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Adsorption of Mono- and Divalent Metal Cations on Hydroxyapatite in Water

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The order of affinity of various metal ions for synthetic hydroxyapatite (HAP) in water was determined by measuring the sedimentation volume, mean particle diameter, suspension pH, and the amounts of metal chloride adsorbed and of cetylpyridinium chloride adsorbed on HAP in competition with metal ions. Direct chemical analysis of divalent alkaline earth cations showed that the binding affinity to HAP is in the order $Ca^{2+} > Ba^{2+} > Mg^{2+}$, in accordance with that deduced from the other experimental results; Ca^{2+} presumably has the highest affinity because it is the parent ion of HAP. By comparing the effects of mono- and divalent cations, it was concluded that the order of binding affinity of monovalent alkali metal cations is $Na^+ > K^+ > Li^+$; Na^+ presumably has the highest affinity because its crystal ion radius is almost the same as that of Ca^{2+}. It was also shown that these ions bind electrostatically by at least two type of mechanism, ion-exchange with Ca^{2+} on HAP and specific adsorption on HAP. It was assumed that the binding sites are Ca^{2+}-defects or dislocations on HAP, and that adsorbate ions are dehydrated when they are adsorbed. Some properties of biological mineralization can be explained on the basis of the results presented here.

Keywords——hydroxyapatite; adsorption of metal ion; suspension pH; sedimentation volume; mean particle diameter; competitive adsorption; biological mineralization; adsorption of cetylpyridinium chloride

The major constituent of biological hard tissues and human renal calculi is crystalline hydroxyapatite(HAP), $Ca_{10}(PO_4)_6(OH)_2$. In addition to calcium ions, many kinds of inorganic cations, such as Na^+ and Mg^{2+}, are present in biological minerals[1] and body fluids[2] which are in contact with calcified tissues. Some of these inorganic cations may be adsorbed on the HAP crystal surface, trapped in lattice defects such as dislocations, or ion-exchanged with the lattice ions.[3] Biological apatite, therefore, has a variable composition, and many studies on ionic interactions have been done with synthetic hydroxyapatite as a model substance for biological apatite.

Calcium ions can be easily adsorbed and result in a positive charge on the surface of HAP, irrespective of the pH of the solution.[4] The point of zero charge obtained for HAP in aqueous KCl solution is 8.5, but there is a shift in the point of zero charge to 7.6 when NaCl is used as a supporting electrolyte, indicating substitution of Na^+ for Ca^{2+} on the surface, because the crystal ion radius of Na^+ is almost the same as that of Ca^{2+}.[5] It was also shown that Sr^{2+} and Ba^{2+} can easily replace Ca^{2+} in dental enamel, but Mg^{2+} is too small to fit into any of the Ca^{2+} positions of HAP.[3] Ni^{2+} exchanges with Ca^{2+} on HAP and follows an adsorption isotherm of Langmuir type, but Cu^{2+}, on the other hand, forms a complex on the surface of HAP, represented tentatively as $Cu_3(PO_4)_2 \cdot Cu(OH)_2$.[6] Higuchi *et al.* also have found that a complex such as $Ca_6Sr_4(PO_4)_6(OH)_2$ appears on the crystal surface of synthetic HAP while it dissolves in an acidic solution of $SrCl_2$.[7] Other kinds of surface complex reported are $Sn_3F_3PO_4$[8] and CaF_2[9] when Sn^{2+} with F^-, or Ca^{2+} with F^- are added, respectively, to HAP in water.

In this article, the affinity of metal cations for HAP will be discussed taking the effect of valence and crystal ion radius, r_c, into consideration.[10] Li^+(r_c=0.68 Å), Na^+ (0.97 Å) and K^+ (1.33 Å) were used as monovalent cations, and Mg^{2+} (0.66 Å), Ca^{2+} (0.99 Å) and Ba^{2+} (1.34 Å) as divalent cations. Since the radii of Li^+ and Mg^{2+}, Na^+ and Ca^{2+}, and K^+ and Ba^{2+} are almost the same, it becomes possible to compare the effect of valence of the metal ion at fixed r_c, as well as the effect of r_c at fixed valence. This investigation should provide fundamental data relevalent to the formation and growth of crystals of hard tissues and urinary stones.

Experimental

Material——All reagents were purchased from Nakarai Chemicals Ltd. or Wako Pure Chemical Industries Ltd. Water used was doubly distilled. HAP was prepared as described elsewhere.[11] The X-ray powder diffraction pattern and infrared spectra were typical of hydroxyapatite and chemical analysis showed it to be stoichiometric (Ca/P=1.67).

Methods——All adsorbate metal ions in this work were used as the chlorides. HAP (2 g) was suspended in 20 ml of a given adsorbate solution of known concentration at 30°C, and vigorously shaken from time to time. After at least 3 days, the filtrate (Millipore filter, pore size 0.22 μm) was analyzed by EDTA chelatometry for Ca^{2+}, Mg^{2+}, and Ba^{2+} with 1-(2-hydroxy-4-sulfo-1-naphthylazo)-2-hydroxy-3-naphthoic acid (NN indicator) at pH 13, 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid (BT indicator) at pH 10, and BT indicator with Mg–EDTA at pH 10. Cetylpyridinium chloride (CPC) was analyzed by the methylene blue diphasic titration method (Epton method) using a standard solution of sodium dodecyl sulfate with chloroform. The amount of adsorption was then calculated.

pH was measured with a pH-meter (TOA type HM-5A). The pH's of the water used, and of aqueous salt solutions (0.5 M, for example) of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$ were 6.50, 5.43, 5.72, 5.83, 5.50, 6.23, and 5.52, respectively. The pH of 0.5 M LiCl was the lowest, probably because of the effect of localized hydrolysis, as will be discussed later. The equilibrium pH of HAP suspension was measured in the supernatant solution before chemical analysis.

The mean diameter, d_m, of the secondary particles of HAP was measured in 0.25 M metal chloride solution at a HAP concentration of 1 g/100 ml by means of a sedimentation balance (Shimadzu type SA-II) at room temperature by the method described previously.[12]

Sedimentation volume was measured by placing 5 g of HAP in a 20 ml graduated cylinder to which was added 15 ml of a solution of 1 M metal chloride, and then the cylinder was shaken vigorously for 2 minutes. Sedimentation volume was recorded after 7 days, and expressed as the ratio, V_2/V_1, of apparent volume, V_2, in the cylinder at equilibrium to the real volume, V_1, of HAP calculated from its density (3.16 g/cm^3) and the weight (5 g) of added HAP.

Results

Ion Exchange and Adsorption of Divalent Cations

Although HAP is practically insoluble in water, the solution concentration of Ca^{2+} increases with that of added cation, such as Mg^{2+} or Ba^{2+}. HAP, therefore, seems to behave like an ion-exchanger. The relationship between the increase of the concentration of Ca^{2+} in the supernatant and the decreases of the concentration of added metal ion, Me^{2+}, by sorption on HAP is shown in Fig. 1, where the slope of the experimental curve is a little smaller than that of the dotted line of slope 1 which shows the hypothetical exact ion-exchange between Ca^{2+} and Me^{2+}. The horizontal distance between the dotted line and the experimental curve, therefore, represents "excess adsorption" of metal ions on HAP with respect to pure ion exchange. It is clear from Fig. 1 that Ba^{2+} is more effectively adsorbed than Mg^{2+}.

The isotherms of the excess adsorptions of Ba^{2+} and Mg^{2+} are shown together with that of Ca^{2+} in Fig. 2; Ca^{2+} is most extensively adsorbed. Ion-exchange will not change the surface charge of HAP, but excess adsorption of Ba^{2+} or Mg^{2+} and total adsorption of Ca^{2+}, which is one of the constituent ions of HAP, produce positive charges on the surface of HAP. In this sense, Fig. 2 shows the relative density of surface charge if the effect of counter anions, mostly Cl^-, is assumed to be almost the same on each divalent cation in the electric double layer and on the surface of HAP. Although Misra *et al.*[6] obtained the adsorption isotherm of Ni^{2+}, they did not divide the total amount into ion-exchange and excess adsorption categories.

Equilibrium pH and pH Titration

The equilibrium pH of the suspension is shown in Fig. 3 as a function of concentration of added electrolyte at a fixed concentration of HAP, where the starting pH of 7.3 on the ordinate is the value in pure water. Although the solution pH of each electrolyte without

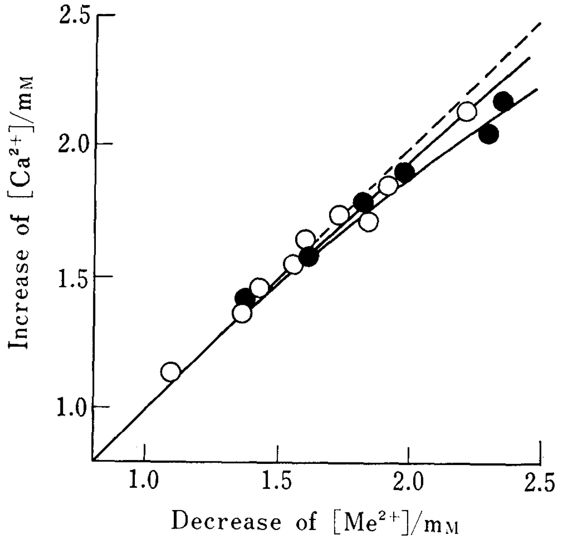

Fig. 1. Relationship between Concentration Increase of Ca^{2+} and Concentration Decrease of Ba^{2+} or Mg^{2+}

The dotted line shows the hypothetical exact ion exchange between calcium ion and divalent metal cation. ●: Ba^{2+}, ○: Mg^{2+}.

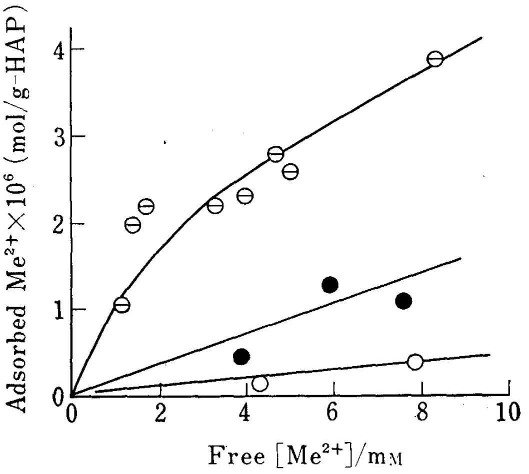

Fig. 2. Adsorption Isotherm of Divalent Cations

The amounts of Ba^{2+} (●) and Mg^{2+} (○) adsorbed are shown by subtracting the amount ion-exchanged with Ca^{2+} from the total amount adsorbed on HAP. The amount of Ca^{2+} (⊖) adsorbed is calculated from the difference between the initial and the final concentration of calcium in the sample solution.

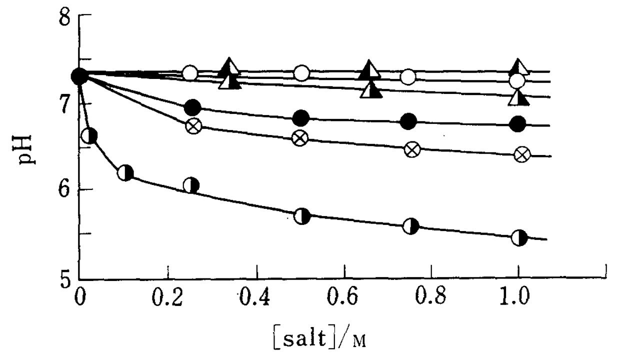

Fig. 3. Variation of Equilibrium pH of HAP Suspension

The pH was measured at a concentration of 10 g HAP/100 ml solution.
Added salt: △ KCl, ○ NaCl, ▲ LiCl, ⊗ $BaCl_2$, ◑ $CaCl_2$, ● $MgCl_2$.

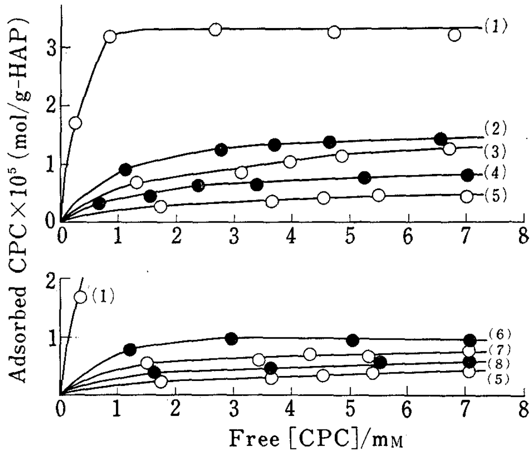

Fig. 4. Adsorption Isotherm of Cetylpyridinium Chloride (CPC)

Additive: (1) none, (2) 50 mM LiCl, (3) 50 mM KCl, (4) 50 mM NaCl, (5) 25 mM $CaCl_2$, (6) 5 mM $MgCl_2$, (7) 5 mM $BaCl_2$, (8) 5 mM $CaCl_2$.

HAP depends only very slightly on its concentration, the suspension pH decreases with concentration of added electrolyte in each case. The dependence on the concentration is more marked in the case of divalent metal chloride than monovalent metal chloride. The order of decrease in pH is $Li^+ > Na^+ > K^+$ for monovalent cations, and $Ca^{2+} > Ba^{2+} > Mg^{2+}$ for divalent cations. The latter sequence is the same as that shown in Fig. 2. The relationship between the crystal ion radius, r_c, of mono- and divalent cations and the equilibrium pH at 0.5 M electrolyte added is shown in Fig. 7, and will be discussed later.

A suspension of 20 g of HAP in 200 ml was titrated with 1 N NaOH in the presence of 1 M monovalent alkali metal chloride or 0.5 M divalent alkaline earth chloride. The titration curves are not shown here, but shift to lower pH from the reference titration curves of the salt solution without HAP, and of the HAP suspension without any salt. The titration curves also show different slopes, depending on the species of added salt, compared with the reference titration curves. The order of extent of both shift and slope change was LiCl>NaCl>KCl, and $CaCl_2$>$BaCl_2$>$MgCl_2$. The latter sequence is the same as that obtained from Fig. 2. Fig. 3 and the results mentioned above show that HAP with calcium ions consumes most OH^- (or releases most H^+). It was also found that there is a small lag at the initial part of each titration curve which presumably represents a buffer function against pH change by HAP particles. These phenomena will be discussed elsewhere.[13]

Adsorption Isotherm of Cetylpyridinium Chloride

Fig. 4 shows the adsorption isotherm of cetylpyridinium cation(CP^+) on HAP from cetylpyridinium chloride(CPC) solutions containing various kinds of added metal chloride. If the salting-out effect of added electrolyte, or the ionic product of $[CP^+]\times[Cl^-]$ as an approximation to the thermodynamic activity[14] of CPC affects the amount of CP^+ adsorbed, it should increase with increasing concentration of metal chloride, irrespective of species. If the ionic strength predominantly affects it, it will decrease irrespective of the species of supporting electrolyte. The amount of adsorbed CP^+ in fact decreases with concentration of added electrolyte, such as $CaCl_2$, as shown by curves (1), (8) and (5) in Fig. 4. Each electrolyte seems to inhibit the adsorption of CP^+ on HAP. The inhibitory effect of 25 mM $CaCl_2$ is stronger than that of 50 mM NaCl, and the latter is almost the same as that of 5 mM $BaCl_2$. Divalent cations are more effective than monovalent cations in inhibiting CP^+ adsorption . It can, therefore, be concluded that CP^+ is adsorbed on HAP electrostatically, but is excluded from the adsorption site by competitive adsorption of metal cations. The order of inhibition of CP^+ adsorption is Na^+>K^+>Li^+ for monovalent cations, and Ca^{2+}>Ba^{2+}>Mg^{2+} for divalent cations at a fixed concentration of added electrolyte and at a constant equilibrium concentration of free CP^+. The latter sequence is the same as that obtained from Fig. 2. The relationship between crystal ion radius and amount of adsorbed CP^+ at a constant concentration of added electrolyte and at a fixed concentration free CPC is shown in Fig. 6. and will be discussed later.

Sedimentation Volume and Mean Diameter of HAP Particles

The variation of the ratio of sediment volume, V_2/V_1, and mean diameter, d_m, of secondary particles of HAP is shown in Figs. 5-A and -B as a function of crystal ion radius of the added metal cation, for comparison with Figs. 6 and 7. Variables such as V_2/V_1 and d_m are parameters of the dispersity of HAP particles, as mentioned later. It was found that the order of the effects of metal ions on V_2/V_1 and $d_m$was same as that obtained from Figs. 2 and 4.

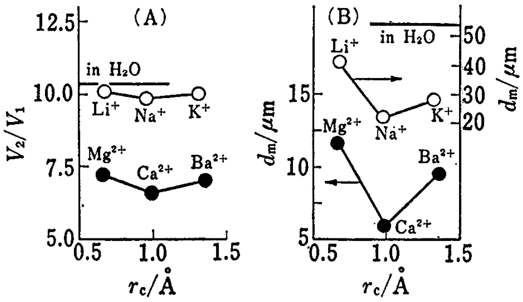

Fig. 5. Dependence of the Dispersity of HAP on Crystal Ion Radius, r_c, of Metal Cation Added

(A) ratio of sedimentation volume, V_2/V_1, in solution containing 1 M metal chloride
(B) mean diameter of HAP particles, d_m, in solution containing 0.25 M metal chloride
The value in pure water is shown by a short bar near the top of the figure.

Discussion

It is known that many physico-chemical phenomena in aqueous solution depend on the size of either the hydrated ion or the dehydrated crystal ion, and follow the sequence of the periodic table downwards or upwards in the group. In the case of adsortion of metal ions on a solid surface, it is known from the literature that the results depend on whether the adsorbent surface promotes water structure or breaks it down. For example, TiO_2 (rutile) and α-Fe_2O_3 (haematite),[15] which are water structure makers, adsorb alkali metal cations in the order $Li^+ > Na^+ > K^+ > Cs^+$, but Hg and AgI,[15] which are water structure breakers, adsorb Cs^+ more strongly than Li^+, the reverse of the sequence mentioned above.

Breeuwsma *et al.*[16] concluded that the specific adsorbability of Li^+ and Mg^{2+} on α-Fe_2O_3 is perhaps related to the fact that the crystal ion radii of Li^+ (0.68 Å) and Mg^{2+} (0.66Å) are almost identical with that of Fe^{3+}(0.64 Å), allowing them to penetrate and occupy an Fe^{3+}-site. The affinity of Li^+ for TiO_2 (Ti^{4+}: 0.68 Å)[16] or of Na^+ (0.97 Å) for calcium oxalate (Ca^{2+}: 0.99 Å)[17] may also be ralated to the crystal radius of the ion contained in the adsorbent crystal structure. A special case of ion-size fitting is the adsorption of a parent metal ion on the corresponding adsorbent, that is, adsorption of Fe^{2+} and Fe^{3+} on Fe_3O_4 (magnetite)[18] and Ca^{2+} on $CaCO_3$ (calcite and aragonite).[19] The parent metal ion generally exhibits a very great affinity for the adsorbent. In these cases, the cation is assumed to be dehydrated when it binds to the adsorbent surface, in contrast to the formation of water structure and also in contrast to the swelling of montmorillonite by sorption of hydrated metal cations.[20]

Going back to Fig. 2, the order of adsorption of divalent cations was $Ca^{2+} > Ba^{2+} > Mg^{2+}$, which was neither in the sequence of hydrated ion radius nor in that of crystal ion radius, but Ca^{2+}, the parent cation of HAP, exhibited more affinity for HAP than Ba^{2+} or Mg^{2+}. Dehydrated Ca^{2+} is assumed to fit adsorption sites formed by dislocations or defects of Ca^{2+} on HAP, but the ion size of Ba^{2+} or Mg^{2+} is too large or too small to fit the site and form a stable state on the surface.

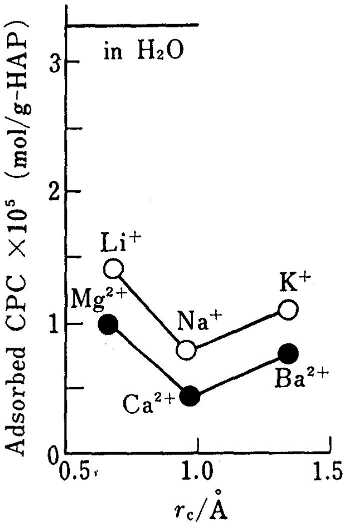

Fig. 6. Inhibitory Effect of Metal Ions on the Adsorption of CPC as a Function of Crystal Ion Radius, r_c

The amount of adsorbed CPC was read at 5 mM free CPC in Fig. 4.

The added electrolyte was 50 mM alkali metal chloride or 5 mM alkaline earth chloride. The short bar near the top shows the value without any electrolyte.

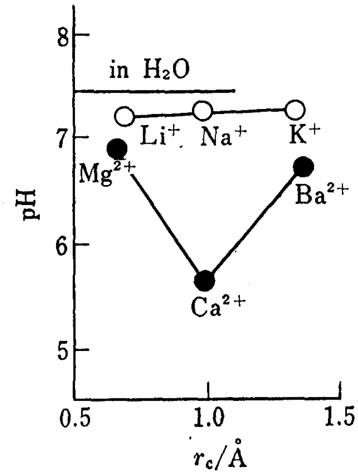

Fig. 7. pH Variation of HAP Suspension as a Function of Crystal Ion Radius, r_c, of Added Metal Ion

The pH value was read at 0.5 M electrolyte in Fig. 3. The short bar near the top shows the value for the HAP suspension without any electrolyte.

The results for divalent cations, shown in Figs. 5, 6 and 7, can be easily explained by considering that the binding of divalent cations increases the positive charge on the surface, and the electrostatic repulsion becomes larger with the amount of Me^{2+} adsorbed. This is directly reflected in the dispersion properties of HAP, such as sedimentation volume and mean diameter of HAP particles. Binding of Me^{2+} also decreases the number of adsorption sites available to other cations. The changes in the amount of CP^+ adsorbed and pH, which is determined by the equilibrium of hydrogen ion concentration between the solution and the HAP surface, therefore, decrease in the same sequence as mentioned above. The latter effect may also be explained either by ion-exchange of Me^{2+} in solution with H^+ bound to surface phosphate, or by adsorption of OH^- due to the positive surface charges, however.

The effect of monovalent cations on the properties of HAP suspension except pH are in the order $Na^+ > K^+ > Li^+$. As the crystal ion radius of Na^+ is almost same as that of Ca^{2+}, it can be concluded that Na^+ is easily adsorbed at adsorption sites of Ca^{2+}, but K^+ or Li^+, approximately the same size as Ba^{2+} or Mg^{2+}, respectively, is too large or too small to fit the site and to be adsorbed stably. Monovalent cations affect these values less than divalent cations of almost the same size because of the smaller electrostatic force exerted by small electric charges.

The properties of HAP suspensions examined here (except pH) originate mainly from the HAP surface, but the pH is a property of the suspending medium. It is, therefore, natural that there is some discrepancy between the effects of different ions on them. The sequence $Li^+ > Na^+ > K^+$ found in Fig. 7 is different from that of $Na^+ > K^+ > Li^+$ found in Figs. 5-A, -B and 6. This may be explained in terms of "localized hydrolysis"21) by lithium ions in water but not on the surface of HAP, due to the fact that the smaller the cation, the more highly polarized are the water molecules and the greater the repulsive force acting upon the water protons, resulting in an increase of proton activity. For the same reason, Mg^{2+} seems to show localized hydrolysis and to decrease the suspension pH more than Ca^{2+}, but the effect of Mg^{2+} on pH, shown in Fig. 7, was not exceptionally large and the effects of divalent cations were in the same order as that found in Figs. 2, 5 and 6. This is probably because the effect of divalent cations adsorbed on the surface is larger than that of ions remaining in the solution.

The results mentioned above may be useful in accounting for the growth of biological HAP crystals and urinary stones, and remineralization of hard tissues such as dental enamel,22) which selectively adsorb Ca^{2+} from body fluids containing various kinds of metal ions. The relatively higher content of Na^+ than other monovalent cations in hard tissues23) can also be explained analogously.

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