

Studies on Solid Solutions of Hydroxyl Apatite of Calcium and Some Micronutrient Metals

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Formation of solid solutions of hydroxyl apatites of calcium and some micronutrient metal ions viz., Mn^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+} has been studied. Solid solutions of composition, $Ca_7M_3(PO_4)_6(OH)_2$ and $Ca_5M_5(PO_4)_6(OH)_2$ (where M = micronutrient metal) were prepared by co-precipitation method. Solid solutions were characterized by analytical studies. The molar g-atom ratio (Ca + M)/P was found to be closer to the theoretical value for hydroxyl apatites suggesting their homogeneity. X-ray diffraction studies showed the decrease of lattice parameter values and contraction of unit cell volume consequent upon substitution of micronutrient metal ion into the calcium hydroxyl apatite suggesting the formation of homogeneous solid solutions. Infrared spectra of solid solutions suggested a coordinated mode of phosphate. Covalence of cation-phosphate bonding seem to increase with the induction of trace metal ion to the apatite. Spectra further suggested the OH of solid solutions to be hydrogen bonded. Implications of the results in phosphate urolithology have been discussed.

Key Words: Hydroxyl apatites, Solid solutions, Micronutrient metals, Urolithiasis, Urinary stones, Urolithology.

INTRODUCTION

Calcium hydroxyl apatite forms an important constituent of urinary stones. Phosphate stones mostly contain this mineral. Other phosphate minerals in the stone might be whitlockite [β - $Ca_3(PO_4)_2$], brushite ($CaHPO_4 \cdot 2H_2O$), newberyite ($MgHPO_4 \cdot 3H_2O$) and struvite [$MgNH_4PO_4 \cdot 6H_2O$]. Calcium hydroxyl apatite is also the primary crystalline inorganic component of human skeletal system^{1,2}. It is known to undergo a series of cationic and anionic exchange reactions³⁻⁵. Such reactions would also be of biological relevance. Exchange reactions of calcium hydroxyl apatite in the urinary tract would be interesting in understanding the role of urinary tract milieu in urolithology of phosphate. A number of cations, other than calcium, are also encountered in the urinary tract. Some of these cations having ionic radii closer to Ca^{2+} are likely to co-precipitate with the later (Ca^{2+}) to form mixed apatites. Micronutrient metal ions have good coordinating abilities. As such these metal ions are also likely to compete with Ca^{2+} ions to precipitate out the phosphate in the urinary tract. There may be co-precipitation resulting in solid solutions of mixed apatites of varying compositions. This, in turn, might result in the modification of bonding, as well as, solubility and stubbornness of phosphate portion of the urinary stones.

With the above views in mind, we have presently prepared some solid solutions of hydroxyl apatite of calcium and some micronutrient metals, by co-precipitation method. Compo-

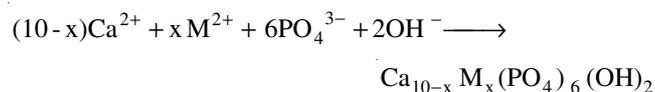
sitions of these solid solutions were characterized analytically. Depending upon the composition of precipitating media, the solid solutions were found to be of general formula, $Ca_7M_3(PO_4)_6(OH)_2$ and $Ca_5M_5(PO_4)_6(OH)_2$ where, M = Mn(II), Fe(II), Ni(II), Cu(II) or Zn(II). Homogeneity of solid solutions was ascertained by X-ray diffraction studies. Mode of bonding of phosphate in the species was studied by spectroscopically.

EXPERIMENTAL

All chemicals used were of AR quality. Various metal salts used were, $Ca(CH_3COO)_2$, $MnSO_4 \cdot 4H_2O$, $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O \cdot CO_2$ – free conductivity water was used for making the solutions. 0.05 M solutions of metal salts were prepared. 0.03 M solution of ammonium dihydrogen phosphate ($NH_4 \cdot H_2PO_4$) was also prepared.

Preparation of calcium hydroxyl apatite: 50 mL of calcium acetate solution (0.05 M) was added drop wise into a 50 mL solution of ammonium dihydrogen phosphate (0.03 M), maintaining the pH at 7.4. A 0.05 M NaOH solution was added drop wise to maintain the pH during precipitation. CO_2 -free N_2 gas was bubbled through the reaction mixture to eliminate the possibility of formation of carbonate apatite. The reaction mixture was refluxed for 4 h and then left overnight (well covered) at room temperature. The precipitate was filtered and washed with CO_2 – free distilled water till the washings were free from ammonium salts. The precipitate was dried at 100 °C and preserved over fused calcium chloride.

Preparation of solid solutions of hydroxyl apatites of calcium and micronutrient metals: The solid solutions were prepared according to the following reaction:



where, $\text{M}^{2+} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ or Zn^{2+} ; $x = 3$ or 5

Solutions of Ca^{2+} (0.05 M) and M^{2+} (0.05 M) were mixed in appropriate volumes (35 mL Ca^{2+} 15 mL M^{2+} , for $x = 3$ and 25 mL Ca^{2+} and 25 mL M^{2+} , for $x = 5$) and added drop wise to an appropriate volume (50 mL) of $\text{NH}_4\text{H}_2\text{PO}_4$ solution (0.03 M) maintaining the pH at 7.4. A 0.05 M NaOH solution was added dropwise to maintain the pH during precipitation. CO_2 -free N_2 gas was bubbled through the reaction mixtures to eliminate the possibility of formation of carbonate apatite. The reaction mixtures were refluxed for 4 h and then left overnight (well covered) at room temperature. The precipitate was filtered and washed with CO_2 -free distilled water till the washings were free from ammonium salts. The precipitates were dried at 100 °C and preserved over fused calcium chloride.

Analysis of samples: The apatites, prepared above, were analyzed for their calcium, micronutrient metal and phosphorous contents. Mn, Fe, Ni, Cu and P were estimated colorimetrically, Ca was estimated flame photometrically and Zn was estimated titrimetrically. All estimations were made by adopting standard methods⁶. Molar g-atom ratios, $(\text{Ca} + \text{M})/\text{P}$ (where M = micronutrient metal) were calculated out.

X-ray diffraction and infrared spectra: The X-ray diffraction patterns of the sample were obtained with siemens powder diffractometer with NaCl (TL) counter employing $\text{CuK}\alpha$ (Ni filtered) radiation with a scanning speed of 1° (2 θ)/min. Infrared spectra (FTIR) of the samples were recorded in the range 4000-500 cm^{-1} in KBr phase, on a Shimadzu 8201 PC infrared spectrophotometer.

RESULTS AND DISCUSSION

Analytical data of solid solutions of apatites are recorded in Table-1 and composition of the solid solutions has been assigned on the basis of analytical results. The molar g-atom ratio of $(\text{Ca} + \text{M})/\text{P}$ (M = micronutrient metal) of solid solutions has been found to vary in the range 1.64-1.71. This closely agrees with the theoretical value of 1.67 for hydroxyl apatites, suggesting homogeneity of solid solutions⁴.

X-ray diffraction studies: Formation of solid solution can be confirmed by X-ray diffraction analysis. The value of a and c parameters and corresponding unit cell volume of the samples were calculated from their X-ray diffraction patterns by standard methods^{7,8} (Table-2). Apatites are known to crystallize in a hexagonal structure^{4,5} with space group $\text{P6}_3/\text{m}$. Presently the lattice parameter values showed a regular decrease with the introduction of smaller trace metal ions (ionic radii 0.69 to 0.80 Å) in place of bigger Ca^{2+} (ionic radii 0.99 Å). The corresponding unit cell volume also thus decreased with the substitution of Ca^{2+} by the trace metal ions in the hydroxyl apatite. Consequent upon substitution of calcium by trace metal, the unit cell volume contraction was larger for solid solutions of $\text{Ca}_5\text{M}_5\text{POW}_6(\text{OH})_2$ series than those of $\text{Ca}_7\text{M}_3(\text{PO}_4)_6(\text{OH})_2$

TABLE-1
ANALYTICAL DATA OF SOLID SOLUTIONS OF APATITES

Solid solution	Elemental analysis (%):			Molar g-atom ratio (Ca+M)/P
	Found (calcd.)			
	Ca	M	P	
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	39.25 (39.84)	–	18.12 (18.53)	1.68
$\text{Ca}_7\text{Mn}_3(\text{PO}_4)_6(\text{OH})_2$	26.23 (26.69)	15.30 (15.73)	17.21 (17.53)	1.69
$\text{Ca}_7\text{Fe}_3(\text{PO}_4)_6(\text{OH})_2$	26.35 (26.62)	15.42 (15.97)	17.26 (17.68)	1.68
$\text{Ca}_7\text{Ni}_3(\text{PO}_4)_6(\text{OH})_2$	26.12 (26.41)	16.36 (16.61)	17.18 (17.55)	1.68
$\text{Ca}_7\text{Cu}_3(\text{PO}_4)_6(\text{OH})_2$	26.14 (26.06)	17.36 (17.73)	17.09 (17.31)	1.68
$\text{Ca}_7\text{Zn}_3(\text{PO}_4)_6(\text{OH})_2$	25.73 (25.95)	17.86 (18.07)	17.35 (17.24)	1.64
$\text{Ca}_5\text{Mn}_5(\text{PO}_4)_6(\text{OH})_2$	18.26 (18.54)	25.15 (25.49)	16.92 (17.24)	1.67
$\text{Ca}_5\text{Fe}_5(\text{PO}_4)_6(\text{OH})_2$	18.17 (18.45)	25.48 (25.83)	16.81 (17.16)	1.68
$\text{Ca}_5\text{Ni}_5(\text{PO}_4)_6(\text{OH})_2$	18.36 (18.22)	26.41 (26.74)	16.52 (16.95)	1.71
$\text{Ca}_5\text{Cu}_5(\text{PO}_4)_6(\text{OH})_2$	17.38 (17.83)	28.10 (28.31)	16.14 (16.58)	1.68
$\text{Ca}_5\text{Zn}_5(\text{PO}_4)_6(\text{OH})_2$	17.63 (17.71)	28.51 (28-79)	16.19 (16-47)	1.68

where M = Mn(II), Fe(II), Ni(II), Cu(II) or Zn(II)

TABLE-2
LATTICE PARAMETERS AND UNIT CELL VOLUME OF SOLID SOLUTIONS OF APATITES

Solid solution	Lattice parameter (Å)		Unit cell volume (Å ³)
	A	c	
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	9.42	6.87	527.96
$\text{Ca}_7\text{Mn}_3(\text{PO}_4)_6(\text{OH})_2$	9.40	6.81	521.11
$\text{Ca}_7\text{Fe}_3(\text{PO}_4)_6(\text{OH})_2$	9.37	6.78	515.53
$\text{Ca}_7\text{Ni}_3(\text{PO}_4)_6(\text{OH})_2$	9.30	6.69	501.09
$\text{Ca}_7\text{Cu}_3(\text{PO}_4)_6(\text{OH})_2$	9.27	6.65	494.93
$\text{Ca}_7\text{Zn}_3(\text{PO}_4)_6(\text{OH})_2$	9.35	6.74	510.32
$\text{Ca}_5\text{Mn}_5(\text{PO}_4)_6(\text{OH})_2$	9.38	6.80	518.17
$\text{Ca}_5\text{Fe}_5(\text{PO}_4)_6(\text{OH})_2$	9.34	6.76	510.73
$\text{Ca}_5\text{Ni}_5(\text{PO}_4)_6(\text{OH})_2$	9.28	6.68	498.21
$\text{Ca}_5\text{Cu}_5(\text{PO}_4)_6(\text{OH})_2$	9.24	6.63	490.22
$\text{Ca}_5\text{Zn}_5(\text{PO}_4)_6(\text{OH})_2$	9.33	6.72	506.60

series. Within the series also smaller the ionic radii of substituting trace metal larger was the volume contraction. These observations suggest the formation of homogeneous solid solutions.

Infrared studies: Selected infrared bands of the apatites are recorded in Table-3. The ideal symmetry of tribasic phosphate ion in free or undistorted state is tetrahedral-a member of T_d point group. It generally shows four IR absorption modes, namely, asymmetric P-O stretch (ν_3), symmetric P-O stretch (ν_1) and two O-P-O bending modes (ν_2 and ν_4). In the ideal symmetry conditions, ν_3 and ν_4 are clearly seen. In a non-equivalent force field around the PO_4^{3-} , however, there occurs distortion from the tetrahedral symmetry. In the case of ionic phosphate, the totally symmetric P-O stretching mode (ν_1) is Raman active. In the case of coordinated phosphates, however, this band (ν_1), has been found to become IR active⁹ and show at 970 cm^{-1} . In case of coordinated phosphates, the (ν_3) band splits into two when unidentate and into three when bidentate⁹.

TABLE-3
SELECTED INFRARED BANDS (cm⁻¹) OF
SOLID SOLUTIONS OF APATITES

Solid solution	v(OH) & v(O-H...O)	Asym. P-O stretch. (v ₃)	Sym. P-O stretch. (v ₁)	O-P-O Bending mode (v ₄)
Ca ₁₀ (PO ₄) ₆ (OH) ₂	3425	1123	962	563
	2825	1066		
	2368			
Ca ₇ Mn ₃ (PO ₄) ₆ (OH) ₂	3407	1090	950	579
	2368	1024		
Ca ₇ Fe ₃ (PO ₄) ₆ (OH) ₂	3351	1071	974	602
		1025		553
Ca ₇ Ni ₃ (PO ₄) ₆ (OH) ₂	3426	1079	955	577
	2368	1061		
Ca ₇ Cu ₃ (PO ₄) ₆ (OH) ₂	3431	1056	Obscured	568
	2366	1061		
Ca ₇ Zn ₃ (PO ₄) ₆ (OH) ₂	3414	1140	953	596
	2370	1055		560
Ca ₅ Mn ₅ (PO ₄) ₆ (OH) ₂	3433	1070	951	574
	2340	1027		
Ca ₃ Fe ₃ (PO ₄) ₆ (OH) ₂	3423	1096	955	601
	2369			
Ca ₅ Ni ₅ (PO ₄) ₆ (OH) ₂	3430	1112	951	599
	2368	1043		
Ca ₅ Cu ₅ (PO ₄) ₆ (OH) ₂	3404	1092	993	563
	2368			
Ca ₅ Zn ₅ (PO ₄) ₆ (OH) ₂	3430	1111	951	620
	2367	1018		

Presently, in the infrared spectra of pure calcium hydroxyl apatite two medium sharp bands occurring at 1123 and 1066 cm⁻¹ may be assigned to two components of asymmetric P-O stretching vibration (v₃). Symmetric P-O stretch (v₁) is seen, rather very weakly, at 962 cm⁻¹. O-P-O bending mode (v₄) is found positioned at 563 cm⁻¹. Split of v₃ hints at some coordinated nature of PO₄ in the apatite. v(OH) is seen at rather low position, at 3425 cm⁻¹. This shows that the OH groups are involved in hydrogen-bonding in the apatite.

In the infrared spectra of solid solutions of apatite, a general lowering of v₃ (assym. P-O stretch) as well as v₁ (sym. P-O stretch) bands is observed. In most of the cases the v₃ band is found split into two, one component being in the region 1140-1070 and the other at 1061-1018. In case of a single v₃ band, it invariably occurred below 1100 in the region 1096 to 1056 cm⁻¹. The v₁ band, which was not very clear in pure calcium hydroxyl apatite, appears rather clearly in most of the solid solutions. The v₄ band (O-P-O bending) was also found to be split into two in some cases.

The splitting as well as lowering of v₃ and clear occurrence of v₁ in the spectra of solid solutions indicate a coordinated nature of phosphate. The extent of covalence between cation and anion (phosphate) seem to increase with the substitution of calcium by transition metal ion in the apatite. This might be due to a greater polarizing power of transition metal ions compared to Ca²⁺. As the cation-anion bond becomes stronger, the frequencies of the internal modes of the anion should become cation-dependent and inturn more sensitive to cation mass. This, Perhaps, has contributed to the lowering of frequencies¹⁰.

It has been generally observed that the splitting of v₃ band is more pronounced and v₁ band is also more clear in solid solutions of Ca₅M₅(PO₄)₆(OH)₂ composition as compared to Ca₇M₃(PO₄)₆(OH)₂ (M = transition metal). Thus, it looks, the covalent character of phosphate bonding increases with an increase in transition metal content in the apatite.

The v(OH) band of the solid solutions, once again, appear rather low (3433-3351 cm⁻¹) with an additional weak band at 2370-2340 cm⁻¹ indicating hydrogen-bonded OH groups in the solid solutions of apatites¹¹.

Thus, on the whole, it is revealed that in the presence of micronutrient metal ion the calcium hydroxyl apatite would coprecipitate with the apatite of the former in the form of solid solutions with a higher degree of covalence. This, inturn, would effect the intra crystalline forces as well as cementation in the apatite.

Conclusion

The present observations indicate that the micronutrient metal ions viz., Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺ or Zn²⁺ can coprecipitate with calcium hydroxyl apatite to form solid solutions of varying compositions. It is also observed that the mode of phosphate bonding is affected by such coprecipitation. Calcium hydroxyl apatite forms the chief phosphate mineral in the urinary stones. Its precipitation is likely to be interfered with and modified by the micronutrient metal ions in the urinary tract, leading thus to formation of solid solutions under a suitable milieu. Altered intra-crystalline forces, as a result of mixed apatite formation, would affect the level of cementation as well as embedment of crystals with the matrix in the stone. Solubility and stubbornness of the stone might also be affected in this process. Thus, present work would be of applied value in understanding the effect of micronutrient metal ions on the process of biomineralization in the urinary tract and related phosphate urolithology.

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