SOME FACTORS AFFECTING THE SYNTHESIS OF CRYPTOCRYSTALLINE STRENGITE FROM AN AMORPHOUS PHOSPHATE COMPLEX

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ABSTRACT

Four experiments were initiated to examine the effects of pH, Eh (dissolved oxygen), agitation and concentration of key reactants (Fe and P) on the reaction of P with amorphous iron oxyhydroxide under conditions encountered in natural systems. pH and dissolved oxygen content are the most important variables controlling initial P uptake in the aqueous phase. The pH range (4-7) is optimal for uptake when Fe is greater than 0.25 mg/l and dissolved oxygen concentration is >15% saturation. Digestion of the resultant iron oxyhydroxide-phosphate under conditions of neutral pH, oxidizing Eh and $T = 100°C$, produced a mixture of cryptocrystalline strengite and phosphosiderite. This end-product verifies the thermodynamic predictions of Nriagu (1972b).

RÉSUMÉ

Quatre expériences ont été entreprises afin d'examiner les effets du pH, du Eh (oxygène dissous), de l'agitation et de la concentration des réactifs clés (Fe et P) sur la réaction du P avec de l'oxyhydroxyde ferreux amorphe dans des conditions rencontrées dans les systèmes naturels. Le pH et le contenu en oxygène dissous sont les variantes les plus importantes controllant la fixation du P initial de la phase aqueuse. La portée du pH (4-7) est au maximum pour la fixation lorsque Fe est plus grand que 0.25 mg/l et que la concentration d'oxygène dissous est plus grande que 15% de saturation. La digestion de l'oxyhydroxyde de phosphate ferreux dans des conditions de pH neutre, oxydant Eh et $T = 100°C$, a produit un mélange de strengite cryptocristalline et de phosphosiderite. Ce produit final confirme les prédictions thermodynamiques de Nriagu (1972b).

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INTRODUCTION

The reaction of phosphate ions with amorphous iron oxide has been suggested as a probable inorganic control on the availability of phosphorus in water (Mortimer 1941). Experiments undertaken by Einsele (1938) showed that in the pH range between 5 and 8, significant removal of inorganic phosphate from solution by precipitation with amorphous iron oxide did occur. Subsequent studies (Williams *et al.* 1971a,b,c) have suggested that this reaction may be of considerable importance in natural water systems. Mortimer (1971) found that the uptake and release of P in natural waters could be related to the oxidation state of the sediments. Oxygen depletion resulted in increased P concentrations in the overlying water.

The thermodynamic properties of the iron phosphate system have been examined in detail in a series of papers by Nriagu (1972a,b, 1974). He has summarized the available thermochemical data from the basic iron phosphate minerals and has developed theoretical models of the solubilities and stabilities of these minerals in aqueous systems.

No complete experimental description of the reaction of phosphorus with amorphous iron oxides exists, although Patrick & Khalid (1974) have provided good experimental information about five different soil types.

The effects of Eh and pH on the sorption of P onto ferric oxyhydroxide motivated the work described here. These experiments were designed

  (i) to describe experimentally the effects of Eh and pH in a simple aqueous Fe-P system, and

  (ii) to define the conditions of formation of a possible crystalline end-product of this interaction.

EXPERIMENTAL

In all experiments the simplest possible chemical systems were used so that extraneous chemical species would not interfere with the processes being investigated. 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.

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TABLE 1. SUMMARY OF 3 EXPERIMENTS CARRIED OUT TO DEFINE PO_4-IRON OXIDE ASSOCIATION

Experiment Number	Purpose of Experiment	Key Variables Observed	Results
1 (i)	To determine effect of pH on PO_4^{-3} uptake by amorphous iron oxide	pH	Uptake dependent on pH.
(ii)	To determine the stability of the phosphate iron hydroxide complex at different pH's.	pH	Defined pH range of stability of complex.
(iii)	To determine time of reaction	Time	Reaction complete in 2 min.
2 A	Effect of oxygen conc. on stability of complex	Eh	Complex dissolves when dissolved oxygen 2mg O_2/l.
B	If oxygen re-enters system when does complex reform?	Eh	Reforms when oxygen content 1-2mg O_2/l.
3	Can complex form a stable insoluble mineral?	Eh, pH, conc. PO_4^{-3}	Crystalline product forms and follows the thermodynamic predictions of Nriagu.

For experiment 2A results read dissolved oxygen <2 mg.

The phosphorus and iron concentrations employed in these experiments closely approximate those encountered in anoxic hypolimnetic waters. Lake Erie hypolimnetic waters contain between 0.35-2.5 mg/l of Fe and 90-275 μg PO_4/l (Burns & Ross 1972). Total P varied between 216-240 μg PO_4/l in these experiments, total Fe was maintained at 2.5 mg Fe/l. The key parameters of Eh and pH were investigated one at a time in order to keep the system simple and deterministic.

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 endproducts in a time short enough to be useful in this study. All other experiments were run at room temperature, which varied between 20-23°C.

Table 1 is a summary of the experiments, and the following are details of each:

Experiment 1: Two groups of seven solutions, each containing 2.5 mg/l Fe and 216 μg PO_4^{-3}/l were prepared as described in Appendix A. The pH's of the first group of seven solutions were raised from an initial value near 2.0, by the slow addition of 1.0 N NaOH, to final values of 3.0, 4.0, 5.0, . . . 10.0, care being taken to ensure that the final recorded value of pH was not exceeded at any time during the NaOH addition.

For the second group of seven solutions, the pH was raised quickly to about 7 long enough to form a solid; then the pH was quickly lowered to about 2. The pH of each beaker was again slowly increased to a final value of 3.0, 4.0, 5.0, . . . 10.0, as in the first group.

In both sets of experiments, once the final pH value had been attained, the solutions were stirred for about 20 minutes. They were then covered and left to stand for 24 hours, at which time the top 25 ml were decanted and analyzed for phosphate.

Two additional solutions were prepared. Each had its pH raised to 7 or 8 for about 10 seconds, then quickly had it lowered to 1.5 with a pre-measured amount of HCl. Finally, the pH of each solution was raised quickly to a final value of 4 and 5 respectively. The solutions were transferred immediately to 250 ml centrifuge tubes and spun at 2680 rpm for two minutes. Fifty-ml samples were decanted from the tubes and analyzed for phosphate.

Experiment 2: Two groups (A and B) of three solutions each were prepared as in Experiment 1.

Each solution initially contained 216 μg PO_4^{-3}/l, 2.5 mg Fe/l and had a pH between 6 and 8.

The six solutions were then treated in a manner identical with those of Experiment No. 1, except that this time, after the formation of the solid, they were not agitated, but were left undisturbed for 24 hours. At the end of the 24 hours, the top 20 ml were decanted and analyzed for phosphate. The Eh and pH of each solution was then measured.

The flasks were made airtight, and flushed with ultra-pure nitrogen for 24 hours. The stoppers were then removed, the Eh and pH of each solution was immediately recorded, and a 40 ml aliquot was decanted and analyzed for phosphate. This completed the work with group A.

The three solutions of group B were left stoppered for a further 48 hours, but air contact was available through the presence of two 4mm-diameter holes in each stopper. After this 48 hour exposure to air, a further 40 ml sample was decanted from each solution and analyzed for Eh, pH and phosphate.

Experiment 3: About 0.4 g of the amorphous ferric oxide were placed in a sealed glass bottle containing 250 ml solution of D.D. water having a pH of between 6.0 and 7.3. Varying concentrations ($3.9 \times 10^{-5}M$ to $3.9 \times 10^{-3}M$) of $KHPO_4$ were added in liquid and solid form as per Table 1. The mixture was then digested at 90°C for varying periods of time up to 20 days.
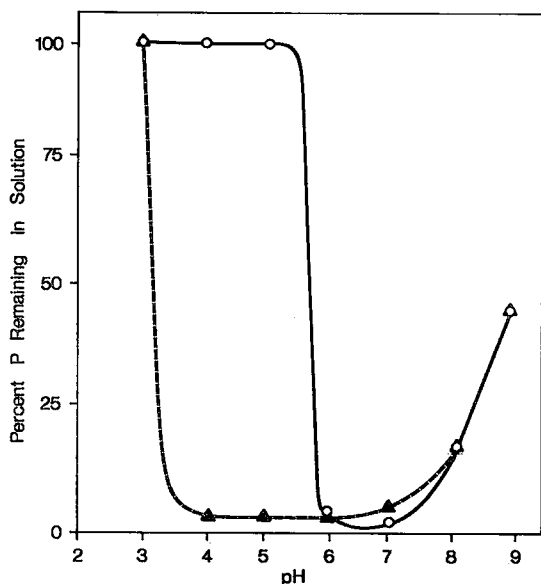
FIG. 1. P remaining in solution vs pH. Solid line is the result for no precipitate existing below pH = 6; dashed line is result for precipitate initially present. When iron-oxide precipitate is present, uptake of P onto the solid occurs down to pH = 4; in addition, P uptake is not as efficient above pH 7 for both experiments as in the neutral pH range. Initial Fe = 25 mg/l, initial P = 216 μg PO₄/l, See Table 4 for other details.

After digestion, the solid material was filtered on a 0.45 μm Millipore filter, dried in air, examined microscopically and x-rayed with a Guinier diffraction camera.

METHODS

All glassware was washed thoroughly in sulfuric acid and allowed to soak in 1.0 N acid for at least 2 days prior to its use in any experiments.

Total phosphate was determined using the molybdenum-blue method with extraction in isobutanol after Sutherland *et al.* (1966). The sensitivity of this method is about 0.5 μg PO₄/l. Iron was measured spectrophotometrically as its orthophenathroline complex, after Shapiro & Brannock (1962). All standard solutions were prepared using reagent-grade chemicals and distilled-deionized water.

Reagents used in the experiments are: Fe(S) in HCl, NaOH, HCl and KH₂PO₄.

RESULTS AND DISCUSSION

Figure 1 shows the removal of P as a function of pH (Experiment 1). Actual data are given in Table 2. Almost all P is removed from solution in the pH range 5.5-7.5 when no solid is present initially. Outside this pH range, considerable P remains in solution.

The results from the second set of solutions of Experiment No. 1 (with initial iron oxide present) are also shown in Figure 1. In the pH region between 3 and 6, more than 95% of the total phosphate is seen to have been removed in the second set of solutions, whereas none was lost in the first set. The only difference between the groups is that the second set contains solid particles of amorphous iron oxide in the pH range between 4 and 6, whereas the first set does not. Evidently, the solid is capable of removing more than 95% of the phosphate from the aqueous phase. In terms of concentrations, the amount of total phosphate was reduced to less than 10 μg PO₄/l from 240 μg PO₄/l. We can conclude that particulate amorphous ferric oxyhydroxide scavenges phosphate very efficiently from aqueous solution in the pH range between 4 and 7.

Inefficient phosphate removal at pH values greater than 7.5 is seen in both experimental sets. This becomes so pronounced, that at a pH of 9, only 50% of the P has been removed from solution. Since the solubility of the amorphous ferric oxide complex does not increase appreciably at this pH (Stumm & Morgan 1970), the removal of phosphate by the complex must not proceed very well at pH's greater than 7.5.

Parks (1969) has shown that the Z.P.C. of iron oxide particles in aqueous solution is 8.5. Below this pH, the oxide is positively charged and easily sorbs negatively-charged phosphate ions. As this pH value is approached, however, the positive surface charge on the iron oxide particles decreases and these particles become less efficient in attracting the phosphate. The

TABLE 2. SUMMARY OF EXPERIMENT 1[*]

Initial pH	Final pH	Total Initial Fe (mg/1)	Total Initial PO₄⁻³ (μg/1)	Eh (mV)	% PO₄⁻³ Remaining
2.17	2.99	2.5	216	362	100.0
2.13	4.05	2.5	216	357	100.0
2.20	4.97	2.5	216	368	100.0
2.04	5.97	2.5	216	366	4.4
2.07	6.99	2.5	216	373	2.2
2.11	7.99	2.5	216	367	14.0
2.15	9.02	2.5	216	374	46.5
2.1-2.2	3.00	2.5	216	460-350	100.0
"	3.99	2.5	216	"	4.2
"	5.01	2.5	216	"	3.8
"	6.03	2.5	216	"	4.4
"	6.98	2.5	216	"	4.5
"	8.00	2.5	216	"	14.0
"	9.01	2.5	216	"	47.0
2.11	4.01	2.5	216	365	1.5
2.09	5.00	2.5	216	361	1.0

[*]Effect of varying pH on uptake and release of P on iron oxides. First set are results with no initial solid; second set are results for initial Fe-oxide precipitate.

amount of phosphate in solution then increases relative to the amounts in solution when adsorption is proceeding at full capacity, *i.e.*, at pH's <7.5.

The results of the centrifuging experiment (solutions C-1 and C-2, Experiment 1, Table 2) show that the reaction time for the adsorption to occur is less than 120 seconds. This represents the total time required to form the ferric phosphate complex and to centrifuge it out of the top few mm of solution. This fast reaction can be explained as a physical sorption reaction, as a chemisorption reaction, or as a simple chemical precipitation of the ferric phosphate complex. Unfortunately, no further differentiation as to which mechanism is operative in this system can be made using the results of Experiment 1.

Experiment 2 relates P removal to the oxidation state of the solution. The influence of Eh on the ferric phosphate complex is found in Table 3. Here we see that lowering the Eh of the system to between 192 and 200 mV from the original 370 mV resulted in the disappearance of the complex and an increase in phosphate concentration in the solution. After oxygen had been allowed to re-enter the vessel, it was noted that the precipitate reappeared and that the phosphate had been removed again from its soluble phase. This phenomenon is identical to that described by Mortimer (1971) for natural systems.

The Eh value of 192 mV in this experiment is equivalent to a dissolved oxygen concentration of about 0.2 mg/l. This represents about 2% of the oxygen that was originally in the solution. The first reappearance of precipitate was confirmed at an Eh of 249 mV; this corresponds to a dissolved oxygen content of 1.2 mg O_2/l or 15% saturation.

Dissolved-oxygen values measured by Mortimer (1971) as being necessary for the release of phosphate and iron into water from lacustrine sediments ranged between 1 and 2 mg O_2/l. Comparison of his values with those of this study (0.2-1.2 mg O_2/l) provides good agreement between laboratory measurements and field observations.

The third experiment provides two notable results. The first is that a crystalline ferric phosphate mineral can form from the amorphous ferric phosphate complex; the second is that its conditions of formation conform to those defined thermodynamically by Nriagu (1972b). The findings of experiment 3 are summarized in Table 5.

As seen in the Table, only one set of conditions results in the formation of a uniquely

TABLE 3. SUMMARY OF EXPERIMENT 2.[*]

	Total Initial Fe (mg/l)	Total Initial PO_4^{-3} (g/l)	Eh	pH	PO_4^{-3} Remaining in Water (5)
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

[*]Effect of Eh upon retention of P on Fe-oxide.

TABLE 4. SUMMARY OF EXPERIMENT 3.[*]

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

[*]Effect of phosphate addition on $Fe(OH_3)$ diagenesis.

TABLE 5. RESULTS OF EXPERIMENT NO. 3[*].

Digestion Product	Digestion Time	Solid KH_2PO_4 Added	Dissolved KH_2PO_4 Added	Final PO_4^{-3} concentration, moles/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}

[*]Effect of phosphate addition on $Fe(OH)_3$ diagenesis.

In Table 3, for g/l read ug/l.

identifiable crystalline product. These conditions are: $\Sigma PO_4 = 3.9 \times 10^{-3}$ moles PO_4^{-3}/l, pH = 7.0, Eh = 359 mV, digestion time = 18 days, temperature = 90°C.

The product was identified by its *x*-ray pattern recorded with the Guinier diffraction camera. After the major reflections were indexed, the product was identified as a combination of cryptocrystalline strengite, $FePO_4 \cdot 2H_2O$ and phosphosiderite, $FePO_4 \cdot 2H_2O$ (Table 6). These minerals are chemically identical but structurally dimorphic, their sole difference being in the tilt of their phosphate tetrahedra with respect to their metal-oxygen octahedra. For structural details of these minerals the publications of Moore (1966) and Borensztajn (1966) should be consulted. Table 6 provides a brief structural comparison of these minerals.

The conditions of formation described above (Figure 2) fall within the thermodynamic boundaries of strengite as defined by Nriagu (1972a).

In the natural environment, strengite is not

likely to be a major constituent of lacustrine sediments (Nriagu 1974) because (i) it is unstable relative to tinticite and cacoxenite, two other ferric phosphate minerals, and (ii) most lacustrine sedimentary environments are reducing a few mm below the sediment-water interface. The formation of cryptocrystalline strengite in oxidized microzones at the sediment-water interface cannot be ruled out though and, in fact, one occurrence of cryptocrystalline strengite has been reported by Halbach (1974). He identified the strengite in ferromanganese concretions from the sediments of some Finnish lakes. In this case, the formation of strengite was attributed to the upward migration of ferrous ions to the surface sediments, where they were oxidized to ferric ions and reacted with the phosphate to form strengite.

SUMMARY AND CONCLUSIONS

These experiments have revealed the following characteristics of the reaction between in-organic orthophosphate ions and amorphous iron oxide in an isolated experimental system:

(1) Phosphate removal from solution by amorphous iron oxide proceeds efficiently only between pH values of 4 and 7. In addition, solid particles of amorphous iron oxide are necessary for the reaction to proceed.

(2) The reaction between the solution and the solid ferric oxide is rapid; so rapid in fact, that it is complete in less than 120 seconds.

(3) The iron oxide-phosphate complex is stable in the pH range from 4 to at least 10, provided that the Eh is greater than 250 mV. If thte redox potential becomes less than 200 mV, the complex becomes unstable and dissolves.

(4) This complex can be altered to cryptocrystalline strengite and/or phosphosiderite after a 2-week digestion at 90°C.

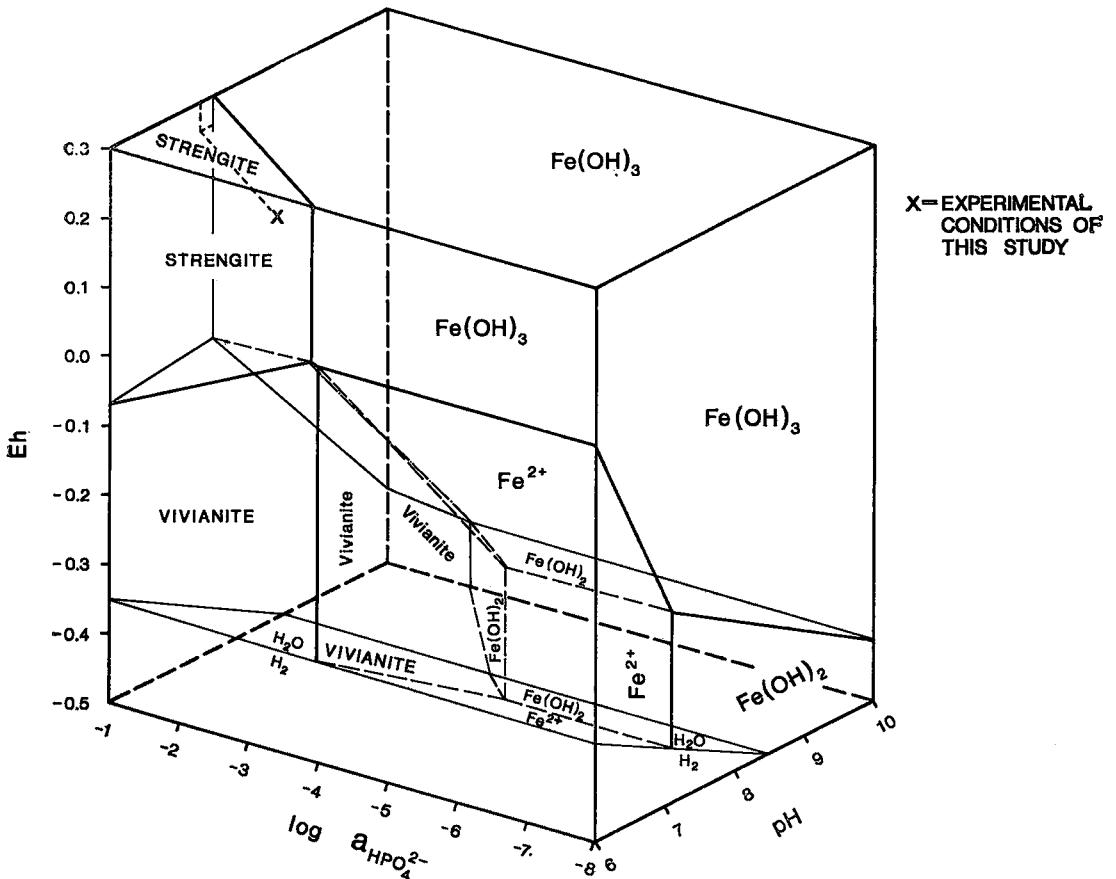These results are applicable to the short-term phosphorus budget of lakes that are shallow

FIG. 2. Stability relations of iron phosphates and hydroxides in the absence of H_2S (after Nriagu 1972a).

(P uptake into particulate iron oxyhydroxide), lakes that undergo periods of extreme oxygen depletion (P release from sediments) and lakes subject to high loadings of iron and phosporus (phosphate-mineral formation). Anoxic conditions (<2 mg/l dissolved oxygen) are a major, though not unique, contributor to the release of phosphorus from sediments; anoxic conditions commonly occur in the hypolimnion of eutrophic lakes, such as in the central basin of Lake Erie (Burns et al. 1972).

Lakes having their pH buffered above the pH range of maximum P removal (pH$>$7) probably can attribute part of their labile P to the decreasing sorption of this nutrient by amorphous iron oxide above this pH. Most hard water (carbonate) lakes have pH's about 8, so this mechanism is probably operative in them.

The formation of phosphate minerals should be an important control on phosphate availability in fresh-water and sedimentary environments where total iron is in large excess over sulfur. In most natural environments, the phosphate minerals vivianite, lipscombite, beraunite and rockbridgeite should constitute the most stable mineral suite (Nriagu 1974), as opposed to the strengite minerals synthesized in this study. Vivianite is probably the most common, and has been identified in sediments from Lakes Superior, Erie and Ontario (Dell 1973).

A different application of these results could be in the field of nutrient removal from domestic wastewater. If solutions containing ferric iron were applied to oxygenated wastewater under near-neutral pH conditions, large amounts of soluble phosphate should be removed. In our experiments, more than 95% of the original phosphate was removed from solution. Comparable results in domestic wastewater treatment plants would go a long way towards alleviating the problem of anthropogenic addition of phosphate to our lakes and streams.

APPENDIX

Standard solutions

Two standard solutions were employed in this research. The iron standard was prepared by dissolving 1.2523 g of pure iron powder in 100 ml of 12 N HCl. This solution was then diluted with distilled-deionized (D.D.) water to a final volume of 500 ml in a volumetric flask. 10.00 ml of this stock solution were pipetted into a 1000 ml volumetric flask and diluted to volume with D.D. water. The resultant concentration of Fe^{+3} in this solution was 25 mg Fe^{+3}/l and its pH was less than 1. The phosphate standard was made by diluting

TABLE 6. COMPARISON OF STRENGITE ($FePO_4.2H_2O$), PHOSPHOSIDERITE ($FePO_4.2H_2O$), AND CRYSTALLINE PRODUCT DIGESTED AT pH 7

Strengite PDF 15-513		Phosphosiderite PDF 15-390		pH 7 Digest	
I	$d(\mathring{A})$	I	$d(\mathring{A})$	I	$d(\mathring{A})$
80	5.50	40	6.51	80	5.50
60	4.95	60	4.90	60	4.90-4.95
		80	4.69	50	4.69
100	4.38	80	4.37	100	4.37-4.38
		40	4.12	-	4.12
60	3.98			40	3.99
40	3.72			20	3.72
		80	3.61	40	3.62
20	3.29	10	3.34		
80	3.11	10	3.20	50	3.11
60	3.00			40	3.00
60	2.95			40	2.96
		100	2.78	50	2.76-2.80
10	2.69				
		10	2.65		
10	2.63				
80	2.54	60	2.57	50	2.54-2.57
40	2.445	10	2.46	20	2.43-2.45
10	2.400				
10	2.360	20	2.342		
10	2.273	20	2.258		
40	2.180	10	2.220		
10	2.134	10	2.168		
40	2.101	20	2.122	-	2.101
10	2.035	10	2.072	-	2.010
40	2.001	60	2.010	-	2.001

40.0 ml of a 12.0 mg PO_4^{-3}/1 working solution to 2000 ml with D.D. water. This produced a solution containing 240 μg PO_4^{-3}/l. The working solution was prepared by dissolving 0.01569 g of KH_2PO_4 in 1000.0 ml of D.D. Water.

Experiment 1

The fourteen solutions of experiment 1 were prepared by mixing together 10.00 ml of the iron standard (25 mg Fe^{+3}/l) with 90.0 ml of the phosphate standard (240 μg PO_4^{-3}/l) in a 250 ml beaker. All of the solutions prepared for experiments 1 and 2 were prepared in this manner.

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