Zeta Potential of Apatite in Aqueous Solutions and Its Change during Equilibration

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Streaming potential experiments showed that the isoelectric point of apatite, in aqueous solutions, is initially at pH 4 and shifts towards a final value of pH 6 with time. Measurements of solution pH changes gave a value of 7 for the point of zero charge of apatite. Hydrogen, hydroxyl, and phosphate species were found to have a major role as potential-determining species. Zeta potential changes due to the addition of calcium and fluoride also are significant. The major effect of calcium appears to be due to its specific adsorption characteristics. Mechanism of charge development at the apatite surface is discussed in terms of pH-dependent hydrolysis of the surface species.

Apatite is one of the most important commercial minerals processed by methods involving operations such as flotation and flocculation. The performance of such operations depends primarily on the electrochemical properties of the apatite surface, about which very little is known. A knowledge of the apatite surface properties is also important from a biological viewpoint since apatite is a major constituent of tooth and bone. Most electrokinetic work (1-4) on apatite has been conducted without equilibration of the system or control of system variables and the results from these studies are often conflicting. For example, while Dobias and co-workers (1) obtained a negative zeta potential for apatite, Borisov (2) obtained a positive zeta potential throughout the pH range of their study (pH 2-12). Mattson and co-workers (3), on the other hand, in their electrophoretic mobility measurements on tertiary calcium phosphate, found it to be positively charged below and negatively charged above pH 7.6. Our work on the electrokinetic properties of calcite (5) has shown that unlike the widely studied insoluble oxides and silicates, soluble minerals behave in a complex manner. We observed that the calcite-aqueous solution system attained equilibrium only after several weeks of mixing. Solubility studies on calcium phosphate have indicated similar time effects which have obviously contributed to the considerable inconsistency among the reported experimental data on apatite solubility (6, 7). As pointed out by Rootare and co-workers (7), irreproducibility and inconsistency in the data was probably a result of a failure to achieve equilibrium, even though the mixtures have been, in some cases, mixed for times varying from 18 hours to 30 days. A study of the properties of apatite surfaces and their changes with time, besides being helpful in understanding the above complications, is also essential for determining optimum conditions for processes such as flotation.

The present paper reports the zeta potential of apatite in 10^{-2} M KNO3 solutions and aqueous solutions of salts with one species of it common to that of apatite in the presence of air, with due regard to equilibration. The potential-determining role of pertinent inorganic ions and the mechanism of the generation and of the changes of surface charge are discussed.

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EXPERIMENTAL METHODS
Fluorapatite [Ca$_3$(PO$_4$)$_2$(F,OH)] particles of 35-65 mesh size originally containing 5% calcite were used, after cleaning by leaching with dilute nitric acid and then washing with conductivity water until free from nitrate ions. The sample was then stored in conductivity water until used. The water used for the experiments had an initial conductivity of less than $7 \times 10^{-7}$ ohm$^{-1}$-cm$^{-1}$.

The experiments consisted of measuring the zeta potential of the apatite, and also the pH and the calcium and phosphate concentrations of the supernatant solution after allowing the particles to settle. The techniques used in the experiments have been described in detail in earlier papers (5, 8, 9), and will only be briefly mentioned here.

The zeta potential of the apatite was measured by a streaming potential technique employing a plug of the mineral (100 gm) and 500 ml of the electrolyte solution. Streaming through the plug was repeated until there was no difference apparent between successive readings. The solution with mineral in it was then transferred into a 1-liter flask and mixed on a tumbler for several weeks. At regular intervals, the mineral was transferred into the streaming potential cell, and measurements made. This was continued until an apparent equilibrium, as indicated by a constancy of the measured properties for at least 2 weeks, was attained. The concentration of calcium in solution was measured by atomic absorption and that of phosphorous by a colorimetric technique as vanadophosphomolybdate.

Earlier experiments (10) with apatite in water indicated considerable increase of ionic strength upon prolonged mixing of the systems. Therefore, the results reported here were obtained under conditions of constant ionic strength by using a 10$^{-2}$ M KNO$_3$ solution. The potential-determining role of calcium, phosphate, and fluoride species was investigated by using aqueous solutions to which Ca(NO$_3$)$_2$, K$_2$PO$_4$, or KF was added to make 10$^{-2}$ M concentration before dissolution of apatite.

RESULTS AND DISCUSSION
The zeta potential of apatite in 10$^{-2}$ M KNO$_3$ solution is given as a function of pH in Fig 1. Change of isoelectric point$^1$ with time is shown in the diagram by plotting the values that were obtained before and after equilibration by mixing.

The isoelectric point of apatite was initially around pH 4 and on equilibration continuously shifted towards a higher value. A final value of 6 was obtained after mixing for more than 2 weeks. This value can be compared with the results obtained from flotation of apatite with cationic and anionic reagents (1, 11). Cationic reagents floated apatite above and the anionic reagents below pH 6. Since flotation is the result of adsorption of these reagents on apatite, and since a physically adsorbing

$^1$ The isoelectric point describes that condition of the system at which the potential at the plane of shear, i.e., the zeta potential ($\phi_z$), as obtained from electrokinetic measurements is zero. This point is the same as the "zero point of charge" used in some of the earlier papers (5, 8, 12). There is considerable confusion prevalent in the literature in the terms used to describe such conditions in a solid-solution system. The condition at which the zeta potential is zero has, since as early as 1900, been called the "isoelectric point" by most workers (13-16). In recent years, while the above usage continued, the use of "zero point of charge" to describe the same condition developed side by side among one school (17) and led to the use of isoelectric point to describe other conditions such as "that point at which the net surface charge is zero" (18). Since the zeta potential is not necessarily always zero when the net surface charge is zero, especially in the presence of specifically adsorbing species such as pyrophosphate or surfactant ions, the latter definition of isoelectric point is different from the one stated earlier. The author uses the following definitions. The conditions under which the zeta potential is zero, probably best called "zero-zeta point," will be referred to as "isoelectric point" and that under which the net surface charge, commonly denoted by the symbol $\sigma_z$, is zero, will be called "point of zero charge". The species which determine the surface potential will be called potential-determining ions and the species which determine the difference between the surface potential and the zeta potential will be called countercations or co-ions, depending on whether their charge is opposite or the same as that of the surface charge.
ZETA POTENTIAL OF APATITE

Reagent would adsorb mostly when the mineral has a charge opposite to its own, the flotation experiments support the finding that apatite is negatively charged above and positively charged below pH 6.

Figures 2 and 3 show the change of zeta potential and pH with the conditioning time. The figures show that even though the isoelectric point has shifted towards higher pH values with conditioning making the general electrochemical nature of the surface more positive, particles in acidic solutions have actually become less electro-positive during a test due to the predominant effect of the change in solution pH with conditioning time.

It can also be seen from Fig. 3 that the addition of apatite to a solution at about pH 7 will cause no net change in pH. At this pH equal amounts of hydrogen and hydroxyl ions in solution will be consumed in the reactions between apatite with water, and since this will require the formation of equivalent amounts of positive and negative potential-determining ions in solution, pH 7 is actually the point of zero charge of apatite in water. An indication of point of zero charge can be obtained also from the point of minimum solubility because of the close correspondence between the two (19). Measurements of calcium and phosphate concentrations indicated minimum solubility in the pH region 7-9; Mattson and

Fig. 1. Zeta potential of apatite as a function of pH showing its isoelectric point and the change on equilibration with 10^{-2} M KNO3 solution and air.

Fig. 2. Change of zeta potential of apatite with conditioning in 10^{-2} M KNO3 solution and air at different pH values. Corresponding pH values and calcium and phosphorous concentrations are given in Fig. 3. *Initial zeta potential values obtained after streaming (until no difference apparent between successive readings) and before conditioning by mixing.

Fig. 3. Change in pH of the 10^{-3} M KNO3 solution with conditioning in presence of apatite and air. *pH of the solution before contacting it with apatite. Final total calcium and phosphorous concentration in M were, respectively: Expt. 1, ~5 \times 10^{-2}, 1.5 \times 10^{-3}; Expt. 2, 1.6 \times 10^{-3}, ~8 \times 10^{-4}; Expt. 3, 1.8 \times 10^{-3}, ~5 \times 10^{-2}; Expt. 4, 6.9 \times 10^{-4}, ~6.4 \times 10^{-4}; Expt. 5, 2.3 \times 10^{-3}, 9.6 \times 10^{-5}; Expt. 6, 3.5 \times 10^{-3}, 2.0 \times 10^{-3}; Expt. 7, 9.3 \times 10^{-3}, 7.6 \times 10^{-3}.
The role of chemical constituents of fluorapatite as potential-determining ions was investigated by conducting streaming potential experiments in the presence of an added salt, one ion of which was common to fluorapatite and the other to potassium nitrate, and the data were compared with that obtained by using only potassium nitrate as supporting electrolyte. It is assumed that neither potassium nor nitrate has any potential-determining or specifically adsorbing characteristics, an assumption found valid in experiments showing that the concentration of potassium nitrate in solution had no effect on isoelectric point. Figures 4, 5, and 6 show the effect of calcium, phosphate, and fluoride ions on the zeta potential of apatite at different pH values and at various stages of conditioning. The results show that phosphate, calcium, and fluoride ions play a major role in determining the zeta potential of apatite. Addition of phosphate made the mineral more negative in the complete pH range, and that of calcium made it more positive, but only above the isoelectric point. Fluoride addition caused an increase in negative zeta potential of apatite, but the effect was less than that produced by the addition of phosphate. Such changes in zeta potential can either be due to the potential-determining nature of these ions or because of their specific adsorption in the Stern plane as counterions and co-ions, due to their polyvalency or chemical and van der Waals interaction with other ions in the interfacial region.

Even though it is difficult from the above data alone to confirm the nature of the effect of the calcium, phosphate, and fluoride ions, the fact that added phosphate gives

**Fig. 4.** Zeta potential of apatite as a function of pH after streaming only, and before conditioning by mixing, in $10^{-3}$ M solutions of potassium dihydrophosphate, potassium fluoride, potassium nitrate, and calcium nitrate in the presence of air.

**Fig. 5.** Zeta potential of apatite as a function of pH after conditioning for one day in $10^{-3}$ M solutions of potassium dihydrophosphate, potassium fluoride, potassium nitrate, and calcium nitrate in the presence of air.

**Fig. 6.** Final values obtained for zeta potential of apatite as a function of pH after conditioning for several days in $10^{-3}$ M solution of potassium dihydrophosphate, potassium fluoride, potassium nitrate, and calcium nitrate in the presence of air.
negative values of much greater magnitude than that given by nitrate in the complete pH range, including the range in which apatite is originally negatively charged, indicates that phosphate ion is actually potential-determining. Addition of calcium, however, made the zeta potential more positive only when the system is above the isoelectric point of apatite. Since most of the calcium present in the pH region near isoelectric point is in the form of a Ca\(^{2+}\), and since it affects the zeta potential only when the mineral is oppositely charged, the major effect of calcium is probably due to that of specific adsorption of the ions in their hydrated state on apatite. Any potential-determining influence of added calcium is probably masked in the acidic region by possible competition of hydrogen ions with calcium and the effect of calcium dissolved from apatite in the acidic KNO\(_3\) solution.

Figure 7, in which the zeta potential and solution pH is plotted as a function of time of conditioning in 10\(^{-2}\) M Ca(NO\(_3\))\(_2\), shows that calcium is being adsorbed in increasing quantities with continued conditioning making the mineral surface increasingly more positive, even though solution pH is increasing. Such increases in positive zeta potential with an increase in pH is normally, even though not exclusively, a characteristic of the presence of specific adsorption due to polyvalency and indicates adsorption of calcium on apatite. The increase of positive zeta potential with an increase in pH (see Fig. 6) is also indicative of specific adsorption of Ca\(^{2+}\) assuming that the CaOH\(^+\) complexes formed with an increase in pH does not have a greater influence than Ca\(^{2+}\). This is because an increase in pH would decrease the negative surface charge of the apatite and, as a result, the specific adsorption of calcium ions due to its divality would increase.

The change of zeta potential and pH on
conditioning in 10−3 M KH2PO4, shown in Fig. 8, exhibits a more complex behavior. Experiments in the alkaline pH range show a reproducible decrease of negative zeta potential in the initial stages followed by an increase in the final stages. The increase in negative zeta potential in the final stage was accompanied by the slow development of cloudiness in the system; this indicates that slow formation of an insoluble complex is probably responsible for the observed change in the zeta potential in the final stages.

Fluoride also has shown an effect on the zeta potential of apatite, but to a lesser degree than phosphate. In past studies (20), it has been shown to have a specific adsorption effect on many other minerals, ascribed to its small size and resultant high electronegativity. Extensive work (21) on the effect of fluoride on tooth materials indicated the possibility of an additional effect of fluoride on apatite due to its substitution in the apatite lattice, favored by the better fit of the fluoride ions than the hydroxyl ions in the apatite lattice.

Mechanism of Charge Generation

To establish the mechanism of surface charge generation, it is first necessary to know the chemical nature of the surface species. Solubility product studies have shown the complexity of this problem. Bjerrum (22) and Hayes et al. (23) observed that hydroxyapatite is a mineral which did not possess a constant solubility product. This is supported by the considerable discrepancy in the reported values (24) for the solubility product. As mentioned earlier, this effect has been ascribed by some to the incomplete equilibrium reached during the experiments. It can be seen from the results reported here that conditioning for more than 2 weeks was often necessary to reach equilibrium. Various authors (7, 25) discussed their results for the solubility of apatite by assuming the presence of complexes such as dicalcium phosphate, dicalcium phosphate dihydrate, and octacalcium phosphate. Routare et al. (7) resolved most of the problems mentioned above by postulating that, in the case of hydroxyapatite, terminal phosphate ions hydrolyze resulting in a complex of the formula Ca2(HPO4)(OH)4, which subsequently covers the solid surface and, as a result the following reactions take place:

\[
\text{Ca}_{10}^{}(PO_4)^{6-}(OH)_2 + H_2O \rightleftharpoons 4 \text{Ca}^{}(HPO_4)^{-} \quad (\text{OH})_2 + 2\text{Ca}^{2+} + 2\text{HPO}_4^{2-} \quad \text{(1)}
\]

\[
\text{Ca}^{}(HPO_4)^{-} \quad (\text{OH})_2 \rightleftharpoons 2\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{OH}^- \quad \text{(2)}
\]

Whether it is the complex Ca10(PO4)6(OH)2 or the original Ca10(PO4)6(OH)2 which undergoes dissolution to produce Ca2+, and HPO42−, these ions would undergo further hydrolysis and complex formations according to the reactions given below:

\[
\text{Ca}^{2+} + \text{OH}^- \rightleftharpoons \text{CaOH}^+ \quad \text{(3)}
\]

\[
\text{CaOH}^+ + \text{OH}^- \rightleftharpoons \text{Ca(OH)}_2 \quad \text{(4)}
\]

\[
\text{Ca(OH)}_2(aq) \rightleftharpoons \text{Ca(OH)}_2(s) \quad \text{(5)}
\]

\[
\text{PO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^- \quad \text{(6)}
\]

\[
\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{OH}^- \quad \text{(7)}
\]

\[
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4^- + \text{OH}^- \quad \text{(8)}
\]

\[
\text{Ca}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{CaHPO}_4^- \quad \text{(9)}
\]

\[
\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CaH}_2\text{PO}_4^+ \quad \text{(10)}
\]

The fluoride ions present in the fluorapatite would also undergo similar reactions.

\[
\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^- \quad \text{(11)}
\]

\[
\text{Ca}^{2+} + 2\text{F}^- \rightleftharpoons \text{CaF}_2 \quad \text{(12)}
\]

Surface species such as −Ca2+, −F, and −PO4 would similarly undergo hydrolysis according to the reactions given above and the extent of such hydrolysis for each species, depending upon the solution pH, would essentially determine the surface charge. An alternate mechanism would be the hydrolysis of the ions in the bulk, followed by its adsorption at the interface. Both mechanisms are thermodynamically indistinguishable and of the same final result. When apatite is contacted with solutions at pH values above the point of zero charge, equilibrium points of reactions (2), (6), (7), (8), and (11) are shifted towards the left side of the equations and those of reactions (3) and (4) towards the right side, making the solid surface acquire a net negative charge. These equilibrium point shifts also explain the decrease of solu-
tion pH shown in Fig. 3. When apatite is contacted with acidic solutions, the material acquires a net positive charge, and the solution pH rises due to the shift of equilibrium point of reactions [6], [7], [8], and [11] towards the right side, and that of reactions [3] and [4] towards the left side of the equations.

Continuous changes in zeta potential and solution pH shows the presence of a slow step in the mechanism, possibly diffusion of products or reactant species through the double layer (3, 26). Such behavior has been observed in the case of calcite also (5), the dissolution of which has been shown to be diffusion controlled (27). The continuous zeta potential change observed when apatite is agitated with aqueous solutions could be due simply to pH changes, but experiments done with added phosphate do not support such an argument. For example, Fig. 5 shows that in experiments done at pH 7.03, while the pH remained constant throughout the experiment, the zeta potential exhibited marked changes. Also the experiment done at a lower pH value showed different behaviors for zeta potential and solution pH for zeta potential and solution pH with time. Increasing specific adsorption of Ca\(^{2+}\) ions on the negatively charged apatite is possibly responsible for the shift of isoelectric point with conditioning. Surface deposition of calcium carbonate (which has an isoelectric point of 0.5 (5)), formed in solutions during equilibration in the presence of air, might also be partly responsible for it; but this would only be a minor factor because of the low carbonate and calcium concentrations in the solutions at pH values in the region of the isoelectric point of apatite. Any preferential dissolution of potential-determining ions from the surface on conditioning could also contribute to the observed time effects. Such dissolution has been found in the case of magnesium silicate minerals.\(^1\) In the case of apatite, however, measurements of calcium and phosphorous solution concentrations did not yield a systematic evidence for this, probably due to the very small change in solution concentration produced by the preferential dissolution. Further detailed study of the time effects would be necessary to ascertain the role of the above mechanisms in controlling the change in the surface charge of apatite with conditioning time.

**SUMMARY**

The isoelectric point of apatite under equilibrium conditions lies about pH 6. It has an initial value of 4 and it is necessary to condition the mineral in solutions for more than 2 weeks to obtain constancy in the measured properties. Measurements of pH changes on contacting aqueous solutions with apatite gave a value of 7 for the point of zero charge. Besides hydrogen and hydroxyl phosphate species also are major potential-determining ions. Calcium and fluoride ions also have a major influence on the zeta potential of apatite. The major effect of calcium appears to be due to its specific adsorption characteristics. The mechanism of charge generation at the apatite surface is discussed in terms of preferential hydrolysis of calcium, fluoride, or phosphate ions, depending on the solution pH.

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