PHYSICAL AND CHEMICAL CHARACTERIZATION OF SELECTED NATURAL APATITES IN SYNTHETIC AND NATURAL AQUEOUS SOLUTIONS

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Abstract. Several natural calcium-phosphate apatites, chosen to be representative of the apatite which enters aquatic environments in ground water, runoff and erosion material, were characterized by X-ray diffraction and chemical analyses. Samples were selected to include apatites with widely different structural stabilities and ionic compositions. The solubility of apatite increased as the pH of water and the particle size of apatite crystals were decreased. The concentrations of dissolved ortho-PO_4^{3-} increased in proportion to the amount of apatite added to water and apatite generally increased the pH of water at low slurry densities. The solubility of apatite decreased as the concentrations of ions in water were increased and apatite increased the pH and levels of ortho-PO_4^{3-} in lake water containing relatively high endogenous concentrations of Ca^{2+} and ortho-PO_4^{3-}.

Increases in soluble ortho-PO_4^{3-} concentrations in limnetic solutions following apatite addition suggest that partial dissolution of apatite crystals can contribute dissolved ortho-PO_4^{3-} to the P-cycle of aquatic ecosystems. The contribution would probably be of significance under oligotrophic conditions, in areas where anthropogenic P loadings are reduced or in regions receiving high inputs of apatite in the form of erosion material.

1. Introduction

The properties of apatites have been under active investigation for many years due to the widespread distribution of this mineral in nature (see McConnell, 1973, for review of apatite literature). Geologically, apatite is ubiquitous in igneous rocks, usually being the sole locus of P and is also associated with metamorphic, sedimentary and lunar rocks (Albee and Chodos, 1970; McConnell, 1973). Minerals having the general formula $(M)_{10}(XO_4)_6(Z)_2$ are called apatites when M is Ca, Na, K or Mg and pyromorphites when M is a metal (Corbridge *et al.*, 1966). Various ions can occupy the positions X (P, As, Si, S, Cr, and Ge) and Z (F, OH, Cl, Br). Evidence has also been presented to show that H_3O^+ (McConnell, 1970, 1973), CO_3^{2-} (Gulbrandsen *et al.*, 1966; Corray, 1970) and rare earths (Grisafe and Hummel, 1970; Nash, 1972) can be found in the crystal lattices of apatites in significant concentrations. Isomorphous substitutions within the crystal lattices of apatites occur during the process of igneous differentiation (Nash, 1972). The degree of substitution affects the color (Grisafe and Hummel, 1970) and stability of the lattice (Wier *et al.*, 1972) and consequently influences the solubility of the mineral in aqueous environments.

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The calcium phosphates are by far the most important forms of apatite but the role of apatite, predominantly hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and fluorapatite ($Ca_{10}(PO_4)_6F_2$), in aquatic ecosystems is not well understood. It is generally believed that apatite need not be considered as a significant source of soluble ortho-PO_4^{3-} in limnetic situations due mainly to its relatively low solubility in alkaline water (Williams *et al.,* 1976b). It has also been suggested that 'apatite does not enter into the P-cycle of Lake Erie' (Burns *et al.,* 1976). Other workers, however, have suggested that increases in total plankton in the western basin of Lake Erie are attributable in part to increasing degrees of saturation of the water with respect to hydroxyapatite (Snow and Thompson, 1968).

The present investigation was conducted to examine the behavior of several natural apatite samples in synthetic and natural aqueous solutions and to determine the factors which affect the release of ortho-PO_4^{3-} from apatite crystals.

2. Materials and Methods

2.1 APATITES

Apatite samples (#1 and 3 to 10) were obtained from various locations around Lake Ontario. Fluorapatite (#2); representative of apatite in Monmouth Township, Ontario (Royal Ontario Museum), francolite (#11), collophane (#12) and fluorapatite from Mexico (#13) were used for comparative purposes. The samples were ground with mortar and pestle, and were passed through sieves to obtain crystals of the following particle sizes: 1000 to 2000 μm; 500 to 1000 μm; 250 to 500 μm; 100 to 250 μm; 30 to 100 μm, and <30 μm. The crystals were washed in distilled water (pH 8.0) and were stored in sterile plastic petri dishes. Each of the 13 apatite samples (30 to 100 μm) was characterized by X-ray diffraction using a Philips Type PW 1011/60 X-ray diffractometer (Cu tube, 20 mA and 40 kV) at a scanning rate of 1° min^{-1} (10° to 65°).

Each apatite sample (50 mg) was weighed into a 200 ml BOD bottle containing 20 ml of 95.5% H_2SO_4. The samples were autoclaved at 121°C for 20 min and after cooling were diluted to 200 ml with H_2SO_4. The samples were analyzed for Ca, P (as ortho-PO_4^{3-}), Cl, Na, K, Mg, Pb, Al, Fe, Hg, Ni, Zn, Co, Cu and Si (Analytical Methods Manual, 1974).

2.2 APATATE-WATER SYSTEMS

After the chemical analyses and X-ray diffraction studies were completed, apatite samples 2, 3 and 4 were selected to examine the behavior of apatite in various aqueous solutions since they represented samples with considerable variation in ionic composition and structural stability.

In all cases, the glassware used in this study was soaked in concentrated H_2SO_4, washed four times in hot water and rinsed three times with glass-distilled water. Distilled water was used for all solutions unless stated otherwise. The pH of water was adjusted to acidic levels with 1 N H_2SO_4 and to basic levels with 1 N KOH. Apatite #4 crystals (30 to 100 μm) were added to BOD bottles containing water of pH levels ranging from 1 to 8 to yield concentrations of 100 $\mu g\ ml^{-1}$.

To determine the effect of the quantity of apatite on the concentrations of ions released from the lattices, apatite #4 crystals (30 to 100 μm) were weighed into BOD bottles containing water of pH 7 to yield concentrations of 50, 100, 200, 400, 600, 800, 1000, 1500, 2000 and 2500 $\mu g\ ml^{-1}$. To examine the influence of particle-size distribution on the solubility of apatite, crystals of sample #3 were added to water of pH 7 to yield concentrations of 100 $\mu g\ ml^{-1}$ as particles ranging from 1000 to 2000 μm to <30 μm. Apatite #4 crystals (30 to 100 μm) were added to water of pH 6.4 to yield concentrations of 250, 500, 1000, 1500 and 2500 $\mu g\ ml^{-1}$ in order to determine the effect of apatite on the pH of the water. To investigate the effects of ionic composition of water on apatite solubility, apatite #2 crystals (<30 μm) were added to P-free (<1 $\mu g\ l^{-1}$ total P) Bristol's (PfB) medium (pH 7) containing the recommended ionic composition (Nichols and Bold, 1965) to yield 500 $\mu g\ ml^{-1}$. Apatite #4 crystals (30 to 100 μm) were added to PfB medium of pH 7 containing 10^{-1} to 9×10^{-1} times the normal ionic concentration to yield 100 $\mu g\ ml^{-1}$. In this experiment, water from Lake Ontario (pH 7.93) containing endogenous ortho-PO_4^{3-} and Ca^{2+} concentrations of 51.0 $\mu g\ l^{-1}$ and 40.7 $\mu g\ ml^{-1}$, respectively, was used as the solution for comparison with distilled water. Apatite #2 crystals (30 to 100 μm) were added to yield 100, 1000 and 2500 $\mu g\ ml^{-1}$.

In all cases, BOD bottles containing apatite-water slurries were incubated for 24 h at 20°C before the concentrations of ortho-PO_4^{3-} and/or Ca^{2+} were determined. The pH of each solution was determined using a model PHM 62 standard pH meter (Bach-Simpson Ltd., London, Canada).

3. Results and Discussion

The apatite samples used in this study were analyzed by X-ray diffraction to gain some information on the crystalline nature and stability of each sample. Samples were selected to include apatites which would range from unstable, distorted, defective, highly substituted forms with inferior crystalline structure (apatite #4) to forms which were stable, relatively unaltered and closely approximating the nature of synthetic fluorapatite (apatite #1). The X-ray diffractograms presented in Figure 1 display the apatitic character (Berry *et al.*, 1974) of samples 2 through 5. The diffraction patterns confirm that apatite #4 as compared to #2 had an inferior crystalline structure due to the absence of peaks between 40 and 50° and to the presence of two additional strong peaks between 45 and 55° indicating a high degree of isomorphous substitution. Apatite #2 was superior in structure as indicated by the well-defined diffraction patterns. The X-ray diffractograms of the remaining samples (excluding #11 and #12) were similar to that of #5.

According to the chemical analyses (Table I), all samples contained Ca^{2+} and ortho-PO_4^{3-} as the major ionic constituents but the ratios of Ca^{2+}/ortho-PO_4^{3-} and the

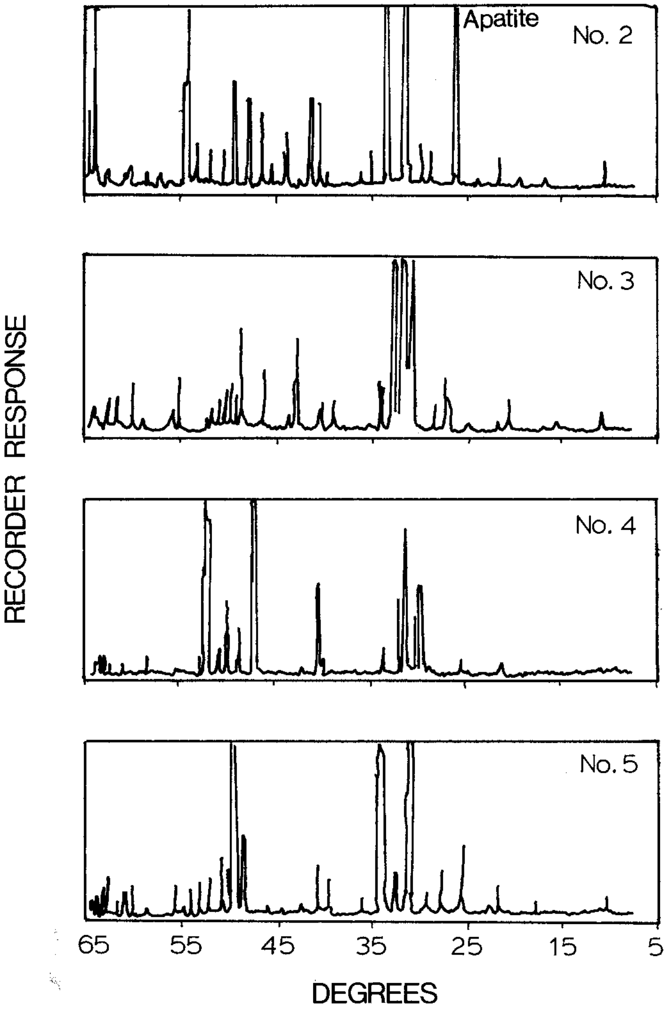

Fig. 1. X-ray diffraction patterns of selected apatite samples.

abundance of other elements within the crystal lattices of the samples were highly variable. The samples varied in Ca^{2+} and ortho-PO_4^{3-} content from 372 and 172 mg g^{-1}, respectively, in apatite #5 to 480 and 212 mg g^{-1}, respectively, in apatite #1. Apatite #2 contained 0.12 mg g^{-1} of Mg and 4.8 mg g^{-1} of Cu whereas apatite #4 contained 3.6 and 1.3 mg g^{-1}, respectively. Francolite (apatite #11) contained more than 100 times as much Al and more than 50 times as much Fe as the well-structured apatite #3. Apatite #2 contained a substantial quantity of Pb and apatites #2, #3, and #4 were characterized as having high levels of Cu.

The apatite samples differed considerably in solubility due to the great differences in ionic composition of the crystals and degrees of crystallinity based on X-ray diffraction

TABLE I

Chemical analyses of apatite samples

Sample	Ca^{2+}	PO_4^{3-}	Al	Fe	Mg	Cu	Pb	Zn	Ni	Si	Hg	Na	K	Cd
1	480[a]	212	0.92	0.23	0.12	0.29	0.15	0.08	0.01	5.2	0.0006	78.4	1.3	0.012
2	388	188	0.76	0.60	0.12	4.80	1.0	1.32	0.012	8.4	0.0006	3.7	1.3	0.012
3	412	188	0.64	2.12	0.40	3.50	0.11	1.24	0.028	8.4	0.0008	1.3	1.2	0.012
4	400	176	0.76	0.80	3.60	1.28	0.11	0.48	0.028	9.2	0.0006	1.3	1.2	0.012
5	372	172	0.72	0.32	0.92	0.03	0.33	0.012	0.028	7.6	0.0006	2.9	4.2	0.012
6	388	176	0.80	0.32	1.1	0.012	0.08	0.012	0.028	7.6	0.0006	3.7	1.2	0.012
7	400	184	0.68	0.32	1.1	0.012	0.11	0.012	0.028	6.8	0.0006	2.6	1.2	0.012
8	412	188	0.76	0.36	1.1	0.012	0.08	0.012	0.028	4.8	0.0006	2.9	1.2	0.012
9	412	192	0.76	0.32	2.28	0.012	0.08	0.012	0.028	6.0	0.0006	4.0	1.2	0.012
10	428	196	0.88	0.64	0.40	0.004	0.08	0.012	0.028	6.8	0.0006	4.8	1.2	0.012
11[b]	132	108	84.0	11.6	1.2	0.004	0.05	2.92	0.028	6.8	0.0006	1.7	1.2	0.200
12[c]	368	156	6.0	0.92	0.52	0.012	0.08	0.068	0.012	6.0	0.0006	2.6	2.2	0.012
13	380	184	1.1	0.40	0.28	0.012	0.07	0.012	0.012	4.8	0.0006	2.9	1.2	0.012

[a] All values are given as mg g^{-1}.

[b] Francolite.

[c] Collophane.

patterns. The relative instability of the crystalline structure of apatite #4 under acidic conditions is depicted in Figure 2. These results are in agreement with the general behavior of apatites in solutions with acidic pH levels (Brown, 1966). Thus, the pH of aquatic habitats will have a profound influence on the solubility of apatites. The amount of apatite that was added to an aqueous environment at any given pH was also found to have a direct bearing on the total amounts of Ca^{2+} and ortho-PO_4^{3-} that were released from the crystal lattices (Figure 3). As the amount of apatite was increased in a given volume of solution, the Ca^{2+} and ortho-PO_4^{3-} concentrations in solution increased in a non-linear fashion. The experimental evidence shows that as the amount of apatite was increased, the changes in concentration of dissolved ions became less pronounced.

Data presented in Figure 4 indicate that there was an inverse relationship between particle-size distribution of apatite crystals and the amounts of Ca^{2+} and ortho-PO_4^{3-} released from the crystals. Thus, at any given pH, the solubility of a given amount of apatite increased as the particle size was decreased. This effect can be attributed to surface area. Apatite crystals associated with the fine-grained (<62.5 μm) sediment that is entering Lakes Erie and Ontario (Williams and Mayer, 1972; Williams *et al.*, 1976a) has been shown to be sufficiently small to be transported considerable distances by water currents (Burns *et al.*, 1976).

The presence of OH^- ions within the lattices of the apatite samples was confirmed by the evidence presented in Figure 5. When apatite #4 crystals of one particle size were added to water of pH 6.4 to yield 250 μg ml^{-1}, the pH of the solution after 24 h at 20°C was 6.7 and a level of 2500 μg ml^{-1} resulted in a pH change of 1.2 units. The effects of apatite on the pH of water with higher pH values was much less pronounced due to the reduced solubility of apatite under alkaline conditions and the addition of as

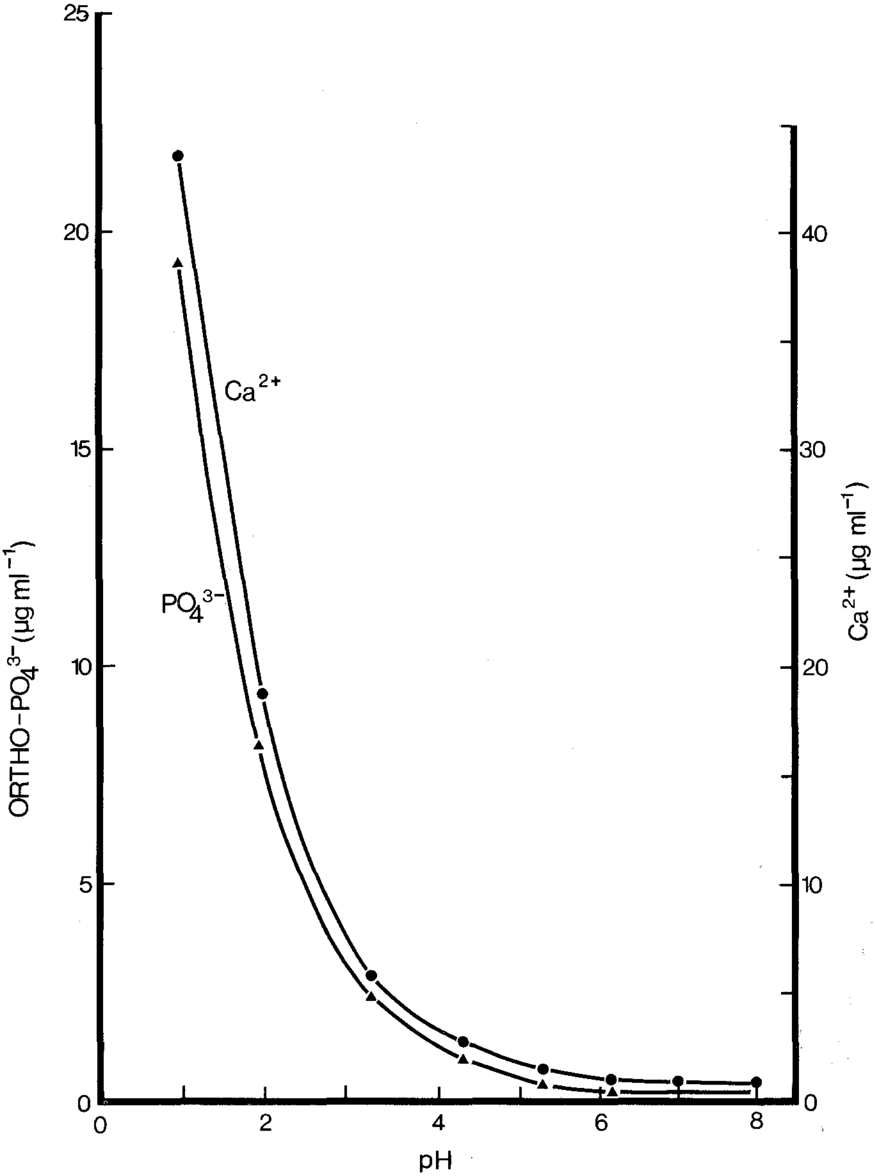

Fig. 2. Effect of pH of water on the solubility of apatite #4 crystals (30–100 µm) after 24 h at 20°C at a slurry density of 100 µg ml^{-1}.

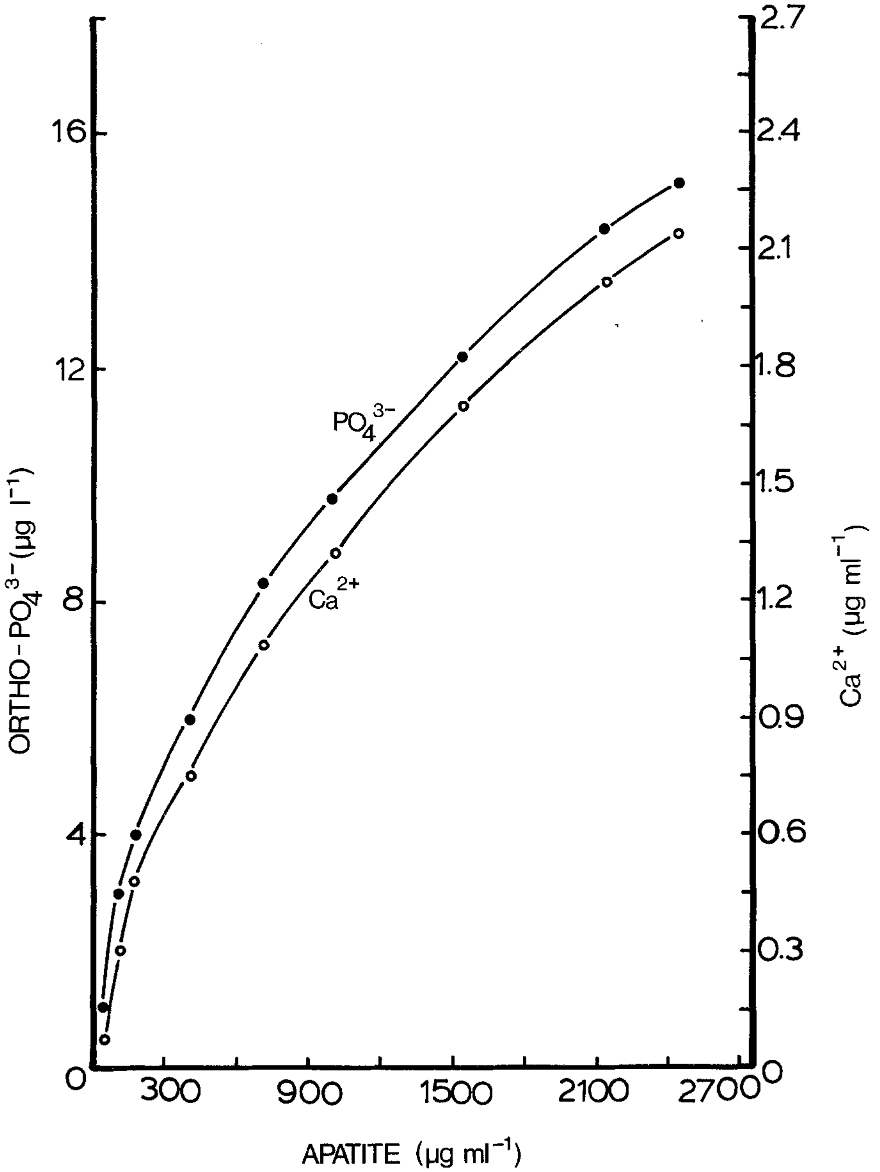

Fig. 3. Effect of quantity of apatite #4 crystals (30–100 µm) added to water (pH 7) on concentrations of ortho-PO_4^{3-} and Ca^{2+} in solution after 24 h at 20°C.

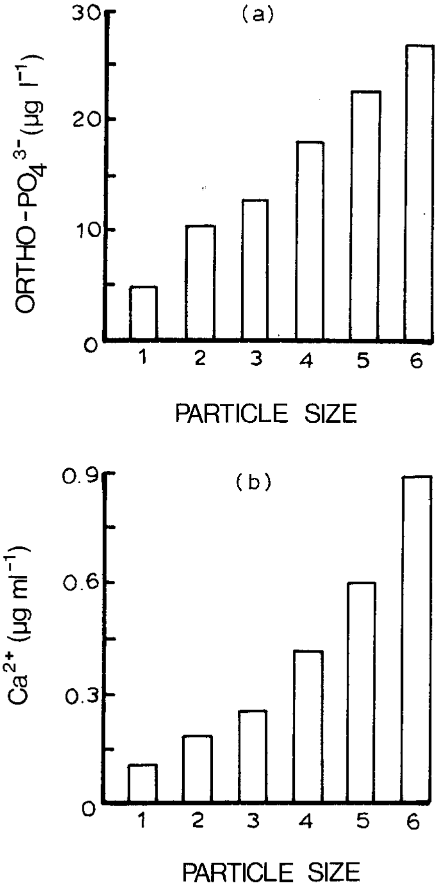

Fig. 4. Effect of particle-size distribution of apatite crystals on solubility of apatite. Crystals of apatite #3 were added to water (pH 7) to yield 100 μg ml^{-1}. Concentrations of ortho-PO_4^{3-} and Ca^{2+} were determined after 24 h at 20°C for slurries containing the following particles sizes: 1 (1000–2000 μm), 2 (500–1000 μm), 3 (250–500 μm), 4 (100–250 μm), 5 (30–100 μm) and 6 (<30 μm).

much as 2500 μg ml^{-1} of apatite #2 to lake water containing relatively high concentrations of Ca^{2+} and ortho-PO_4^{3-} increased the pH of the water by only 0.23.

The presence of other ions in solution reduced the solubility of apatite (Figure 6). For a given amount of apatite #4 crystals at a slurry density of 100 μg ml^{-1}, one particle size (30 to 100 μm) and a single pH of 7.0, the concentrations of ortho-PO_4^{3-} in solution after 24 h at 20°C in PfB medium containing 1 and 10^{-1} times the recommended level of nutrients were 6.2 and 9.9 μg l^{-1}, respectively. Similarly, the concentrations of ortho-PO_4^{3-} from apatite #2 crystals (<30 μm) added to 1, 10^{-1} and 10^{-2} times normal ionic-strength PfB medium of pH 7.0 were 21, 39 and 90 μg l^{-1}, respectively (Figure 6).

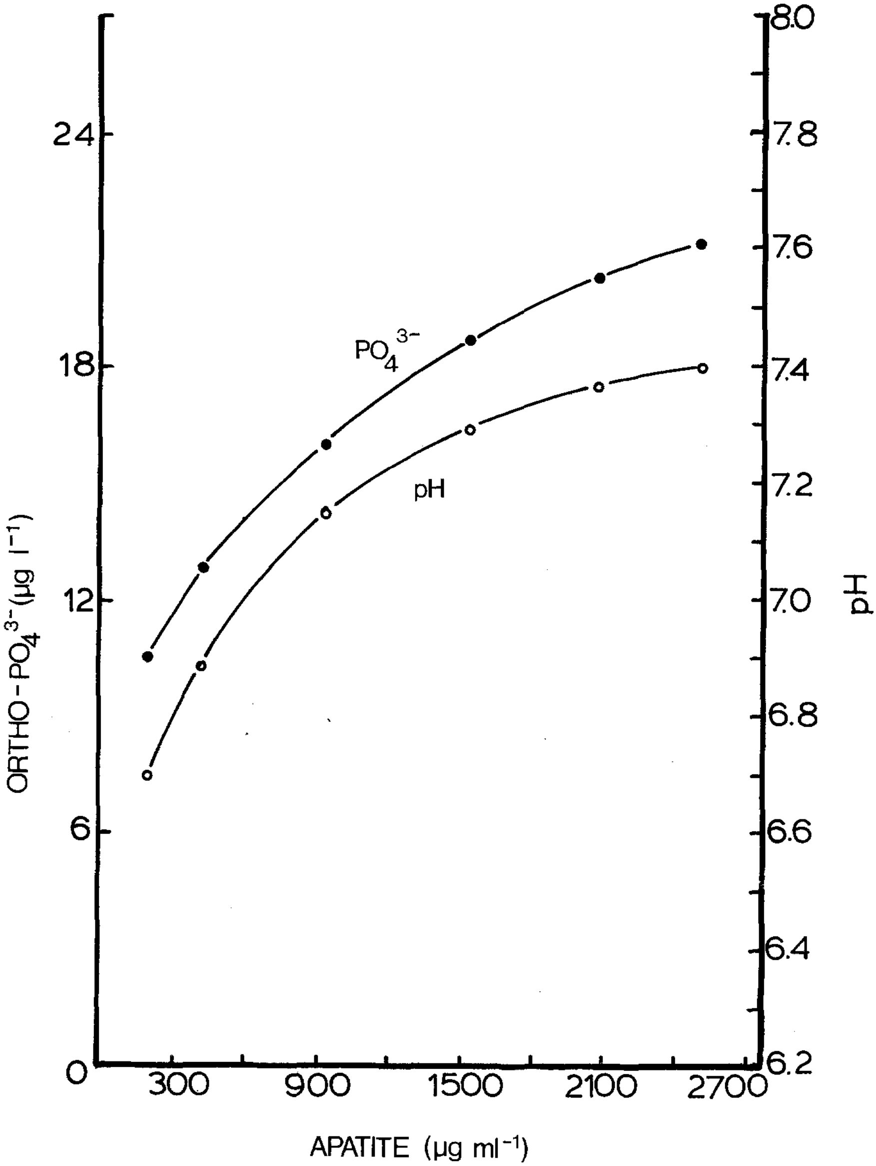

Fig. 5. Effect of apatite on the pH of water. Apatite #4 crystals (30–100 µm) were added to water (pH 6.4) to yield concentrations from 250–2500 µg ml^{-1}. After 24 h at 20°C, ortho-PO$_4^{3-}$ and pH were determined for each slurry.

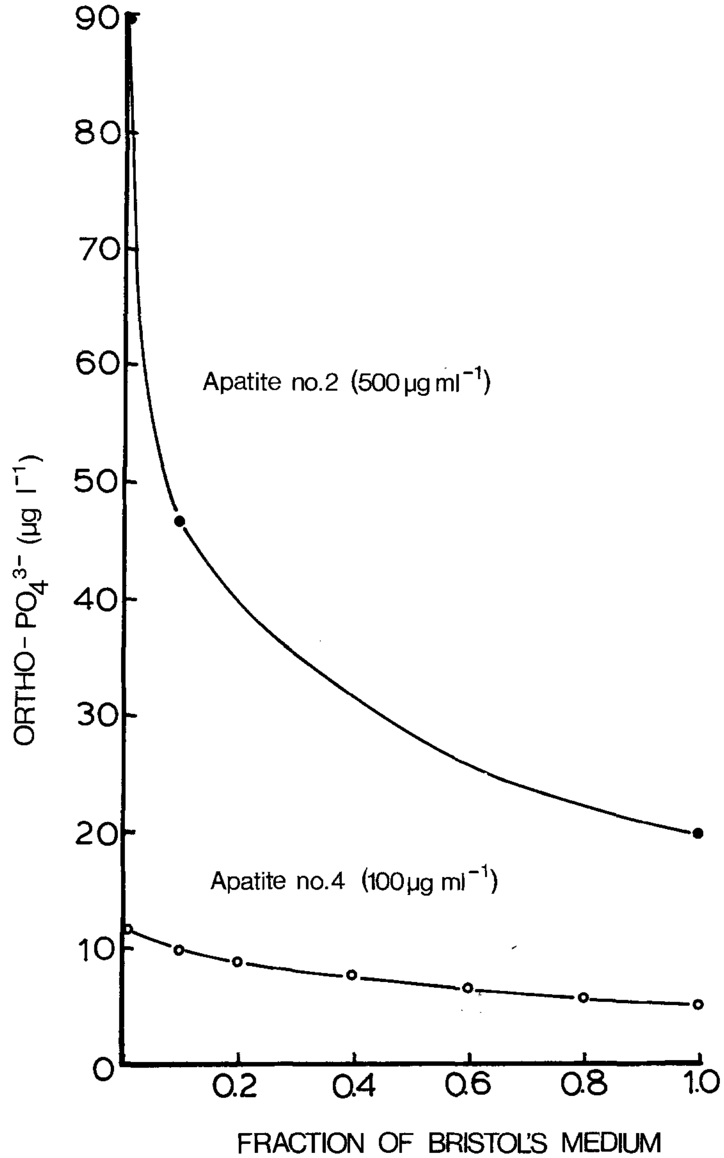

Fig. 6. Effect of ionic composition of water on apatite solubility. Apatite #4 crystals (30–100 µm) were added to PfB medium (pH 7) containing various fractions of the recommended ionic composition to yield 100 µg ml^{-1}. Similarly, apatite #2 crystals (<30 µm) were added to PfB medium to yield 500 µg ml^{-1}. The concentrations of ortho-PO$_4^{3-}$ in the slurries were determined after 24 h at 20°C.

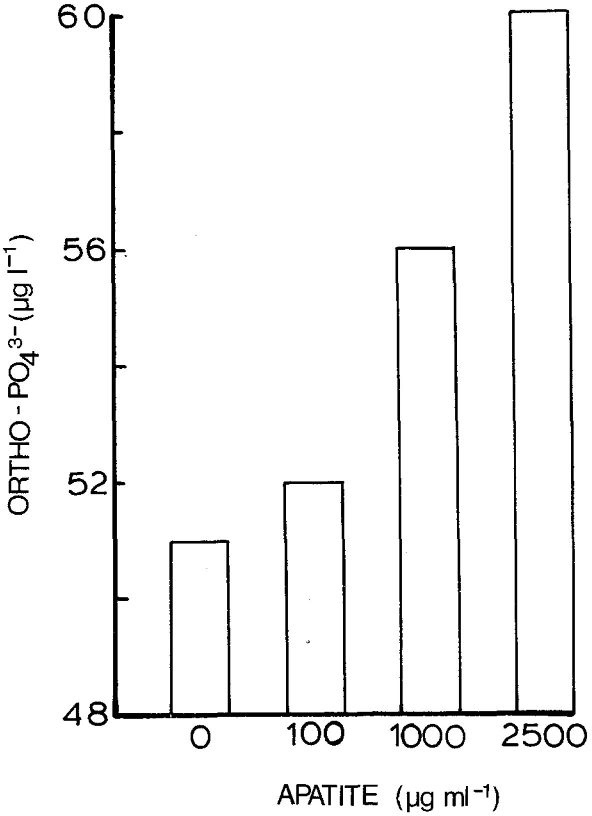

Fig. 7. Effect of apatite on ortho-PO_4^{3-} concentrations in nutrient-rich lake water (pH 7.93). Apatite #2 crystals (30–100 µm) were added to lake water containing endogenous levels of ortho-PO_4^{3-} and Ca^{2+} of 51 µg l^{-1} and 40.7 µg ml^{-1} respectively to yield 100, 1000, and 2500 µg ml^{-1}. A control was included and the ortho-PO_4^{3-} concentrations were determined for each slurry after 24 h at 20°C.

Even though the solubility of apatite was noticeably reduced under alkaline conditions, when fluorapatite was added to lake water, relatively small quantities still resulted in detectable increases in ortho-PO_4^{3-} (Figure 7). Stumm and Morgan (1970) have determined that in a hypothetical water of pH 7, in the presence of hydroxy-apatite and with a Ca^{2+} concentration of 40 µg ml^{-1}, total soluble-P is limited to 9 µg l^{-1}. In this study, the level of dissolved ortho-PO_4^{3-} in distilled water of pH 7 and containing <1 µg ml^{-1} of soluble Ca^{2+} and <1 µg l^{-1} of soluble ortho-PO_4^{3-} at a slurry density of 1000 µg ml^{-1} of apatite was 10 µg l^{-1} after 24 h at 20°C before equilibration of the system. A level of 1000 µg ml^{-1} of apatite in lake water of pH 7.93 containing endogenous concentrations of soluble Ca^{2+} and ortho-PO_4^{3-} of 40.7 µg ml^{-1} and 51.0 µg l^{-1}, respectively, increased the level of dissolved-P to 56 µg l^{-1}. Thus, even under conditions of alkaline pH and in the presence of other dissolved nutrients (including ortho-PO_4^{3-} and Ca^{2+}) small quantities of ortho-PO_4^{3-} were released from the lattices of apatite crystals.

These findings suggest that even under environmental conditions that do not favor apatite dissolution, the mineral still contributes some ortho-PO_4^{3-} as well as other elements to the water mass; the contribution being dependent upon quality and quantity of apatite. As long as these ions remain in solution, assuming they are not immediately precipitated out of solution by Al^{3+} or Fe^{3+} (Williams *et al.,* 1976b), they have the potential for entering into the nutrient cycling of aquatic environments.

There is little information available detailing the concentrations of apatite in various rivers and lakes (Brown, 1966). It should be emphasized that the behavior of naturally-occurring apatite crystals in these aqueous solutions may be considerably different than crystals of hydroxyapatite or fluoraptite synthetically-prepared under carefully controlled laboratory conditions. During mineral differentiation, ions within the lattices of apatite crystals are replaced by other ions by isomorphous substitution and lattice positions may be left unoccupied (Nash, 1972). It has been established that slight differences between certain apatites can reflect great differences in crystal chemical behavior (Kreidler and Hummel, 1970) and although the effects of structural factors on the solubility of apatite are poorly understood (Brown, 1966), it appears that solubility increases as the degree of crystal impurity increases (Brown, 1966). Brown (1966) also emphasized that uncertainties involving several studies on solubilities of laboratory preparations of hydroxyapatite present problems in application of solubility principles to limnetic situations.

A naturally-occurring fluorapatite from Faraday Township, Ontario (used as a reference fluorapatite in Danas' System of Mineralogy (Palache *et al.*, 1951)) contained more than 20 different elements including sufficient CO_3^{2-} and Na^+ ions to be included in the structural formula $(Ca_{9\cdot84}Mn_{\cdot02}Sr_{\cdot02}Na_{\cdot06}(RE)_{\cdot6}(P_{5\cdot87}C_{\cdot13}O_{23\cdot87}F_{\cdot13})F_2)$ (Gulbrandsen *et al.,* 1966). The behavior of this mineral and those used in this study would not necessarily be identical to a mineral such as fluorapatite which contains only 4 elements arranged in a crystal lattice which characteristically displays the lowest solubility of the calcium phosphates.

Deitz *et al.* (1964) have suggested that a complex forms by the hydrolysis of the exposed PO_4^{3-} ions on the crystal surface planes of hydroxyapatite. They postulated the following reaction: $Ca_{10}HPO_4(OH)_2 \rightarrow 4\,Ca_2HPO_4(OH)_2 + 2\,Ca^{2+} + 2\,HPO_4^{2-}$. The complex was considered to dissolve according to the following reaction: $Ca_2HPO_4(OH)_2 \rightarrow 2\,Ca^{2+} + HPO_4^{2-} + 2\,OH^-$. The theoretical solubility products for hydroxyapatite and fluorapatite in negative-logarithmic form have been given as $10\,pCa + 2\,pOH + 6\,pPO_4 = 113.7$ and $10\,pCA + 2\,pF + 6\,pPO_4 = 118.4$ (Lindsay and Moreno, 1960) and the solubility product of the surface complex was determined as $2\,pCa + 2\,pOH + pPO_4 = 26.3$ (Rootare *et al.,* 1962).

Care is taken to reduce impurities in commercial preparations of apatite to simplify the study of solubility phenomena and although the water-extract technique commonly employed to examine crystal solubility has the advantage of reducing the concentration of soluble surface impurities (Deitz *et al.,* 1964), such impurities may be important in governing solubility of apatite crystals and also may affect the reactions at the crystal boundary planes. Although it has been suggested that formation of a surface complex accounts for the solubility of synthetic hydroxyapatite crystals, there is little evidence to suggest the formation of a similar surface complex in naturally-occurring apatites with distinctly different surfaces. Although the amounts and particle sizes of apatite crystals which enter aquatic ecosystems will be important in determining the amounts of ortho-PO_4^{3-} released into the water, pH would likely be the single most important factor in setting the solubility of apatite (Brown, 1966).

Apatite has been shown to constitute a considerable amount of the phosphorus in some locations. In Florida rivers alone, there is an estimated 40 million tons of apatite (Mansfield, 1942). If, as some workers have suggested, only 1% of the apatite which is entering the aquatic environments dissolves (Williams *et al.,* 1976b), about 130 000 t of ortho-PO_4^{3-} have entered the P-cycle of Florida rivers. Similarly, based on the estimates of Van Wazer (1961) that 10^{21} g of P is trapped in marine sediments and that 10 000 times this amount is still to be weathered into aquatic environments (apatite P being the only important form), if apatite constituted 50% (conservative estimate) of the total P of the earth, 5×10^{20} g of apatite has at some time entered aquatic habitats. Based on the ratio 1.667 for Ca^{2+}/ortho-PO_4^{3-} in $Ca_{10}(PO_4)_6(F, OH_2)$ even if 0.1% of the apatite dissolved, according to Van Wazer's estimates, this would mean that 1.3×10^{19} g or 1.3×10^{14} t of apatite ortho-PO_4^{3-} has entered aquatic environments. Thus, despite the fact that apatite characteristically displays low solubility, particularly under alkaline conditions, the contribution of ortho-PO_4^{3-} as well as Ca^{2+} and other elements to various aquatic ecosystems cannot be completely ignored.

Other more readily available forms of P may be more important in determining the extent of primary production at a particular time in a given water body and there is no doubt that anthropogenic-PO_4^{3-} which enters the environment in the form of sewage, detergent, and industrial pollution is much more significant in influencing the behavior and development of those ecosystems than less available forms such as the detrital P associated with apatite. Golterman (1973) has stated that 'the real cause of the present phosphate eutrophication is that man will mobilize an amount of 3×10^{16} g of phosphate very rapidly perhaps in 100 instead of several million years and by doing so speeds up the natural process to such a degree that our lakes and rivers are no longer able to maintain their equilibrium'.

Under oligotrophic conditions, the contribution to the P-cycle of ortho-PO_4^{3-} from the partial dissolution of apatite crystals would be greater than in eutrophic water masses, particularly where high erosion rates increase the loadings of apatite.

4. Summary and Conclusions

Characterization of several natural calcium-phosphate apatites by X-ray diffraction and chemical analyses has shown that the apatites were highly variable in ionic composition and structural stability and that the degree of isomorphous substitution and the crystalline nature of an apatite lattice influenced the solubility of that apatite in any given solution.

The following is a summary of the findings of this study:

(1) The solubility of apatite increased as the pH of water was decreased.
(2) The concentrations of ortho-PO_4^{3-} and Ca^{2+} increased as the amount of apatite added to water was increased.
(3) The solubility of apatite increased as the particle-size distribution of crystals was decreased.
(4) Apatite increased the pH of water indicating the release of OH^- ions from apatite crystals.
(5) The solubility of apatite decreased as the concentration of ions in water was increased.
(6) Apatite increased the pH as well as levels of ortho-PO_4^{3-} and Ca^{2+} in lake water containing relatively high concentrations of dissolved nutrients including Ca^{2+} and ortho-PO_4^{3-}.

Under oligotrophic conditions, particularly in areas where large quantities of apatite are entering water as erosion material, the contribution of ortho-PO_4^{3-} from the partial dissolution of apatite crystals to the P-cycle would be more significant than in lakes which are eutrophic or are receiving high loadings of anthropogenic-PO_4^{3-}.

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