

STUDIES ON SOME PHYSICO-CHEMICAL ASPECTS OF PHOSPHATE AND VANADATE APATITES OF CALCIUM

Abstract

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A THESIS
SUBMITTED IN FULFILMENT OF
THE REQUIREMENTS OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY



To



THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG-793001

SEPTEMBER, 1984

SYNOPSIS

Introductory Aspects

It has been established that calcium and phosphorus present in human bones and teeth exist as calcium phosphate apatite (PHA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is a member of large series of isomorphous compounds known collectively as "Apatites" which belongs to the hexagonal pattern of crystals. A characteristic property of them is to undergo a series of both anionic and cationic exchange reactions without a disruption of crystal lattice, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. It is evident that a partial exchange leads to the formation of solid solutions of the isomorphs involved while a complete exchange gives the isomorph itself. Significant among such replacements are: (i) Ca^{2+} by Sr^{2+} , Ba^{2+} , Pb^{2+} and Cd^{2+} ; (ii) PO_4^{3-} by AsO_4^{3-} , VO_4^{3-} and (iii) OH^- by F^- , Cl^- , Br^- and I^- .

Such exchange reactions are of extensive biological and physico-chemical significance, since they constitute the basis of incorporation of these ions into the human skeletal and dental systems. The radiation hazards caused by incorporation of β -active Sr-90 as well as the toxic effects of fluorine are, among several processes of biological importance, explained on the basis of such isomorphous replacement on calcium hydroxylapatite of bones and teeth.

Significance of the Present Studies

The principal processes occurring at the bone/body fluid and tooth/saliva interfaces are the dissolution and the precipitation of calcium hydroxylapatite, the processes being known as resorption and calcification respectively. While an equilibrium exists between these two processes maintaining an optimum level of calcium and phosphorus in body-fluids and saliva in a healthy system, the incorporation of extraneous ions causes a disturbances to it leading to pathological conditions. The seat of action of these processes is calcium hydroxylapatite.

It is an established fact that elemental vanadium and its salts are toxic to the human system. Inhalation of them through nose and mouth as well as through exposure of the skin causes symptoms such as paralysis, convulsions and sleepiness leading to bronchitis and bronchopneumonia prevalence of such ailments is common among workers of industrial establishments involving the element. It gets incorporated into the human skeletal system through $\text{PO}_4^{3-} \rightleftharpoons \text{VO}_4^{3-}$ exchange on PHA leading to the formation of its isomorph calcium vanadate apatite (VHA), $\text{Ca}_{10}(\text{VO}_4)_6(\text{OH})_2$, constituting the basis of toxicity of vanadium. Any attempt in the direction of elimination or minimisation of such a toxicity is associated with a study of the solubility of PHA as well as the products of the exchange reactions mentioned above under simulated biological conditions.

Prompted by such a consideration the present work which deals with the preparation, characterization and solubility equilibria of PHA, VHA and a series of nine of their solid solutions spread over the entire compositional range was undertaken.

Preparation and Characterization of the Samples

The samples were prepared through a judicious modification of the existing method taking care to see that the yield were high and the products were of a high order of purity.

Characterization of these samples was brought about through sophisticated instrumental techniques such as x-ray diffraction, electromicroscopy, i.r. spectral studies and thermogravimetry in addition to the conventional chemical analyses. The g atom ratios, $\frac{Ca}{P}$, $\frac{Ca}{V}$ and $\frac{Ca}{(P+V)}$, of the samples were determined through conventional chemical analyses were found to agree well with the stoichiometric values of 1.67. From the Debye-Scherrer powder patterns of the samples, the lattice parameters as well as the unit cell volumes were determined. Vegard's law, which demands that the unit cell volumes of a series solid solutions vary linearly with the composition, offers a convenient means of scrutinizing their homogeneity. As anticipated from the smaller size of PO_4^{3-} , its replacement by VO_4^{3-} brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of VO_4^{3-} observed in the present series of solid solutions confirmed their homogeneity.

The electronmicrographs of a few samples obtained after breaking the conglomeration of individual crystals, their hexagonal pattern confirming the absence of extraneous phases and enabling approximate calculations of their specific surface areas through measurement of dimensions of the individual crystals. The measured surface areas show a gradual increase with an increase in the proportion of VO_4^{3-} . The i.r. absorption spectra while confirming the identity of the samples by proving the absence of extraneous peaks could establish the predominant absorption peaks to be due to PO_4^{3-} and VO_4^{3-} . The pyrolysis curves of the samples obtained through thermogravimetric analyses extending upto about 1000°C were found to be free from discontinuities suggesting that the water associated with samples was not chemically bound and that the stability of the samples was not affected within this temperature range.

Determination of Solubility Products of the Samples

Studies on the solubility of the samples were undertaken at 37°C in order to investigate its dependence on the replacement of PO_4^{3-} by VO_4^{3-} , since it was intended to determine the solubility product of each samples from data resulting from the chemical analyses of the saturated solution, a buffered dissolving medium was used to maintain constancy of the activity of OH^- ions involved in such calculations. In order to investigate the reproducibility of the solubility products so determined, the studies in each case were extended to a few chosen pH values in the range extending from 4.3 to 8.0. In addition, all such buffered dissolving media were maintained at a

molarity of 0.165 with respect to sodium chloride to simulate biological conditions. By adopting such a medium of dissolution the complicated process of evaluating accurately the activity co-efficients of polyvalent ions could be avoided by assuming all of them to be unity without unduly foregoing the accuracy. It is evident that such calculations make the solubility product, K_{sp} , and the ionic product, K_{ip} , synonymous.

Each one of the powdered samples were equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature shaker-bath. The colloidal component of the solute present in its saturated solution due to its low solubility was separated by filtration at 37°C through a 1G4 sintered glass crucible before the solutions were analysed for the products of dissolution. A separate experiment could prove the suitability of such crucibles for colloidal separation.

From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric acid and its dissociation products, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} using the three dissociation constants of the acid and the equilibrium pH of the system, the latter being required also for evaluating OH^- ion concentration needed for the calculation of solubility product.

There exists an ambiguity in the earlier literature regarding the solute phase likely to control the solubility of apatite

systems since the dissolution involved is hydrolytic. That the apatites exhibit stoichiometric dissolution could not unambiguously be established by the earlier workers. In order to investigate this significant aspect of dissolution of apatites, the solubility data of the present investigations were subjected to calculations to establish which among the possible phases exhibited a constancy for the activity product of its ions.

Making allowance for the fluctuations likely to be associated with the calculated ionic products due to error involved in the pH measurement and the microanalytical determinations of the dissolved ions, the constancy in the ionic product of the apatite phase was established. This consideration coupled with value of the g atom ratios, $\frac{Ca}{P}$, $\frac{Ca}{V}$ and $\frac{Ca}{(P+V)}$ of the saturated solutions approaching that of the apatite phase could establish the stoichiometric dissolution of apatites. An additional confirmation of such a dissolution could be provided by a precise response of the ionic products of PHA and VHA to the addition of common ion.

At a given pH, VHA was found to be more soluble than its phosphorus counterpart while the solubilities of the solid solutions were found to range between these two extremities exhibiting a systematic increase with an increase in the proportion calcium vanadate apatite. These aspects could be explained on the basis of the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.

Conclusion

The investigations carried out could suggest a convenient method for preparation of samples of PHA, VHA and a series of their solid solutions spread over the entire compositional range. A high order of purity of the samples could be established through their characterization by conventional chemical analyses as well as x-ray diffraction, electronmicroscopy, i.r. spectroscopy and thermogravimetry. The results on the solubilities of the samples indicated an increase with an increase in vanadium content. The investigations, when taken in totality, are significant to throw light on incorporation of vanadium into human skeletal and dental systems and the possibility of its elimination.

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