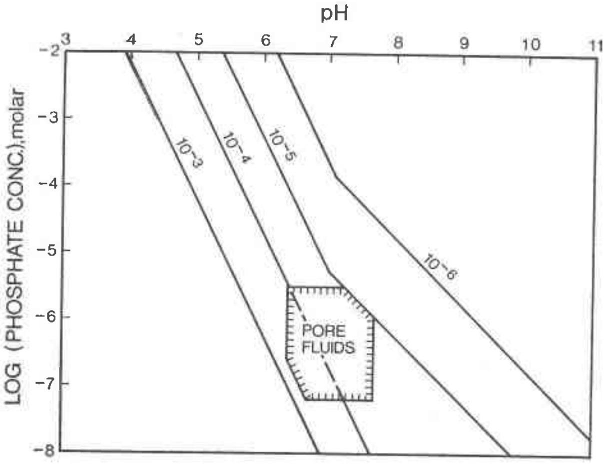

FIG. 8. Effects of pH on the iron and phosphate concentrations required to saturate the interstitial fluids with respect to vivianite. Contours refer to molar iron concentrations. Field measurements mostly fall in the indicated area.

Regeneration of Phosphorus from Lake Sediments

The mechanism of phosphorus regeneration in limnetic environments enunciated by Einsele (1938) and Mortimer (1941) has won widespread acceptance. From observations on the inter-relationships between the limnological cycles of Fe and P, these workers suggested that during overturn, when the hypolimnion is well aerated, most of the iron is oxidized to the ferric form which then engenders extensive removal of P by sorption or direct precipitation. During periods of stagnation, it is further believed that the ferric iron is reduced to the ferrous form with a concomitant release of P and Fe to the overlying water. Such a regenerative mechanism assumes that the oxido-reduction of the phosphated ferric oxyhydroxides is a readily reversible process. Experiments purporting to demonstrate the reversibility of such reactions (*e.g.*, see Warren, 1972), however, fail to recognize the potential reactivity of the precipitated oxyhydroxides towards the ions (notably P-bearing ligands) in the interstitial fluids. In addition, the suggested mechanism cannot explain the aerobic regeneration of P from sediments (see Tessenow, 1972) nor the observation (Burns and Ross, 1972) that the rise in levels of P (and other nutrients) in the hypolimnion commences long before the Eh is low enough to induce the reduction of the ferric oxyhydroxides.

Our studies of iron-phosphate systems lead us to suggest that, in many instances, the ferric oxyhydroxides precipitated from the overlying water are stabilized in the sediments, by their subsequent interaction with the P in the interstitial fluids as follows:

$$n\mathrm{Fe(OH)_3} + m\mathrm{HPO_4}^{2-} \rightarrow \mathrm{Fe}_n(\mathrm{HPO_4})_m(\mathrm{OH})_{3n-2m} + 2m\mathrm{OH}^-$$

As noted earlier, ferrosoferric hydroxyphosphates are most stable at the Eh and pH conditions likely to be encountered at the mud-water interface. Below the mud-water interface, however, the Eh environment may cause these complexes to dissolve incongruently to form vivianite or a mixture of vivianite with reddingite or anapaite. The solubility of the ferrous phosphates apparently controls the P concentrations in the interstitial water (see above) and indirectly the release of P to the overlying water. Thus the development of stagnant conditions during stratification may be expected to induce a large flux of P-laden interstitial fluids into the hypolimnion waters. The mass movement will of course be aided by bioturbation and supported by further dissolution of vivianite. Such a regenerative mechanism has been postulated by Bray, Bricker, and Troup (1973) and shown to be capable of resupplying the overlying water of Chesapeake Bay with 5 percent of its total P content in a period of about a week. Among several evidences which may be cited in support of the suggested mechanism is the familiar increase in P levels of lake waters observed after the disturbance of sediments by large storms. In this situation, the released P is more likely to come from the flushed-out interstitial waters and/or from the dissolution of ferrous phosphates rather than from the reduction of ferric oxyhydroxides.

Appendix

Composition of Interstitial Fluids from Lake Erie Sediments

The results of a partial analysis of interstitial waters extracted from Lake Erie sediments are summarized in Table 1A. It is immediately apparent that the pore fluids are enriched in all components with respect to the lake water. Stations 73-006, 73-015, 73-021, and 73-022 show a general increase of conductivity and concentrations of Ca, Mg, Na, and K with depth below the mud-water interface; the depth-concentration relationship for these parameters is less distinct in the other cores. The concentrations of Fe and Mn are highly variable and in general tend to increase with depth. No depth gradient is apparent for total-P concentrations. The homogeneity of pore fluid compositions in Stations 73-010 and 73-015 is notable.

TABLE 1A. Chemical Composition of Pore Fluids from Lake Erie Sediments

Interval (cm, below interface	pH	Conduc. (umhos)	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Fe (ppm)	Mn (ppm)	ΣP (ppb)
Stn 73-006									
0-2	7.33	140	13.4	4.6	7.2	30.0	2.9	1.7	100
2-4			18.6	2.3	6.8	30.0	2.3	1.5	73.0
4-6	7.29	271	17.0	1.6	7.2	29.0	1.8	0.8	41.0
6-8			15.0	1.5	9.0	30.1	2.7	1.1	110
8-10	7.35	320	19.4	2.4	9.1	31.5	2.6	1.3	52.5
10-12			18.0	2.3	10.0	34.5	2.2	1.4	78.5
13-15	7.39	290	23.6	2.5	10.3	-	3.5	1.6	128
18-20			20.4	2.6	11.2	36.8	2.7	1.6	50.0
28-30	7.58	305	24.0	4.9	12.3	-	7.6	1.4	114
38-40			20.0	2.3	11.8	40.6	3.0	1.7	48.5
48-50	7.46	405	20.8	3.0	15.8	43.5	4.3	2.0	55.0
62-64			23.2	2.6	14.2	49.5	2.5	1.7	44.5
68-70	7.20	478	19.6	3.2	14.2	49.5	5.3	2.0	47.5
78-80			36.4	3.0	16.2	60.0	8.4	2.1	156
Stn 73-007									
0-2	7.39	300	8.4	2.4	8.3	33.1	1.6	0.7	35.0
2-4		293	14.0	1.8	7.9	34.0	2.8	1.5	248
4-6		307	17.2	2.7	10.8	32.0	1.8	1.2	48.0
6-8	7.47	307	16.0	2.9	9.0	36.0	3.9	1.3	100
13-15		342	18.0	2.5	11.0	40.2	3.7	1.6	80
18-20		365	18.4	3.8	10.3	43.5	4.0	1.6	84
28-30	7.33	398	20.0	2.6	7.4	42.0	2.0	1.5	42
38-40			22.0	3.2	8.1	49.0	3.4	1.6	68.0
48-50	7.50	445	20.4	2.8	7.1	47.0	2.4	1.5	48.0
Stn 73-010									
0-2	7.18	340	17.6	1.9	7.5	37.0	1.2	1.5	34
2-4	7.23	331	17.4	2.4	8.2	39.0	3.2	2.1	90.0
4-6		330	17.6	2.4	7.5	35.5	1.9	0.9	50.0
6-8	7.14	330	16.6	3.4	7.5	35.0	2.0	1.6	54.0
8-10		325	18.0	2.5	8.2	36.4	3.1	1.7	58.0
13-15	7.22	325	16.3	2.7	7.4	34.0	2.8	2.0	62.0
18-20		342	20.8	2.4	7.5	32.5	2.9	1.9	56.0
28-30		339	22.0	3.0	7.5	33.0	3.1	1.4	45.0
38-40		335	18.0	2.8	8.3	35.0	2.8	1.5	50.0
48-50	7.46	342	16.6	3.0	8.3	35.8	3.4	1.8	62.0
Stn 73-015									
0-2	6.92	320	15.2	4.0	8.0	36.0	2.0	1.7	34.5
2-4	7.12	330	19.6	2.5	8.0	35.0	1.6	1.5	50.0
4-6		320	21.0	4.6	8.8	36.0	5.1	1.3	80.0
6-8	7.53	335	20.8	4.0	8.0	35.5	1.7	1.5	48.5
8-10		299	23.6	2.6	8.1	35.2	3.3	1.2	70.0
Stn 73-015 (Cont.)									
13-15	7.60	329	17.2	2.7	9.5	40.0	4.5	1.8	170
18-20		329	18.6	2.8	12.7	45.6	4.2	1.2	375
28-30	7.59	320	21.0	2.4	9.8	41.0	3.7	1.2	76.0
38-40		342	21.8	2.4	11.5	40.8	5.4	1.3	230
48-50	7.48	343	20.4	2.7	10.1	39.7	4.5	1.2	130
Stn 73-016									
0-2	7.34	341	20.4	2.9	8.2	37.0	1.8	1.3	82.0
2-4	7.48	330	20.6	3.2	8.0	36.0	2.2	1.7	100
4-6		355	19.8	2.8	8.2	38.0	2.0	1.5	34.0
6-8	7.41	370	23.2	3.0	8.8	37.2	1.9	1.4	44.5
8-10		368	20.0	2.1	8.8	38.2	1.7	1.2	60.1
13-15	7.66	364	18.7	4.6	10.2	41.0	1.9	1.4	136
18-20		406	23.9	2.5	9.8	41.4	1.8	1.3	66.0
28-30	7.46	370	20.0	2.1	9.3	-	2.7	1.2	60.0
38-40		389	19.0	2.4	9.3	40.0	2.5	0.9	43.0
48-50	7.61	424	23.2	5.1	10.2	-	3.4	1.0	72.5
Stn 73-021									
0-2	7.81	378	16.4	3.2	8.2	39.1	1.8	7.7	44.0
2-4	7.31	440	17.2	3.2	9.4	49.0	3.0	7.9	60.0
4-6	7.19	458	16.1	3.5	10.0	51.3	2.4	6.8	40.0
6-8	7.41	512	17.8	4.5	10.9	57.0	2.3	7.5	25.0
8-10	7.10	522	16.8	3.9	11.5	58.0	7.2	8.0	24.5
13-15	7.12	560	21.8	4.8	12.5	62.0	5.3	8.3	25.5
18-20	6.96	590	20.2	4.6	13.1	66.0	5.5	8.4	22.0
28-30	6.99	599	16.0	4.5	13.8	72.0	6.7	8.2	27.0
38-40	6.95	601	18.3	4.7	13.3	67.0	2.6	8.9	25.0
48-50	7.12	599	19.8	4.6	13.2	67.0	2.8	6.5	23.0
Stn 73-022									
0-2	7.23	331	16.0	2.5	7.4	35.5	2.2	2.4	34.0
2-4	7.23	382	16.4	2.7	8.2	41.8	2.3	3.0	38.5
4-6	7.19	423	17.5	3.3	9.2	47.0	2.5	3.4	39.5
6-8	7.10	448	18.0	3.2	9.8	52.0	4.8	3.7	44.0
8-10	7.13	463	18.3	3.1	10.5	54.0	2.0	3.6	48.5
13-15	7.06	510	16.3	3.5	12.5	60.0	7.5	3.8	27.5
18-20	7.06	530	20.0	3.8	12.5	59.5	8.5	3.8	34.0
28-30	7.03	490	17.0	3.7	12.5	56.4	5.3	3.5	27.0
38-40	7.12	496	16.5	3.5	12.6	59.0	6.3	3.7	38.0
48-50	7.21	502	19.0	3.9	12.6	56.0	6.0	3.6	30.0

Minor differences exist among stations. The conductivity (a measure of the total ionic concentration) of the interstitial waters from Station 73-006 is remarkably low at the sediment-water interface but increases rapidly with depth. By contrast, Stations 73-021 and 73-022 are highly enriched in dissolved ions throughout the core profile. Also, Stations 73-021 and 73-022 contain inexplicably high levels of dissolved Fe and Mn. These variations in chemical composition do not show any recognizable regional pattern.

Table 2A compares the compositions of pore fluids from the Great Lakes sediments. It is seen that there are significant differences in the (dissolved) major ion (specially Na, Mg, and Ca) concentrations in these lake sediments. The ranges in Fe, Mn, H^+ (and possibly other trace elements) concentrations, however, are similar. Notice the differences in the capacities of the lake sediments to concentrate the nutrients from the overlying water. For instance, Lake Superior sediments have a higher enrichment factor for Ca and Mg than the other lake sediments; Lake Erie surficial sediments are in fact depleted in these two elements relative to the lake water. The highest levels of dissolved Na is found in Lake Erie even though Lake Ontario waters have a higher Na concentration. In this connection, the depletion of Na with depth which has been reported for Lake Ontario pore fluids (Weiler, 1974) has not been observed in lake sediments; in many instances the reverse situation (*i.e.*, increasing Na concentration with depth) appears to be the case in Lake Erie sediments.

TABLE 2A. Comparison of Average Lake and Interstitial Water Compositions for the Great Lakes

Lake	pH	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Fe (ppm)	Mn (ppm)	ΣP (ppb)	Conduct. (μmhos)
Erie									
Lake water	8.1	11.5	1.23	8.3	37.4	0.067*	0.11*	20.1*	-
Surface sed.†	7.29	16.5	2.8	8.0	34.2	2.2	2.6	73.1	323
Deep sed.†	7.34	19.6	3.2	10.3	44.2	3.8	2.7	71.0	411
Ontario									
Lake water	7.9	12.6	1.35	8.1	40.3	-	-	-	
Surface sed.	7.7	13.5	2.1	9.2	51.4	0.72	2.8	-	
Deep sed.	7.7	12.9	2.1	10.1	50.0	1.78	3.36	-	
Michigan									
Lake water	8.0	3.4	0.9	10.0	32.0	0.005**	0.003**		
Surface sed.	8.0	5.8	2.4	13.6	42.9	0.29	0.41		
Deep sed.	7.2	13.9	2.2	17.0	43.9	1.2	0.94		
Huron									
Lake water	8.0	3.2	0.84	6.7	28.1	-	-		
Surface sed.	7.2	5.5	1.6	7.5	42.0	1.2	4.1		
Deep sed.	6.8	5.9	1.9	8.3	49.7	4.2	7.5		
Superior									
Lake water	7.8	1.3	0.54	2.7	13.2	0.011**	0.002**		
Surface sed.	7.0	2.3	1.2	3.7	26.0	1.8	0.99		
Deep sed.	7.0	4.4	1.7	4.9	30.8	5.2	1.8		

Unless otherwise specified, the chemical data for the lake waters are from Weiler and Chawla (1969). The sources for the interstitial water compositions are this report (Lake Erie), Callender, 1969 (Lakes Michigan, Huron and Superior) and Weiler, 1974 (Lake Ontario).

† surface sed. refers to depths of 0-5 cm below mud-water interface; deep sed. refers to core profiles below 6 cm.
* data from Burns and Russ, 1972.
** data from Callender, 1969.

Several authors (Callender, 1969; Weiler, 1974) have discussed the biogeochemical processes which control the compositions of pore fluids in the other Great Lakes sediments. Lake Erie, however, contrasts sharply with the other lakes in its physicochemical characteristics. A detailed examination of the diagenesis of Lake Erie sediments is now in progress.

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