STUDIES ON SOME PHYSICO-CHEMICAL ASPECTS OF SOLID SOLUTIONS OF PHOSPHATE AND ARSENATE APATITES OF STRONTIUM

SYNOPSIS

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DEPARTMENT OF CHEMISTRY
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NEHU

A THESIS
SUBMITTED
IN
FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF
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To

THE NORTH-EASTERN HILL UNIVERSITY
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SYNOPSIS

Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of substances known as apatites. It has been the subject of extensive investigations because of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. Among such diverse exchange reactions a few have attained significance during the recent past consequent upon the toxicity of the elements involved, such an exchange being the mechanism of their incorporation into human skeletal system

Based on the contemporary importance given to the toxicity to the human system by arsenic and β-active Sr-90, a product of atomic explosions, studies on the replacement of calcium by strontium (ionic radii 0.99 and 1.13Å respectively) and of phosphate by arsenate covalent radii (1.10 and 1.18Å respectively) have been chosen for the present investigations. Among heteroionic cationic substitutions on calcium hydroxylapatite replacement of Ca^{2+} by Sr^{2+} is significant since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90. Such an incorporation even in trace amounts, can be fatal because

of the long half-life period of Sr-90 (28.5 years). It is evident that a complete replacement of Ca^{2+} ions by Sr^{2+} ions leads to the formation of strontium phosphate apatite, $Sr_{10}(PO_4)_6(OH)_2$, while that of PO_4^{3-} by AsO_4^{3-} on strontium phosphate apatite leads to strontium arsenate apatite $Sr_{10}(AsO_4)_6(OH)_2$, both being iosmorphs of calcium hydroxylapatite. A partial replacement in either case leads to formation of solid solutions of the concerned end-members.

The toxicity of elemental arsenic and its salts is well known. There is prevalence of arsenic poisoning among workers employed in the manufacture of insecticides, paints and dyes containing the element. Inhalation of arsenic through nose and mouth and exposure of the skin to it are supposed to be responsible for the ailment. In spite of the fact that arsenic is distributed primarily throughout the soft tissues in living organisms its incorporation in the human skeletal system through $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ exchange on calcium hydroxylapatite of bone is probable.

It could be unambiguously established that ions incorporated in the human skeletal system through exchange reactions on calcium hydroxylapatite of bones play a significant role in two principal bone processes, namely, calcification and resorption, the deposition and dissolution respectively of calcium hydroxylapatite at the interface of bone and body fluids. Consequently, any attempt in the direction of elimination or minimization of such a toxicity is associated with a study of the solubility of calcium hydroxylapatite

as well as of 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 strontium phosphate apatite, strontium arsenate apatite and a series of six of their solid solutions spread over the entire compositional range, was undertaken. Adopting co-precipitation of the end-members in aqueous media through a judicious modification of the existing methods, the samples were prepared at 37°C to simulate biological conditions.

Characterization of these samples was brought about through sophisticated instrumental techniques such as x-ray diffraction, electronmicroscopy, i.r. and Laser Raman Spectral studies in addition to the conventional chemical analyses. Vegard's law demands that the unit cell volume of a homogeneous series of solid solutions varies linearly with the composition and offers a convenient method of scrutinizing their homogeneity. As is to be expected from the bigger size of the arsenate ion, a replacement of phosphate by it brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of arsenate ion replacing phosphate ion, observed in the present series of solid solutions, confirmed their homogeneity. The electronmicrographs of a few representative samples revealed the hexagonal pattern of the crystals confirming the absence

of extraneous phases and enabling approximate calculation of the specific surface areas from the measured average dimensions of the individual crystals.

The i.r. and Laser Raman spectra could confirm the identity of the samples. The predominant absorption peaks recorded in the traces of the samples were found to be due to the PO_4^{3-}, AsO_4^{3-} and OH^- ions.

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-} ion by AsO_4^{3-} ion on strontium phosphate apatite. Since it was intended to determine the solubility product of each sample from data resulting from the chemical analyses of the saturated solutions 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 product so determined, the studies in each case were extended to a few chosen pH values, the range being restricted to the limits, 5.5 and 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 coefficients of polyvalent ions could be avoided by assuming all of them to be unity without foregoing accuracy. It is evident that such calculations make the solubility product, Ksp, and the ionic product, Kip, synanymous.

Each one of the powdered samples was equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature shakerbath. 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 $1G_4$ sintered glass crucible before the solutions were analyzed for the products of dissolution. A separate experiment could prove the suitability of such crucibles for colloidal separation.

While phosphorus and arsenic were determined spectrophotometrically, atomic absorption spectroscopy was adopted for the determination of strontium, the attainable accuracy in all the cases being scrutinized by analyses of solutions of known compositions.

A scrutiny of attainment of saturation and the minimum period of equilibration required for the purpose were determined through dissolution kinetics of a couple of representative samples. From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric-acid and its three 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. Similar calculations were done with ortho arsenic acid in the case of systems having arsenate -

containing samples as solutes.

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 be unambiguously 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. It is evident that for the phosphate containing apatites such phases are the primary and secondary phosphates of the metal concerned in addition to the apatite phase. By analogy with a double salt, $Ca_2(HPO_4)(OH)_2$, a phase reported to control the solubility product of calcium hydroxyl apatite by functioning as a surface coating, the ionic product of its strontium counterpart, $Sr_2(HPO_4)(OH)_2$, was also calculated for the present systems. Examination of the data on solubility of all the phases mentioned above reveals that the ionic product of apatite showed a constancy over the entire pH range investigated and the calculated set of values were found to lie within the error limits. It is evident that the corresponding arsenate phases are relevant for strontium arsenateapatite while the phases of both phosphate and arsenate are to be considered for the systems involving the solid solutions. Such calculations were done on the data of solubility of all these samples. That the apatite phase

controlled the solubility was further supplemented by the fact that the g atom ratio, Sr/(P+As), of the saturated solutions of all the samples was in the proximity of the theoretical value (1.67) confirming unambiguously the occurrence of stoichiometric dissolution of apatites.

It could be established further that the solubility product of each sample of the series while remaining constant at all the pH values investigated, decreased systematically with an increase in the extent of replacement of PO_4^{3-} by AsO_4^{3-}. An interpretation of these results could be provided by the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.

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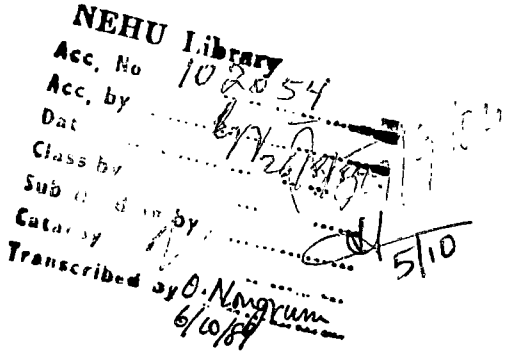

Dedicated

To

My Parents

phone : 0593
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North-Eastern Hill University

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I certify that a thesis entitled "**Studies on Some Physico-Chemical Aspects of Solid Solutions of Phosphate and Arsenate Apatites of Strontium**" submitted by Km. Grace George to the North-Eastern Hill University, Shillong for the Degree of Doctor of Philosophy, embodies a record of original investigations carried out by her under my supervision. I further certify that the results included in the present dissertation have not been submitted in full or in parts to any other University for any degree.

T S B Narasaraju

Signature of Supervisor

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This is to cerify that Miss Grace Geoege has satisfactorily completed the following Pre-Ph.D. courses, as prescribed by the University:

1. Bio-Inorganic Chemistry	CHEM	608
2. Chemical kinetics	CHEM	640
3. Experimental technique	SPS	630
4. French language	SPS	601

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SECTION III

SOLUBILITY EQUILIBRIA OF PHOSPHATE AND ARSENATE APATITES OF STRONTIUM AND THEIR SOLID SOLUTIONS

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PREFACE

It is well known that calcium and phosphorus are significant among the elements essential for human existence. They have been shown to be present in bones and teeth as calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the prototype of which belongs to a large family of naturally occurring isomorphous substances known as "Apatites".

A remarkable characteristic of apatites is that they are able to undergo a series of anionic and cationic substitutions without a disruption of the crystal lattice being inflicted. During the recent past, such substitutions have been the subject of extensive biological and physicochemical investigations. While $OH^- \rightleftharpoons F^-$ exchange on calcium hydroxylapatite is of importance in explaining the mechanism of occurrence of fluorosis and of the prophylactic action of fluorine in the occurrence of dental caries, a disease caused by the attack of tooth enamel by acidogenic bacteria, replacement of calcium by toxic ions such as Pb^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+} explains the incidence of pathological conditions, consequent upon the incorporation of these ions into the human skeletal system. In addition, radiation damage caused to human skeletal system by incorporation of Sr-90, a product of atomic explosions, has been shown to be a consequence of $Ca^{2+} \rightleftharpoons Sr^{2+}$ exchange.

Among the principal anionic exchange reactions of calcium hydroxylapatite, mention may be made of the replacement of PO_4^{3-} by VO_4^{3-} and AsO_4^{3-} (covalent radii, 1.10, 1.22, 1.18 Å respectively). An insight into the mechanism of incorporation of these toxic ions and the role played by them in influencing the physiology of bones and teeth can be achieved through studies on solubilities of this and its appropriate isomorphous compounds. The principal bone proccesses, calcification and resorption, are governed respectively by the deposition and dissolution of this compound at the bone/body-fluid interface. A similar equilibrium exists at the tooth/saliva interface. It is evident that any attempt in the direction

of removal of the incorporated toxic ions is based on a knowledge of the solubility phenomena of the samples under simulated biological conditions.

While the solubility of strontium phosphate apatite has earlier been investigated that of strontium arsenate apatite and its solid solutions with the former was not undertaken and therefore motivated the present investigations. In spite of the fact that studies on apatites are scattered over several disciplines, a physical chemist is considered to be better suited for investigating the aspects mentioned above providing thereby an additional justification for undertaking the present studies.

A prerequisite for such a series of investigations is to arrive at an optimum set of experimental conditions to prepare samples of these apatites and a series of their solid solutions spread over the entire compositional range and to characterize them through sophisticated physico-chemical techniques.

The thesis has been divided into three sections. Section I has been an attempt at a judicious compilation of information about calcium hydroxylapatite based on the earlier investigations carried out in diverse branches of research, the physico-chemical aspects being naturally given more emphasis. The experimental work carried out by the author has been included in sections II and III which have been presented in the conventional form of a research publication. The preparation of strontium phosphate apatite, strontium arsenate apatite and their solid solutions along with the confirmation of their homogeneity through, chemical, x-ray, electron microscopic, infrared and Laser Raman analyses has been included in Section II. Section III is constituted by the details of investigations on the solubility equilibria of these samples.

A consolidated list of books and journals consulted has been given at the end of the thesis to facilitate easy reference. References pertaining to each section have not been separately listed to avoid duplication. For such of the references, the originals of which could not be

consulted due to non-availability, the particulars about their 'Chemical Abstracts' have also been given. The journals have been abbreviated based on the pattern followed in 'Chemical Titles' published by the American Chemical Society.

A synopsis of the work and reprints of two research publications given as an appendix conclude the thesis.

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SECTION I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1.1 Apatites - An Isomorphous Series

It is a well known fact that human bones and teeth[1] contain calcium and phosphorus. In addition, these elements occur in nature as fluorapatite, $Ca_{10}(PO_4)_6F_2$, which is a member of an isomorphous series of minerals named by Werner[2] as "Apatites" ("Deceivers" in Greek). The name is justified because of the difficulties involved in their identification due to their non-stoichiometric existence consequent upon the tendency of these isomorphs to be present in nature as combinations[3]. Names of some of the important members of this isomorphous series[4-13] along with their molecular formulae and lattice constants are given in Table 1-1.

Each member of the series can undergo a series of cationic and anionic isomorphous substitutions leading to the formation of the corresponding isomorphs or their solid solutions depending upon the extent of substitution. It is evident that 100 per cent substitution leads to the formation of an isomorph while a partial replacement results in a solid solution[14]. Hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, a compound of extensive biological importance results from the replacement of F^- by OH^- on fluorapatite. Bones and teeth of human beings and animals are shown to be having hydroxylapatite as the principal inorganic constituent meriting

Table 1.1 Name, molecular formulae and lattice constants of a few principal members of apatite series.

S. No.	Name	Molecular Formula	Lattice constants(Å) a	c
1	2	3	4	5
1.	Barium hydroxylapatite	$Ba_{10}(PO_4)_6(OH)_2$	10.19	7.70
2.	Cadmium Arsenic-chlorapatite	$Cd_{10}(AsO_4)_6Cl_2$	10.07	7.26
3.	Cadmium hydroxylapatite	$Cd_{10}(PO_4)_6(OH)_2$	9.01	6.61
4.	Cadmium chlorapatite	$Cd_{10}(PO_4)_6Cl_2$	9.62	6.49
5.	Calcium hydroxylapatite	$Ca_{10}(PO_4)_6(OH)_2$	9.42	6.88
6.	Chlorapatite	$Ca_{10}(PO_4)_6Cl_2$	9.63	6.78
7.	Fermorite	$Ca_{10}(AsO_4)_6F_2$	9.75	6.92
8.	Fluorapatite	$Ca_{10}(PO_4)_6F_2$	9.35	6.58
9.	Hydroxyl vanadinite	$Ca_{10}(VO_4)_6(OH)_2$	9.82	6.98
10.	Lead hydroxylapatite	$Pb_{10}(PO_4)_6(OH)_2$	9.90	7.29
11.	Magnesium Apatite	$Mg_{10}(PO_4)_6(OH)_2$	9.30	6.89
12.	Mimetite*	$Pb_{10}(AsO_4)_6Cl_2$	10.36	7.52
13.	Pyromorphite*	$Pb_{10}(PO_4)_6Cl_2$	9.95	7.32
14.	Strontium hydroxylapatite	$Sr_{10}(PO_4)_6(OH)_2$	9.76	7.28
15.	Vanadinite	$Pb_{10}(VO_4)_6Cl_2$	10.47	7.43

*Also reported as members of pyromorphite series.

thereby a status for hydroxylapatite as a subject of extensive physico-chemical and biological investigations. Consequently a knowledge of its location and role played in bones and teeth is a prerequisite for undertaking a meaningful series of investigations on it.

1.2 Hydroxylapatite in Calcified Tissues- Its Biological Significance

Calcified tissues of the body can be divided into two different groups, namely mesodermal and ectodermal; bone, dentine and cementum belonging to the former and tooth enamel to the latter groups. The two groups differ in biological and chemical activity as well as in composition and ultra-structure.

Bone is an important tissue of the body. Its biological and structural significance is extensive. Biologically it acts as a reservoir of calcium in addition to providing a seat for production of blood cells. Structurally, bone provides the architecture of the human body. It is hydroxyl-apatite which plays an important role in both biological and structural aspects of bone. It is constituted by organic and inorganic compounds. The organic constituent amounting to about 30 per cent by weight, is made up of collagen a cement substance and a cellular component. Collagen is a complex inter-woven net-work of a fibrous protein and constitutes an extra cellular matrix of bone, while the cement substance consists of a few hexoses linked with the

protein. The cellular component, in turn, consists of cells designated as osteoblasts, osteoclasts and osteocytes which are concerned respectively with dissolution , deposition and nourishment of bone. The inorganic part of bone consists of an amorphous and a crystalline phase, the former being tricalcium phosphate while the latter is hydroxylapatite. The amorphous phase is predominant[15] in younger bones and gets partially transformed into crystalline phase with age. About 40 per cent by weight of an adult human bone was found to be hydroxylapatite. Mineral phase in bone is deposited as minute needles or platelets (100-600 Å long, 20-60 Å wide) within the collagen fibres such that their long axes line up with the fibres[16-18]. In addition, bone contains about 20 per cent of water by weight, present mostly in the organic matrix and in traces in hydroxylapatite crystals.

Tooth enamel consists of an outer part known as crown, a neck which is surrounded by gum and one or more roots or fangs fitting into the sockets of the jaw-bones. The principal dental tissues are enamel, dentine and cementum. The crown is covered by enamel which rests on dentine and the latter occupies the bulk portion of tooth. The cementum helps in the fixation of tooth in the socket of the jaw-bones. As in the case of bone the dental tissues are made up of inorganic and organic constituents. Hydroxylapatite admixed principally with ions such as magnesium and carbonate[1] was shown to be the inorganic constituent. The weight percents of it in enamel, dentine and cementum amount to

about 95, 75 and 35 respectively. Unlike other calcified tissues which are in equilibrium with the internal fluids, enamel equilibrates with saliva and is thus a seat of action for locally administered prophylactic agents of dental caries,[19,20], a tooth decay caused by acidogenic bacteria. Tooth enamel is almost fully mineralized and the crystals are much larger. Average length, width and thickness of 600, 1000 and 350 Å respectively have been reported[19,21] for these crystals. It is generally agreed that this tissue consists mainly of prisms or rods constituted by dense groupings of hydroxylapatite crystals.

The bone tissue serves as a reservoir for the body-minerals while the tooth enamel protects the inner layers of the tooth. In accordance with these functions, bone is chemically and biologically more reactive than tooth enamel.

1.3 $CaO-P_2O_5-H_2O$ Phase Diagram - Stability Ranges of Calcium Salts of Ortho Phosphoric Acid

The precipitation of phosphates of calcium is of considerable biological significance since the hard tissues of vertebrates contain them as the mineral constituents[22]. Among such phosphates the ones which are sparingly soluble and relatively more stable in aqueous systems deserve a mention in the present context. A specific calcium phosphate phase is preferred in a particular tissue depending upon the prevalent conditions such as temperature, pH and the chemical reactivity of the phase. Studies on (i) inorganic

constituents of human bones[23], (ii) utilisation of phosphatic minerals by plant kingdom[24] and (iii) geological aspects[25] of several naturally occurring phosphates contributed to our present knowledge of the phosphates of calcium. Preliminary studies intended to establish[6,26-27] the conditions of existence of phosphates of calcium were restricted to the solid phase reactions of the binary system, $CaO-P_2O_5$. It was not, however, recognised that an imperceptible inclusion of traces of water elevates this binary system to a ternary one, $CaO-P_2O_5-H_2O$. Earlier investigations on this ternary system were restricted exclusively to chemical analysis, the results being unreliable due to absence of a proof of homogeneity of the phases. The amorphous nature of the constituent phases added to the complications involved in their identification . These considerations necessitated the application of phase rule to the system and exposed the limitations of the exclusive use of chemical analysis[28] for the purpose. It is well known that important pre-requisites for the validity of phase rule are the attainment of equilibrium and the existence of homogeneous phases separated by sharp boundaries. Fulfilment of these conditions in the $CaO-P_2O_5-H_2O$ system was found to be complicated due to a slow attainment of equilibrium[29,30] and the amorphous nature of products formed.

A criterion of attainment of equilibrium in a precipitation reaction is the availability of identical results both from the sides of supersaturation and undersaturation.

In addition, solid phases are characterized by a high degree of reactivity due to their large surface areas. Further, they exist as colloidal suspensions causing additional complication in their filtration. The preliminary experimental data on the conditions of existence of calcium phosphates became repetitive, disorganised and contradictory since the factors mentioned above were not given proper considerations. Cameron[31] and Bassett[32] independently carried out investigations on the applicability of phase rule to $CaO-P_2O_5-H_2O$ system and the results obtained at 25°C are incorporated in the phase diagram[33] given in Fig. 1.1. The abscissa and the ordinate of a given point on the phase diagram represent the weight per cent of phosphorus pentoxide and calcium oxide respectively, the rest being water. The possible solid phases of the system are:-

(i) Anhydrous monocalcium phosphate, $Ca(H_2PO_4)_2$.

(ii) Monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2.H_2O$.

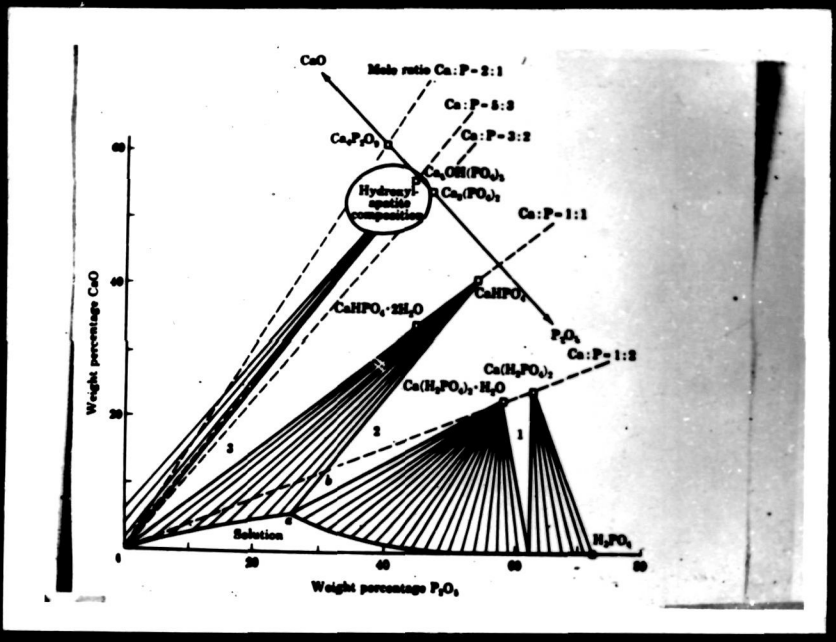
(iii) Anhydrous dicalcium phosphate, $CaHPO_4$.

(iv) Dicalcium phosphate dihydrate, $CaHPO_4.2H_2O$, and

(v) A crystalline precipitate of a variable composition with an x-ray diffraction pattern similar to that of an apatite.

All these phases could be identified through their distinct x-ray diffraction patterns supplemented by their chemical analyses. The blank regions of the phase diagram represent the solution phase while the solid phases are indicated by areas marked by convergent lines. Anhydrous monocalcium phosphate and its monohydrate exist as well-defined crystals

Fig 1.1 Phase diagram of Cao-P_2O_5-H_2O system at 25°C


CaO
Mole ratio Ca : P = 2 : 1
Ca : P = 5 : 3
Ca : P = 3 : 2
$Ca_4P_2O_9$
$Ca_5OH(PO_4)_3$
$Ca_3(PO_4)_2$
Hydroxyapatite composition
Ca : P = 1 : 1
$CaHPO_4 \cdot 2H_2O$
$CaHPO_4$
P_2O_5
Ca : P = 1 : 2
$Ca(H_2PO_4)_2$
$Ca(H_2PO_4)_2 \cdot H_2O$
Solution
H_3PO_4
Weight percentage CaO
Weight percentage P_2O_5
0
20
40
60
80
1
2
3
4
5
6

in acidic regions of the phase diagram which correspond evidently to the compositional ranges having a high proportion[34] of phosphorus pentoxide; they can thus be obtained by cooling solutions of such compositions. The acidic region is also found to be favourable for the formation of dicalcium phosphate[34]. The aqueous acidic solutions are to be heated to an optimum temperature for the percipitation of dicalcium phosphate as it follows a retrograde solubility. Dicalcium phosphate dihydrate exists over a limited range of experimental conditions making its isolation difficult. Since a crystalline precipitate of variable composition exhibiting the X-ray diffraction pattern of naturally occurring apatites constitutes one of the phases of the diagram the region of its existence is indicated by an elliptical area. This phase is given the formula, $Ca_{10}(PO_4)_6(OH)_2$, and represented in Fig.1.1 as $Ca_5(PO_4)_3OH$, neglecting its variable composition and water content.

Most of the investigations done on the calcium phosphates deal with hydroxylapatite phase which is characterized by a variable composition and constitutes phosphates of calcium having a g atom ratio[22] ranging from 3/2 to 4/2; the limiting ratios correspond respectively to tricalcium phosphate(TCP), $Ca_3(PO_4)_2$, and tetra calcium phosphate, $Ca_3(PO_4)_2.CaO$, as shown in the phase diagram. It is evident from the diagram that in the alkaline region which is characterized by a higher proportion of calcium oxide, the only solid phase capable of existence is that of hydroxylapatite.

The phases stable in the acidic region get transformed into hydroxylapatite for compositional ranges indicated by an upward arrow in the diagram. Some of these conclusions could be confirmed by Seuter[35] on the basis of studies on this phase diagram at temperatures higher than 800°C. The existence of an additional solid phase called octa calcium phosphate (OCP), $Ca_3(PO_4)_2.CaHPO_4$, in the neutral region of the ternary system was suggested by Hayek **et al**[36]. OCP could be demarcated from hydroxylapatite through its X-ray diffraction pattern and electronmicrographs. However, OCP has not been indicated in the phase diagram as a separate phase. Formation of OCP could be substantiated by Chaikina **et al**[37], on the basis of recent studies on this phase diagram at 25°C.

In addition to what has been mentioned in the present context involving $CaO-P_2O_5-H_2O$ phase diagram, it is considered appropriate here to make a mention of a few more phase diagrams such as those of (i) $Ca(OH)_2-H_2O-H_3PO_4$[21,38,39] (ii) calcium-carbonate-phosphate[40,41] (iii) $Na_3PO_4-CaCl_2$[40,42]. It is evident that in these cases also, as in the case of $CaO-P_2O_5-H_2O$ phase diagram, the phases preferred to be formed are dependent, among others, on activities of calcium and phosphate ions and the initial pH.

1.4 Preparative Techniques Based on Conditions of Formation

It was shown in the phase diagram of $CaO-P_2O_5-H_2O$ system that for a wide range of compositions formation of hydroxylapatite is favourable as substantiated by X-ray diffraction

patterns which are similar to those of naturally occurring apatites. Since such a phase is shown to be stable over a wide area in the phase diagram, the corresponding g atom ratio, Ca/p, was found to range from 1.5 to 2.0. These results facilitate the establishment of experimental parameters optimum for the formation of hydroxylapatite. It is evident[43] that hydroxylapatite is the stablest of the different calcium phosphates in weakly acidic, neutral and basic media. Consequently hydrolysis of other calcium phosphates leads to the formation of hydroxylapatite. Bassett[29] reported the precipitation of hydroxylapatite from solutions of calcium oxide and phosphorus pentoxide of appropriate concentrations which is in accordance with the suggestion offered by the phase diagram. Lorah **et al**[44] investigated the time-dependence of g atom ratio, Ca/p, of the compounds, calcium monophosphate, $Ca(H_2PO_4)_2$, calcium diphosphate, $CaHPO_4$, calcium pyrophosphate, $Ca_2P_2O_7$, and tricalcium phosphate(TCP), $Ca_3(PO_4$ when treated with sodium hydroxide solution. They found that the g atom ratio attained constancy equal to that of naturally occurring apatite within about 50 hours substantiating the statement that hydrolysis of calcium phosphates leads to the formation of hydroxylapatite. Schleede **et al**[27] obtained similar results by refluxing TCP with a dilute solution of potassium hydroxide for about 7 hours. Isolation of hydroxylapatite from bones and teeth is found to be complicated consequent upon changes sustained by the sample due to the techniques adopted. Synthetic samples which can

be prepared with a high degree of purity are better suited for purposes of physico-chemical investigations. A survey of different methods of formation of hydroxylapatite indicates that very few of them are suited for its preparation. Synthesis of apatites can be brought about by wet , dry and hydrothermal methods.

1.4.1 Wet Methods

Among the available methods those based on precipitation from aqueous solutions are the most suited for preparation of appreciable quantities of apatites. A method suggested by Hayek and Stadlemann[45] is widely used for the purpose because of the simplicity of experimental operations, the accompanying high yield and purity of the samples. This method is based on the following equation:

$$10\ Ca(NO_3)_2+6(NH_4)_2\ HPO_4+8NH_4OH=Ca_{10}(PO_4)_6(OH)_2+6H_2O+20NH_4NO_3 \quad .....(1.1)$$

1600 ml of a solution containing 79g of diammonium hydrogen phosphate maintained at a pH greater than 12 by the addition of ammonium hydroxide were dropped under constant stirring into 1200ml of a solution containing 230g of calcium nitrate, $Ca(NO_3)_2.4H_2O$, also maintained like-wise at the same pH. The amounts of the reactants taken were intended to give an yield of about 100g of the sample on the basis of the above equation. Based on the dissociation constants[46-48] of phosphoric acid, it can be shown that only the orthophosphate

ions are predominant at the pH maintained and thus likely complications due to co-precipitation of acid phosphates can be avoided. The accompanying volatile ammonium salts were sublimed off by heating the filtered product to about 250°C. Introducing minor alterations O'Shea et al[49] made use of this method to prepare samples of hydroxylapatite desired for X-ray diffraction and spectral studies. With appropriate modifications, this method could be extended to the preparation of a few more isomorphs of hydroxylapatite[50], the principal modifications being complexing[51] of the metal ions with appropriate ligands. This method was subsequently modified by Collin[52] and Narasaraju[50], important among the modifications being the replacement of ammonium hydroxide by ethylenediammine. Adriana Bigi et al[53] applied a modification of the method of Hayek and Stadlemann[45] for preparation of samples of solid solutions of calcium and barium hydroxylapatites spread over a limited compositional range extending upto about 25% substitution of Ca^{2+} by Ba^{2+}. They adopted solutions of the acetates of these metals and stoichiometric amounts of disodium monohydrogen phosphate, the temperature of precipitation being 100°C. No additional reagents were added to maintain the alkalanity of the medium of precipitation. This method could be extended for the preparation of a continuous series of solid solutions of cadmium and calcium hydroxylapatite[53]. A mention may be made of another wet method proposed by Rathje[43,54] known as "acidimetric precipitation" which is based on the following equation:

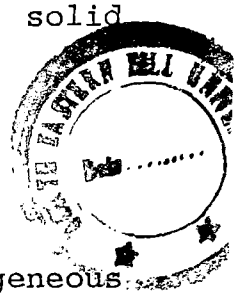
$$10\ Ca(NO_3)_2+6KH_2PO_4+14NaOH=Ca_{10}(PO_4)_6(OH)_2+6KNO_3+14NaNO_3+12H_2O \quad \ldots\ (1.2)$$

Convenient volumes of solutions of calcium nitrate and potassium dihydrogen phosphate containing the reactants in the proportions suggested by the above equations were simultaneously dropped into boiling water. The medium was maintained pink to phenolphthalein by the addition of a solution of sodium hydroxide. By a judicious selection of appropriate dilutions and rate of mixing of the solutions, crystals upto about 50μ in length could be obtained.

By another wet method hydroxylapatite of a high order of purity could be obtained by Arnold[55] involving a simultaneous addition of ammoniacal solutions of calcium acetate and of ammonium phosphate to about 10 litres of a mechanically stirred ammonium acetate solution also maintained alkaline. These methods which involve the precipitation of hydroxylapatite at high dilutions have low yields and hence are unsuitable for a rapid preparation of appreciable quantities of the samples. Kani **et al**[56] could prepare samples of hydroxylapatite similar to human dental enamel in crystallinity and g atom ratio, Ca/p, through appropriate modification of the above methods. Adopting a judiciously modified method of Hayek and Stadlemann[45], Narasaraju **et al**[57] obtained calcium hydroxylapatite of phosphorus and arsenate and a series of their solid solutions over the entire compositional range, the method being successful for the preparation of a similar series of compounds involving phosphate and vanadate apatites of lead[58] and phosphate and arsenate apatites of

barium[59]. During the recent past[60,61] several investigators adopted the wet methods mentioned above with minor alterations to prepare samples of hydroxylapatites intended for a specific purpose. An interesting recent wet method suggested by Meyer **et al**[62] was based on the use of a reaction between solid calcium sulphate and highly alkaline solutions of sodium phosphate. This method could be extended by Narasaraju **et al**[63] for the preparation of calcium vanadate apatite and of its solid solutions with hydroxylapatite.

Samples of hydroxylapatite and carbonate apatite of calcium were obtained by Iino-shinji[64] by refluxing suspensions of stoichiometric amounts of calcium hydroxide and calcium carbonate respectively and either mono, di- or triphosphate of calcium. The medium of suspension consisted of mixtures of water and pentane, the constant temperature chosen being in the range, 30-200°C. The homogeneity of the sample obtained was confirmed by X-ray diffraction. The method offered a simplified procedure for the preparation of hydroxylapatite of calcium and seems to be capable of being extended to the preparation of other apatites as well as their solid solutions.



1.4.2 Dry Methods

It is an established fact that an intimate heterogeneous mixture of appropriate solid ingredients when heated to an optimum temperature can lead to the formation of a desired lattice through solid state diffusion of the constituent ions.

Trömel[65,66] investigated the optimum conditions for the formation of hydroxylapatite through a solid state reaction between TCP and tetracalcium phosphate, $Ca_3(PO_4)_2.CaO$, or alternatively of TCP-calciumoxide. Solid mixture of these ingredients in appropriate compositions with a g atom ratio, ca/p, equal to 5/3 gave hydroxylapatite on heating for a few hours at 1050°C in a current of moist air as represented by the following equations:

$$2Ca_3(PO_4)_2+Ca_4P_2O_9+H_2O = Ca_{10}(PO_4)_6(OH)_2 \quad .... \quad (1-3)$$

$$3Ca_3(PO_4)_2+CaO+H_2O = Ca_{10}(PO_4)_6(OH)_2 \quad .... \quad (1-4)$$

Narasaraju **et al**[67] confirmed the utility of this method for preparing samples of hydroxylapatites of a high order of purity as investigated through x-ray, i.r., electron microscopic and chemical analysis. In addition, fusion of a sample of calcium phosphate, $CaHPO_4$, and calcium carbonate or alternatively heating of a sample of finely divided naturally occurring fluorapatite[68] at about 1400°C under a stream of moist air resulted in the formation of hydroxylapatite.

$$12CaHPO_4+8CaCO_3 = 2Ca_{10}(PO_4)_6(OH)_2+8CO_2+4H_2O \quad .... \quad (1-5)$$

$$Ca_{10}(PO_4)_6F_2+2H_2O = Ca_{10}(PO_4)_6(OH)_2+2HF \quad .... \quad (1-6)$$

An extension of the above methods to prepare chlorapatite and a series of its solid solutions with hydroxylapatite was brought about by Rai **et al**[69] as shown below:

$$3Ca_3(PO_4)_2+3CaCl_2 \xrightarrow{770\text{-}1040^\circ} 3Ca_3(PO_4)_2.CaCl_2 \longrightarrow Ca_{10}(PO_4)_6Cl_2+2CaCl_2 \quad \ldots\ldots (1\text{-}7)$$

$$2Ca_{10}(PO_4)_6(OH)_2+nCaCl_2 \longrightarrow 2Ca_{10}(PO_4)_6(OH,Cl_n)+nCa(OH)_2 \quad \ldots\ldots (1\text{-}8)$$

where n changes from o to 2

$$Ca(OH)_2 \longrightarrow CaO + H_2O \text{ (vapour)} \quad \ldots\ldots (1\text{-}9)$$

This method could be extended for the preparation of arsenic chlorapatite[70], $Ca_{10}(AsO_4)_6 Cl_2$, and its solid solutions with arsenic hydroxylapatite, $Ca_{10}(AsO_4)_6(OH)_2$, using arsenic hydroxylapatite and $CaCl_2$ as the starting materials.

A similar attempt to prepare solid solutions of hydroxylapatites of calcium and barium extending over compositional ranges of 60 to 100% replacement of calcium by barium was successfully carried out by Adriana Bigi **et al**[14], the temperature chosen for the solid state reactions of appropriate intimate mixtures of the end-member being 1200°C.

1.4.3 Hydrothermal Methods

Hydrothermal methods[71], as the name implies, deal with the application of high temperatures to aqueous solutions to facilitate the precipitation of crystals of dimensions bigger than those attainable using ordinary wet methods. Since an aqueous precipitating medium at atmospheric pressure has its boiling point as the upper limiting temperature, heating under high pressure enables this limit to be exceeded. In an autoclave the desired high pressure is produced by the vapour of the solvent of the precipitating medium since

the system is subjected to a high temperature in a sealed enclosure. The principal advantage of such methods has been to enhance considerably the crystallinity and purity of the product. Such sets of results were achieved by Hayek[72] et al and by Perloff and Posner[73] as substantiated by formation of homogeneous crystals of about 0.1mm in length in the form of hexagonal prisms. For this purpose 2g of precipitated hydroxylapatite were heated at 380°C in an autoclave for 24 hours with 15ml of 2M sodium hydroxide solution. The X-ray diffraction pattern of the sample was characterized by sharp peaks as expected from its crystal dimensions. Young and Sudarsanan[74] adopted a similar method to prepare a sample of strontium hydroxylapatite for crystallographic studies. Perloff and Posner[73] obtained hydroxylapatite by the hydrolysis of dicalcium phosphate and the probable reactions involved are the following:

$$10CaHPO_4 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4H^+ + 4H_2PO_4^- \quad .... \quad (1\text{-}10)$$

$$14CaHPO_4 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4Ca^{2+} + 8H_2PO_4^- \quad .... \quad (1\text{-}11)$$

This process was brought about by heating 0.1g of dicalcium phosphate with 10ml of water at 300°C for 10 days in a platinum - lined hydrothermal bomb and the product was found to be in the form of prismatic crystals. Another suitable method for the preparation of single crystals of hydroxylapatite for purposes of X-ray, neutron diffraction and thermogravimetric investigations was suggested by Elliot and Young[75]. A crystal sphere of 0.1mm in diameter of synthetic chlorapatite

when heated electrically on a piece of platinum foil at about 1300°C under steam at atmospheric pressure for two weeks formed a single crystal of hydroxylapatite of a high order of purity. A further extension of hydrothermal methods for preparation of hydroxylapatite was brought about independently by Akoi and Hideki[76] and Kazov **et al**[77].

1.5 Chemical Analysis

Quantitative separation of calcium and phosphate, which is a prerequisite for an accurate chemical analysis of hydroxylapatite needs special analytical procedures, the details of which have been worked out by Washburn and Shear[78]. Gravimetric[78], complexometric[79] and spectrophotometric[80] techniques are usually employed for the accompanying determinations of these separated ions. Application of atomic absorption spectroscopy to determine the metal ion concentration in apatites without a quantitative separation was brought about by Hivo **et al.** These techniques[14,53,82-87] can be extended to quantitative analysis of other systems involving the isomorphs of calcium hydroxylapatite as well as their solid solutions.

1.6 Structural Aspects

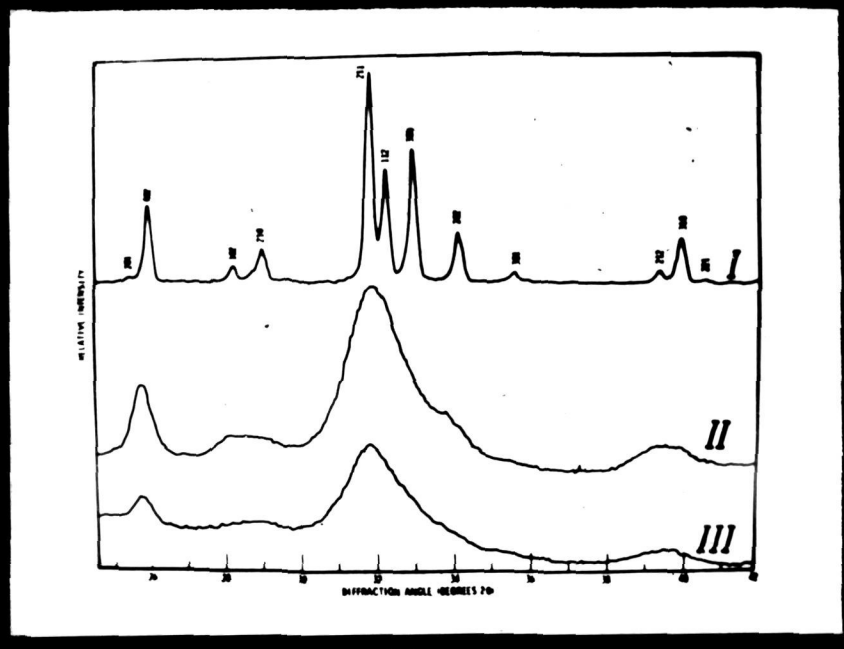
The basic structural features[88] of the apatite lattice were first worked out independently by deJong[89], Mehmel[90] and Naray-szabo[91]. deJong showed for the first time, with the then relatively new technique of *X-ray diffraction*, that the mineral in bone bore a close structural resemblance

to the naturally occurring hydroxylapatite. In this pioneering diffraction study, deJong also observed that the apatite crystals in bone were extremely minute and ill-defined. However, the detailed spatial arrangement of the constituent ions in the apatite structure was not firmly established. It was only after about 25 years that Posner **et al**[92] could arrive at these structural aspects from x-ray diffraction studies on synthetically prepared single crystals of hydroxyapatite, and by Kay **et al**[93] from neutron diffraction studies. These studies revealed the most striking feature of the hydroxylapatite structure namely the hexagonal arrangement of Ca^{2+} and PO_4^{3-} ions about columns of monovalent OH^- ions. That animal bones and teeth contain hydroxylapalite as an ingredient was proved[94] by the identity of x-ray diffraction patterns of the former with those of the naturally occurring hydroxylapatites as shown in Fig. 1-2(a). In addition, a representative Debye-Scherrer powder pattern of synthetic hydroxylapatite is given in Fig. 1.2(b).

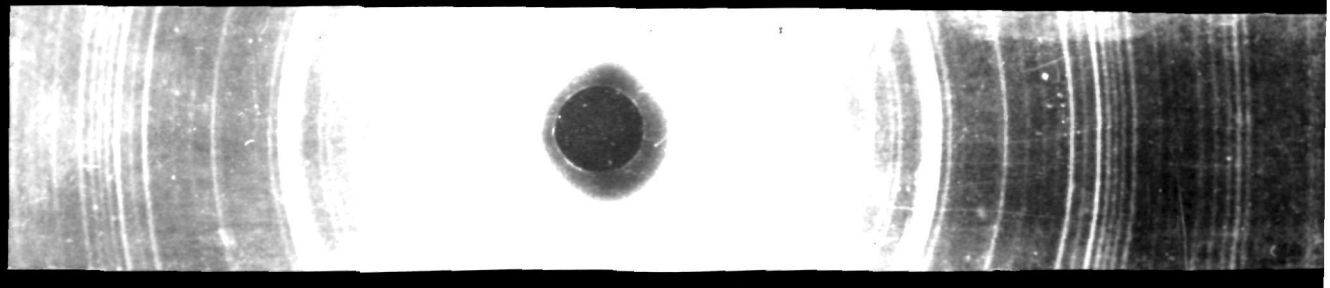
Hydroxylapatitė, both of biological and synthetic origin crystallises in hexagonal $P6_3/m$ space group with lattice constants, 'a' and 'c' equal to 9.42 and 6.88Å respectively. The details of the crystal structure of apatites were studied independently by Naray-Szabo[91] and Mehmel[90] and their conclusions were subsequently confirmed by Hendricks **et al**[9]. The structure proposed by them was later modified by Beevers and McIntyre[95] and a few more refinements were suggested by Posner **et al**[92]. Sudarsanan[8] studied the structure of

Fig 1.2 (a) X-ray diffraction patterns of
(i) Crystalline synthetic hydroxylapatite
(ii) Amorphous synthetic hydroxylapatite
(iii) Hydroxylapatite obtained from Bone

Fig 1.2 (b) A representative Debye-Scherrer powder pattern of crystalline synthetic hydroxylapatite.



a



b

cadmium apatites and proved them to be iso-structural with naturally occurring fluorapatite. The lattice of hydroxylapatite is constituted by the ions Ca^{2+}, PO_4^{3-} and OH^- and their arrangement[15] in the unit cell is indicated in Fig.1.3. The ions are distributed in two planes one over the other such that each half is a mirror image of the other. It is evident that the whole volume of the unit cell is closely packed with the constituent ions and only for purposes of clarification of their relative positions, they are represented in the figure as if they are wide apart from one another.

Out of a total of fourteen calcium ions, six are located within the unit cell and thus belong to it entirely and the remaining eight peripheral ions are shared by adjacent unit cells, such that there is an allocation of four per each. Similarly, it can be shown that out of ten phosphate groups (2 situated inside and 8 at the periphery) only six belong to each unit cell, (2 situated inside and four out of the eight peripheral ions). Likewise two out of eight hydroxyl groups represented in the figure belong to the unit cell. The number of ions present per unit cell of hydroxylapatite can thus be correlated with its molecular formula accounting thereby for the basic chemical repeat unit in the three dimensional symmetry pattern.

Fig. 1.4 represents a cross-section of hydroxylapatite lattice parallel to the c-axis and provides a further clarification[9] of the relative lattice position of the atoms. It can be shown from the figure that O- Ca-O chains

Fig 1. The unit cell perspective of hydroxylapatite.

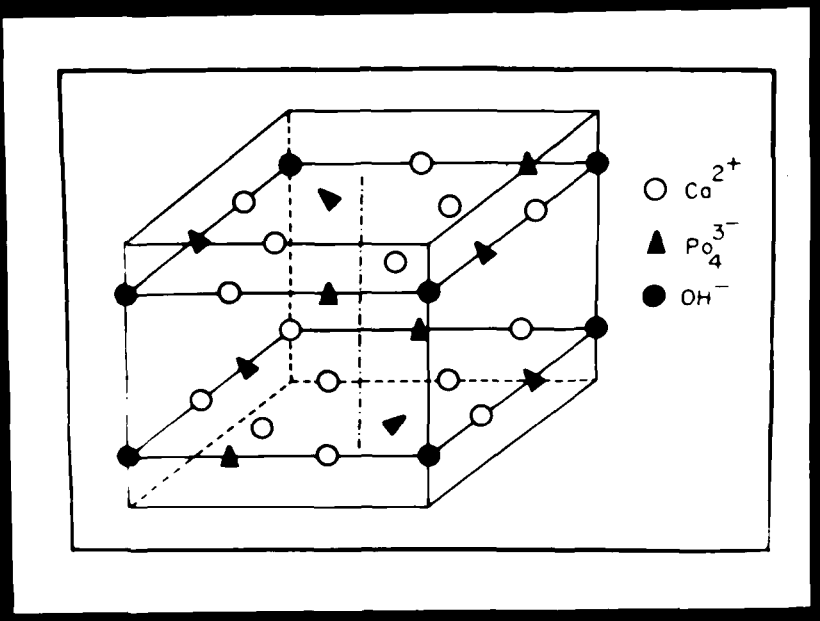
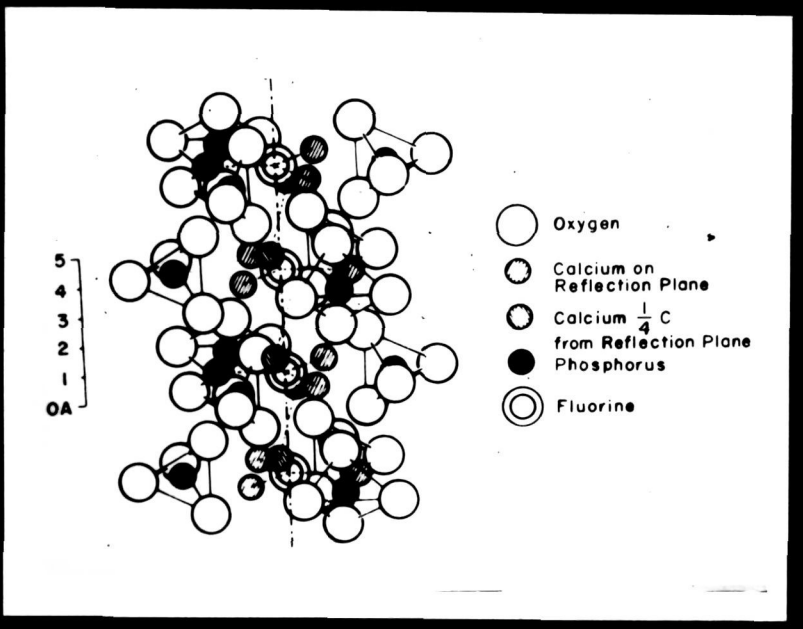
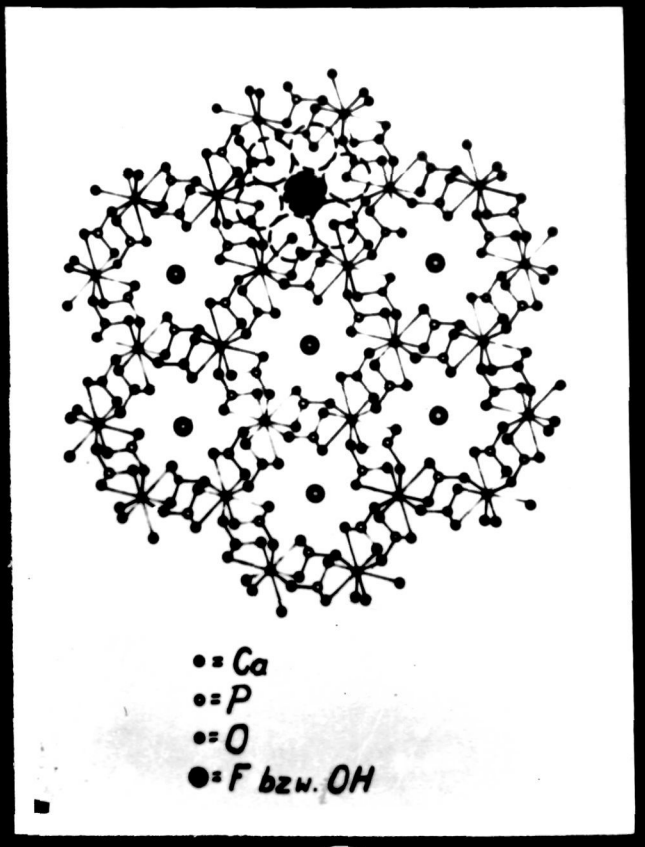

Ca^{2+}
PO_4^{3-}
OH^-

Fig 1.4 (a) A cross-section of the apatite lattice parallel to the c-axis.

Fig 1.4 (b) Apatite lattice viewed from the plane 001 as reported by Beevers and McIntyre.


5
4
3
2
1
0A
Oxygen
Calcium on Reflection Plane
Calcium $\frac{1}{4}$ C from Reflection Plane
Phosphorus
Fluorine

a

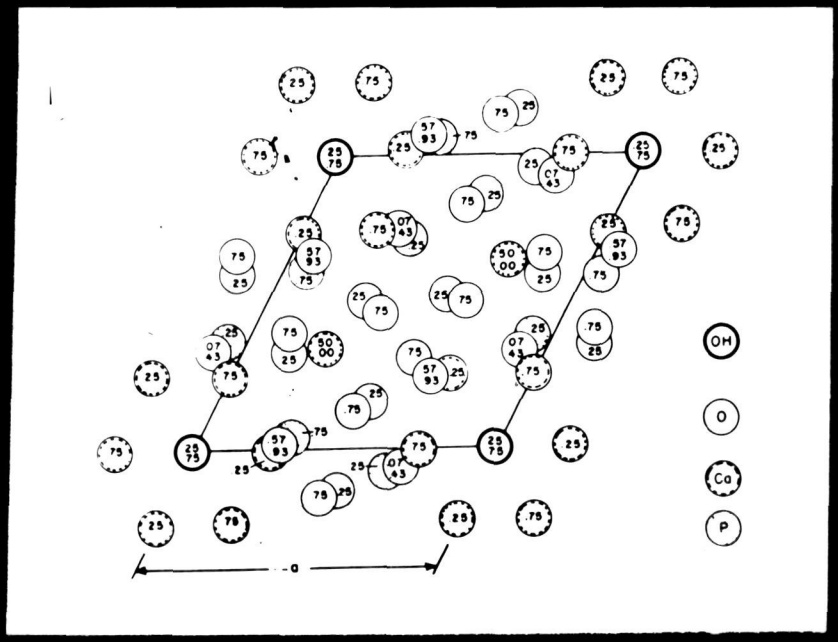

●= Ca
●= P
●= O
●= F bzw. OH

b

exist running parallel to the c-axis. The chains are joined together by phosphorus atoms constituting the inner lining of an elongated cavity which runs parallel to the c-axis and accommodates the F^- ions. It is evident that depending upon ionic size and charge, other ions can replace fluoride ions. In addition every phosphorus atom is surrounded by four oxygen atoms forming a tetrahedron. The existence of cavities in the crystal structure accounts for the porosity and the consequent surface activity of apatites. X-ray line broadening experiments[18] using low angle scattering revealed the apatites to be thin tabular hexagons elongated in the direction of the c-axis. A refinement of the crystal structure of hydroxylapatite was suggested by Posner **et al**[92] based on the three dimensional x-ray diffraction studies on single crystals. The bond lengths and the atomic positions were determined more accurately than those already available. It was further shown that the phosphate tetrahedra have P-O distances shorter than those reported earlier. In addition, the Ca atoms situated around the hexagonal screw axis are shown to be co-ordinated to the hydroxyl ions and oxygen atoms of the phosphate tetrahedra. It was further shown that the calcium atoms among themselves constituted triangles one over the other in the direction of the c-axis. Based on these refinements, the arrangement of the constituent atoms of hydroxylapatites as projected upon the basal plane of its structure is shown in Fig. 1-5.

Attempts to determine the orientation of hydroxyl groups

Fig 1.5 Arrangement of the constituent atoms of hydroxylapatite as projected upon the basal plane of its structure (The number in each circle represents the c-axis parameter perpendicular to the basel plane).


OH
O
Ca
P
a

in the crystal structure of hydroxylapatite were made by Kay et al[93] through neutron and X-ray diffraction studies. They concluded that the hydroxyl groups occur in columns parallel to the C-axis and that these columns pass through the centres of the calcium triangles. The X, Y and Z co-ordinates of the constituents of the hydroxylapatite lattice are given in Table 1.2. Depending upon their relative positions in the unit cell of hydroxylapatite, the calcium and oxygen atoms are designated through the subscripts given to their symbols.

Table 1.2 Listing of position-parameters for the constituent atoms of hydroxylapatite.

Atom	No. of atoms per unit cell	Position parameters		
		X	Y	Z
Ca_i	4	0.333	0.667	0.001
Ca_{ii}	6	0.246	0.993	0.250
P	6	0.400	0.369	0.250
O_i	6	0.329	0.484	0.250
O_{ii}	6	0.589	0.466	0.250
O_{iii}	12	0.348	0.259	0.073
OH	2	0.000	0.000	0.250

Extensive work on the crystal structure of apatites was carried out by Young and his co-workers[96-99], the samples used being prepared exclusively by thermal methods. As mentioned earlier apatites are normally expected to be hexagonal belonging

to the space group $P6_3/m$. Young could establish that a stoichiometric synthetic sample of chlorapatite is pseudohexagonal belonging to the monoclinic space group, $P2_1/b$ with 'a' equal to 9.628Å and 'c' 6.764Å. while the monoclinic and hexagonal structures are very similar, the former is characterized by an ordered arrangement of the Cl^- ions in chlorapatite resulting in the transformation of the mirror plane of the hexagonal structure to a glide plane in the monoclinic structure with the accompaniment of the doubling of one of the cell dimensions. Subsequent single crystal analysis of hydroxylapatite by these workers confirmed that the analogy regarding the monoclinic structure could be extended to this compound and the lattice constants 'a' and 'c' reported were shown to be 9.4214Å and 6.8814 Å respectively. Single crystal of hydroxylapatite used for these studies was prepared by a conversion of that of chlorapatite by heating in steam at 1200°C. However, the significance of the monoclinic space group for biological considerations could not be established. In addition, optimum range of temperatures desired for the phase transformation from monoclinic to hexagonal form is yet to be investigated to know whether the monoclinic form exists under in vivo conditions. It will be of interest to investigate the role of trace impurities like F^-, Cl^-, CO_3^{2-} and Mg^{2+} in bringing about such a phase transformation. Recently Elliot **et al**[100] substantiated the findings of Young[96] by reporting that a sample, $Ca_{10}(PO_4)_6CO_3$, termed as carbonate-apatite, exhibits a pseudohexagonal symmetry with monoclinic

space group, P_b, with lattice parameters 'a' and 'c' being equal 9.557Å and 6.872Å and b approximately equal to 2a.

For purposes of characterisation of samples of synthetic apatite such refinements in the structure brought about by precise x-ray diffraction studies may not be of great relevance. In addition, as these structural refinements were carried out using samples obtained by dry methods, the divergence, if any, shown by precipitated samples of apatites from the hexagonal structure is not yet established.

The conclusions drawn from x-ray diffraction studies on the structural aspects of apatites can be supplemented by its electronmicroscopic pattern which can confirm the homogeneity of the samples by proving the absence of extraneous phases. In addition they provide information regarding the geometry and dimensions of its individual crystals. Though x-ray diffraction patterns of bone help in proving the presence of hydroxylapatite and determining its lattice constants, they do not permit one to see the shape of bone crystals or to visualise directly the relationship these crystals hold to the other ingredients of bone. These aspects can be fulfilled by the electronmicroscopic investigations of bone, the corresponding in vitro studies being carried out by Hayek **et al**[36]. Extensive in vivo electronmicroscopic studies carried out by Robinson[15] could throw light on the uniformity in size of the inorganic crystalline component and the spatial relationship existing between the collagen fibres, the cement substance and the calcium hydroxylapatite in bone.

1.7 Isomorphous Substitution

Isomorphous substitution may be defined as the replacement of one ion by another in a crystal lattice without disrupting its geometry. This can be classified as isoionic and heteroionic substitutions. The former may be defined as a process by which ions from the solution phase exchange with identical ions of a solid phase in contact with it, the composition of the two phases being unaltered. In heteroionic substitution an ion of a solid phase is being displaced by a different ion from a solution in contact with it altering thereby the compositions of both the phases . A characteristic property of hydroxylapatite is its ability to undergo a series of iso- and heteroionic substitutions[101] involving both cations and anions, the criteria being the similarity in charge and size of the ions concerned. It was shown by Clement and Zureda[102] that bivalent metal ions with ionic radii of about 1.0Å can form apatites, the most important among them being Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} and Cd^{2+} with ionic radii 0.99, 1.13, 1.35, 1.20 and 0.97Å respectively. Both iso- and heteroionic substituions involving these ions are therefore possible .

1.7.1 Isoionic Substitutions

Isoionic substitutions of calcium and phosphate have been investigated extensively on synthetic calcium hydroxylapatite, human bones and teeth[103,104]. Such investigations are of significance in providing an explanation for the skeletal fixation of calcium and phosphorus and also for throwing

light on the phenomenon of resorption, a process by which portions of bone during growth are dissolved and returned to blood stream. Such substitutions were investigated by tracer techniques in which a slice of the labelled tissue is placed in contact with a photographic film which functions as a radiation detector.

1.7.2 Heteroionic Substitution

Based on their extensive biological significance heteroionic substitutions are considered relevant and merit a mention in the present context:

(a) $Ca^{2+} \rightleftharpoons Sr^{2+}$, (b) $Ca^{2+} \rightleftharpoons Ba^{2+}$

(c) $Ca^{2+} \rightleftharpoons Pb^{2+}$, (d) $Ca^{2+} \rightleftharpoons Zn^{2+}$

(e) $F^- \rightleftharpoons OH^-$ and (f) $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$

(a) $Ca^{2+} \rightleftharpoons Sr^{2+}$ substitution.

Ca^{2+} — Sr^{2+} substitution on hydroxylapatite is one of the most important heteroionic substitutions since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90 produced in atomic explosions. The substitution reaction can be explained as follows:

$$Ca_{10}(PO_4)_6(OH)_2 + nSr^{2+} \rightleftharpoons \underset{\text{A Solid solution of hydroxylapatites of calcium and strontium.}}{Sr_nCa_{10-n}(PO_4)_6(OH)_2} + n\ Ca^{2+} \quad ...(1\text{-}12)$$

Due to its long half-life period (about 28.5 years) Sr-90 can prove fatal even when it is present in traces in the human skeletal system. Investigations on the substitution reactions

are consequently supposed to be helpful in suggesting a possibility of removal of the incorporated strontium. The time-dependence of this substitution using β-active Sr-89 as a tracer was investigated by Knappwost and Ehret[105]. An equilibrium was brought about in solutions of strontium nitrate, labelled with Sr-89, with synthetic samples of hydroxyl apatite having different surface areas. Adsorption of strontium ions and their subsequent diffusion into the crystal interior accompanied by a simultaneous recrystallization of the equlibrated hydroxylapatite were shown to be the factors governing such a substitution.

Collin[106] showed through coprecipitation that a series of homogeneous solid solutions of hydroxyapatites of calcium and strontium over the entire compositional range could be formed confirming thereby the occurrence of isomorphous substitution between these ions. These results were subsequently confirmed by Chickerur et al[107,108]. Through X-ray diffraction studies Khudolozhkin et al[109] could conclude that replacement of calcium by strontium or barium on the apatite lattice, occurs preferentially on Ca(II) sites in comparison with those of Ca(I). A substantiation of these results was provided by using i.r. spectroscopy and thermoanalytical studies. Based on in vivo studies on isomorphous substitutions on apatite crystals, Baud[113] could show that the dimensions of the unit-cell were dependent on the chemical composition; the alteration in the former offers an evidence for the occurrence of substitution. As mentioned earlier

the replacement of Ca^{2+} by Sr^{2+} on the hydroxylapatite of human bones is of extensive biological importance. Commensurate with its contemporary significance extensive work[114-121] on this substitution has been reported during the recent past which deserves a brief mention in the present context. These aspects are an addition to what has been mentioned in the earlier paragraphs. Roushdy et al[114] investigated the levels of retention of Sr-85, and Sr-89 in rat femur. It was observed that the retention levels are inversely proportional to the proportion of calcium in the diet. In addition, vitamin D-deficient diet caused a decreased retention level of radio strontium. Dehos[115,116] could prove through an analysis of teeth of children of different age groups that the uptake of Sr-90 by the human teeth is proportional to the levels of fall-out of the isotope from the atmosphere consequent upon nuclear test explosions. An extension of this work by them to human bones among West German residents indicated that the uptake of Sr-90 was higher in 15-25 year age group than that for the 25-55 year age group. Based on investigations on rabbit lense Grub et al[117] found that the presence of Sr^{2+} reduced the replacement of Na^{+} by K^{+}. In addition they could get evidence to show that the Sr^{2+} present interacted with the cell surface of the crystalline lense.

The uptake and turnover of Sr^{90} in human skeleton were investigated by Papworth and Vennart[118]. They estimated the fraction of dietary intake of Sr^{90} that reaches the skeleton

as well as its turnover. The age dependence of these parameters was also investigated. It was suggested by them that these results can be used to predict the future levels of Sr^{90} in human bones from measurements of the dietary levels of the radionuclide. Park[119] investigated the incorporation of Sr^{90} in beagles using the technique of radionuclide ingestion. The results could lead to equations which stabilised Sr^{90} retention and distribution. It was found that the Sr^{90} distribution matched closely with that of calcium distribution in skeletal component. Bang **et al**[120] investigated the skeletal distribution of stable Sr^{2+} and its incorporation in the bone mineral in vivo. They observed that bone mineralization in mice decreased with a strontium-high diet intake. In addition they observed an exchange of strontium for calcium in bone mineral as substantiated by x-ray and i.r. studies. Marie **et al**[121] studied the dependence of bone metabolism in rates on oral doses of strontium. These seral and bone levels of strontium were found to be proportional to the intake of the element.

(b) $Ca^{2+} \rightleftharpoons Ba^{2+}$ substitution

Because of the toxic effects of elemental barium and its soluble salts, replacement of Ca^{2+} by Ba^{2+} on hydroxyl apatite is another heteroionic substitution[67] of importance.

Analogous to strontium, β-active Ba-140 (half life, 12.8 days), a product of atomic explosions, also gets incorporated in the human skeletal system based on the following equation:

$$Ca_{10}(PO_4)_6(OH)_2 + nBa^{2+} \rightleftharpoons Ca_{(10-n)}Ba_n(PO_4)_6(OH)_2 + nCa^{2+} \quad (1\text{-}13)$$

A Solid solution of hydroxylapatites of calcium and barium.

The relatively smaller half-life period of Ba-140 makes the radiation damage caused by it less toxic than that by Sr-90. Unlike strontium the non-active barium is also toxic and consequently the studies on such a substitution are of importance to explore a possibility of elimination of the incorporated barium.

Detailed aspects of Ca^{2+} – Ba^{2+} substitution were investigated by Narasaraju **et al**[67]. Adopting a thermal method, samples of hydroxylapatites of calcium and barium and a series of their solid solutions were prepared over the entire compositional range. The characterization of the sample was brought about by chemical, i.r. x-ray diffraction and electronmicroscopic analysis. It could be shown through tracer techniques by Samachson **et al**[122] that there is a preferential uptake

of Ba-133 over Ca-47 and Sr-85 by human bones. In addition Samachson and Schmidt[123], could show that traces of Zn^{2+} ions when present in the equilibrating solution increase the uptake of Sr-85 and Ba-133. These results were explained on the basis of the supposition that Zn^{2+} distorts the surface of calcium hydroxylapatite facilitating thereby a replacement of Ca^{2+} by larger alkaline earth ions. The replacement of calcium by barium in the hydroxylapatite lattice by solid state reaction at different temperatures and by precipitation from an aqeuous system have been investigated by x-ray diffraction and i.r. absorption analyses. The products obtained by solid-state reaction at 1200°C are solid solutions over the range of barium concentration, 60-100 atom%.

(c) $Ca^{2+} \rightleftharpoons Pb^{2+}$ substitution

"Lead Poisoning"[124] also known as "Plumbism" is caused by inhalation of lead in the form of dust or its adsorption through skin, the mechanism involved being attributed to isomorphous substitution of Ca^{2+} by Pb^{2+} on bone leading to formation of solid solutions[125] of hydroxylapatites of calcium and lead. Such a formation was shown by Müller[10] to be possible over the entire compositional range through co-precipitation in aqueous media as substantiated by Narasaraju et al[50] and also by Rao and Chickerur[126]. The following is the chemical equation involved:

$$Ca_{10}(PO_4)_6(OH)_2 + nPb^{2+} \rightleftharpoons Ca_{10-n}\,Pb_n(PO_4)_6(OH)_2 + nCa^{2+} \quad \ldots(1\text{-}14)$$

A Solid solution of hydroxylapatites of calcium and lead.

It could be shown recently that lead-poisoning occurs through the coating of pottery in Mexico, the damage being termed as "Problem of lead in Mexican Pottery"[127].

(d) $Ca^{2+} \rightleftharpoons Zn^{2+}$ substitution

Detailed investigations on the replacement of Ca^{2+} by Zn^{2+} on calcium hydroxylapatite of bones were carried out by Samachson et al[128-130]. Detailed radio chemical studies on this exchange using solutions labelled with Zn-65 could prove 100 percent uptake of Zn^{2+} by calcium hydroxylapatite within five minutes. Chelating agents such as EDTA were found to be considerably effective in hindering this process. An estimation of the amount of extra calcium which entered the solution during equilibration consequent upon an ion to ion replacement of lattice Ca^{2+} by Zn^{2+} present in the equilibrating solution confirmed the occurrence of such an exchange. As in the case of other exchanges, this processes was also found to be rapid initially, the subsequent process controlled by a diffusion of Zn^{2+} in to the crystal lattice being slow.

(e) $F^- \rightleftharpoons OH^-$ substitution

Neutron and x-ray diffraction studies carried out by Kay et al[93] could confirm the earlier findings that OH^- groups are located in the cavities running parallel to the c-axis of the apatite lattice. It can be shown that, among others, ions of the type F^-, OH^- and Cl^- with ionic radii 1.32, 1.68 and 1.81 Å respectively fit into these cavities. In addition spherical symmetry of F^- ion makes it better suited for the

purpose than OH^- ion. A replacement of OH^- ion by F^- ion therefore brings about a contraction of the unit cell of hydroxylapatite[4,8,131]. The OH^--F^- exchange is of significance in explaining the occurrence of dental caries which involves the attack of the apatite inorganic phase of enamel by acidogenic bacteria existing in the vicinity of the enamel surface. Knappwost[19,20,132,133] and co-workers investigated the various aspects of this substitution and the role of F^- ion as a prophylactic in the occurrence of dental caries. He proved that the tooth surface enriched with F^- ions was more resistant to caries. He could suggest a convincing mechanism of the caries prophylactic action of fluorine. Deposition of fluorapatite layers on the tooth surface resulting, inter alia, in alteration in the viscosity of saliva, was found to be caused by an oral daily dose of 1-5 mg of fluorine. Fluorapatite being less soluble than calcium hydroxyl apatite, the corrosion by acidogenic bacteria on the tooth surface can be retarded by such a deposition which was found to be preferentially formed on the affected regions of the tooth surface. The substitutions can be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + xF^- \rightleftharpoons Ca_{10}(PO_4)_6(OH)_{2-x}F_x + x(OH^-) \quad .... \quad (1\text{-}15)$$

A Solid solution of calcium hydroxylapatite and fluorapatite

The product of this substitution is a solid solution of calcium - hydroxylapatite and fluorapatite known as fluor -hydroxylapatite. Calcium fluoride formed simultaneously during the progress of this substitution reaction was found to inter-

fere with the exchange reactions as shown by Liang and Higuchi,[134] Stearns and Berndt[135] and Higuchi et al[136]. A measure suggested for the prevention of the dental caries has been the application of appropriate amounts of F^- ions in some suitable form to the dental tissue. This process known as fluoridation[1] has been in vogue since a few decades. 1 ppm of fluorine in drinking water was found to be an optimum level for caries control, a level higher than this was found to lead to mottled enamel and also to certain toxic effects. Several mechanisms are suggested to explain the prophylactic action of fluorine in the occurrence of dental caries, the most important among which is based on the exchange of OH^- ion of calcium hydroxylapatite of tooth by F^- ion resulting in the formation of fluorohydroxyapatite. Narasaraju[137] could show that fluorhydroxylapatite is less soluble than calcium hydroxylapatite accounting thereby for the caries-resistance imparted to the dental tissues by fluoridation. Results of recent investigations[138-143] on F^--OH^- exchange could substantiate these findings. The principal conditions favourable for the occurrence of OH^--F^- exchange on hydroxylapatite were shown by Narasaraju et al[144] to be (i) an increase in the concentration of F^- ion, (ii) a decrease in pH of the medium of exchange and (iii) a reduction in the grain size of the sample of calcium hydroxylapatite. The location of F^- ions present in traces in calcium hydroxylapatite and a mechanism to explain the prophylactic action of fluorine in the occurrence of dental caries were suggested by Young et al[145] through NMR

studies. Further the role played by internuclear distance in the formation of hydrogen bonding between OH^- and F^- ions in the apatite lattice was explained by Van-der Lugt et al[146]. NMR studies on F^--OH^- exchange on hydroxylapatite were further carried out by Lundin et al[147] and Knubovets et al[148]. Based on Laser Raman spectral studies, O'Shea[49] et al could show that a halide substitution of OH^- ion on apatite is possible. The physico-chemical changes undergone by amorphous and apatite calcium phosphate, could substantiate the prophylactic action of fluorine in the occurrence of dental caries[149-151].

(f) $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ substitution

The toxic effects[152-154] of arsenic and its soluble salts are attributed to a replacement of PO_4^{3-} by AsO_4^{3-} or calcium hydroxylapatite which is another example of a hetero-ionic substitution[155]. The substitution reaction can be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + xAsO_4^{3-} \rightleftharpoons Ca_{10}(PO_4)_{6-x}(AsO_4)_x(OH)_2 + xPO_4^{3-} \quad \ldots\ldots (1\text{-}16)$$

A Solid solution of phosphorus and arsenic hydroxylapatites.

The existing literature confirms the occurrence of this substitution reaction[155,156] spread over the entire compositional range and can be utilized to throw light on the mechanism of this substitution with a view to arrive at a possibility of removal of incorporated arsenic. In addition it could be shown by Rao[157] that such a substitution is possible on

lead hydroxylapatite.

The arsenate ion is isoelectronic with phosphate facilitating thereby the $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ ion exchange on apatite as well as in a few enzyme catalyzed[146] reactions. Lindgren et al[158,159] could prove from autoradiographic studies conducted on mice and hamsters that PO_4^{3-} can be replaced by AsO_4^{3-}.

(g) Miscellaneous substitutions

While systematic investigations were carried out by different workers on the heteroionic substitutions described above, a few scattered results on certain aspects of some more substitutions are available.

It is an established fact that human bones contain CO_3^{2-} ion although the concept that it exists due to heteroionic substitution on calcium hydroxylapatite is still debatable[160,161] and deserves further investigations[162,163]. A mineral, francolite, $(Ca, Mg, Na, K)_{10}[(P,C)O_4]_6(F,OH)_2$, which is a carbonate-containing fluorapatite, when subjected to x-ray studies[162] indicated the absence of free calcium carbonate and proved the similarity of its X-ray patterns with that of fluorapatite suggesting thereby the presence of CO_3^{2-} ion in the apatite lattice. These findings were substantiated by Le Geros et al[164] and Bonel and Montel[165-167]. Contrary to these findings[168] the solubility of francolite was found to indicate a preferential dissolution of CO_3^{2-} ion which can be attributed to its free existence. As mentioned

above whether CO_3^{2-} ion exists as a separate submicroscopic phase or as a substituent in an apatite lattice is yet to be confirmed.

Radiochemical studies carried out by Knappwost[169] showed that $PO_4^{3-} \rightleftharpoons SiO_4^{4-}$ substitution was possible on calcium hydroxylapatite when it was accompanied by a compensation of the surplus negative charge through introduction of a univalent metal ion like Na^+ into apatite lattice. Further studies on this substitution were carried out by Azimov et al[170,171] and by Gaude et al[172]. Based on the proximity of ionic radii of Na^+ and H_3O^+ (0.95 and 1.00Å respectively) with that of Ca^{2+} ion (0.99Å), evidence for a partial replacement of Ca^{2+} by Na^+ and H_3O^+ could be shown by Neuman[24], the charge compensation being brought about by appropriate depletion of some of the boundary ions. Mayer et al[173] could show that Ca^{2+} - Eu^{2+} exchange is possible on calcium hydroxylapatite. Fluor –, chlor - and hydroxylapatites of europium as well as a few solid solutions of some of these isomorphs were also prepared by them. The possibility of replacement of Ca^{2+} by Mn^{2+} ions, the latter being capable of occupying both Ca(I) and Ca(II) lattice[93] positions, was proved by Gilinskaya and Shicherba Kova[174]. A substantiation of these results was provided by Dubrov et al[175] through EPR studies which were extended to fluoro- and chlorapatites by Vinnikov and Gugel[176]. Oxyapatites of composition, $M_4,Nd_6(SiO_4)_4(EO_4)_2O_2$, where M stands for Ca or Sr and E for P, As or V were synthesised by Federov et al[169], the characterization of the sample

being done by X-ray diffraction studies. Similar investigations were extended by Mayer et al[178] to systems such as $Ln_xM_{(10-2x)}Na_x(PO_4)_6F_2$, where Ln stands for La, Pr, Nd, Sm, Eu, Dy, Er, Lu or Y and M for Ca, Sr, or Ba.

Through Mössbauer studies Khudolozhkin et al[179] could provide evidence for Ca^{2+}-Fe^{2+} substitution on calcium hydroxylapatite over a limited compositional range. Rao[180] could confirm these findings through chemical analyses. Replacement of Ca^{2+} by Ni^{2+} and Cu^{2+} ions on the apatite lattice through equilibration studies of calcium hydroxylapatite with solutions containing these ions was shown by Misra et al[181].

The existence of a new series of compounds having a general formula, $Ba_{10}(ReO_5)_6X_2$, where X stands for Br or I, named as 'New rhenium apatites' was proved by Baud and Besse et al[182,183]. A series of apatites containing S^{2-} and SO_4^{2-} ions was reported by Schiff Francois et al[184]. A sample of strontium oxyapatite could be prepared by Berak et al[185]. Mayer et al[186] could prepare samples of Lead and strontium phosphate apatites substituted by rare earth and silver ions having the formula $M_{10-2x}Ln_xAg_x(PO_4)_6Z_2$ (M=Sr, Pb, Ln=La, Nd, Eu, Z=F, Cl, X=1,2). Calco-europium dioxyapatite and its solid solutions with phospho calcium oxyapatite were prepared by Taitai et al[187].

1.8 Studies on Solubility

1.8.1 Significance

During the recent past phenomena associated with dissolution[24,105,188-192,203] of hydroxylapatite have attracted considerable attention because of their significance in diverse fields. Such studies are of importance to understand the physiology of bones and teeth from the point of view of calcification and resorption. In addition, consideration of the occurrence of dental caries and the prophylactic action of fluorine[19,20] are based on information about the solubility of hydroxylapatite. Such solubility studies have an additional utility in soil chemistry to account for the mechanism of availability of phosphate containing fertilizers to the plant kingdom. The interdisciplinary significance of solubility behaviour of hydroxylapatite explains its ability to demand the attention of physical chemists, bone biologists, dentists, chemical engineers and geologists, to mention only a few. A survey of literature on solubility of hydroxylapatite shows that the results can be classified under (i) Non-stoichiometric and (ii) Stoichiometric dissolutions. The reported investigations, in general, were carried out with either synthetic or natural samples obtained from bones and teeth.

1.8.2 Non-Stoichiometric Dissolution

Extensive studies on solubility of hydroxyl apatite carried out independently by Neuman and co-workers[188] and Rootare et al[190] could provide ample evidence to show that the sample

exhibits a non-stoichiometric dissolution based on a divergence of g atom ratio, Ca/P, of its saturated aqueous solutions from the stoichiometric value of 1.67. The divergence was attributed to the formation of a surface coating on the solute consequent upon its hydrolytic dissolution. While Rootare et al[193-195] could prove this surface coating to be a complex, $Ca_2(HPO_4)(OH)_2$, others could provide evidence that it is one among calcium monohydrogen phosphate, $CaHPO_4$, calcium pyrophosphate, $Ca_2P_2O_7$ and octacalcium phosphate, $(Ca_4H)PO_4)_3$. Simulation of biological conditions and maintainance of a constant ionic environment in the medium of dissolution were achieved by Levinskas and Neuman[188] through use of a 0.165M aqueous solution of sodium chloride as a solvent to study the solubility of hydroxylapatite. It was reported by them that for a given set of experimental conditions the g atom ratio, Ca/p, of the saturated solution was different from that of the solute and that no reproducible values for the solubility product, Ksp, could be obtained. It was therefore supposed that the compound deviated from the established laws of solubility.

The solubility products of a number of commercial and laboratory-made samples of hydroxylapatite were determined by Rootare et al[190]. While observing divergent values of the solubility product of hydroxylapatite, they attributed it to a dependence of solubility on solute to solvent ratio, defined by them as slurry density. Further as shown by Levinskas and Neuman[188], the g atom ratio, Ca/p, of the saturated

solution is not constant at the stoichiometric value of 1.67. These investigators gave a convincing explanation to account for the observed behaviour from the point of view of established physico-chemical principles. Their theoretical considerations were subsequently substantiated by La Mer[191]. Hydroxylapatite being the salt of a weak acid, undergoes hydrolysis in aqueous solutions yielding a solid surface complex, $Ca_2(HPO_4)(OH)_2$, which was found to dominate the solubility equilibria according to the following equations:-

$$Ca_{10}(PO_4)_6(OH)_2+6H_2O = 4Ca_2(HPO_4)(OH)_2+2Ca^{2+}+2HPO_4^{2-} \quad .... \quad (1\text{-}17)$$

$$4Ca_2(HPO_4)(OH)_2 = 8Ca^{2+}+4HPO_4^{2-}+8OH^- \quad .... \quad (1\text{-}18)$$

Thus it is evident that when equation 1.17 predominates the g atom ratio, Ca/p, in the solution is unity while it becomes 2 with the establishment of equation (1.18). When both the equations contribute equally to the solution process this ratio becomes 10/6 as expected for the stoichiometric dissolution. Complications involved in the accurate determination of individual activity coefficients of the ions involved in the system employed were supposed to be responsible for the non-reproducibility of Ksp of hydroxylapatite as reported by Levinskas and Neuman[188] and substantiated by La Mer. La Mer[191] pointed out that consequent upon its biological significance an aqueous 0.165M solution of sodium chloride, which is the solvent employed by Neuman, functions as a standard solvent of reference in which all ion activity co-efficients can be assumed to be unity. The problem of evaluating the individual ion activity co-efficients involved in the

solubility equilibria of hydroxylapatite can thus be avoided. The solubility of hydroxylapatite was shown by La Mer to respond precisely to the principles of solubility product, on the basis of a recalculation of Neuman's data based on the foregoing considerations. These studies were subsequently extended to natural samples of hydroxylapatite[192,193]. The solubility of dental enamel with saliva as a medium of dissolution was investigated by Brudevold et al[193]. According to them calcium monohydrogen phosphate, $CaHPO_4$, functions as a phase controlling the solubility since it gives rise to a constant Ksp in the pH range 4.5-7.5. In solutions buffered to a pH range, 3.5-6.0 the solubility of synthetic hydroxylapatite, dental enamel and a few more allied natural phosphatic minerals were investigated by Francis[192]. The formation of a coating of calcium monohydrogen phosphate, $CaHPO_4$, on the surface of these samples when equilibrated with acid buffers was shown through chemical analysis. Formation of a complex of the products of dissolution of hydroxylapatite in acetate, lactate and phosphate buffers necessitated the application of correction for the evaluation of Ksp of the samples. The deposition of calcium monohydrogen phosphate, $CaHPO_4$, on the surface of hydroxylapatite was shown to be responsible for the change in composition of the solution during dissolution. The role played by parameters such as particle size, solute to solvent ratio, type and concentration of buffers and pH in deciding the composition of hydroxylapatite solution was explained by Francis[192].

The role of a surface coating of calcium pyrophosphate, $Ca_2P_2O_7$, was investigated by Fleisch et al[194] in controlling the solubility of hydroxylapatite. By extending the analogy to the bone processes a mechanism was suggested for the calcification and resorption.

Dissolution kinetic studies of synthetic samples of hydroxylapatites of calcium and strontium were investigated by chickerur et al[195] at 37°C using $1G_4$ sintered glass crucible for separating the colloidal component of the solute from the saturated solutions. A non-stoichiometric dissolution was reported. The process was found to obey first order kinetics which could be explained on the basis of the surface complex theory suggested by Rootare et al[190].

Blitz et al[196] studied the solubility equilibria of hydroxylapatite obtained from animal bones and teeth in order to characterize the phases likely to be formed as a result of the reactions occurring on the surface of the samples and also to study the role of such phases in governing the solubility of the samples. They concluded that octa calcium phosphate, $Ca_4H(PO_4)_3$, formed during dissolution of hydroxylapatite controlled its solubility. Bell et al[39] investigated the solubility product of synthetic hydroxylapatite. While the value was found to be constant within a pH range, 4.6-9.7, ionic strength range 0.0003-1.03 and a solid/solution ratio ranging from 0.06-5.6 g/200 ml, the dissolution was found to be non-stoichiometric. They supported the view of formation of a surface layer on synthetic hydroxylapatite, the composi-

tion of which, however, was not studied by them.

1.8.3 Stoichiometric Dissolution

The credit of proving for the first time that hydroxylapatite obeys the established laws of solubility goes to Clark[189]. He investigated the solubility equilibria of hydroxylapatite over a wide range of experimental conditions, the samples used being obtained by mixing solutions of calcium hydroxide and orthophosphoric acid. He analyzed the saturated solutions obtained from the mother liquor of the precipitate. In addition, the precipitate was subjected to the conventional solubility equilibria to obtain the saturated solutions which were also analyzed. It could be confirmed from both the sets of investigations that hydroxylapatite exhibits stoichiometric dissolution resulting in a definite Ksp at 25°C, the pKsp reported being 115.5. Using precipitated samples of hydroxylapatite, its solubility was investigated by Brandy **et al**[197] taking the solute in the form of a pellet mounted on an electrically operated stirrer fixed in a buffered dissolving medium containing excess of potassium chloride to maintain a constant ionic environment. The activity coefficients of the dissolved species were therefore found to be constant and a stoichiometric dissolution was observed by them. Fassbender **et al**[198,199] could also substantiate the stoichiometric dissolution of hydroxylapatite. It was further shown by them that the observed dissolution rate was controlled by a combination of several consecutive partial reactions

and was dependent on the pH and surface area of the solute and independent of the temperature in the range, 15-35°C. A mathematical theory proposed by Zimmerman[200] on the basis of the data on the solubility of enamel could establish the pH range vulnerable for the onset of dental caries. Based on a study of solubility isotherms of well-characterized samples of synthetic hydroxylapatite over a pH range, 5.0-7.0, Moreno et al[201] could provide evidence for stoichiometric dissolution. The interfacial properties associated with solubility equilibria of hydroxylapatite were investigated by Chander and Fuerstenan[202] through application of thermodynamics. They further studied the role played by electrical double layer properties in the solubility of apatites.

Wier et al[203] investigated extensively the solubility behaviour of hydroxylapatite. Commercial samples were used as solutes after subjecting them to a detailed procedure of purification consisting of either refluxing for 24 hours in contact with water or by auto-claving in presence of ~ 1N ammonium chloride solution for 50 days at 120°C under a pressure of 1.06 kg/cm^2, the wash-liquid being periodically replaced. Systematic characterization of the samples was done through X-ray, petrographic and chemical analyses. The samples were equilibrated in media at pH values ranging from 4.3-6.7 and choosing 0.1, 0.5, 1.0 and 10.0 g of the solute per 100 ml of the solvent. The colloidal component of the solute present was removed by using specially prepared cells made of plexiglass and fitted with cellulose acetate dialyzing membranes.

Based on the results of chemical analyses of the saturated solutions and calculating the activities of the ionic species present, they could convincingly establish a stoichiometric dissolution of hydroxylapatite, the observed average pKsp being 116.5. Divergence observed in the results of solubility of hydroxylapatite was attributed by them[193] to the presence of trace impurities which get eliminated on rigorous purification. The dissolution kinetics and solubility studies of hydroxylapatite and chlorapatite and a series of their solid solutions spread over the entire compositional range were undertaken by Narasaraju and Rao[204] in buffered media extending over a pH range of 4.9-7.5 which could convincingly establish the occurrence of stoichiometric dissolution. The pKsp values determined by them at 37°C were found to be 110.6 and 115.4 respectively for hydroxylapatite and chlorapatite. Valyashko et al[205] investigated the influence of temperature on solubility of apatites and found that it decreased with an increase in temperature exhibiting, what is known as retrograde solubility.

1.8.4 Some Additional Aspects of Solubility

A systematic survey of the existing literature on the solubility of apatites indicates that a major part of the results can be put under the above mentioned categories of non-stoichiometric and stoichiometric dissolutions. Over and above these aspects, a few significant scattered results are available which merit a mention in the present context.

Benedict and Kanthak[206] found that the pH dependence of solubility of dental enamel was similar to that of tricalcium phosphate establishing thereby compositional similarities between the two. Similar studies on dental enamel coupled with those on synthetic hydroxylapatite were carried out by Ericsson and coworkers[207,208] and the optimum pH range for solubility of hydroxylapatite was calculated by them. The increased solubility of the sample in the presence of CO_3^{2-} ions, serum and saliva was attributed to the formation of complexes involving Ca^{2+} ions. Further light on the solubility of such complexes was thrown by Davies and Hoyle[209]. Studies on the pH dependence of the solubility of hydroxylapatites of strontium and calcium and a series of their solid solutions distributed over the entire compositional range carried out by Narasaraju **et al**[108] established an increased solubility with a decrease in pH. The salting-in effect of SO_4^{2-} ions on the solubility of synthetic hydroxylapatite at a series of pH values was established by Paunio and Makinen[210]. Studies on the kinetics of release of PO_4^{3-}, HPO_4^{2-} and CO_3^{2-} ions from powdered samples of normal human tooth enamel region were carried out by Vogel **et al**[211]. In addition, the influence of F^- ions on this dissolution in the acidic region was investigated by them. The solubility of hydroxylapatite, fluorapatite and a few of their solid solutions was investigated by Narasaraju[137] in the pH range, 5.3-8.2. The solubilities calculated exclusively from the experimentally determined phosphate contents of the saturated

solutions were found to decrease with an increase in pH as well as with an increase in fluoride content of the samples. The significance of these results in the context of prophylactic action of fluorine in the occurrence of dental caries was emphasised. Proof for anisotropic dissolution of a single crystal of hydroxylapatite was exclusively established by Jongebloed **et al**[212] using citric and lactic acids as dissolving media. The dissolution parallel to c-axis was found to be much faster than that perpendicular to it. Scanning electronmicroscopic patterns of the solute after attainment of saturation would show that the single crystal was twisted along c-axis confirming thereby the existence of a screw dislocation parallel to it. Daculsi **et al**[213] used high resolution transition electronmicroscopy to study the acid dissolutions of biological and synthetic apatite crystals and their dependence on the lattice pattern. According to them the dissolution starts at the regions of dislocation and progresses preferentially across the 'c' axis.

1.8.5 Divergent Solubility Data

Literature on the solubility of hydroxylapatite is characterized by divergence and mutual contradictions of the conclusions as indicated in the foregoing account. When a critical assessment of the results is made, it is possible to throw light on the factors responsible for such disparities The observed divergence could be attributed to the fact that the earlier investigators ignored one or more of the factors

mentioned below:-

(i) An attempt to clarify the reported divergence in the g atom ratio, Ca/P, of calcium hydrogen phosphate solutions was made by Smith **et al**[214] by dissolving a synthetic sample in hydrochloric acid at a pH of 4.5. The g atom ratio, was found to be higher than the stoichiometric value when 500 g of the solute were equilibrated in 1 litre of the dissolving medium. A resuspension of the solute under identical conditions exhibited stoichiometric dissolutions. Similar results could be observed in the case of systems having lower solute/solvent ratios. It could be established that the non-stoichiometric dissolution could be attributed to the higher proportion of surface impurities dissolved along with the solute when the slurry density was low the errors caused by surface impurities were less than the experimental errors associated with the microanalytical determinations of calcium and phosphorus and were not therefore perceptible.

(ii) The low solubility and its minute particle size enable hydroxylapatite to exist partially as a colloidal component in its aqueous solutions. This component is to be separated before the solution is analyzed for the determination of solubility[195].

(iii) Proof for the attainment of saturation by solutions of hydroxylapatite can be achieved only by getting identical values for the solubility determined both from sides of undersaturation and supersaturation[190]. Absence of such a proof

leads to uncertainties in the values of solubility reported.

(iv) The possibility for existence of more than one solid phase[215] functioning as solute in systems used for the determination of solubility of hydroxylapatite is evident from $CaO-P_2O_5-H_2O$ phase diagram and demands adequate precautions in determining the phase controlling the pKsp calculated.

(v) Impurities caused by contamination[45,216] through adsorption of foreign ions facilitated by high surface areas of the samples contribute towards vitiating the solubility data.

(vi) Inaccuracies in the measurement of pH of the dissolving medium cause aberrations in the computed solubility data since the pH exerts a sensitive control over the solubility of apatities[189,191].

(vii) Ingredients of the buffer combinations adopted for the solubility determination of hydroxylapatite exhibit a tendency to form soluble complexes[209] with calcium affecting thereby the measured solubility.

(viii) Hydroxylapatite, being the salt of a weak acid undergoes hydrolysis in aqueous media resulting in the precipitation of insoluble phases and causing thereby errors[190,191] in solubility determination.

(ix) Microdeterminations of Ca^{2+}, PO_4^{3-} and other ions when present together as in apatite solutions involve errors which get magnified in the computation of values of Ksp of apatites

because of the high power to which the concentrations are to be raised.

Savage[22] investigated the solubiity of calcium phosphates by choosing a three component system of calcium hydroxide, water and phosphoric acid. The relative solubilities of different calcium phosphates of biological importance could thus be compared. He found that the solubilities increased in the order hydroxylapatite, β-tricalcium phosphate, octacalcium phosphate, dibasic calcium phosphate dihydrate and monobasic calcium phosphate. While hydroxylapatite is shown by him to be the most stable phase in media with pH values above 4.3, below this point dicalcium phosphate dihydrate becomes more stable than hydroxylapatite. He further suggested that at a pH of 4.3 hydroxylapatite undergoes a conversion to dicalcium phosphate dihydrate, the pH of the medium remaining constant till the conversion was complete. It was further suggested by him that the solubility of hydroxylapatite is stoichiometric.

1.9 Calcification

The physiology of human bone is goverened by the phenomenon of calcification[217,218] which involves an orderly precipitation of hydroxylapatite within the organic matrix of bone. In the light of the fact that a knowledge of the solubility equilibria of hydroxylapatite plays an important role in understanding the mechanism of calcification, it has been considered appropriate to mention a few aspects of it in the present context.

The results of **in vivo** and **in vitro** investigations on the solubility of hydroxylapatite facilitated the understanding of the mechanism of calcification[1]. It has been established that the process occurs only at certain regions of the body known as sites of calcification. An essential prerequisite for the process to occur is the transport of the assimilated calcium and phosphorus to these sites which is brought about by the body fluids. For the promotion of calcification, optimum environmental conditions should be prevalent at these sites. The mechanism of establishment of these conditions was suggested by Robison's scheme[1]. It involves a local increase in phosphate concentration brought about at the sites of calcification when a substrate of phosphate ester is hydrolysed by an enzyme known as phosphatase resulting thereby in the deposition of hydroxylapatite. Studies on the solubility phenomena of hydroxylapatite could show that blood serum is supersaturated with respect to it and its spontaneous precipitation is therefore expected. Since such a precipitation is found to take place only at the sites of calcification due to local action as mentioned by Robison's scheme, it is supposed that the prevention of calcification in the non-calcifying regions is due to a possible chemical binding of calcium and/or phosphate. The theories suggested to explain the ability of only certain regions of the body to function as sites of calcification are controversial.

It could be shown[219] that about one-third of the calcium of blood is bound to protein fraction through chelation while the rest of it exists in the ionised form or as soluble

complexes involving ions such as citrate and phosphate[208]. The phosphorus of blood serum exists principally as HPO_4^{2-} ions and to some extent as $H_2PO_4^-$ and PO_4^{3-} ions. The composition of blood serum suggests that it is complicated to apply the principles of solubility product to account for the deposition of hydroxylapatite. The calcium and phosphate concentrations of blood serum are higher than those corresponding to the solubility product of hydroxylapatite and approximate to those of saturated solutions of dicalcium phosphate. It was therefore supposed by Neuman[188] that precipitation of dicalcium phosphate takes place initially. Hydroxylapatite which is the stablest among the calcium phosphates, is likely to be formed due to a subsequent hydrolysis.

Samachson[217,218] could provide a clear insight into the basic requirements of calcification. While he agrees with earlier theories as far as the role of HPO_4^{2-} ion as a prerequisite for calcification is concerned, he considers the removal of H^+ ion as a factor essential for the process as indicated by the following equation:-

$$10Ca^{2+}+6HPO_4^{2-}+2H_2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2+8H^+ \quad (1.19)$$

It is evident from the equation that the deposition of hydroxylapatite is facilitated when there is the presence of a proton acceptor and a local increase in pH at the sites of calcification. The foregoing account shows that a plausible mechanism of calcification is possible only with the availability of a more comprehensible interpretation of the factors controlling the solubility of hydroxylapatite.

1.10 Calcium-Deficient Apatites

It has been an established fact that synthetic calcium phosphates prepared by wet methods have x-ray diffraction patterns similar to hydroxylapatite. On the other hand a deviation in stoichiometry was found as indicated by fluctuations in g atom ratio, Ca/P, ranging from 1.33 to 1.67. Such compounds are defined as calcium deficient apatites. These non-stoichiometric apatites are of biological importance since the g atom ratio, Ca/P, of bone is lower than the stoichiometric value of hydroxylapatite. They have an additional significance since they are found to act as catalysts[220-223] in several organo-chemical reactions such as dehydration and dehydrogenation of primary alcohols, leading to the formation of aldehydes and ketones, the catalytic activity of hydroxylapatite being proportional[221] to the calcium deficiency of the sample. Halogen-deficient cadmium haloapatites with the structure, $Cd_5(MO_4)_3X$, where X stands for Cl, Br or I, were studied by Wilson **et al**[224]. Many theories[227], the salient aspects of which have been presented here were proposed to explain the structure and composition of these compounds. Cameron[225], Hodge[226], Schleede[27] and Trömel **et al**[227] have advanced independently a theory based on the adsorption of HPO_4^{2-} ions to account for the non-stoichiometry of apatites. This theory was rejected by Posner[228,229] on the basis that, the non-stoichiometry was not exclusively due to surface adsorption since the measured surface areas of the samples were too low to account for the expected uptake by HPO_4^{2-} ions. The calcium deficiency was instead accounted for by

Posner on the basis of a statistical model depicting the absence of Ca^{2+} ions from the columnar positions of the apatite lattice, the charge balance being maintained by the introduction of two protons. Winand et al[230,231] could explain the maintenance of charge balance through a compensation of the two positive charges of each missing Ca^{2+} ion by addition of a proton and removal of a structural OH^- ion. Additional theories[232-234] on non-stoichiometric apatites were advanced among others by Bett and Christner[225], Brown et al[235], Berry[236], Young[237] and Feenstra and De Bruyn[238].

1.11 Recent Trends in Apatite Research

The trend of recent investigations[239-245] in the field of apatites establishes convincingly their interdisciplinary significance. In a brief review like the present one, only a few significant aspects other than these given earlier merit a mention.

Apatites find an increasing application as catalysts[239] in synthesis of organic compounds such as sugars and their phosphoric esters, in addition to a few dehydration and dehydrogenation reactions mentioned earlier. In addition they function as luminophosphors[240-245] and as starting materials for several phosphatic fertilizers[246,247]. The observation that kidney and prostrate stones[248-251] contain hydroxylapatite further enhances the biological and physico-chemical significance of these compound since its solubility behaviour can throw light on their possible elimination by dissolution.

A knowledge of solubility of hydroxylapatite can play a role in preventing a few occupational diseases caused by inhalation[252] of dust containing toxic ions. Another significant role of apatites in biology is the utility of apatite coated ceramics as dental prosthesis[253] and artificial bons[254-257].

While the use of hydroxylapatite as a column in chromatographic separation[258] was well known, recent trends have been in the direction of its use in significant separations such as those of protein mixtures.

Though extensive[1,24,31,32,188-193] work was carried out during the recent past on various aspects of apatites in different disciplines, a researcher in the field suffers from the absence of an up-to-date review containing a consolidated and systematic account of all these aspects. The present review has been an attempt to compensate for this lacuna with a judicious emphasis on all the essential aspects of hydroxylapatite.

SECTION II

PHOSPHATE AND ARSENATE APATITES OF STRONTIUM AND THEIR SOLID SOLUTIONS — PREPARATION AND CHARACTERIZATION

2.1 Introduction

Among heteroionic cationic substitutions on calcium phosphate apatite(CPA) replacement of Ca^{2+} by Sr^{2+} is significant since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90 produced in atomic explosions. Such an incorporation, even in trace amounts, can be fatal because of the long half-life period of Sr-90 (28.5 years)[259]. Papworth and Vennart[118] showed that the uptake of Sr-90 in the human skeletal system causes radiation damage in the bone marrow leading to incidence of leukemia.

According to Collin[106] the criterion facilitating the incorporation of strontium in the human skeletal system is the formation of solid solutions of hydroxylapatites of calcium and strontium, the factors contributing to such a formation being the isomorphism existing between them and the closeness of the ionic radii of calcium and strontium (0.99 and 1.13Å respectively).

The toxicity of elemental arsenic[152] and its salts[153] is well known. There is prevalence of arsenic poisoning among workers employed in the manufacture of insecticides, paints and dyes containing the element. Inhalation of arsenic through nose and mouth and exposure of the skin to it are supposed to be responsible for the ailment. It is considered to be an occupational disease and is characterized by severe burning of mouth and throat, gastroenteric pains, vomitting, diarrhoea,

haemorrhage and haematuria leading to dehydration, jaundice and paralysis resulting in collapse.

In spite of the fact that arsenic is distributed primarily throughout the soft tissues in living organisms its incorporation in the human skeletal system through $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ exchange on CPA of bone is probable. Consequent upon the fact that tetrahedral AsO_4^{3-} and its isostructural PO_4^{3-} have covalent radii (1.18 and 1.10 Å respectively) close to one another, the latter present in SPA being amenable for isomorphous replacement by the former leading to strontium arsenate apatite(SAA). While extensive work has been done on SPA[260], studies on its solid solution with SAA as well as on SAA itself have not been undertaken, the latter being a compound containing a potentially toxic element such as arsenic. Investigations on such solid solutions are being considered to be extremely significant from the point of view of toxicity to human skeletal system and hence the present work was undertaken.

These investigations deal with preparation of samples of SPA, SAA and a series of their solid solutions spread over the entire compositional range through a method suggested by Collin[52], the samples so prepared being characterized through chemical, x-ray, electron-microscopic, i.r. and laser Raman analyses. The method adopted is the first of its kind for preparation of SAA in appreciable quantities by precipitation.

2.2 Experimental

The experimental work included in this section has been subdivided into (i) Preparation and (ii) Characterization by (a) chemical analyses (b) determination of lattice constants (c) electronmicroscopic investigations and (d) i.r. and Laser-Raman studies.

2.2.1 Preparation of the Samples

The preparation of the samples of SPA, SAA and six of their solid solutions spread over the entire compositional range was based on the following equation

$$10Sr^{2+} + 6XO_4^{3-} + 20H^- \longrightarrow Sr_{10}(XO_4)_6(OH)_2$$

where X = P or As for the end-members and (P+As) for the solid solutions, the proportion of P to As being varied as described. The samples were precipitated at 37°C by mixing stoichiometric quantities of the reactants in the form of their aqueous solutions maintained at a pH of $\sim$ 12. The precipitation was done in an atmosphere freed from carbon dioxide and the chemicals used were of A.R (BDH), G.R (E. Merck) and L.R (BDH) grade. All the solutions were prepared in water freed from carbon dioxide. Based on the above equation, calculated amounts of strontium nitrate, diammonium hydrogen phosphate and disodium hydrogen arsenate were taken such that the yield was about 30 g of the sample. Ethylenediamine was used instead of ammonia since relatively smaller volumes of it were required to maintain the reacting solutions at the desired pH. In addition the unpleasant smell of ammonia could be avoided.

The desired solutions were prepared as described below:-

Solution A

Approximately 0.5M strontium nitrate:-

This was prepared by dissolving about 106 g of strontium nitrate, $Sr(NO_3)_2$, in water and making up the volume to 1 litre, its strontium content being determined complexometrically[261]. A desired volume of this solution was added dropwise under constant stirring to an appropriate volume of ethylenediamine, determined previously by a trial experiment, such that the solution maintained a pH of~12 on making up to 1000 ml. This was taken in a 3 necked round-bottomed flask of 3 litre capacity.

Solution B

Approximately 0.5M solution of diammonium hydrogen phosphate:-

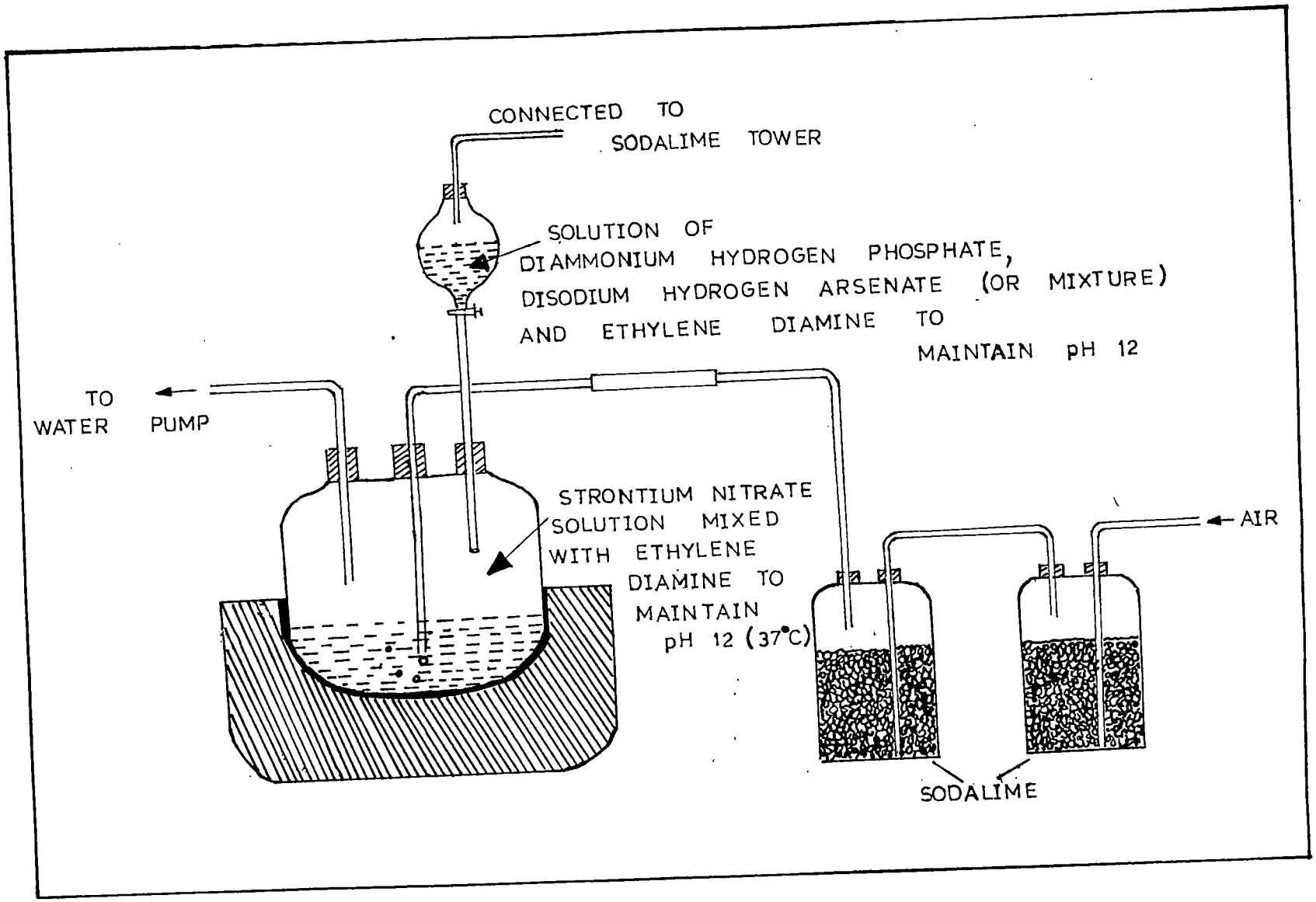
This was prepared by dissolving approximately 70 g of diammonium hydrogen phosphate in water and making up the volume to 1 litre, its phosphorus content being determined by Washburn and Shear's[78] method.

Solution C

Approximately 0.5M solution of disodium arsenate:-

This was prepared by dissolving approximately 156 g of disodium hydrogen arsenate in 250 ml of~ 2 N sodium hydroxide and making up the volume to 1 litre, the arsenate content of the solution being determined iodometrically[262].

Fig 2.1 Assembly of the apparatus used for the preparation of strontium phosphatate apatite, strontium arsenete apatite and their solid solutions.


CONNECTED TO
SODALIME TOWER
SOLUTION OF
DIAMMONIUM HYDROGEN PHOSPHATE,
DISODIUM HYDROGEN ARSENATE (OR MIXTURE)
AND ETHYLENE DIAMINE TO
MAINTAIN pH 12
TO
WATER PUMP
STRONTIUM NITRATE
SOLUTION MIXED
WITH ETHYLENE
DIAMINE TO
MAINTAIN
pH 12 (37°C)
AIR
SODALIME

An appropriate volume of solution 'B' or 'C' or a mixture of them which was in a stoichiometric proportion to that of solution 'A' was treated with a pre-determined volume of ethylenediamine such that it maintained a pH of 12 on making up to 1 litre and was taken in a dropping funnel. The funnel was closed by a hollow groundglass stopper, connected to soda-lime towers and fitted into a quick-fit socket of a 3-necked flask of 3 litre capacity containing solution A maintained at 37°C. While the solution from the dropping funnel was drained drop by drop, CO_2 - free air obtained by use of soda-lime towers and water suction pump was bubbled through the solution 'A' to eliminate the formation of carbonate-apatite and to keep it, in addition, well stirred. The precipitate was refluxed for about 3 hours in contact with the mother liquor, left overnight, filtered through a $1G_4$ sintered glass crucible, washed till washings were neutral and air-dried. A part of it was heated to ~300°C for ~6 hours, for purposes of x-ray diffraction studies. A schematic representation of the assembly of the apparatus used for the preparation of the sample was given in Fig 2.1

2.2.2 Chemical Analyses

The chemical analyses of SPA is complicated by the mutual interference of strontium and phosphate ions and consequently special analytical techniques are desired for the purpose. In presence of arsenate ions these complications become more pronounced as in the case of solid solutions of SPA and SAA. Although instrumental methods of analysis

such as spectrophotometry, x-ray fluorescence and flame photometry have frequently been used for such determinations, they have a limited range of applicability. Special procedures are worked out for the determination of strontium in the presence of (i) phosphate (ii) arsenate and (iii) in the presence of phosphate and arsenate. The accuracies of the procedures adopted were assessed by analysing sample solutions containing known quantities of the respective ions. The solutions used for these determinations were prepared in double-distilled water and preserved in polythene containers.

The following solutions were prepared for the purpose:-

(a) Strontium nitrate solution containing 1 mg of Sr per ml It was prepared by dissolving 2.4153 g of strontium nitrate, $Sr(NO_3)_2$, previously heated to constant weight, in distilled water and making up to 1 litre. The Sr^{2+} content of the solution was determined complexometrically[261] using Eriochrome Black T as indicator at a pH of $\sim$10 obtained by ammonium chloride-ammonium hydroxide buffer.

(b) Potassium dihydrogen phosphate solution containing 1mg of P per ml.

4.3930 g of KH_2PO_4 heated previously to constant weight at 110°C were dissolved and made up to 1 litre.

(c) Disodium hydrogen arsenate solution containing 1mg of As/ml

4.1630 g of $Na_2HAsO_4.7H_2O$, dried previously to constant weight, were dissolved in distilled water and made up to 1 litre.

(d) Standard 0.1M EDTA solution.

The disodium salt of EDTA (ethylene diaminetetra acetic acid) was dried for about 12 hours at 80°C and cooled in a desiccated atmosphere so that the compound attained the composition of its dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$. 1 litre of 0.01 M EDTA solution contained 3.7224 g of this dried substance.

(e) 0.01M Magnesium chloride solution.

A solution of magnesium chloride, $MgCl_2.6H_2O$, of an approximate molarity slightly higher than 0.01M was prepared by taking about 3.0 g of the salt in a litre of the solution. This was subsequently standardised by titrating at a pH of ~ 10 against 0.01M EDTA solution using Eriochrome Black T as an indicator.

(g) Buffer solution of pH ~10

About 70 g of ammonium chloride were mixed with about 570 ml of liquor ammonia (sp.gr, 0.9) and the volume was made upto a litre.

(g) Indicator solution

About 0.2g of Eriochrome Black T, the sodium salt

of 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4 sulfonic acid was dissolved in a mixture of about 15 ml of triethanolamine and about 5 ml of absolute alcohol. Such a solution could be used for about 1 month.

2.2.2.1 Estimation of Sr^{2+} and PO_4^{3-} when present together

A convenient volume of the stock solution of strontium was mixed with a known excess of EDTA to prevent its precipitation on subsequent addition of phosphate. To this solution were added a known volume of stock solution of phosphorus, 2ml of a buffer of pH~10 and 2 drops of indicator solution. The resulting solution was titrated against $MgCl_2$ solution standardised previously by titrating against standard EDTA solution. The end-point is the change of the color from blue to wine red. From the above solution $MgNH_4PO_4.6H_2O$[78] was precipitated by treating with excess of 0.5M magnesium chloride solution followed by the addition of~9M ammonium hydroxide, the presence of excess of Mg^{2+} being confirmed by the absence of further precipitation from the supernatant liquid on addition of the precipitant. It was left overnight in contact with the mother liquor, filtered through a $1G_4$ sintered glass crucible, washed successively with 0.4M ammonium hydroxide, acid-free alcohol and ether till freed from the accompanying ions and then dried overnight at 37°C to constant weight and weighed as $MgNH_4PO_4.6H_2O$. The precipitate was dissolved in~2N HCl, quantitatively made up to a known convenient volume and the Mg content determined complexometrically.

2.2.2.2 Estimation of Sr^{2+} and AsO_4^{3-} when present together

A convenient volume of the stock solution of strontium was mixed with a known excess of EDTA to prevent its precipitation on subsequent addition of AsO_4^{3-} ions. A known volume of stock solution of arsenate was then added to this solution. While strontium was estimated complexometrically, arsenate taken as another aliquot was estimated iodometrically[262].

2.2.2.3 Estimation of Sr^{2+}, PO_4^{3-} and AsO_4^{3-} when present together

Sr^{2+} was determined complexometrically in the presence of PO_4^{3-} and AsO_4^{3-} as described above. The reagents employed for the precipitation of phosphate and arsenate as their respective magnesium ammonium salts for the purposes of quantitative estimation happen to be the same. A method was therefore used to get the combined phosphate and arsenate content of the mixture of these ions by precipitating them quantitatively as a mixture of their magnesium ammonium salts, using a procedure, the details of which were given above. The precipitate was dissolved quantitatively in $\sim$2N HCl, made up to a known volume and Mg^{2+} estimated complexometrically. From this value the total (P+As) content was determined. From another aliquot the arsenate content was determined iodometrically as described earlier. From the above values the phosphate content was determined by subtracting the estimated arsenate content from the total amount of arsenate and phosphate determined by the combined estimate. The above methods were applied for the chemical analyses of SPA, SAA and their

solid solutions, 0.5g of each sample being dissolved in a minimum quantity of ~2N hydrochloric acid and made up to 500ml.

2.2.3 Determination of Unit-Cell Volumes

The criteria for a given pair of substances to form solid solutions are that the two are isomorphous and that the ionic radius of each ion of one is comparable with that of its counterpart in the other. It is evident that SPA and SAA fulfil these requirements. Since the replacement of PO_4^{3-} by AsO_4^{3-} (covalent radii 1.10 and 1.18Å respectively) in an apatite lattice brings about a dilation of the unit cell, a proof for the formation and homogeneity of the resulting solid solutions can be provided by the determination of the lattice constants and the accompanying calculation of the unit cell volumes. The Debye-Scherrer powder method was found to be suitable for the purpose, since the samples are microcrystalline in nature being precipitated from aqueous media. The samples to be subjected to these investigations were previously heated for ~6h at 300°C in order to increase the size of the crystals[52] so that the sharpness of the diffraction lines could be enhanced. The patterns were recorded as paper-traces with a rotating-sample exposed to Cu-K_α radiation, the voltage, current strength and exposure time being 40KV, 25mA and 5h respectively.

2.2.4 Electromicroscopic Investigations

The conclusions drawn from x-ray diffraction patterns

confirming the homogeneity of the samples could be supplemented by their electromicrographs which, in addition, could scrutinize the absence of extraneous phases and provide visual information about the geometry and dimensions of the individual crystals of the samples. Air-dried samples were found to be better suited for the purpose than those heated to 300°C, since the latter operation was found to be leading to fusion of the individual crystals into large crystalline masses[263], preventing thereby the measurement of the dimensions of individual crystals.

A pinch of the sample was dispersed in a few ml of water and the suspension was subjected for a few minutes to ultrasonic radiation at a frequency of a few hundred kilocycles per sec. in order to breakdown the conglomeration of the individual crystals. A drop of the resulting slurry was taken on a copper grid, placed in the vacuum chamber of an electron microscope (Siemens Elmiskop 1, No. 591) with carbon as back-ground and the specimen was exposed to the electron beam after evacuation, the resulting image being viewed on a small fluoroscopic screen. When the field of vision consisted of well-defined individual crystals, it was photographed. From each electron micrograph a few individual crystals, preferably of varying dimensions, were focussed at random under a calibrated eye-piece and through measurement of the length and breadth of these crystals their average dimensions were calculated. An attempt was made to calculate the specific surface areas of a few representative

samples among those prepared using measured length and breadth. The crystals of the samples which are in the form of elongated hexagonal prisms could be considered as cylinders[137] for purposes of evaluation of their approximate specific surface areas using the expression, $\frac{2\pi r^2 + 2\pi rh}{\pi r^2 h\rho}$, where r=0.5 times the average breadth, h=average length, and ρ=density of the samples. It is evident that the rates of dissolution[137] of the samples which decide the period of equilibration required for the attainment of saturation are dependent on their surface areas. In addition, the utility of apatites as luminescent phosphors and ion exchangers[144] is controlled by their surface areas, the measurement of which is therefore justified

2.2.5 Infrared Spectra

Infrared spectra of the samples at room-temperatures were recorded on the Perkin-Elmer model 983 spectrophotometer. The spectra were recorded within the frequency range, 4000cm^{-1} to 180cm^{-1} as nujol mulls as well as by using KBr pellets.

2.2.6 Laser-Raman Spectra

It is evident that Raman Spectroscopy is basically emission spectroscopy. Consequently the instrumental technique involves the use of a typical visible-region spectrometer. It is the source of excitation used that distinguishes the experimental work of Raman spectroscopy. Needless to

say, Raman technique underwent a revolution with the displacement of the traditional mercury vapour lamp by an appropriate easily accessible and relatively inexpensive laser as source of excitation. With the advent of laser as the source of excitation the range of samples which can be studied by the technique increased enormously encompassing virtually all types. In addition, the technique could be applied with smaller volumes of samples and with a curtailed duration of exposure. The narrow highly monochromatic beam of radiation available with lasers can be focussed on to a small sample enabling the laser to be an ideal Raman source. The following are the lacunae associated with the traditional Raman spectroscopy involving mercury discharge lamp as the source of excitation.

(i) A substantial part of radiation is scattered directly into the spectrophotometer masking the Raman lines,

(ii) Considerable quantities of samples are to be used to fill up sample tubes 20-30 cm long and 1-2cm in diameter,

(iii) There is incidence of fluoroscence of the sample under the high frequency mercury radiation causing a masking of the weak Raman spectrum by the resulting fluorescence spectrum of the sample.

These disadvantages can be eliminated by using a laser as a source of excitation. The possibility of multiple passes of the radiation through the sample achieved by the use of a laser beam coupled with a careful alignment of a system of mirrors results in enhancing the Raman signal considerably facilitates a better recording of the spectrum.

Laser Raman(LR) spectra were recorded on a SPEX Ramalog Model 1403 Raman Spectrometer. The Laser line of wavelength 4880Å produced by an Argon ion Laser Model 165-09, was used as the source of excitation. The scattered light was detected with the help of a cooled RCA 31034 photomultiplier tube, accompanied by a photon-count processing system. The sample was in the form of a pressed pellet. The recording was done at ambient temperature.

2.3 RESULTS

Table 2.1 A quantitative separation of strontium and phosphorus - Assessment of attainable accuracy

S. No.	Strontium wt.(mg)		Error. (wt. per cent)	Phosphorus wt.(mg)		Error (wt. per cent)
	Theo.	Exptl.		Theo.	Exptl.	
1	2	3	4	5	6	7
1.	4.95	4.99	+0.8	5.00	5.05	+1.0
2.	9.89	9.97	+0.8	10.00	10.17	+1.7
3.	15.00	14.93	-0.5	15.00	14.98	-0.1
4.	20.00	20.09	+0.5	20.00	19.89	-0.6
5.	25.00	24.98	-0.1	30.00	29.92	-0.3
6.	30.00	29.95	-0.2	40.00	40.09	+0.2

Table 2.2 A quantitative separation of strontium and arsenic - Assessment of attainable accuracy

S. No.	Strontium wt.(mg)		Error (wt. per cent.)	Arsenic wt.(mg)		Error (wt. per cent.)
	Theo.	Exptl.		Theo.	Exptl.	
1	2	3	4	5	6	7
1.	4.95	4.95	0.0	5.00	4.95	-1.0
2.	9.89	9.88	-0.1	10.00	10.07	+0.7
3.	14.82	14.80	-0.6	15.00	14.98	-0.1
4.	19.78	19.67	-0.6	20.00	20.05	+0.3
5.	24.70	24.75	+0.2	25.00	24.91	-0.4

Table 2.3 A quantitative separation of phosphorus, arsenic and strontium __ Assessment of attainable accuracy

S. No	Strontium wt.(mg)			Phosphorus wt.(mg)			Arsenic wt.(mg)		
	Theo	Exptl.	Error (wt. per cent.)	Theo.	Exptl.	Error (wt. per cent.)	Theo.	Exptl.	Error (wt. per cent.)
1	2	3	4	5	6	7	8	9	10
1.	4.95	4.95	0.00	10.00	9.83	-1.7	5.00	5.05	+1.0
2.	9.89	9.97	-0.8	10.00	9.86	-1.4	10.00	10.10	+1.0
3.	19.78	19.67	-0.6	15.00	14.91	-0.6	15.00	14.95	-1.0
4.	19.78	19.70	-0.2	20.00	20.15	+0.8	20.00	19.83	-0.9

Table 2.4 Determination of g atom ratio, Sr/(P+As), of phosphate and arsenate apatites of strontium and their solid solutions.

S. No	Sample	(Wt. %) Sr	P	As	Calculated Molecular formula*	g atom ratio, Sr/(P+As)
1	2	3	4	5	6	7
1.	Strontium phosphate apatite (SPA)	58.96	12.38	-	$Sr_{10}(PO_4)_6(OH)_2$	1.68
2.	Solid Solution I	58.13	11.09	3.14	$Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$	1.66
3.	Solid Solution II	56.47	8.83	8.11	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$	1.64
4.	Solid Solution III	56.44	8.44	8.54	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$	1.67
5.	Solid Solution IV	54.05	5.10	15.69	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$	1.65
6.	Solid Solution V	53.55	4.37	16.58	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$	1.69
7.	Solid Solution VI	51.59	1.85	21.97	$Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$	1.66
8.	Strontium arsenate apatite	50.26	-	25.77	$Sr_{10}(AsO_4)_6(OH)_2$	1.67

*g atom ratio, P/As, in a given weight of a sample gives the ratio in which a total of 6 g atoms of these elements is distributed among the two in a mole of the sample. The OH content is assumed to be stoichiometric. Based on these considerations the calculations of the molecular formulae of the samples are made.

Table 2.5 Lattice constants, unit cell volumes, densities and molar volumes of phosphate and aresenate apatites of strontium and six of their solid solutions.

Sample No	Molecular Formula	Molecular Weight, M	Lattice constants (Å)			
			a		c	
			Direct	Refined	Direct	Refined
1	2	3	4	5	6	7
1	$Sr_{10}(PO_4)_6(OH)_2$	1480	9.757	9.742	7.256	7.244
2	$Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$	1506	9.783	9.811	7.239	7.279
3	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$	1550	9.923	9.926	7.361	7.337
4	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$	1559	9.963	9.949	7.350	7.349
5	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$	1629	10.230	10.132	7.520	7.442
6	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$	1643	10.072	10.166	7.375	7.460
7	$Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$	1700	10.321	10.315	7.530	7.535
8	$Sr_{10}(AsO_4)_6(OH)_2$	1744	10.430	10.429	7.600	7.593

Table 2.5 (contd)

Sample No	Unit cell volume, Vuc, $\frac{\sqrt{3}}{2} a^2 c$ [(Å)^3]		Density, d (g/ml)	Molar volume, Vm(ml/mole)	
	Direct	Refined		M/d	Vuc. N
1	8	9	10	11	12
1	598.22	595.39	4.10	361	359
2	600.00	606.77	4.05	371	365
3	627.46	626.03	4.06	381	377
4	631.83	629.96	4.08	382	379
5	681.55	661.62	4.00	407	398
6	647.92	667.68	3.91	420	402
7	694.65	694.30	3.79	448	418
8	716.00	715.20	3.78	461	430

Table 2.6 Electronmicroscopic studies on Phosphate and Arsenate apatites of strontium — Measurement of average dimensions of individual crystals and determination of their specific surface areas

S.No	Molecular Formula	Density (g/ml)	Average dimensions of individual crystals Å		Approximate Specific surface area (m^2/g)
			Length	Breadth	
1	2	3	4	5	6
1.	$Sr_{10}(PO_4)_6(OH)_2$	4.10	1273	313	35
2.	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$	4.06	1340	340	32
3.	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$	4.08	1440	513	21
4.	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$	4.0	2493	580	18
5.	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$	3.91	3156	648	17
6.	$Sr_{10}(AsO_4)_6(OH)_2$	3.78	13454	783	13

Table 2.7 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_6(OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1075(ss), 1030(ss), 948(m), 592(s), 560(s), 456(sh)	—	3578(ww), 544(ww)
LR spectroscopy	1075(m), 1050(m), 1030(m) 948(ss), 578(m), 592(m), 604(ww), 443(m), 422(m)	—	3594(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.8 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1072(ss), 1028(ss), 947(w), 592(s), 559(s) 452(ww)	851(m), 410(sh)	3575(ww)
LR spectroscopy	1051(w), 1029(w), 946(ss) 596(w), 576(w),443(w)	844(w), 425(w)	3592(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.9 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1068(sh), 1017(ss), 946(w), 591(ss), 559(ss) 452(w)	850(s), 412(w)	3564(ww)
LR spectroscopy	1044(w), 1022(w) 950(ss), 596(w), 577(w), 443(w)	852(sh), 842(m), 423(w)	3590(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.10 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1064(ss), 1018(ss), 945(m), 591(ss), 558(ss), 452(s)	852(ss), 413(s)	3564(ww)
LR spectroscopy	1061(w), 1027(m), 944(ss), 597(ww), 577(w), 444(ww)	837(m), 849(sh), 424(ww)	3583(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.11 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1023(ss), 944(m), 591(s), 559(ss), 451(ss)	853(ss), 409(ss)	3563(ww)
LR spectroscopy	1075(w), 1028(ww), 583(w), 573(ww), 441(ww)	841(ss), 404(ww)	3573(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.12 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1028(ss), 941(ww), 589(m), 562(m)	846(ss), 830(ss), 408(ss)	3562(ww)
LR spectroscopy	1068(ww), 1018(ww), 940(s)	838(ss), 405(w), 363(ww), 344(w)	3579(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.13 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0})OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy	1028(ss), 973(ww), 588(m), 564(m)	846(ss), 821(ss), 372(s), 405(ss)	3556(ww)
LR spectroscopy	1068(w), 938(w)	837(ss), 828(ss), 427(m), 405(m) 342(sh), 361(m)	3578(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Table 2.14 Position and assignment of bands of IR and Laser Raman spectra of $Sr_{10}(AsO_4)_6(OH)_2$.

Technique	Wave number (cm^{-1})		
	PO_4^{3-}	AsO_4^{3-}	OH^-
IR spectroscopy		862(ss), 834(ss), 822(ss), 442(ss), 400(s)	3551(ww), 564(ww)
LR spectroscopy		851(ss), 838(ss), 825(ss), 427(w), 402(w), 361(ww), 342(w)	3577(w)

ss - very strong, s - strong, sh - shoulder, m - medium, w - weak, ww - very weak

Fig 2.2 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_6(OH)_2$ (sample No.1 of Table 2.4)

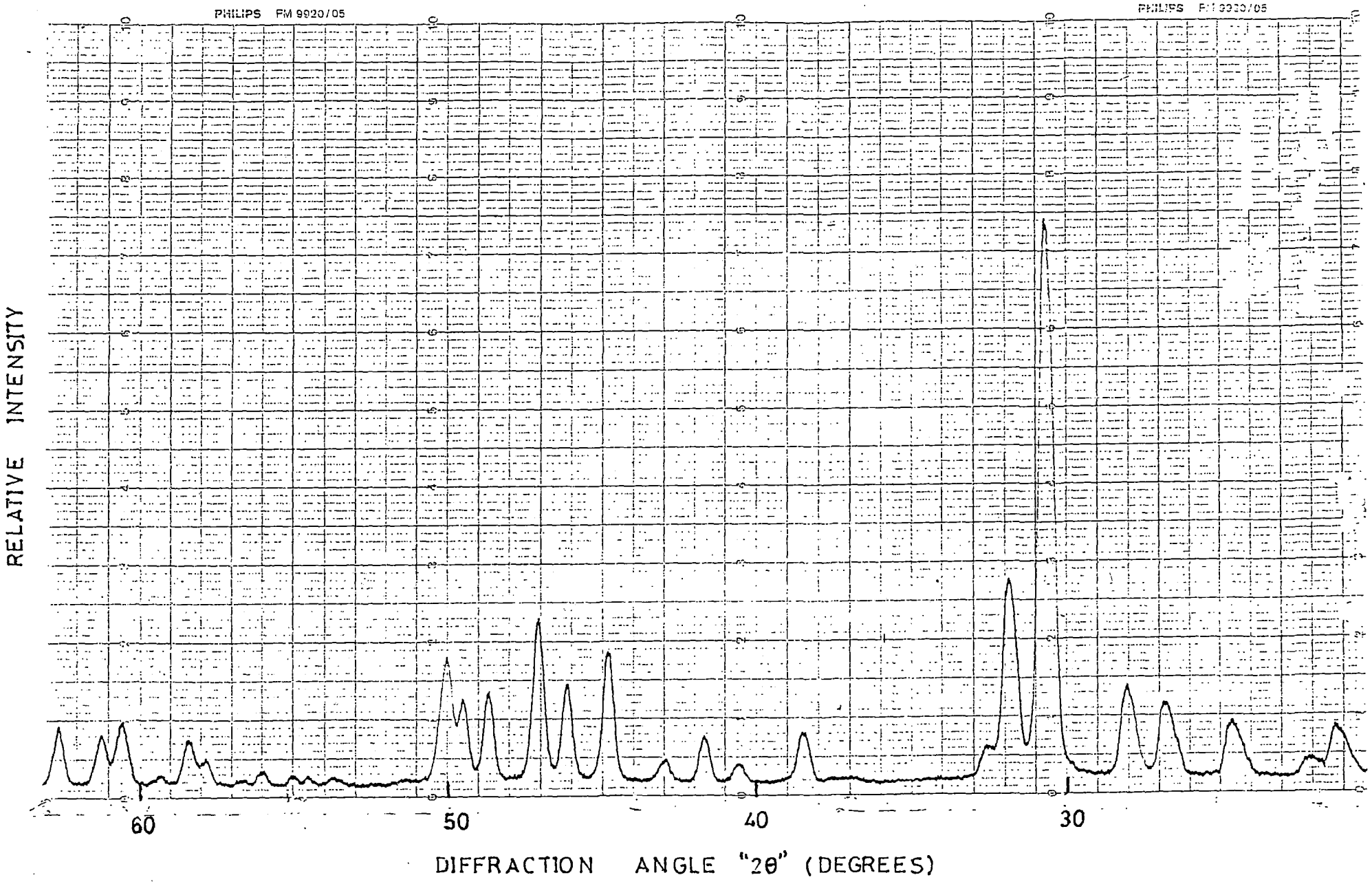

PHILIPS PM 9920/05
PHILIPS PW 9920/05
RELATIVE INTENSITY
60
50
40
30
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.3 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$.
(Sample No. 2 of Table 2.4)

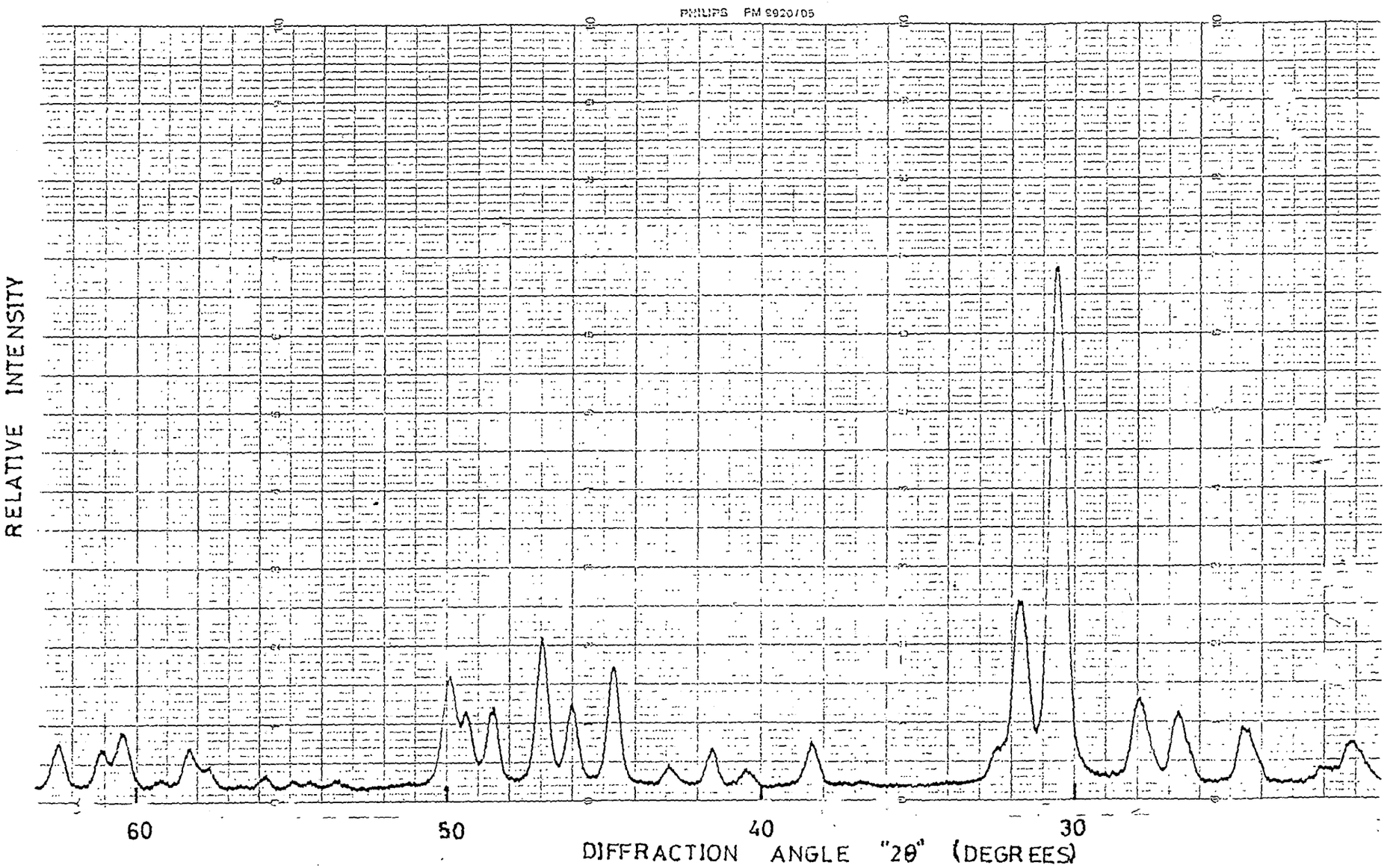

PHILIPS PM 9920/05
RELATIVE INTENSITY
60
50
40
30
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.4 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$.
(Sample No. 3 of Table 2.4)

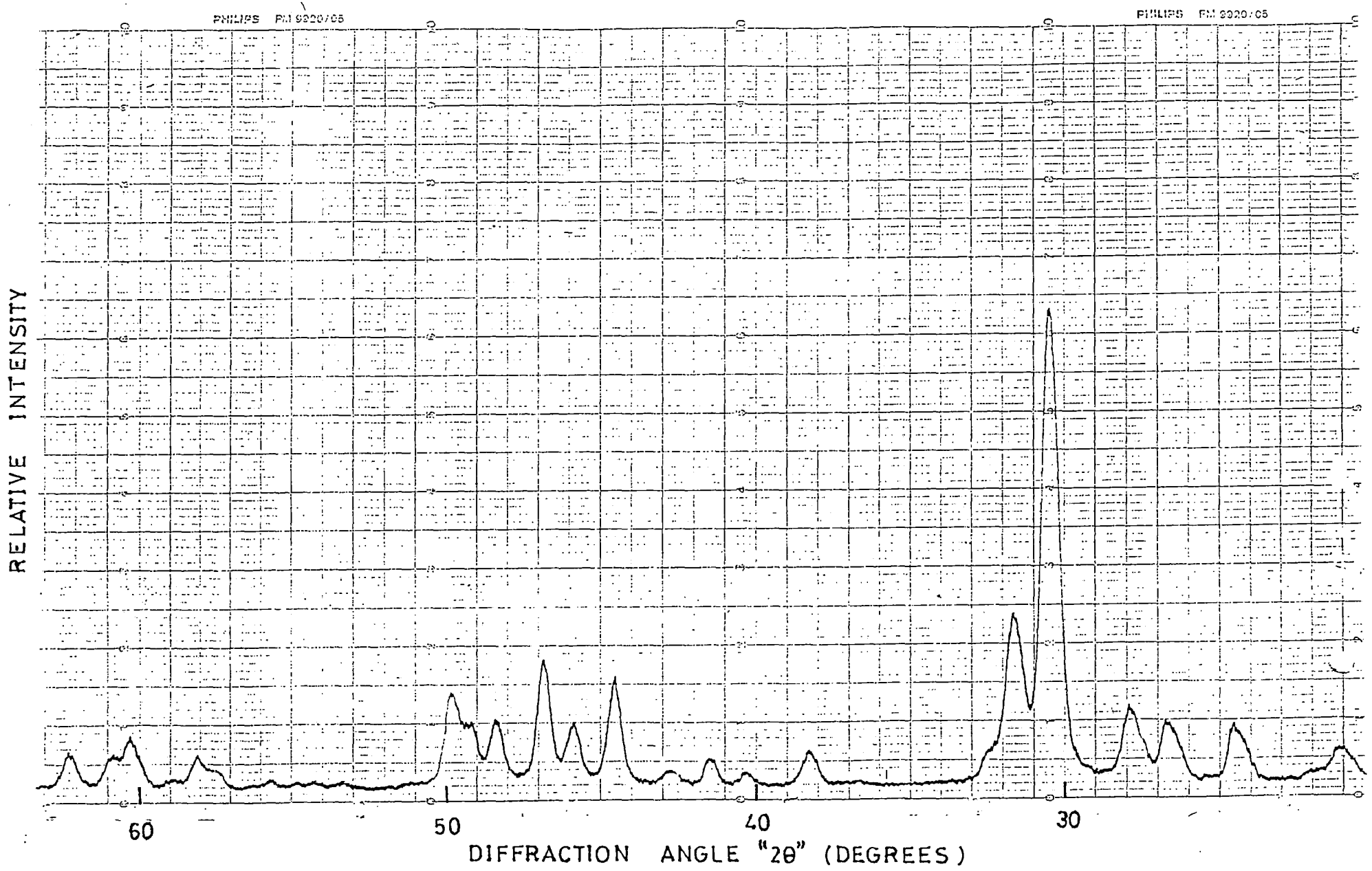

PHILIPS PW 9820/05
PHILIPS PW 9820/05
RELATIVE INTENSITY
60
50
40
30
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.5 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$.
(Sample No. 4 of Table 2.4)

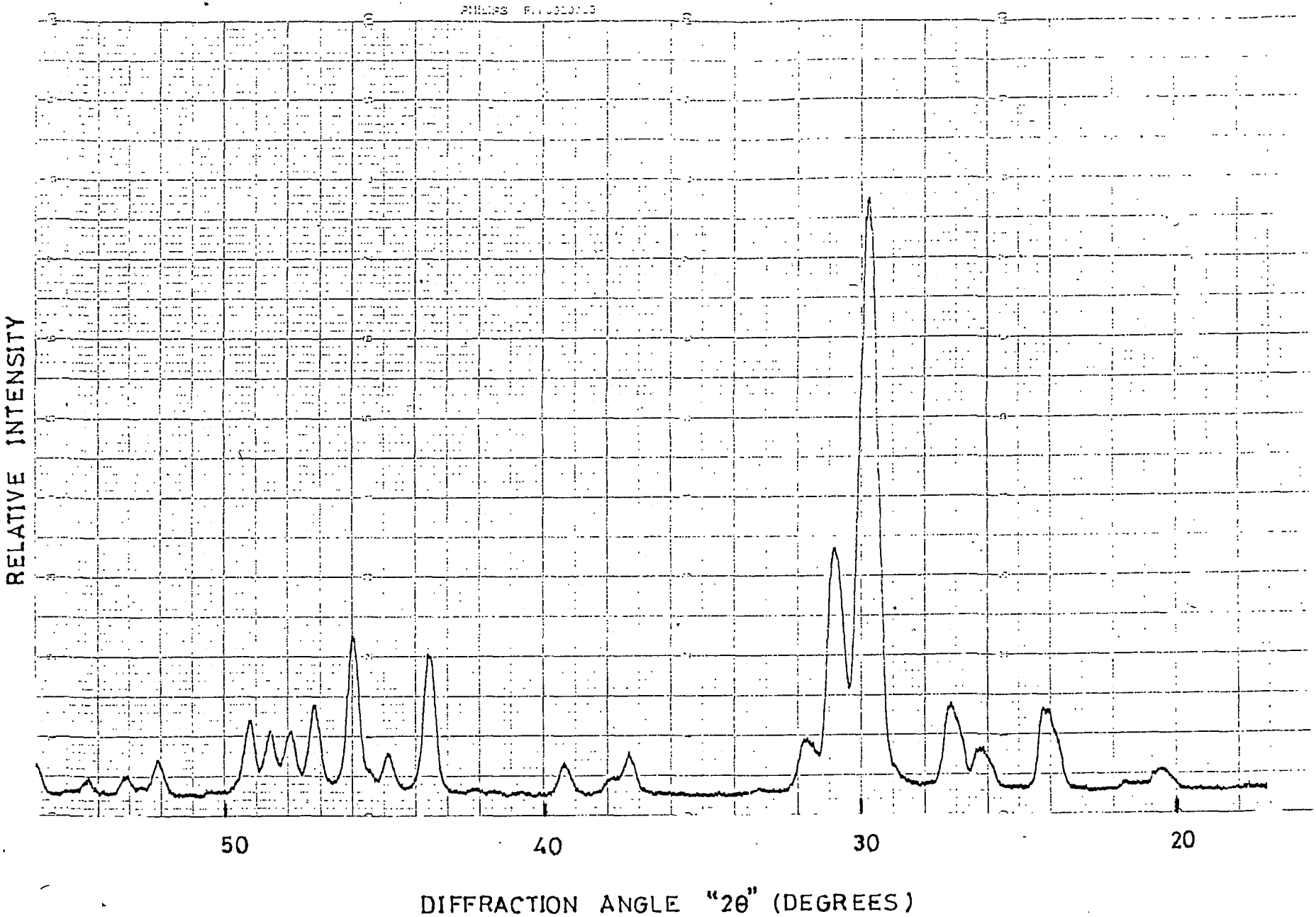

RELATIVE INTENSITY
50
40
30
20
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.6 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$.
(Sample No. 5 of Table 2.4)

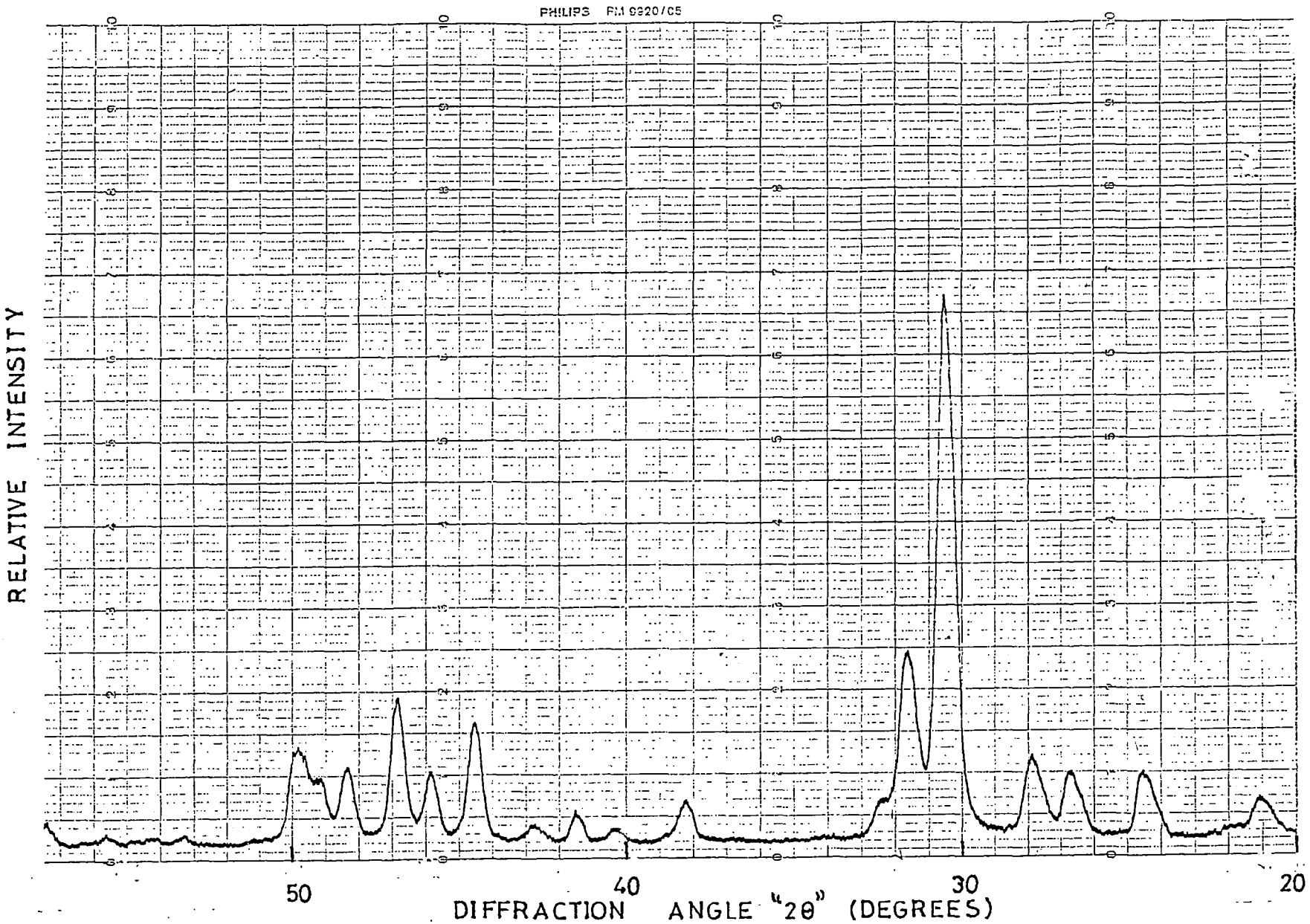

PHILIPS PW 9320/05
RELATIVE INTENSITY
50
40
30
20
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.7 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$.
(Sample No. 6 of Table 2.4)

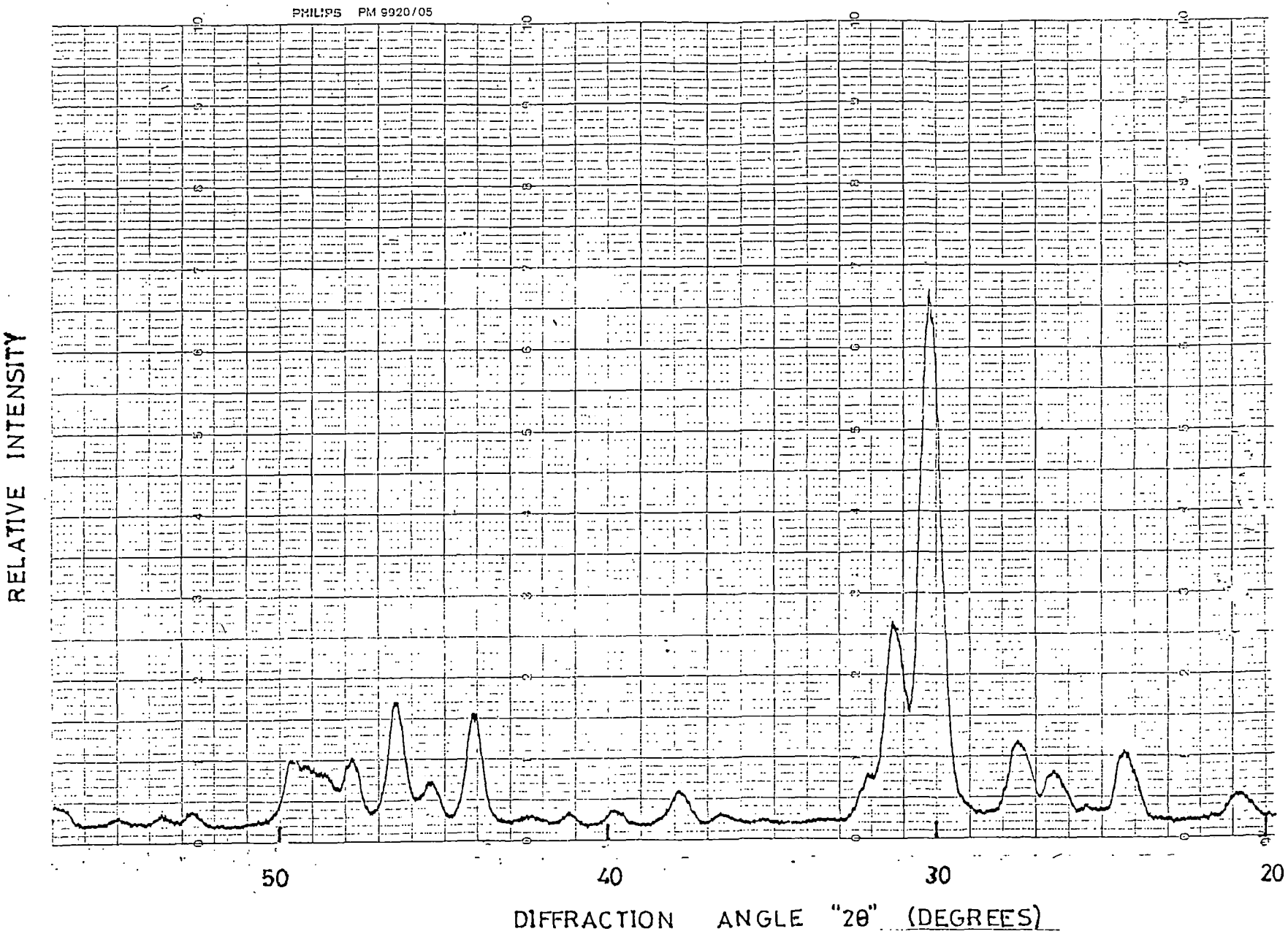

PHILIPS PM 9920/05
RELATIVE INTENSITY
50
40
30
20
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.8 Debye-Scherrer diffraction powder pattern of $Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$.
(Sample No. 7 of Table 2.4)

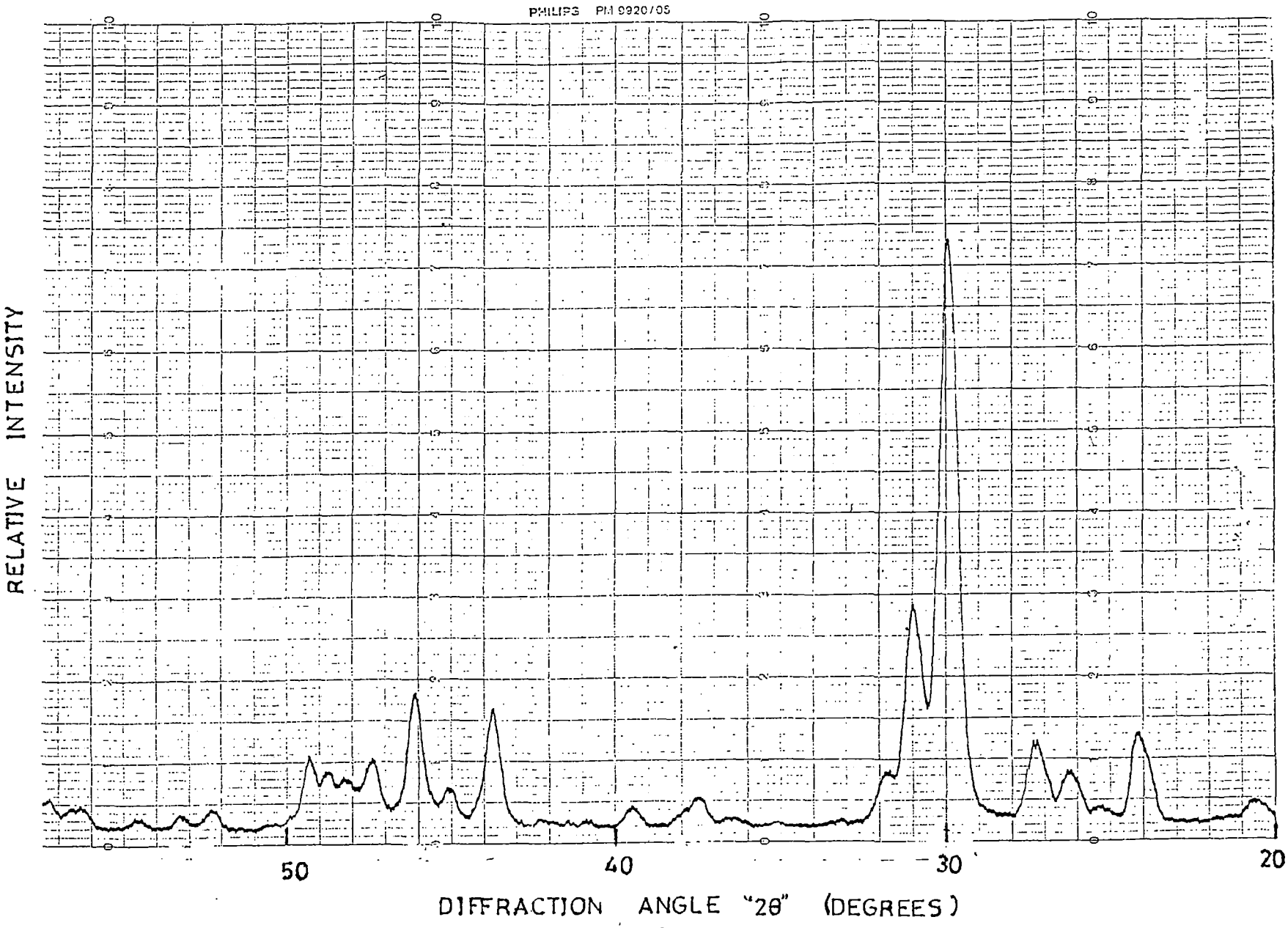

PHILIPS PM 9920/05
RELATIVE INTENSITY
50
40
30
20
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.9 Debye-Scherrer diffraction powder pattern of $Sr_{10}(AsO_4)_6(OH)_2$.
(Sample No. 8 of Table 2.4)

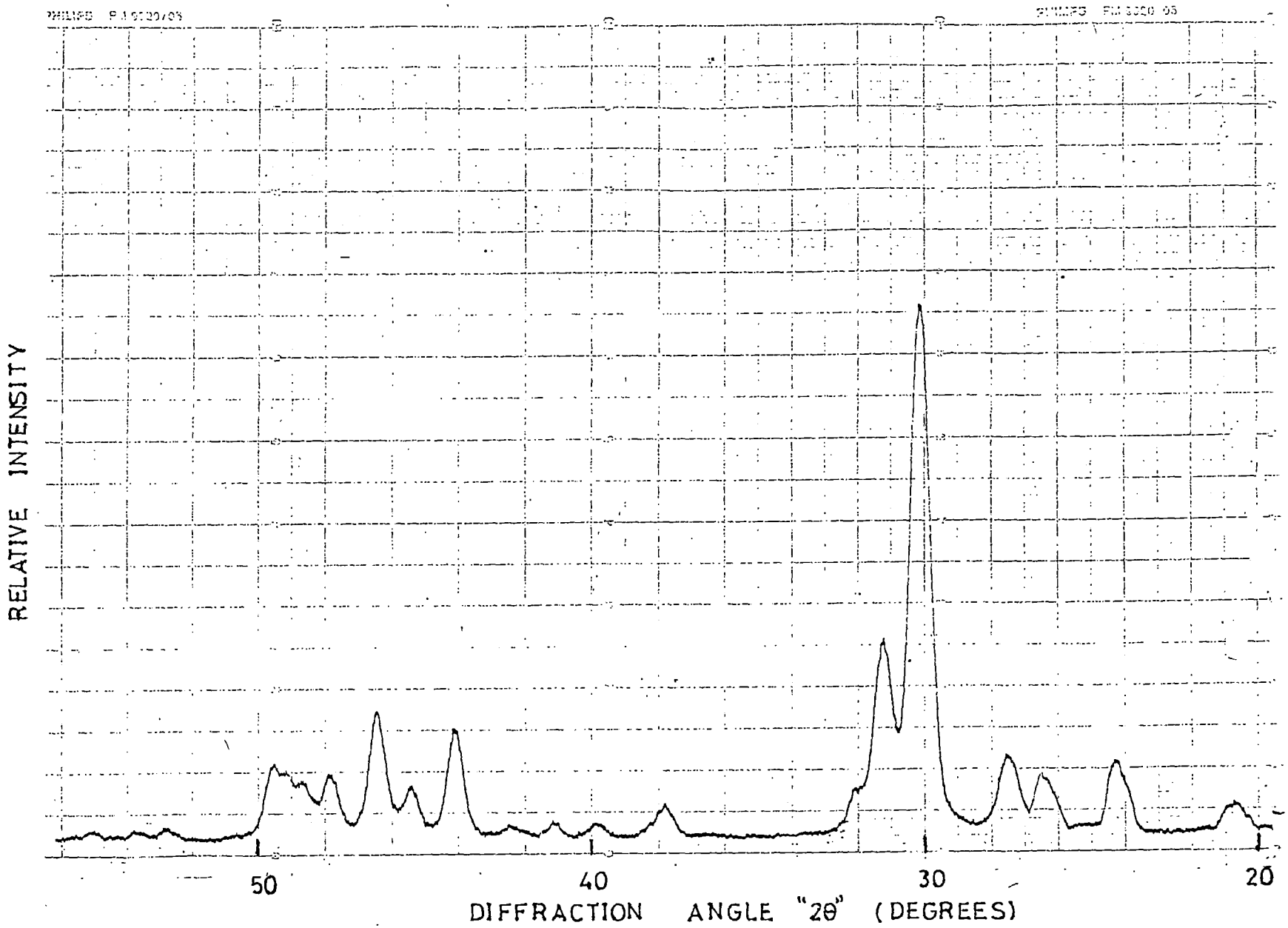

RELATIVE INTENSITY
50
40
30
20
DIFFRACTION ANGLE "2θ" (DEGREES)

Fig 2.10 Dependence of lattice constants of the solid solutions of phosphate and arsenate apatites of strontium on mole per cent of strontium arsenate apatite.
(Column 5 and 7 of Table 2.5).

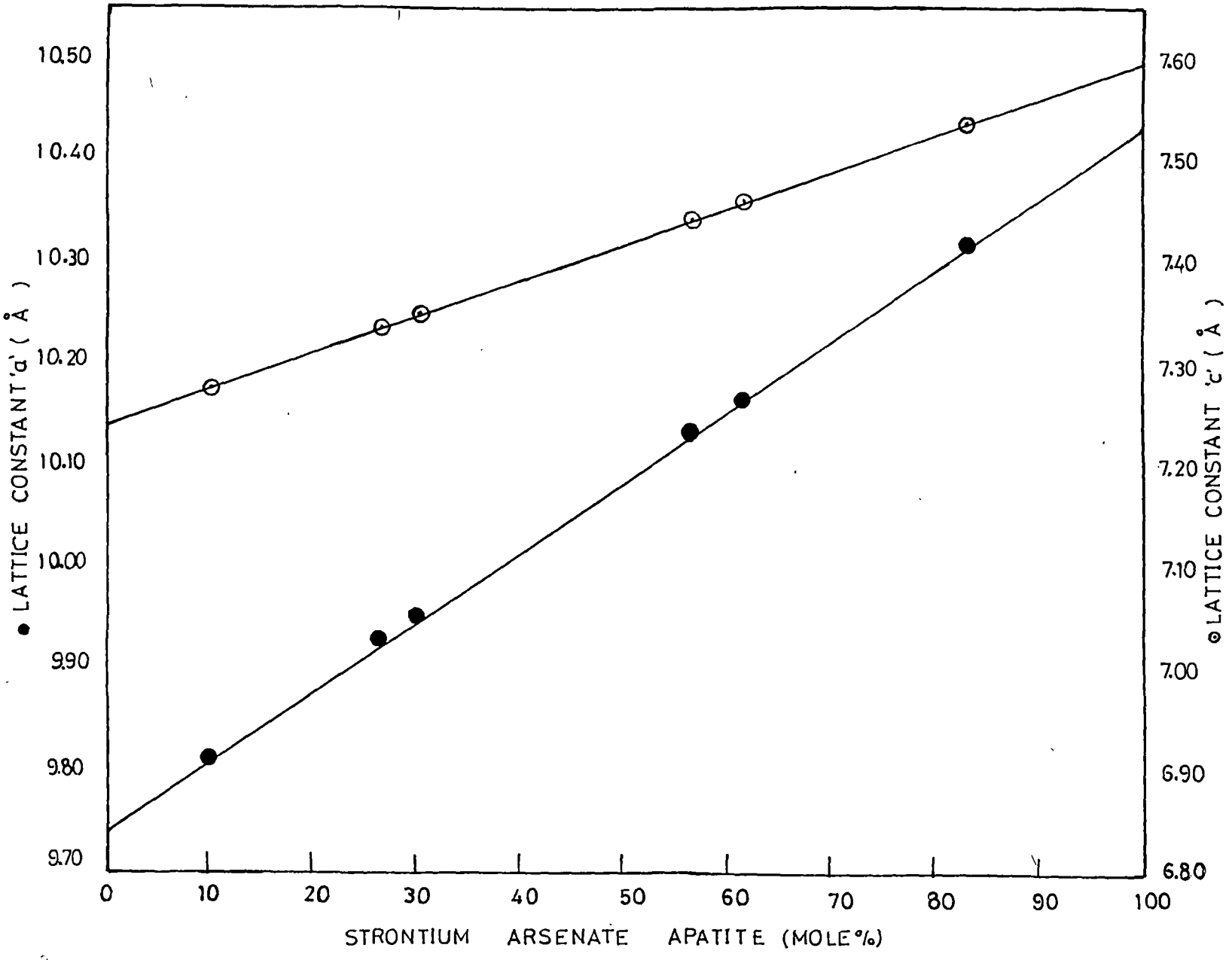

10.50
10.40
10.30
10.20
10.10
10.00
9.90
9.80
9.70
● LATTICE CONSTANT 'a' (Å)
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
⊙ LATTICE CONSTANT 'c' (Å)
0
10
20
30
40
50
60
70
80
90
100
STRONTIUM ARSENATE APATITE (MOLE %)

Fig 2.11 Dependence of unit cell volumes of the solid solutions of phosphate and arsenate apatites of strontium on mole per cent of strontium arsenate apatite.
(Column 9 of Table 2.5)

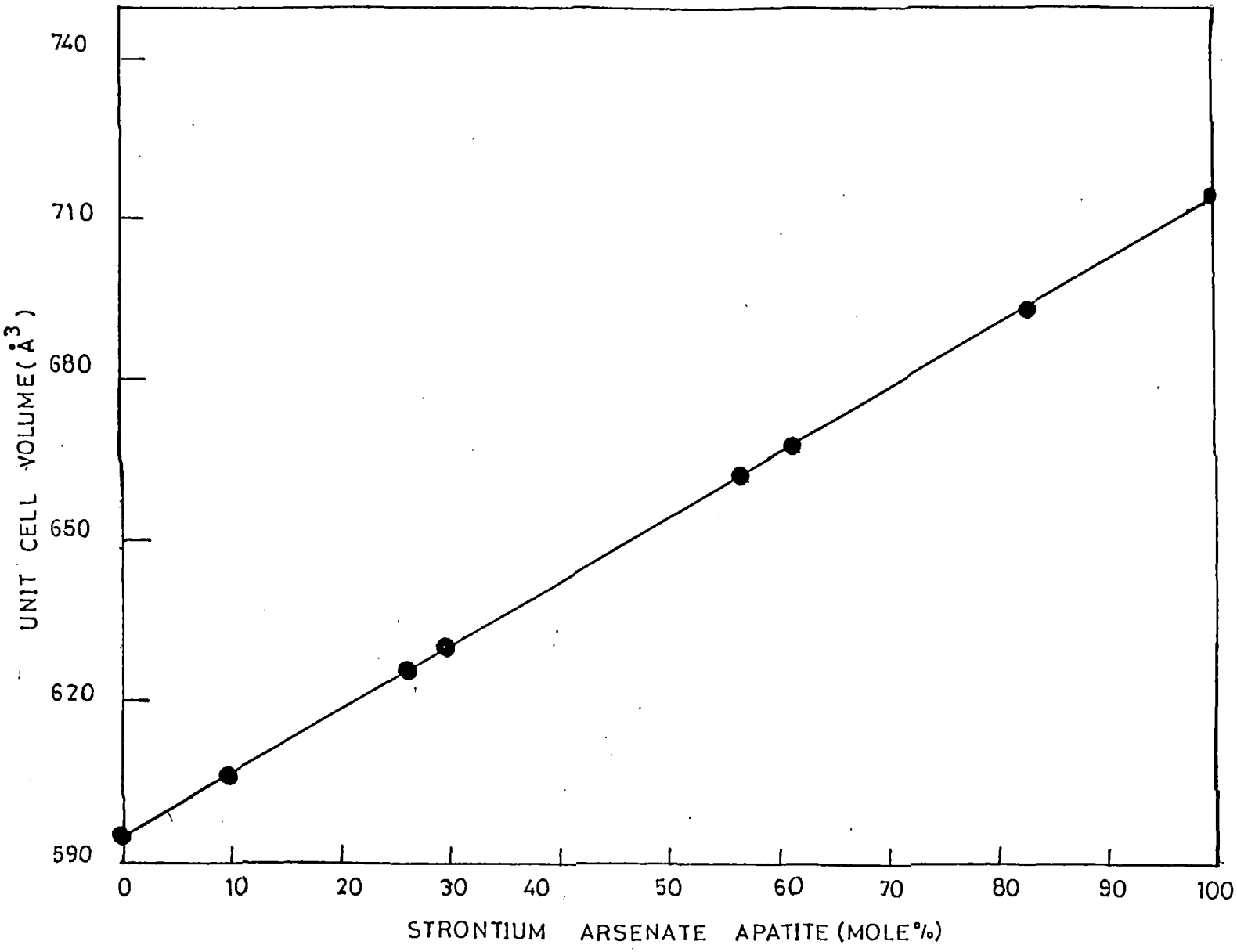

740
710
680
650
620
590
UNIT CELL VOLUME(Å^3)
0
10
20
30
40
50
60
70
80
90
100
STRONTIUM ARSENATE APATITE (MOLE%)

Fig 2.12 Electronmicrographs of the samples.
(S.Nos. 1-3 of Table 2.6)
A. Electronmicrograph of $Sr_{10}(PO_4)_6(OH)_2$
(Sample No. 1 of Table 2.6)
B. Electronmicrograph of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$
(Sample No.2 of Table 2.6)
C. Electronmicrograph of $Sr_{10}(PO_4)_{4.2}(AsO_4^-)_{1.8}(OH)_2$
(Sample No. 3 of Table 2.6)

Magnification, 35,000 x

A

B

C

Fig 2.13 Electronmicrographs of the samples.
(S. Nos. 2-6 of Table 2.6)

A. Electronmicrograph of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$
(Sample No.4 of Table 2.6)

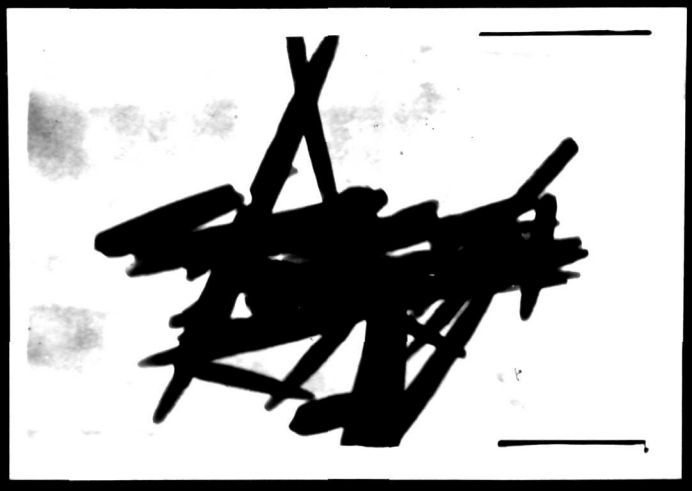
B. Electronmicrograph of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$
(Sample No. 5 of Table 2.6)

C. Electronmicrograph of $Sr_{10}(AsO_4)_6(OH)_2$
(Sample No. 6 of Table 2.6)

Magnification, 35,000 x

A

B



C

Fig 2.14 IR trace of $Sr_{10}(PO_4)_6(OH)_2$
(Sample No.1 of Table 2.4)

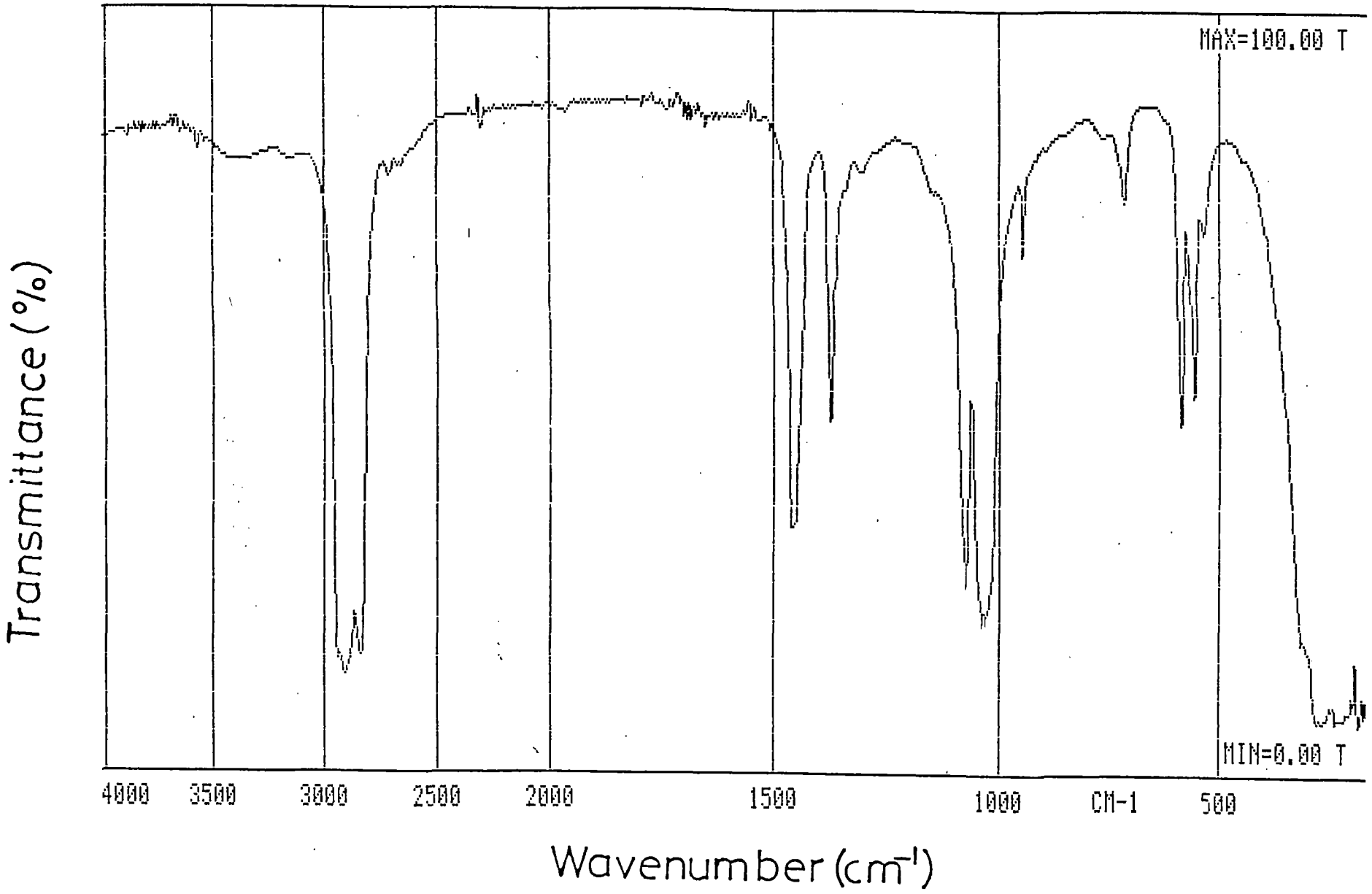

MAX=100.00 T
MIN=0.00 T
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
CM-1
500
Wavenumber (cm⁻¹)

Fig 2.15 IR trace of $Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$
(Sample No.2 of Table 2.4)

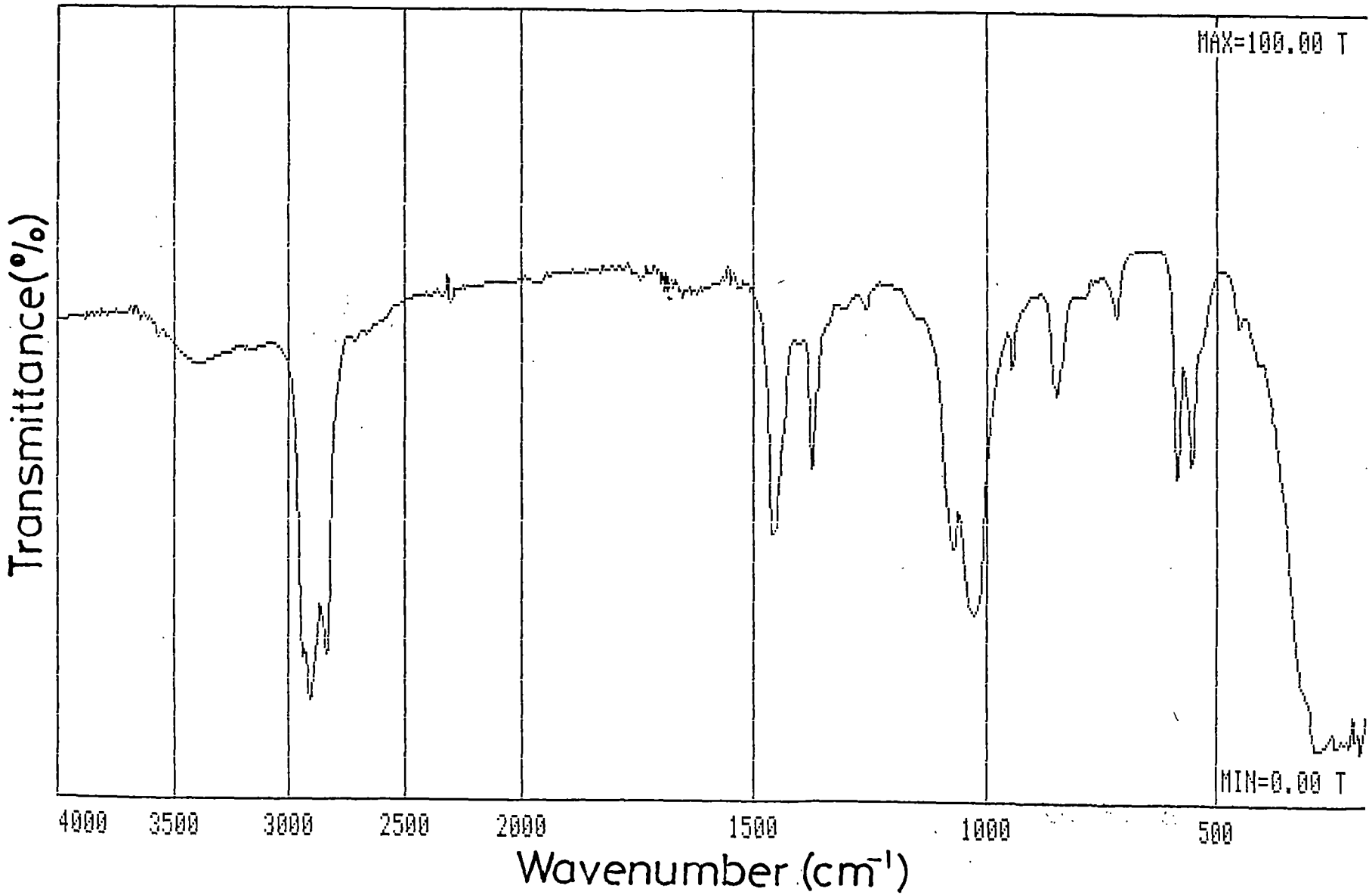

MAX=100.00 T
MIN=0.00 T
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

Fig 2.16 IR trace of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$
(Sample No. 3 of Table 2.4)

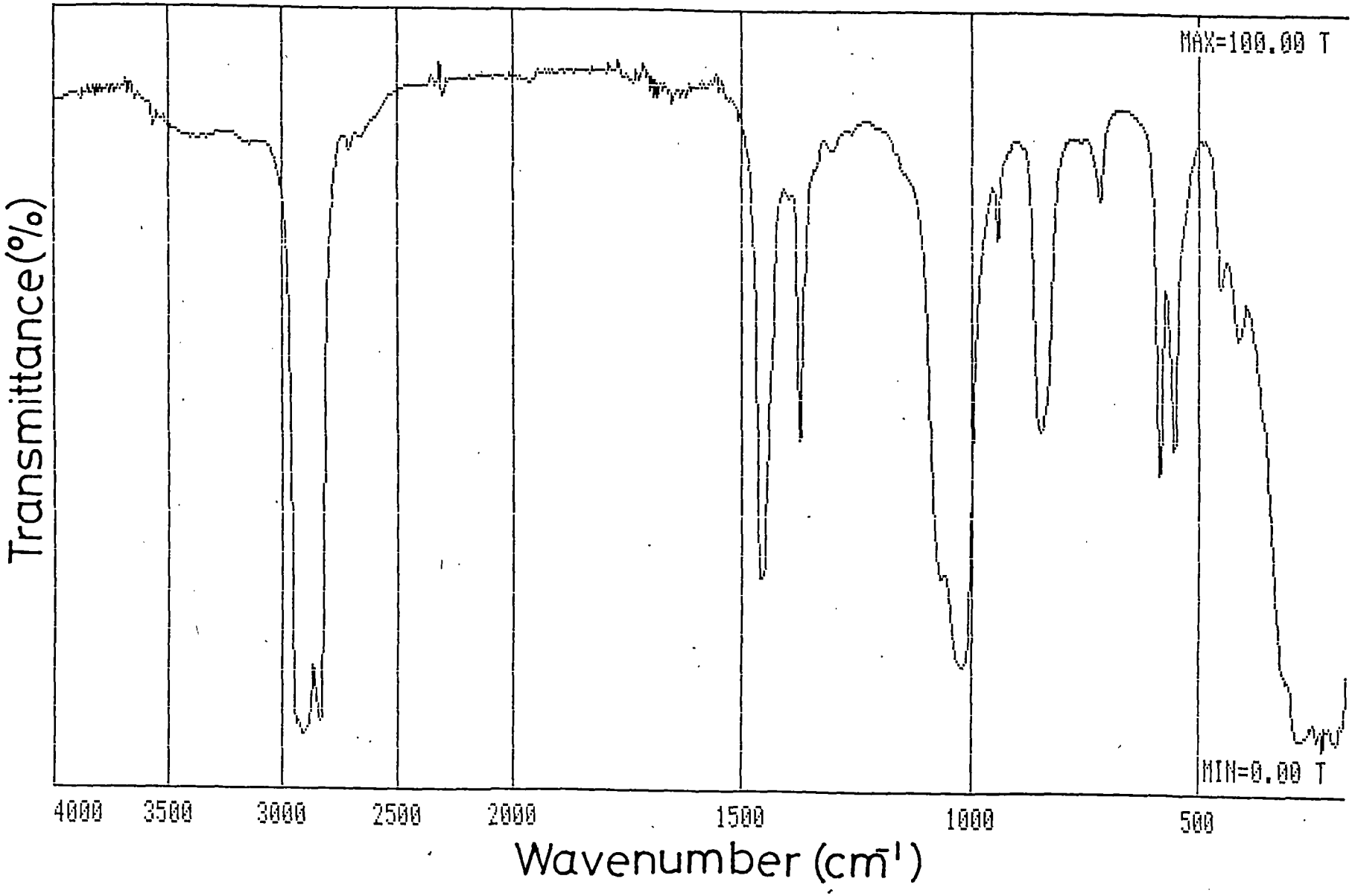

MAX=100.00 T
MIN=0.00 T
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

Fig 2.17 IR trace of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$
(Sample No.4 of Table 2.4)

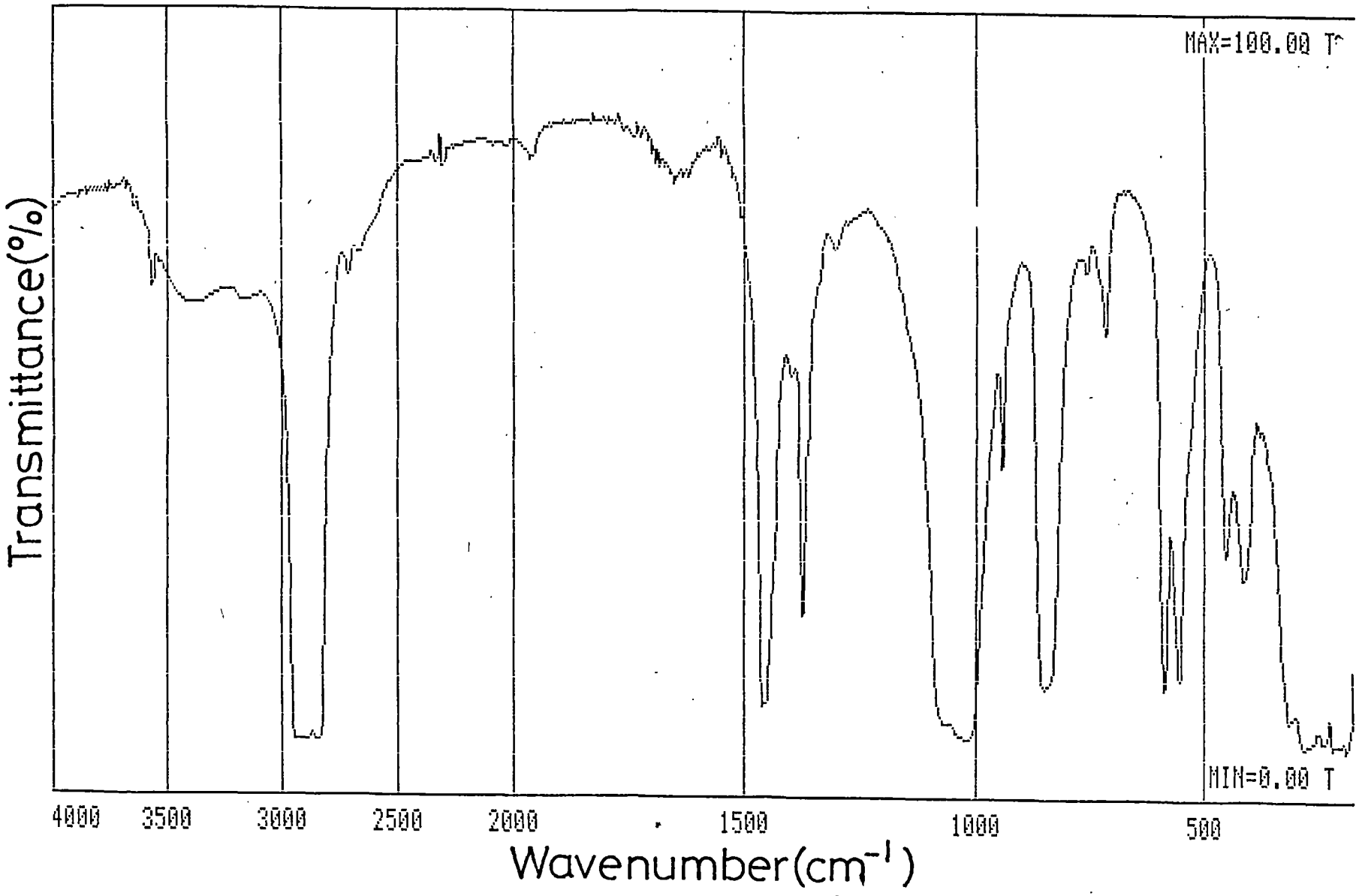

MAX=100.00 T
MIN=0.00 T
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm-1)

Fig 18 IR trace of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$
(Sample No.5 of Table 2.4)

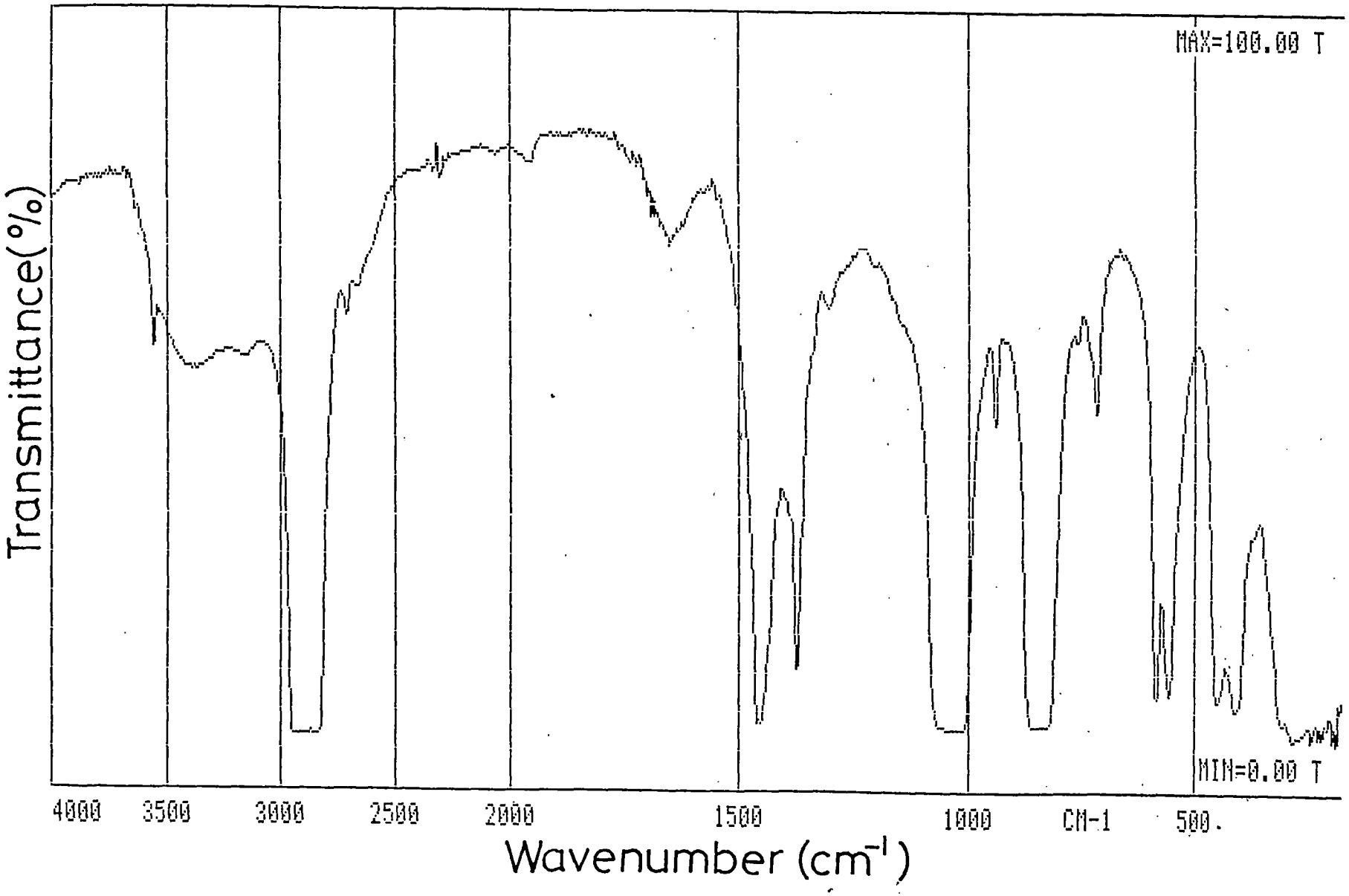

MAX=100.00 T
MIN=0.00 T
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
CM-1
500.
Wavenumber (cm-1)

Fig 2.19 IR trace of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$
(Sample No.6 of Table 2.4)

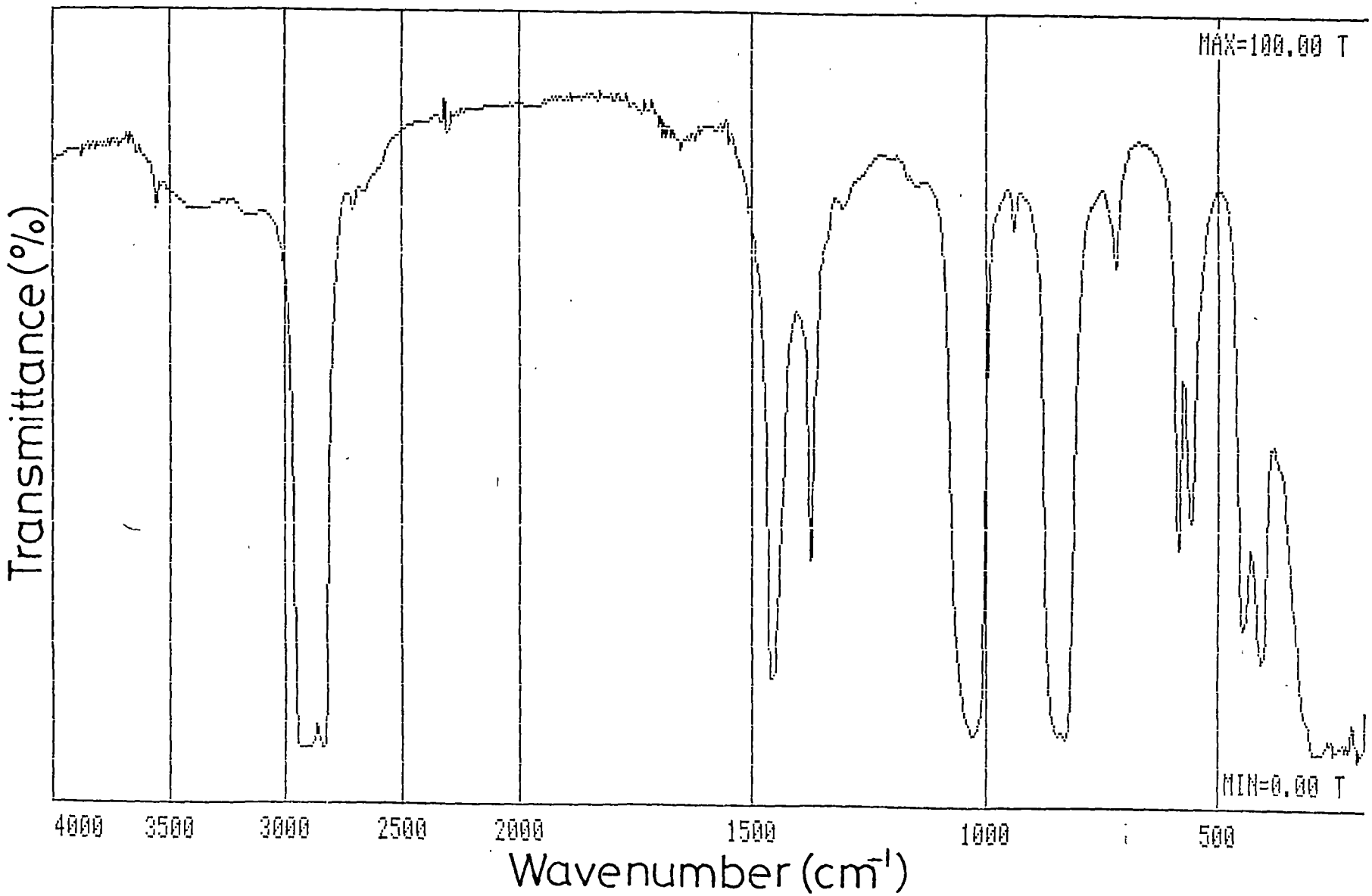

MAX=100.00 T
MIN=0.00 T
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

Fig 2.20 IR trace of $Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$
(Sample No. 7 of Table 2.4)

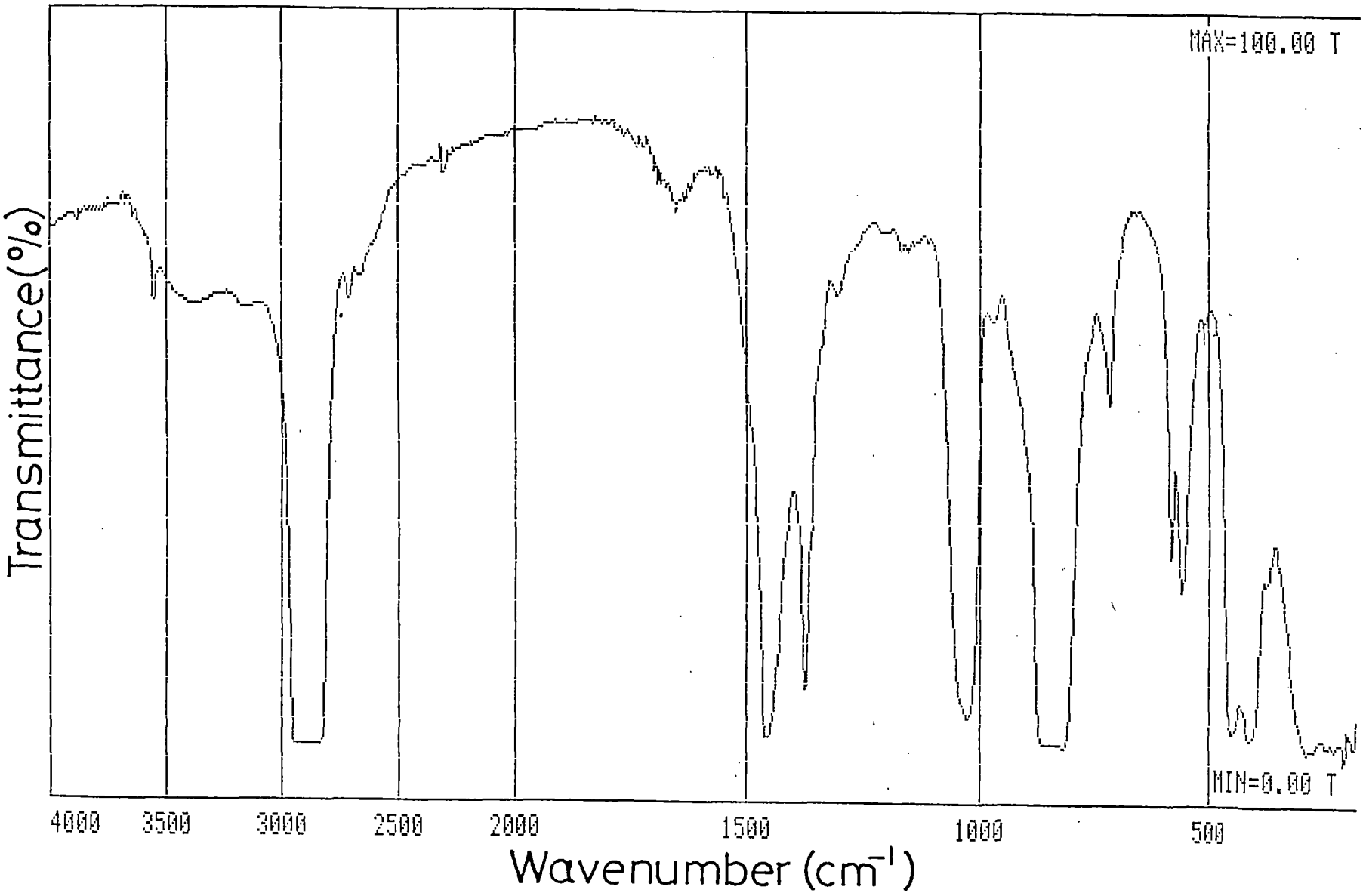

MAX=100.00 T
MIN=0.00 T
Transmittance(%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

Fig 2.21 IR trace of $Sr_{10}(AsO_4)_6(OH)_2$
(Sample No.8 of Table 2.4)

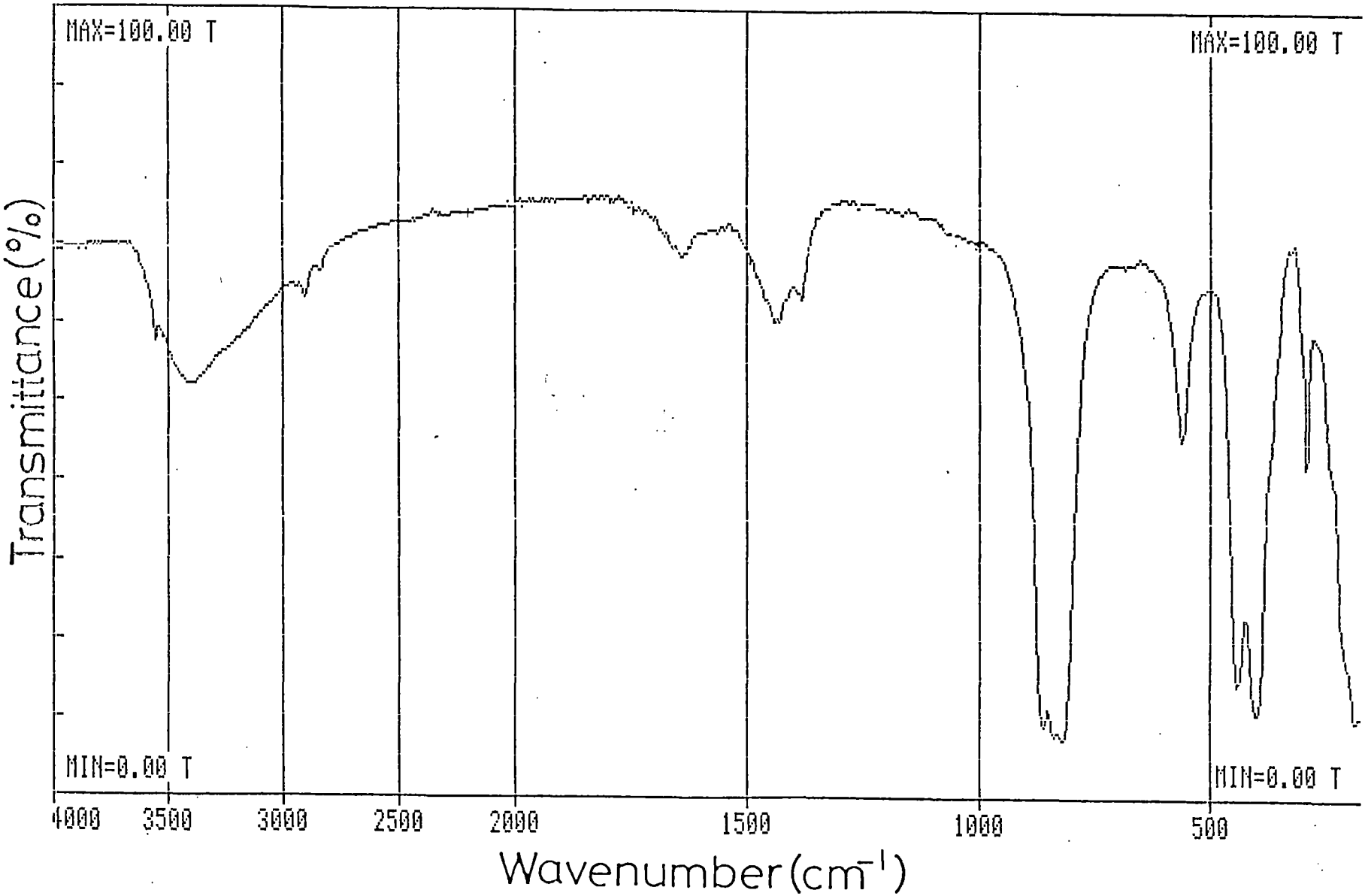

MAX=100.00 T
MAX=100.00 T
Transmittance(%)
MIN=0.00 T
MIN=0.00 T
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm⁻¹)

Fig 2.22 L.R. spectrum of $Sr_{10}(PO_4)_6(OH)_2$
(Sample No.1 of Table 2.4)

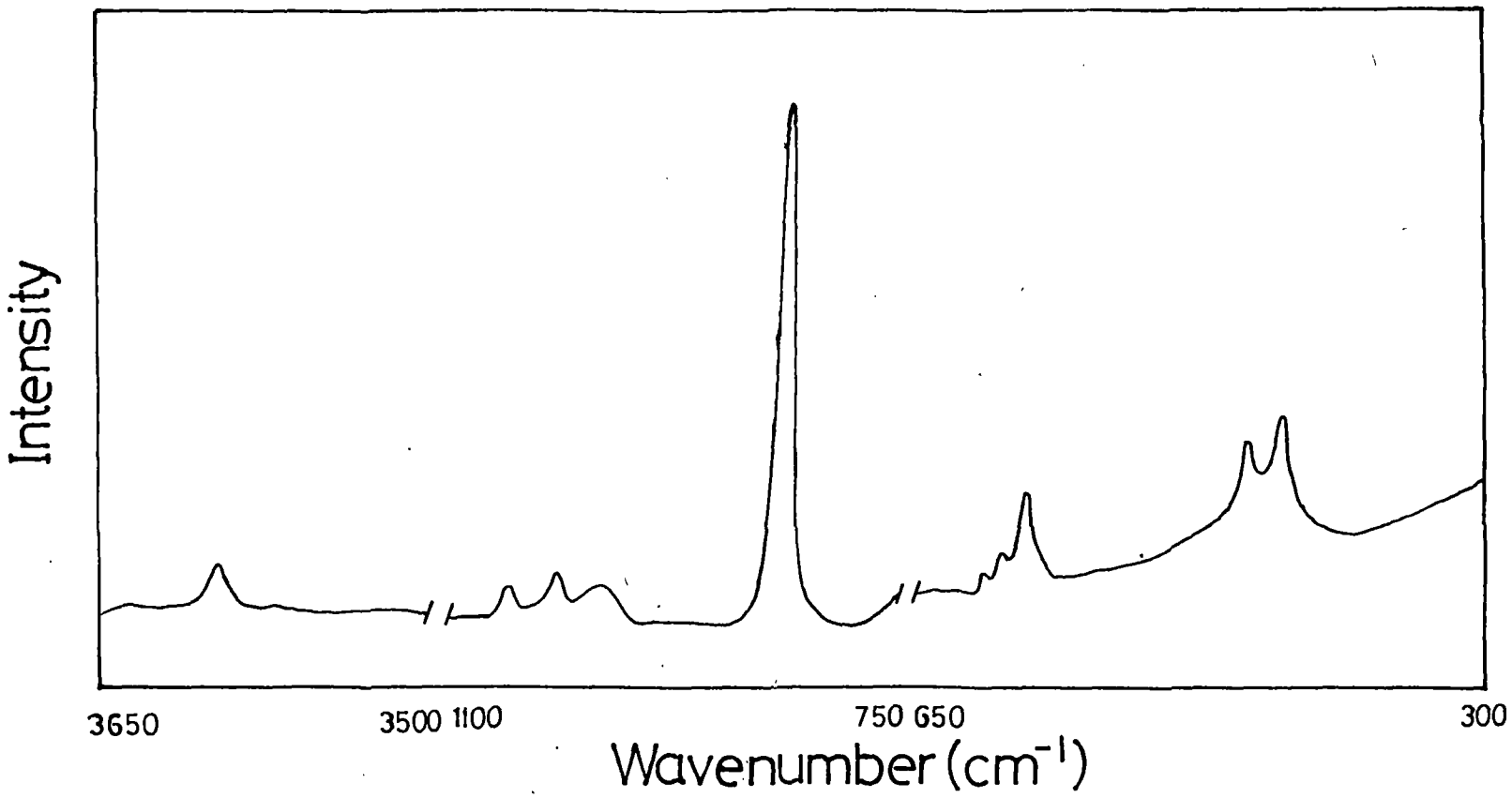

Intensity
3650
3500 1100
750 650
300
Wavenumber (cm⁻¹)

Fig 2.23 L.R. spectrum of $Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$
(Sample No.2 of Table 2.4)

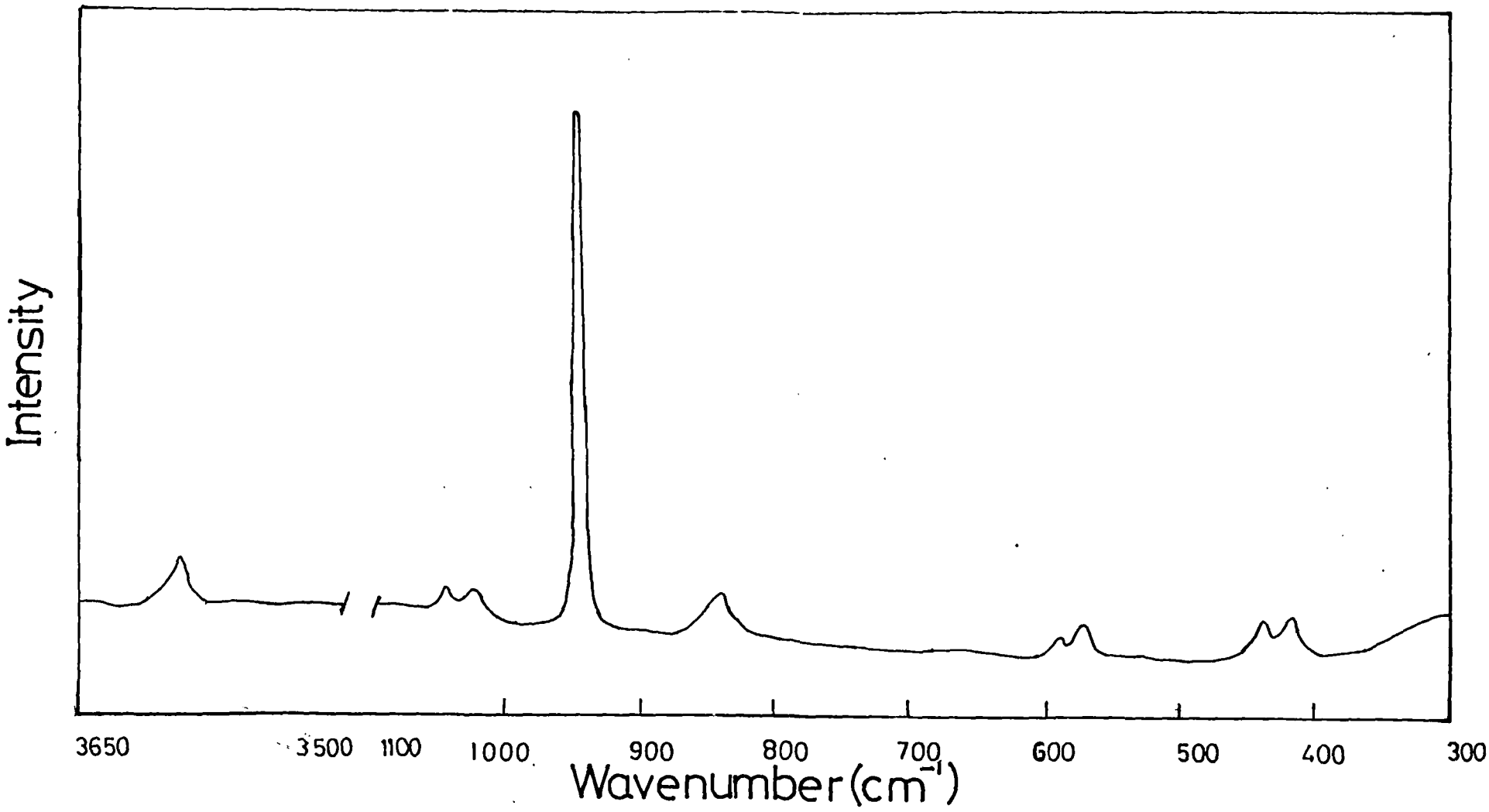

Intensity
3650
3500
1100
1000
900
800
700
600
500
400
300
Wavenumber (cm⁻¹)

Fig 2.24 L.R. spectrum. of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$
(Sample No.3 of Table 2.4)

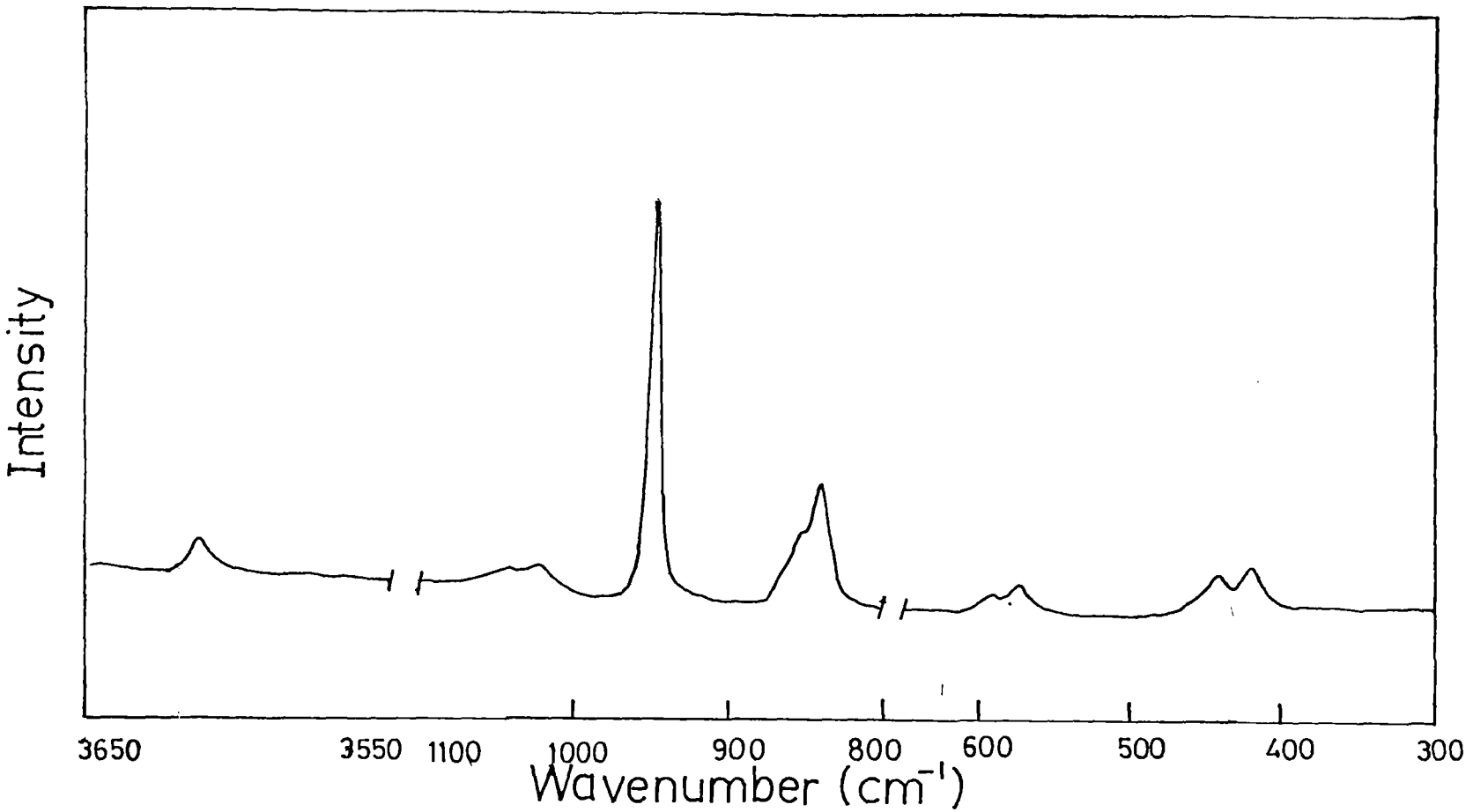

Intensity
3650
3550
1100
1000
900
800
600
500
400
300
Wavenumber (cm⁻¹)

Fig 2.25 L.R. spectrum of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$
(Sample No. 4 of Table 2.4)

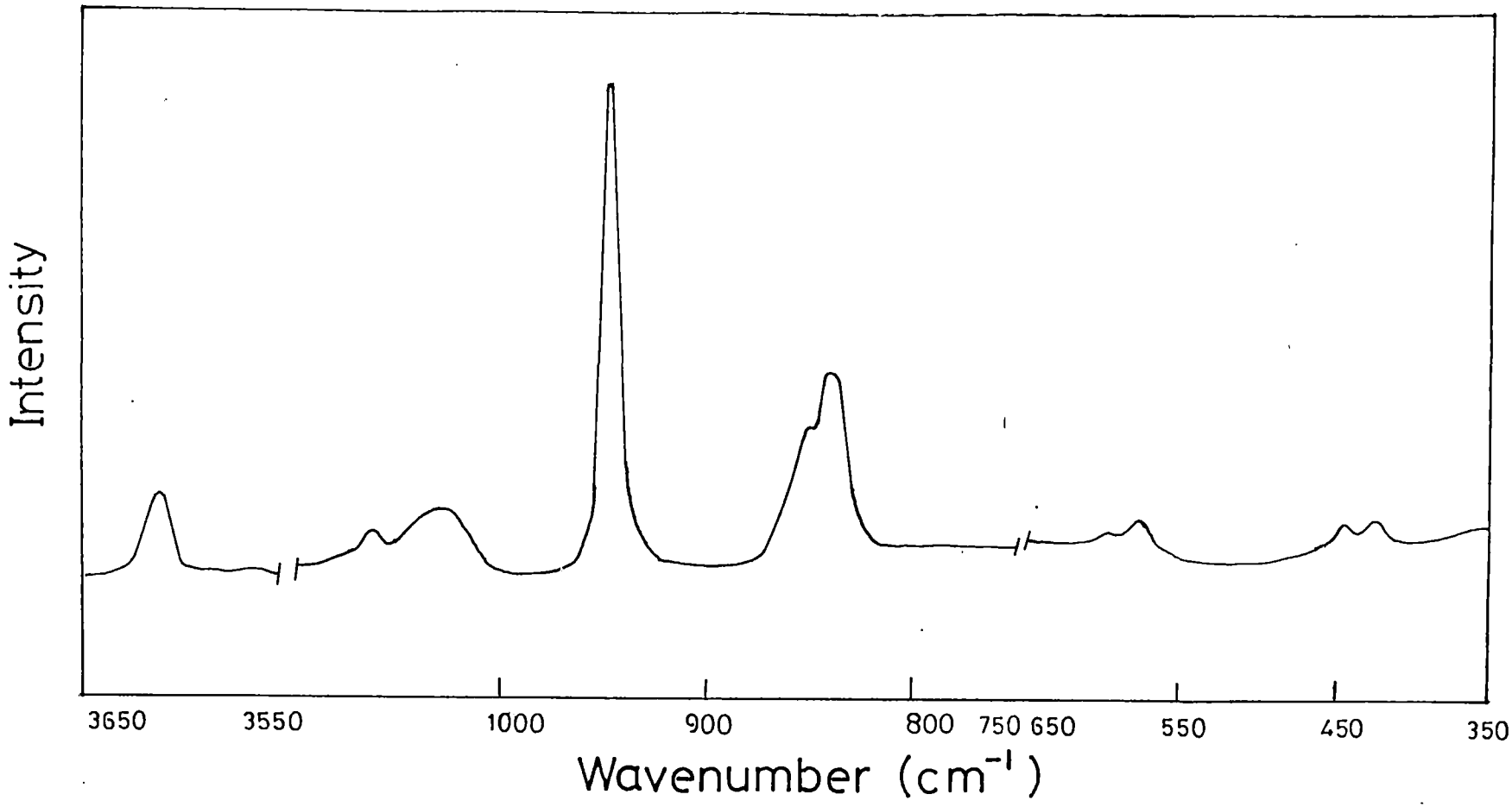

Intensity
3650
3550
1000
900
800
750
650
550
450
350
Wavenumber (cm⁻¹)

Fig 2.26 L.R. spectrum of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$
(Sample No.5 of Table 2.4)

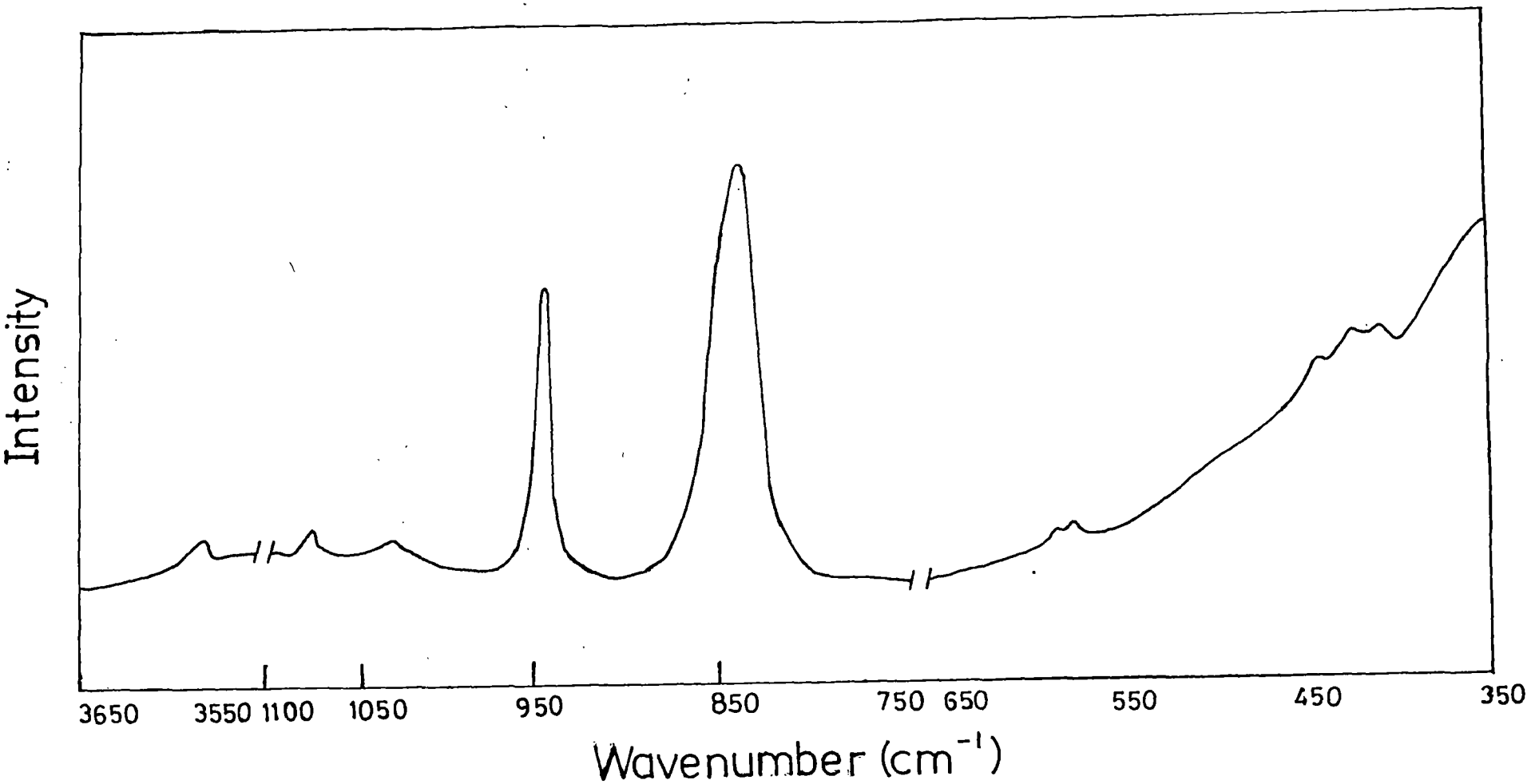

Intensity
3650
3550
1100
1050
950
850
750
650
550
450
350
Wavenumber (cm⁻¹)

Fig 2.27 L.R. spectrum of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$
(Sample No.6 of Table 2.4)

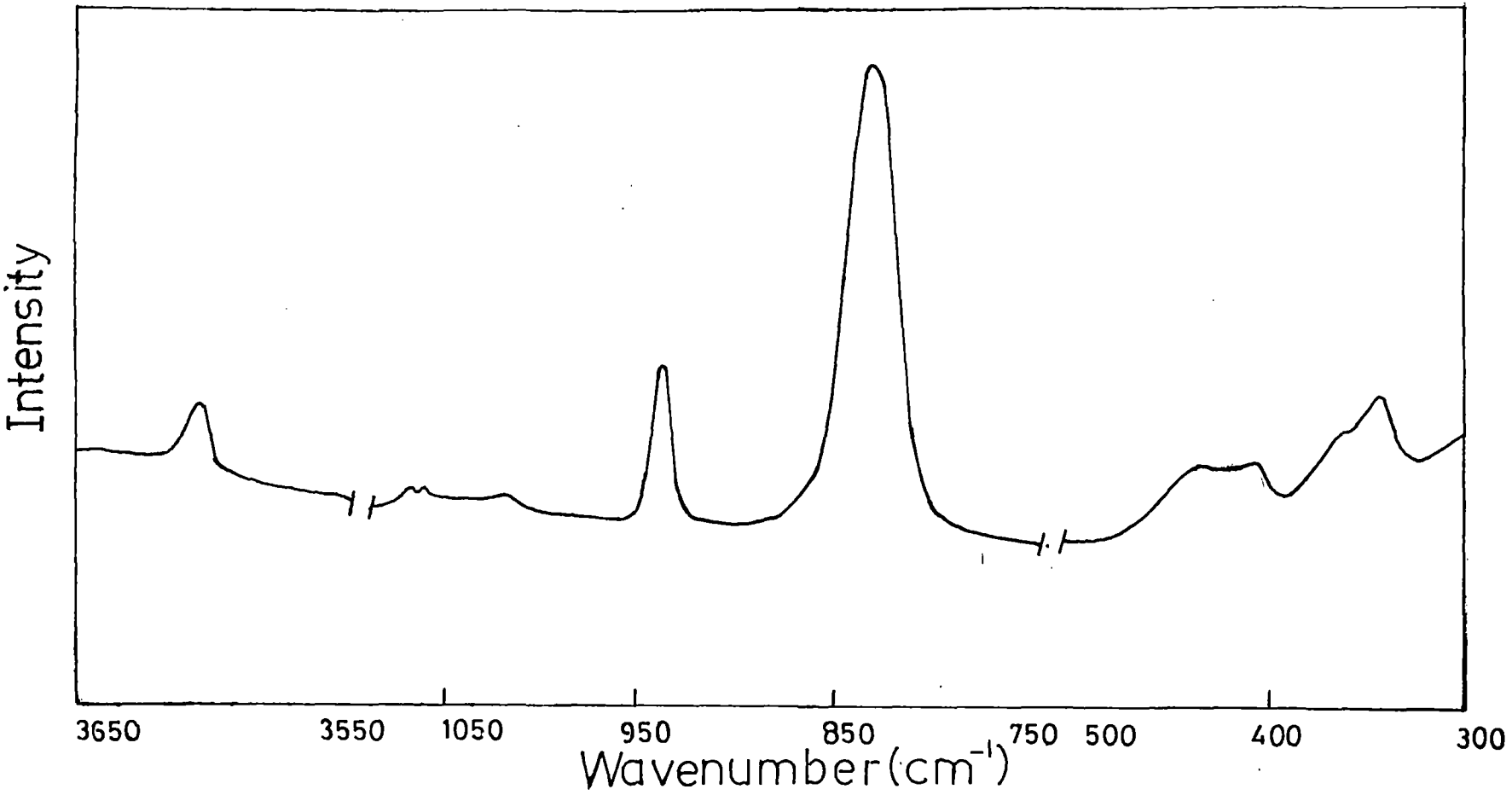

Intensity
3650
3550
1050
950
850
750
500
400
300
Wavenumber (cm⁻¹)

Fig 2.28 L.R. spectrum of $Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$
(Sample No. 7 of Table 2.4)

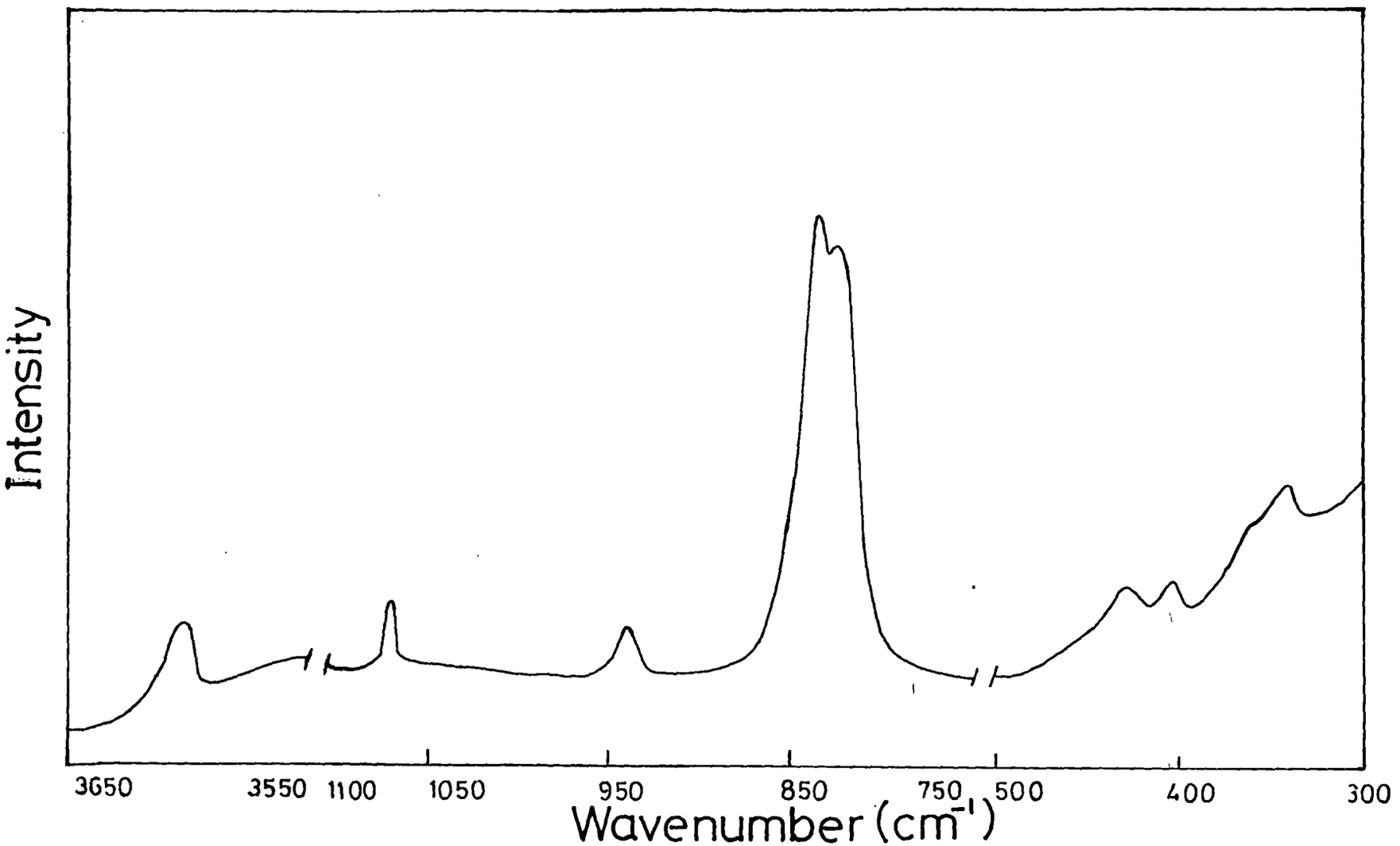
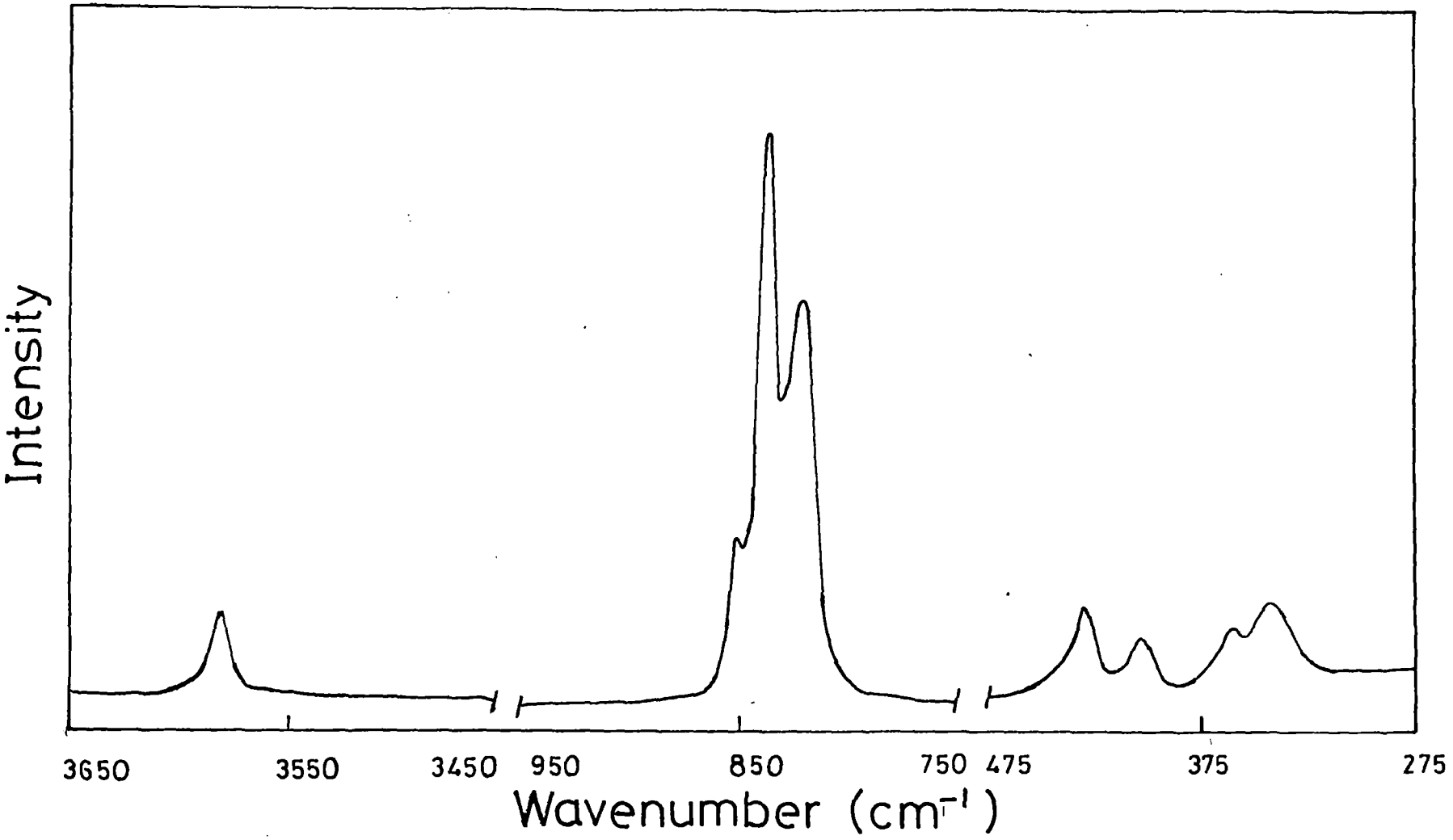

Intensity
3650
3550
1100
1050
950
850
750
500
400
300
Wavenumber (cm⁻¹)

Fig 2.29 L.R. spectrum of $Sr_{10}(AsO_4)_6(OH)_2$
(Sample No.8 of Table 2.4)


Intensity
3650
3550
3450
950
850
750
475
375
275
Wavenumber (cm⁻¹)

2.3 Results

The accuracies of the methods employed for the chemical analyses of SPA and SAA and their solid solutions were scrutinized by analyzing sample solutions containing precisely weighed quantities of the ions concerned and the results are given in Tables 2.1 to 2.3, pp.77-79. The analyses were carried out in each case on a few sets of such solutions preferably of different concentrations and the results of a few representative sets were given in these tables. The errors expressed as weight per cent were found to be ranging from -0.8 to +0.8, -1.7 to +1.7 and -2.0 to +1.0 respectively for strontium, phosphorus and arsenic.

Determination of the weight per cent of strontium, phosphorus and arsenic of each one of the sample was made using the analytical procedures described earlier and the results were given in columns (3), (4) and (5) of Table 2.4, p.80. The samples were numbered serially in the increasing order of their arsenic content. It is evident that for the samples the g atoms of phosphorus and arsenic present in 100 g of the sample can be calculated by dividing the respective percentage by the corresponding atomic weights. It is obvious that this ratio, P/As is independent of the amount of the sample considered. Since the total number of g atoms of (P+As), in a mole of each sample is six, knowing this ratio the number of g atoms of P and As in a mole of each sample could be calculated and the molecular formulae of the samples indicated in column (6) of Table 2.4 were assigned

assuming the number of strontium and hydroxyl ions to remain stoichiometric for the entire series of samples. In addition the g atom ratio, Sr/(P+As), was calculated for each sample from the corresponding weight per cent and included in column (7) of the table. The ratio was found to be varying between 1.64 and 1.69, the theoretical value being 1.67.

Figs. 2.2 - 2.9, pp.92-99 are the x-ray-paper-trace-diffraction patterns of the samples which are distinctly similar as far as the distributions of the diffraction lines are concerned, the observed uniform shift in the lines with increasing proportion of arsenic being a striking confirmation of the homogeneity of the samples as is to be expected from Vegard's law. About fifteen well-defined lines were chosen from each one of the patterns and their corresponding 'θ' values calculated, the corresponding 'd' values being obtained from Bragg's equation. The lattice parameters were calculated for all the patterns by a statistical method using the equations given below:-

$$\alpha\Sigma x^2 + \beta\Sigma xy = \Sigma xz \qquad (2.i)$$

$$\alpha\Sigma xy + \beta\Sigma y^2 = \Sigma y^2 \qquad (2\text{-}ii)$$

where

$$\alpha = \frac{\lambda^2}{3a^2}, \qquad \beta = \frac{\lambda^2}{4c^2}$$

λ = wavelength of incident radiation used, $x = h^2 + hk + k^2$, $y = l^2$ and $z = \sin^2\theta$ (h, k and l being the Miller indices, and θ the angle of incidence). Values of 'a' and 'c', as well as those of unit cell volumes were calculated by solving

the above equations for α and β, and given in column (5), (7) and (9) of Table 2.5'. A refinement of these values was brought about by the method of least squares using a computer, the new set of values being given in columns (5), (7) and (9) of the table. The assigned molecular formulae and corresponding molecular weights of the samples were given in columns (2) and (3) of Table 2.5. A graphical representation of the dependence of 'a' and 'c' and the unit cell volume on the mole per cent composition of the samples was provided by Fig. 2.10 and 2.11, pp.100,101. The experimentally determined densities of the samples and the molar volumes calculated from them were included in columns (10) and (11), while the molar volumes obtained by multiplying the unit cell volumes by the Avogadro number, were given in column (12) of the table.

The electronmicrographs of SPA, SAA and a few representative solid solutions of them were shown in Fig. 2.12 and 2.13 pp.102 and 103. It is evident from these patterns that the individual crystals of apatites were either tabular or ribbon-like in shape tending to look like elongated flattened hexagonal prisms. The crystals of SAA were found to be bigger than those of SPA, the dimensions of the crystals of the solid solutions being found to range between these two extremities. They showed a systematic increase in size with increase in AsO_4^{3-} contents, the experimental conditions of preparation of all the samples being similar. The average dimensions, both length and breadth of the individual crystals were masured taking into consideration the extent of magnification and the values were incorporated in columns (4) and (5) of Table 2.6, p.83. The values would substantiate

that a systematic increase in the average crystal size occurred with increasing AsO_4^{3-} content of the samples. While the average length and breadth of SPA were 1273 and 313 Å respectively the corresponding values for SAA were found to be 13454 and 783 Å, the dimensions of solid solutions being found to range between these two extremities. From the average dimensions of the individual crystals of the samples approximate values of their surface areas could be calculated as described earlier. These calculated values of all the samples incorporated in column (6) of the table, exhibited a marked decrease with increase in the AsO_4^{3-} content of the sample. The specific surface areas of SPA and SAA were found to be 35 and 13 m^2/g respectively, while those of solid solutions ranged between these two values.

Photostat copies of the infrared absorption spectra of all the samples were given in Figs 2.14-2.21; pp.104-112. The experimental details of recording the spectra were given on p. 74. The wavenumber range investigated extended from 4000-180cm^{-1}. The percent transmittance was represented as a function of the wave number of radiation. A consolidated list of absorption peaks of the samples assigned to PO_4^{3-} AsO_4^{3-} and OH^- was given in Tables 2.7 to 2.14. The i.r. patterns of all the samples were found to contain peaks in the range, 3575-3550cm^{-1}. In addition, the end-members were found to contain another OH^- peak in the range, 544-564cm^{-1}. The PO_4^{3-} peaks, six to nine in number, were found in the ranges, 1080-1018, 950-941, 590-559, 450-420cm^{-1} as shown in Tables

2.7 to 2.14. Further the peaks characteristic of AsO_4^{3-} were found in the ranges, 820-862 and 400-442 cm^{-1} for these samples as shown in the Tables. The patterns of the solid solutions were found to contain the entire set of these peaks and were shown in all the Tables, 2.7 - 2.14. All these patterns were found to be comparable with those given in the earlier literature[7,50,62,63,67,145,165,237,264-271]. The absorptions at 2920, 1460, 1375 and 722 cm^{-1} observed in the patterns were of nujol. Results of the laser Raman spectral studies of SPA and SAA and their solid solutions were included in Tables 2.7 to 2.14. In order to facilitate a convenient comparison of the i.r. absorptions of each sample with the corresponding absorptions of the L·R spectra, the two sets of absorptions were included in the same Table. It could be found from such a comparison that there existed a marked identity in the wave numbers of the corresponding characteristic peaks of each sample. Such a similarity in the wave number of the corresponding peaks of each sample observed by using i.r. and Laser Raman Studies confirmed the correctness of the assignments given to the absorptions. It may be mentioned that the results reported in the present work on Laser Raman Spectra of the apatites were observed for the first time as indicated by the absence of such data in the earlier literature[272].

2.4 Discussion

2.4.1 General Aspects

A brief mention of the theoretical aspects of solid solutions[273-275] was considered relevant here since the results of investigations included in this section were mainly concerned with them.

Homogeneous crystals containing variable proportions of isomorphous substances are formed, in general, from mixtures of solutions of the end-members. These are consequently known as "mixed crystals" or more popularly as "solid solutions". The formation of solid solutions sometimes extends to a pair of solids belonging to dissimilar crystallographic types, the permissible range of compositions in such cases is limited and the products are known as "anomalous mixed crystals" A series of solid solutions can be extended to the entire or partial compositional range depending upon the complete or partial miscibility of the solids concerned. Two principal types of solid solutons have been recognized: they are (i) interestitial solid solutions in which atoms of one element are inserted into some of the interstices in the crystal lattice formed by the atoms of a second element, resulting usually in a small increase in lattice constants of the crystal and (ii) substitutional solid solutions in which the replacement of atoms of one kind in the crystal lattice by atoms of a second kind with nearly the same size takes place. The formation of such solid solutions is accompanied either

by an increase or a decrease in the unit cell volume depending on whether the substituent atom is bigger or smaller than the atom replaced. In addition, solid solutions which are non-stoichiometric can be formed when the pairs of ions involved in the replacement are such that charge-neutrality can be maintained in spite of non stoichiometry. These are known as omission solid solutions. Co-precipitation and crystallization from molten mixtures are the methods usually adopted for the preparation of solid solutions.

The criteria for the formation of solid solutions between a given pair of compounds are that (i) there is isomorphism existing between them and (ii) the ionic radii of the pairs of ions competing for a given lattice position of the solid solution should not differ by more than 15 per cent. A convincing proof for the formation of solid solution can be provided by Vegard's law which states that when two isomorphous salts form continuous solid solutions among themselves, the dependence of the lattice spacing on the composition is linear.

It has been established through x-ray diffraction techniques that SPA and SAA constituted a pair of isomorphous substances. The closeness of the atomic radii of phosphorus and arsenic (tetrahedral covalent radii of P and As are 1.10 and 1.18Å respectively) suggests the possibility of formation of substitutional solid solutions between their apatites. Coprecipitation is considered to be better suited for the

preparation of these solid solutions than crystallization from fused mixtures of the end-members, since compounds of arsenic have a tendency to sublime. In addition, the temperature range congenial for the formation of SPA and SAA can be widely different eliminating the possibility of an overlapping set of conditions suitable for the preparation of their solid solutions.

2.4.2 Aspects concerning precipitation of samples

It is evident that PO_4^{3-} and AsO_4^{3-} ions which are required for the coprecipitation of solid solutions of SPA and SAA are the products of the third stage of dissociation of the corresponding ortho acids. Since the three stages of dissociation of these acids are pH-dependent, the selection of an optimum pH is important for such precipitations. It can be shown from a knowledge of the dissociation constants of these acids that a pH in the vicinity of 12 is the most optimum for this purpose. The particle size of the precipitates of apatites is usually in the range of colloidal dimensions resulting consequently in a pronounced surface activity. Such samples are characterized by a series of surface reactions with environmental[45,276] ions of the medium of precipitation. The conditions of precipitation of SPA, SAA and their solid solutions were therefore so chosen that the environmental ions prevalent had no surface interaction with the precipitates. The temperature of precipitation of the samples was maintained at 37°C in order to simulate biological condi-

tions since the subsequent investigations to be undertaken with the samples were intended to understand the mechanism of biological processes like calcification and resorption. The various theoretical aspects associated with the formation, properties and purity of precipitates have been incorporated in an excellent review of Salutskey[274]. It is well known that nucleation governs the nature and purity of the precipitates formed, nucleation being defined as the process of generating the initial fragments of a new and more stable phase capable of further spontaneous development. When numerous nuclei are formed the precipitation will be rapid, individual crystals small, filtration and washing difficult and purity low. Nucleation can be shown to be favoured, inter alia, by an increase in the concentration of the reacting solutions, a decrease in temperature and the presence of suspended impurities which function as seats for its occurrence. The parameters are consequently to be appropriately controlled for the formation of precipitates of desired specifications. The rate of precipitation is another important parameter deciding the crystal size of the resulting samples. A slow precipitation, as shown, results in the formation of large well-shaped crystals minimising the occurrence of crystal defects and imperfections. This can be accomplished by the addition of a very dilute solution of the precipitant accompanied by stirring to a medium in which the precipitate is sparingly soluble. Such a condition favours, in addition, recrystallisation of the precipitate on digestion, promoting

thereby further growth of the individual crystals. Based on a knowledge of the various mechanisms by which impurities may be incorporated, a few conditions such as use of dilute solutions, slow addition of precipitant, maintanance of a high temperature for precipitation, digestion and washing of the precipitate with a suitable wash-liquid are considered optimum for their minimization. The various aspects of the experimental procedures adopted for the preparation of the samples in order to minimize crystal imperfection and to obtain large, well-defined crystals were based on the theoretical principles of precipitation mentioned above. Another important parameter among the post-precipitational operations was the sintering of the samples for about 6 hours at 800°C. This could be justified on the basis of the fact that such a thermal treatment drives out volatile impurities and facilitates the diffusion of PO_4^{3-} and AsO_4^{3-} ions into the appropriate lattice positions of apatite. Crystal imperfections in the samples obtained may thus be eliminated enhancing their homogeneity. In addition, sintering was supposed to enhance the crystal dimensions[263] leading to sharper lines in the x-ray powder patterns[277] of the samples. Care was taken to see that the conditions chosen for the preparation were kept scrupulously the same for all the samples so that the alteration in their properties could be attributed exclusively to the replacement of phosphorus by arsenic.

2.4.3 Theoretical Basis for Characterization of the Samples

A clarification of some of the aspects of the methods employed for the quantitative analyses of the samples deserved a brief mention here since the procedures were specially worked out for the purpose. Since the conditions for the precipitation of the isomorphs, Mg $NH_4PO_4.6H_2O$ and $MgNH_4AsO_4.6H_2O$ are identical, their co-precipitation from an aliquot containing both PO_4^{3-} and AsO_4^{3-} can be brought about. A combined determination of both these ions can be made indirectly through a complexometric estimation of the magnesium content of these co-precipitated samples using standard procedures. While the determination of P and As when present alone in a given sample could be achieved by such a procedure, the quantitative separation of phosphorus and arsenic for the analyses of the solid solutions of SPA and SAA posed problems. Since the coprecipitated magnesium salts could provide a method of determining the total amount of P and As the need was felt for the determination of either of them in a mixture of the two in order to know their individual amounts. Such a quantitative separation is complicated since the conditions of precipitation of the corresponding salts of P and As are identical. Iodometric estimation of orthoarsenic acid is well known. A reversal of this method has been found to be specific only for AsO_4^{3-} in presence of PO_4^{3-}. The equation can be represented as follows:

$$H_3AsO_4+2H^++2I^- \rightleftharpoons H_3AsO_3+I_2+H_2O \qquad (2\text{-}3)$$

It could be shown that the reduction of AsO_4^{3-} to AsO_3^{3-} is quantitative in the presence of I^- ions in a pH range, 2.5 to 11.0, in the absence of atmospheric air. These aspects clarify the theoretical basis for the conditions adopted for the iodometric determination of AsO_4^{3-} in the presence of PO_4^{3-}.

2.4.4 X-ray Diffraction Studies

X-ray diffraction studies were intended to characterize the samples and to provide evidence for the formation of their solid solutions. The similarity of the patterns with those of apatites of well-established[278] composition, furnished evidence for their characterization as well as for the absence of extraneous phases. Based on considerations of the proximity of atomic dimensions of P and As (tetrahedral covalent radii 1.10 and 1.18Å respectively) as well as of the criteria for the formation of solid solutions[274] the possibility for the existence of a series of solid solutions of SPA and SAA over the entire compositional range could be anticipated. In addition, a marginal dilation in the unit cell volume is likely to set in due to the replacement of P by As. Such a dilation with an increase in the proportion of SAA was substantiated by a systematic shift in the corresponding diffraction lines of the samples. A more decisive indication of the dilation was provided by the excellent regularity with which the unit cell volume of the samples, calculated on the basis of the experimentally determined

lattice constants, increased with an increase in the proportion of SAA. The homogeneity of the solid solutions could thus be substantiated by the validity of Vegard's law over the entire compositional range of the solid solutions.

2.4.5 Electronmicroscopy

An additional confirmation of the identity of the samples could be provided by their electronmicrographs which offered a means of visual examination of the shape of the individual crystals. Earlier investigations[92,93,96-99] could prove that crystals of apatites are primarily hexagonal in shape tending to look ribbon-like, tabular or needle-shaped[13,137] depending upon their dimensions. The electronmicrographs of the samples of SPA, SAA and their solid solutiosn could reveal the existence of such a crystal shape, confirming thereby their identity as apatites. The conclusion that crystal dimensions increased with the proportion of SAA as revealed by x-ray diffraction studies could be substantiated by the electronmicrographs of the samples. In addition, as in the case of x-ray powder patterns the electronmicrographs of the samples could prove the absence of extraneous phases.

2.4.6 Infrared Spectroscopy

The similarity of the recorded i.r absorption spectra of SPA, SAA and their solid solutions could confirm convincingly the identity of these samples, supplementing thereby the evidence obtained by chemical, x-ray and electronmicroscopic

analysis regarding the homogeneity of the samples.

Based on an exhaustive survey of earlier literature[7,57,62,264-271] on i.r. absorption spectra of apatites, it could be concluded that principal findings relevant to the present discussion were made independently by Bhatnagar[264] and Fowler[270]. In the case of SPA the bands characteristic of the OH group were found at 544 and 3578 cm^{-1} respectively. The peaks characteristic of PO_4^{3-} were observed at 1075, 1030, 949, 592, 560 and 456cm^{-1}. Similarly, in the case of SAA the bands characteristic of the OH group were found at 564 and 3351cm^{-1} and the characteristic peaks of AsO_4^{3-} were found to be 862, 834, 822, 422 and 400 cm^{-1}. The solid solutions of SPA and SAA were found to have the OH bands in the range, 3572-3551 cm^{-1}. In addition they show peaks characteristic of PO_4^{3-} and AsO_4^{3-}. A broad band in the vicinity of 3390cm^{-} was observed which can be attributed to water of adsorption locked up in the crystal lattice to be given out when the crystal is heated to a fairly high temperature for a long duration. A few of the samples exhibit stray absorption peaks in the range, 1640-1600cm^{-1} which can be attributed to HOH bending[266] motion of free water present in the lattice. The persistance of a peak in the range, 3551-3572cm^{-1} due to OH^{-} group of apatites even in the case of samples sintered at 800°C confirms the thermal stability of the samples up to this temperature since the constitutional water was not given out. As expected, with progressive replacement of PO_4^{3-} by AsO_4^{3-} ion, the area of i.r. absorption peak of the latter increased

at the cost of the former, thereby confirming the homogeneity of the solid solutions, in addition to the evidence provided for the identification of the end-members. However, these studies were intended to be entirely qualitative and desired only for characterization of the samples. The quantitative aspects of i.r. absorption studies on apatites are to constitute the subject matter of the future series of investigations to be taken up soon. A broad narrow band is observed in the range, 1460-1430cm^{-1} which is attributed to the existence of CO_3^{2-} as an impurity caused probably by the interaction of carbondioxide of atmospheric air with the sample.

2.4.7 Laser Raman Spectroscopy

Results on the L.R. spectroscopy of the samples when compared with the corresponding i.r. absorption peaks indicated a similarity in the locations and assignments of the peaks. These results substantiate the wave number and assignment of the groups present in SPA, SAA and their solid solutions. However no quantitative aspects of the L.R and the I.R spectra of the samples could be undertaken with the present set of results since the patterns are mainly intended for characterizing the samples.

2.5 Summary

Strontium phosphate apatite, strontium arsenate apatite and six of their solid solutions, spread over the entire compositional range, were prepared by precipitation from aqueous media at 37°C by a method specially developed for the purpose. They were characterized by the conventional chemical analyses as well as by x-ray, electronmicroscopic, i.r and Laser Raman studies. As was to be anticipated from the covalent radii of P and As (1.10 and 1.18 Å respectively) the x-ray studies could show a systematic increase in the lattice constants consequent upon a dilation of the unit cell with an increase in the proportion of strontium arsenate apatite in the solid solutions in agreement with Vegard's law. The electronmicrographs of a few representative samples confirmed the absence of extraneous phases and enabled calculations of their approximate specific surface areas and the average dimensions of the individual crystals. An additional indication about the homogeneity of the samples was provided by i.r. absorption studies. As anticipated, the area under the arsenate peak increased at the cost of that under phosphate peak with a progressive increase in the extent of replacement of PO_4^{3-} by AsO_4^{3-} in the solid solutions. Results on the Laser Raman spectroscopy of the samples, when compared with the corresponding i.r. absorption peaks indicated a similarity in the location and assignment of the peaks. The homogeneity of strontium phosphate apatite, strontium arsenate apatite and their solid solutions could thus be established.

SECTION III

SOLUBILITY EQUILIBRIA OF PHOSPHATE AND ARSENATE APATITES OF STRONTIUM AND THEIR SOLID SOLUTIONS

3.1 Introduction

It is well known that the incorporation of β-active Sr-90 in the human skeletal system turns out to be fatal[118] because of the long half-life period of Sr-90 (28.5 years). The toxicity of elemental arsenic and its salts is well known[152-155]. The combined presence of these two or their compounds in the body-fluids may result in the precipitation of SPA and SAA at the bone/body fluid interface causing thereby a disturbance of calcium-phosphorus metabolism through a shift in the calcification-resorption equilibrium. Investigations on the solubility of SPA, SAA and their solid solutions under a simulated set of biological conditions may provide an explanation and a means for a possible elimination of such pathological conditions. The solubility equilibria of SAA have not been studied earlier although such equilibria involving several of its isomorphs have extensively been investigated[260]. The toxic effects of arsenic and the absence of information on the solubility equilibria of SAA in the existing literature are the motivations for undertaking the present investigations. In addition, the work was intended to eliminate the lacunae in the information available on solubility behaviour of apatites mentioned above.

The fundamental Physico-chemical aspects governing the dissolution of calcium hydroxylapatite in a solvent like water demand that the following equilibrium is established in its saturated solution:-

$$Ca_{10}(PO_4)_6(OH)_2 \rightleftharpoons 10Ca^{2}+6PO_4^{3-}+2OH^{-} \quad (3.1)$$

It is evident that such a saturated solution is characterized by the fact that the solubility product, Ksp, of the solute, given by $a(Ca^{2+})^{10} \times a(PO_4^{3-})^{6} \times (OH^{-})^{2}$ is a constant at a given temperature, where the terms in brackets represent the activities of the respective ions. Further, the g atom ratio, Ca/P, of the solution should correspond to the value of the solute, namely 1.67.

3.1.1 Salient Aspects of earlier Studies on Solubility Product of Calcium Hydroxylapatite

A careful survey of the existing literature[188-192,203,212,215] on the solubility of apatites indicates that there exist several ambiguities which need clarification. It is considered desirable to take stock of the main factors leading to the existence of such uncertainties and a few such are the following:-

(i) The low solubility coupled with the minute particle size of powdered synthetic samples of apatites leads to the existence of a colloidal component of the solute in its aqueous solution which is to be separated before the solution is analyzed for the determination of solubility[195].

(ii) Since solutions of apatites, assumed to be saturated, were either unsaturated or supersaturated, a scrutiny of attainment of saturation is to be made both from the sides of undersaturation and supersaturation.

(iii) Since several solid phases are present in the $CaO-P_2O_5-H_2O$ system as indicated by its phase diagram (Fig. 1.1 p.8) there is a possibility for the existence of more than one solid phase[215] functioning as solute studied for the determination of solubility of apatites.

(iv) By virtue of the high surface activity of apatites there is a possibility of their contamination[45,279] through adsorption and surface exchange of foreign ions which leads to a divergence in the results on the solubility, the effect being accentuated when the contaminants are highly soluble.

(v) A tendency of the calcium ions to get complexed[209] with some of the ingredients of the buffer combinations used for maintenance of a desired pH in the medium of dissolution causes an additional complication. A scrutiny of this aspect is to be made before deciding the suitability of a given buffer combination.

(vi) Apatites being the salts of a weak acid undergo hydrolysis in aqueous media resulting in the precipitation of insoluble phases which control the solubility equilibria[192].

(vii) It should not be ignored that errors involved in the evaluation of activity coefficient[191] of the products of dissolution of apatites introduce uncertainties in the calculated Ksp values.

In the light of the factors mentioned above which

are responsible for the uncertainties in the solubility data of the apatite systems, it is proposed to effectively eliminate these sources of errors in the present work to lead to a set of dependable solubility product values of the apatites chosen. While preventive measures for the majority of these factors were already reported in the earlier literature[50,144,215], quantitative determination of alkaline earth ions present in the saturated solutions of the systems could not be effectively controlled from the incidence of errors, since techniques such as spectrophotometry and complexometric titrations have been used. It has been proposed to make use of atomic absorption spectroscopy for the determination of strontium in the present series of investigations taking appropriate precautions to mask the phosphate ions likely to cause interference[82,83]. The ease with which the determinations can be carried out coupled with a high level of accuracy afforded by atomic absorption spectroscopy constituted the basis for the preference for this technique. The quantitative determination of phosphate, arsenate, as well as the OH^- ions were carried out in the conventional way.

3.2 Experimental

3.2.1 Selection of Buffers

The selection of appropriate buffers became essential in order to study the solubility equilibria of samples of SPA, SAA and a series of their solid solutions at a few chosen

pH values spread over the acidic and alkaline regions. The criterion of suitability of a given buffer is the non-interference of its constituents in the subsequent microanalytical determination of strontium, phosphate and arsenate. This was found to be fulfilled by the combinations, potassium acid phthalate-sodium hydroxide (pH, 4.3 to 6.2) and boric acid-borax (pH, 6.8 to 8.0) within certain specified concentration limits. The limiting concentration range of each buffer for each determination was established by separate experiments. Care was taken to see that the proportion of the buffer in the medium of dissolution was well within the limiting concentration range established.

3.2.2 Solubility Studies

3.2.2.1 Method of Equilibration

Glass containers were found to be unsuitable for housing the systems for purposes of equilibration since silicate ions dissolved from the glass surface were likely to interfere with the subsequent microanalytical determinations. Polyethylene vessels of about 125 ml capacity provided with air-tight stoppers were found to be suitable for the purpose. By preparing the desired solutions in distilled water collected under an atmosphere free from carbondioxide and by closing the systems air-tight throughout equilibration the presence of carbondioxide could be avoided preventing thereby the formation, if any, of carbonate apatite. Since the activity coefficients of the dissolving species can be maintained

effectively constant in a 0.165M sodium chloride solution, the latter was used instead of water for preparing the buffer solutions. For a pH range 5.0 to 6.2, 0.1M stock solutions of each of the ingredients of the buffer combinations, namely potassium acid phthalate and sodium hydroxide, were prepared. Similarly for the other pH range, 6.8 to 8.0 stock solutions of 0.2M and 0.05M of boric acid and borax respectively were prepared. The molarities of the solutions of the ingredients of the buffer combinations were so chosen that their concentrations in the resulting buffers were within the stipulated concentration limits required for non-interference in the subsequent microanalytical determinations. For each one of the pH values chosen for equilibration, the required proportions of the ingredients of the buffer combinations were found out by separate experiments. A stock solution of such a buffer sufficient in volume for setting up a separate system for each one of the samples was prepared. The pH in all the cases was accurately measured before and after equilibration using a pH meter. A separate system for each one of the chosen pH values was set up taking 0.1g of the solute in a polyethylene bottle dried previously. To this were added exactly 50ml of the stock solution of the appropriate buffer combination. The weight of the solute and the volume of the dissolving medium were thus maintained scrupulously the same for all the systems in order to eliminate the role, if any, of the slurry density[190] (wt. of solute/vol. of solvent), as a parameter in controlling the solubility of the system.

The systems were equilibrated at 37±0.5°C under a controlled rate of shaking using a shaker bath equipped with a thermostatic arrangement.

3.2.2.2 Filtration

Due to their low solubilities and minute particle size, samples of apatites get colloidally dispersed in their solutions resulting in what are known as "slurries". It became necessary to filter off the colloidal component before the solutions were analyzed. Further, the filtration was to be brought about at 37°C, the temperature of equilibration, to avoid any possible alteration in the equilibria consequent upon changes in temperature during filtration.

Based on the earlier investigations it was decided to adopt filtration under suction through IG_4 sintered glass crucibles to eliminate the colloidal component[108,188,215]. In order to bring about this filtration at 37°C, a thermally insulated wooden cabin, specially prepared for the purpose and maintained at 37±0.5°C was used. Heating to the required temperature was done by a couple of 200 watt incandescent bulbs positioned appropriately inside the cabin. The temperature was maintained uniform using an electric fan fabricated specially for the purpose and run at a regulated speed.

An assembly fitted with a $1G_4$ sintered glass crucible suitable for the filtration under suction was housed inside this cabin. A desired volume of the filtrate from each one

of the equilibrated systems could thus be collected and preserved at 37±0.5°C for the subsequent microanalytical determinations.

3.2.2.3 Chemial analysis of the saturated solutions of the samples.

It is evident that for evaluation of solubility products of SPA, SAA and a series of their solid solutions, their saturated solutions are to be analyzed for the activities of strontium, phosphorus, arsenic and hydroxyl ions. While phosphorus and arsenic could be determined spectrophotometrically, strontium could be estimated using atomic absorption spectroscopy. A knowledge of the pH of the saturated solution enabled an evaluation of the OH^- ion activity.

The following is an account of the necessary details of these estimations.

(A) Determination of OH^- ion.

The pH of each one of the systems set up for the determination of the solubility product of the sample was measured after attainment of saturation. It is evident that the relationship, pH+pOH = pKw, is valid for all the aqueous systems where pKw represents the negative logarithm of the ionic product of water Kw, at the temperature of equilibration, 37°C and the OH^- activity could be calculated from a knowledge of the pH of the solution.

A simple and convenient method of determination of concentrations of the remaining ions was provided by the chemical analysis of the saturated solutions of the sample and hence was adopted for the purpose. In the light of the likely interference in the quantitative analysis of systems containing strontium, phosphorus and arsenic, it became essential to modify appropriately the available micro-analytical methods for the quantitative determinations of these ions so that they could be used when the three were present together.

From an aliquot of each one of the filtrates of the systems, strontium^{82} was first determined by atomic absorption spectrometry in the presence of phosphate and arsenate after appropriate masking of the interfering ions. Phosphate^{280} could then be determined spectrophotometrically in the presence of strontium and arsenate. Strontium did not interfere in this estimation since it was carried out in an acidic medium. The interference due to arsenate could be avoided by masking it through the addition of excess of sodium thiosulphate. In a third aliquot of each one of the filtrates molybdenum blue was formed as usual, the solution being subjected to heating on a water-bath for 15 minutes for an expeditious reduction of the heteropoly acids formed. From the extinction of this solution the combined amount of phosphorus and arsenic in the aliquot could be obtained. From a knowledge of the contribution of phosphorus to this extinction,

obtained separately from a calibration curve representing the relationship between the amount of phorphorus and the absorbance under identical conditions, the amount of arsenic could be calculated[280]. The determination of phosphate and arsenate was based on the reaction of the corresponding ortho acids with molybdic acid which resulted in the formation of the heteropolyacids; molybdenum blue formed by the reduction of the latter was determined spectrophotometrically.

B. **Determination of Phosphorus and Arsenic**

The following solutions were prepared for these determinations:-

(a) Ammonium molybdate solution.

About 66g of ammonium molybdate were dissolved in boiling water, cooled and made up to 1 litre.

(b) Ferrous ammonium sulphate solution.

About 3.5g of ferrous ammonium sulphate, $Fe(SO_4)(NH_4)_2SO_4.6H_2O$, were treated successively with about 150ml of water and about 10ml of sulphuric acid (sp.gr. 1.84) and the resulting solution was made upto 250ml, the solution being freshly prepared for each set of determinations.

(c) Approximately 7.5N sulphuric acid.

To about 500ml of water, 210ml of sulphuric acid (sp.gr. 1.84) were added and the resulting solution was made up to 1 litre.

(d) Standard phosphate solutions.

1 litre of a standard solution of potassium dihydrogen phosphate, KH_2PO_4, containing 0.4387 g of it

was prepared, the amount taken being such that each ml of this solution contained 100γ of phosphorus.

(e) Standard arsenate solution.

Approximately 0.50g of disodium hydrogen arsenate $Na_2HAsO_4.7H_2O$ was dissolved in water and the volume was made up to 1 litre, the arsenate content being determined iodometrically. A definite volume of the above mentioned solution was diluted so that each ml contains 100γ of arsenate.

(f) Sodium thiosulphate solution.

Approximately 0.05N sodium thiosulphate solution was prepared by taking about 12g of the salt per litre of the solution. The normality desired for the estimations was obtained by diluting 20ml of this solution to 1 litre.

For obtaining a calibration curve representing the relationship between the amount of phosphorus and the absorbance, about ten systems (Set. No.1) were set up within the concentration range, 20 to 200γ. In each system an appropriate volume of the stock solution of phosphorus was treated successively with 10ml of 7.5N sulphuric acid, 20ml of sodium thiosulphate solution and 10ml each of ammonium molybdate and ferrous ammonium sulphate solutions. The resulting solution was made up to 100 ml, 10 minute after the addition of the reducing agent. The absorbance was measured against a blank at 825 nm using a spectrophotometer (Beckmann Model-26), the cell width being 1.0cm.

For obtaining the calibration curve representing the relationship between the amount of arsenic and the absorbance

a set of systems (Set No. II) identical with the one mentioned above was chosen, the difference being the absence of thiosulphate solution which was intended to mask the contribution of arsenic to the color reaction. Each one of these systems was set up in a 250ml capacity polyethylene beaker and before making up to 100ml, it was heated on a water bath for 15 minutes, cooled, transferred to a standard 100ml measuring flask made up to the mark and the absorbance measured as in the case of phosphorus.

In order to know the contribution of phosphorus to the total absorbance obtained after subjecting the systems to heating, systems of set No. I were set up once again (Set No.III) the absorbance this time being measured by bringing about the color reaction at 100°C as in the case of the arsenic system (Set No. II). The suitability of the procedure was scrutinized by taking a few representative sample solutions containing known amounts of phosphorus and arsenic. In addition the absence of interference due to the presence of strontium and the buffer ingredients was also scrutinized.

Having obtained these calibration curves, two separate convenient volumes of the filtered saturated solutions of each one of the samples of apatite was subjected to the procedure adopted for Sets I and II. It is evident that the absorbance values obtained coupled with the calibration curves of Sets. I, II and III could provide the amount of phosphorus and arsenic present in the saturated solutions of the samples.

C. Determination of Strontium

The following stock solution was prepared: 0.2415g of strontium nitrate dried previously to constant weight at 110°C was accurately weighed, made up to 1 litre. The resulting solution contains 0.1g of strontium per litre which amounts to 0.1 mg of strontium per ml. The strength of the solution so prepared was scrutinized by titrating it against standard 0.001M EDTA solution using Eriochrome black T as indicator maintaining the solution at pH~10. The estimated amount was found to tally with the amount taken.

Using a Perkin Elmer Model No. 297 atomic absorption spectrophotometer the absorbance of the resulting solution was measured at a few chosen concentrations within the range of applicability of Beer-Lamberts law. Since the upper limit of these estimation was found to be 10 ppm care was taken to see that each one of the system chosen had strontium concentration much less than the upper limit.

A correction is to be made for the interference of phosphorus and arsenic in the determination of strontium. For this purpose exactly measured volumes of stock solutions of phosphorus and arsenic prepared as described earlier were added to each one of the systems. Care was taken to see that the ratio between the number of g atoms of strontium present in each system and the total number of g atoms of P and As is equal to the stoichiometric ratio of 1.67.

In order to mask the presence of phosphorus in each

system exactly weighed amounts of 0.5g of KCl and 1g of $LaCl_3$ were added as recommended. Air-acetylene flame was used for atomization of the sample. The absorbance was recorded using a radiation of wavelength 460.7nm. The plot between the amount of strontium taken and the absorbance was found to be linear within the concentration range investigated and served as the calibration curve. The strontium content of the saturated solutions of apatites could be determined after measuring the absorbance on the atomic absorption spectrophotometer.

3.2.2.4 Further purification of Solutes by Equilibration with EDTA

In accordance with the procedure adopted by earlier workers[203] and also keeping in view the fact that trace impurities present in the solutes can markedly vitiate solubility data, about 3 g of each sample were subjected to equilibration in polyethylene containers using a mechanical shaker for about 6 hours with a 2 percent solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide as buffer combination. The samples were subsequently washed repeatedly with double-distilled water till the washings were free from accompanying ions and dried at 110°C.

3.2.2.5 Equilibration Period for Attainment of Saturation

The initial investigations on the solubility of the samples were intended to establish the kinetics of dissolution and to determine the optimum period required for the

attainment of saturation. The investigations were carried out at a couple of pH values representing the acidic and alkaline regions respectively using SPA, SAA and a representative solid solution of them (S. No. 3 of Table 2.4) as solutes. The systems were equilibrated as mentioned earlier. While the strontium content of the filtrate was determined by atomic absorption spectrometry, the amounts of phosphate and arsenate were determined spectrophotometrically as mentioned earlier. The dissolution kinetic studies could be extended in each case to a total duration of about 24 hours by setting up about 10 identical systems, equilibration of each system being interrupted at convenient time-intervals. Equilibration time required for the attainment of saturation, a duration of 12 hours, which was considerably higher than the optimum period determined, was chosen as period of equilibration throughout the investigations.

3.2.2.6 Determination of Solubility

The solubilities of each one of the samples of apatites was determined at about 10 individual pH values in the range, 5.6 to 8.0. From each set of determinations the solubility product, Ksp, was calculated. Care was taken to see that the total experimentally determined activities of P and As were sub-divided into the respective ionic species to be formed by the dissociation of the corresponding ortho acids. The activities of the relevant ionic species needed for the calculation of Ksp of the apatite phase were chosen from the experimentally determined values and the

solubility products were calculated. In order to eliminate the effect, if any, of the presence of the buffer ingredients on the calculated solubility product, a set of investigations on the solubilities of the samples was carried out using exclusively 0.165M NaCl solution as the medium of dissolution.

Table 3.1 *Dissolution kinetics of* $Sr_{10}(PO_4)_6(OH)_2$ *in an acidic medium.*

Solute: 0.1g of $Sr_{10}(PO_4)_6(OH)_2$ (Sample No.1 of Table 2-4) washed with a 2% solution of EDTA maintained at a pH~10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 100 ml of a buffer consisting of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 with respect to NaCl

Temperature: 37±0.5°C

S. No.	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre)		g atom ratio, Sr/P
			Sr $\times 10^{+3}$	P $\times 10^{+3}$	
(1)	(2)	(3)	(4a)	(4b)	(5)
1	0.17	5.59	2.85	1.65	1.72
2	0.33	5.62	3.05	1.86	1.64
3	0.50	5.60	3.15	1.93	1.63
4	0.75	5.60	3.23	1.96	1.68
5	1.00	5.62	3.30	1.97	1.67
6	1.50	5.62	3.50	2.16	1.62
7	2.00	5.62	3.98	2.37	1.68
8	2.50	5.61	4.10	2.41	1.70
9	3.00	5.62	4.23	2.52	1.68
10	4.00	5.62	4.50	2.68	1.68
11	6.00	5.60	4.48	2.60	1.72
12	12.00	5.60	4.50	2.65	1.69
13	24.00	5.50	4.48	2.63	1.70

Table 3.2 Dissolution kinetics of $Sr_{10}(PO_4)_6(OH)_2$ in an alkaline medium

Solute : 0.1g of $Sr_{10}(PO_4)_6(OH)_2$ washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 100ml of a buffer consisting of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

S. No.	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre)		g atom ratio, Sr/P
			Sr $\times 10^{+3}$	P $\times 10^{+4}$	
(1)	(2)	(3)	(4a)	(4b)	(5)
1	0.17	7.80	0.06	0.36	1.65
2	0.33	7.82	0.10	0.62	1.62
3	0.50	7.83	0.15	0.86	1.74
4	0.75	7.82	0.18	1.05	1.72
5	1.00	7.85	0.20	1.19	1.68
6	1.50	7.83	0.22	1.34	1.64
7	2.00	7.82	0.24	1.42	1.69
8	2.50	7.83	0.26	1.59	1.63
9	3.00	7.83	0.26	1.52	1.65
10	4.00	7.85	0.25	1.51	1.65
11	6.00	7.83	0.25	1.52	1.64
12	12.00	7.85	0.24	1.50	1.60
13	24.00	7.83	0.26	1.52	1.71

Table 3.3 Dissolution kinetics of a representative solid solution of strontium phosphate apatite and strontium arsenateapatite in an acidic medium.

Solute : 0.2g of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$ (Sample No.4 of Table 2-4) washed with a 2% solution of EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 100ml of a buffer consisting of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

S. No	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+3}$	g atom ratio, Sr/(P+As)
(1)	(2)	(3)	(4a)	(4b)	(4c)	(5)
1	0.25	5.43	4.56	1.71	0.89	1.75
2	0.75	5.50	4.78	1.76	0.92	1.78
3	1.00	5.50	4.89	1.78	0.98	1.76
4	1.75	5.50	4.96	1.88	1.13	1.64
5	2.50	5.50	5.08	1.81	1.35	1.61
6	4.00	5.50	4.72	1.81	0.98	1.69
7	6.00	5.50	4.89	1.86	1.13	1.63
8	12.00	5.49	4.96	1.81	1.12	1.69
9	2.400	5.47	4.96	1.81	1.13	1.68

Table 3.4 Dissolution kinetics of a representative solid solution of strontium phosphate apatite and strontium arsenateapatite in an alkaline medium.

Solute : 0.1g of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$ (Sample No.4 of Table 2-4) washed with a solution of 2% EDTA maintained at pH 10 using ammonium chloride-ammonium hydroxide on buffer combination.

Dissolving medium : 100ml of a buffer consisting of boric acid-borax brought to a molarity of 0.165with respect to NaCl.

Temperature: 37±0.5°C

S. No	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre)			g atom ratio, Sr/(P+As).
			Sr $\times10^{+3}$	P $\times10^{+3}$	As $\times10^{+4}$	
(1)	(2)	(3)	(4a)	(4b)	(4c)	(5)
1	0.25	7.20	0.40	0.16	0.74	1.66
2	0.50	7.21	0.44	0.16	0.98	1.73
3	0.75	7.10	0.46	0.18	0.97	1.68
4	1.00	7.13	0.49	0.21	0.82	1.67
5	2.00	7.13	0.57	0.25	0.99	1.64
6	4.00	7.18	0.62	0.26	1.16	1.65
7	6.00	7.14	0.60	0.25	1.12	1.65
8	12.00	7.15	0.60	0.26	0.94	1.71
9	24.00	7.17	0.57	0.26	0.89	1.64

Table 3.5 Dissolution kinetics of $Sr_{10}(AsO_4)_6(OH)_2$ in an acidic medium.

Solute : 0.1g of $Sr_{10}(AsO_4)_6(OH)_2$ (Sample No.8 of Table 2-4) washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 100ml of a buffer consisting of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

S. No.	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre)		g atom ratio, Sr/As
			Sr $\times 10^{+3}$	As $\times 10^{+3}$	
(1)	(2)	(3)	(4a)	(4b)	(5)
1	0.17	6.60	4.49	2.82	1.59
2	0.33	6.60	5.00	2.92	1.71
3	0.50	6.62	5.21	2.96	1.76
4	0.75	6.59	5.63	3.19	1.76
5	1.00	6.61	5.99	3.47	1.72
6	1.50	6.62	6.13	3.61	1.69
7	2.00	6.63	6.13	3.56	1.71
8.	2.50	6.62	5.85	3.61	1.61
9.	3.00	6.61	5.71	3.54	1.61
10	4.00	6.62	5.49	3.56	1.54
11	6.00	6.63	5.99	3.52	1.70
12	12.00	6.62	6.06	3.61	1.68
13	24.00	6.62	6.13	3.61	1.69

Table 3.6 Dissolution kinetics of $Sr_{10}(AsO_4)_6(OH)_2$ in an alkaline medium.

Solute : 0.1g of $Sr_{10}(AsO_4)_6(OH)_2$ (Sample No.8 of Table 2.4) washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 100ml of a buffer consisting of boric acid and borax brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

S. No.	Period of equilibration (hours)	Final pH	Measured conc. (g atoms/litre)		g atom ratio, Sr/As
			Sr $\times 10^{+3}$	As $\times 10^{+3}$	
(1)	(2)	(3)	(4a)	(4b)	(5)
1	0.17	7.50	0.80	0.44	1.80
2	0.33	7.53	1.00	0.52	1.92
3	0.50	7.55	1.40	0.82	1.71
4	0.75	7.54	1.60	1.00	1.60
5	1.00	7.50	1.75	1.09	1.60
6	1.50	7.51	1.80	1.18	1.53
7	2.00	7.53	1.95	1.21	1.61
8	2.50	7.55	2.30	1.44	1.59
9	3.00	7.55	2.65	1.60	1.67
10	4.00	7.55	2.80	1.69	1.65
11	6.00	7.54	2.79	1.65	1.70
12	12.00	7.54	2.78	1.61	1.73
13	24.00	7.54	2.70	1.69	1.59

Table 3.7 pH-dependence of the solubility equilibria of strontium phosphate apatite(SPA)

Solute : 0.1g of $Sr_{10}(PO_4)_6(OH)_2$ (Sample No.1 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 50ml of an appropriate buffer combination of Potassium acid phthalate sodium hydroxide or boric acid-borax maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

Dissociation constants of

H_3PO_4: $K_1=7.51\times10^{-3}$, $K_2=6.33\times10^{-8}$ and $K_3 = 4.75\times10^{-13}$

PART A

S. No	Final pH	Measured conc.(g atoms/l)		g atom ratio,	Calculated conc. (g ions/l)			
		Sr $\times10^{+3}$	P $\times10^{+3}$	Sr/P	H_3PO_4* $\times10^{+4}$	$H_2PO_4^-$ $\times10^{+5}$	HPO_4^{2-} $\times10^{+5}$	PO_4^{3-} $\times10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	5.65	4.49	2.65	1.69	769.37	258.11	7.26	1.54
2	5.78	4.28	2.58	1.65	549.76	248.80	9.49	2.71
3	5.92	3.42	2.08	1.64	316.32	197.60	10.40	4.09
4	6.03	2.71	1.67	1.62	194.10	156.20	10.60	5.37
5	7.46	0.57	0.32	1.76	0.53	11.42	20.85	284.60
6	7.52	0.39	0.23	1.71	0.30	7.41	15.53	253.44
7	7.65	0.36	0.22	1.65	0.17	5.62	15.89	336.00
8	7.75	0.28	0.17	1.61	0.09	3.77	13.43	357.50
9	7.85	0.26	0.16	1.62	0.05	2.28	12.90	432.15
10	7.95	0.25	0.14	1.74	0.03	2.20	12.13	500.24

*Conc. in moles/litre.

Table 3.7 - PART B

S. No	Phases expected to be formed and their ionic products							
	$Sr_{10}(PO_4)_6(OH)_2$		$(SrHPO_4)$		$Sr_2(HPO_4)(OH)_2$		$Sr(HPO_4)_2$	
	Kip	pKip	Kip	pKip	Kip	pKip	Kip	pKip
(1)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
1	7.6×10^{-105}	104.1	3.3×10^{-7}	6.5	2.4×10^{-25}	24.6	3.0×10^{-8}	7.5
2	2.4×10^{-103}	102.6	4.1×10^{-7}	6.4	5.2×10^{-25}	24.3	2.6×10^{-8}	7.6
3	6.0×10^{-103}	102.2	3.6×10^{-7}	6.4	7.0×10^{-25}	24.1	1.3×10^{-8}	7.9
4	4.9×10^{-103}	102.3	2.9×10^{-7}	6.5	7.4×10^{-25}	24.1	6.6×10^{-9}	8.2
5	1.3×10^{-96}	95.9	1.2×10^{-7}	6.9	4.7×10^{-23}	22.3	7.4×10^{-12}	11.1
6	1.6×10^{-98}	97.8	6.1×10^{-8}	7.2	2.2×10^{-23}	22.7	2.2×10^{-12}	11.6
7	7.9×10^{-98}	97.1	5.7×10^{-8}	7.2	3.4×10^{-23}	22.4	1.1×10^{-12}	11.9
8	1.5×10^{-98}	97.8	3.7×10^{-8}	7.4	2.7×10^{-23}	22.6	3.9×10^{-13}	12.4
9	3.4×10^{-98}	97.5	3.3×10^{-8}	7.4	3.5×10^{-23}	22.4	2.1×10^{-13}	12.7
10	9.3×10^{-98}	97.0	3.0×10^{-8}	7.5	4.8×10^{-23}	22.3	1.2×10^{-13}	12.9
		Average = 99.4						

Table 3.8 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$ (Sample No.2 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.75 \times 10^{-13}$

(ii) H_3AsO_4: $K_1' = 4.0 \times 10^{-3}$, $K_2' = 1.0 \times 10^{-7}$ and $K_3' = 3.2 \times 10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+4}$	g atom ratio, Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times 10^{+9}$	$H_2PO_4^-$ $\times 10^{+5}$	HPO_4^{2-} $\times 10^{+5}$	PO_4^{3-} $\times 10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	5.79	3.59	1.99	2.21	1.62	413.52	191.48	7.47	2.18
2	5.83	3.47	1.94	2.15	1.61	365.78	185.72	7.94	2.54
3	6.01	2.96	1.61	1.79	1.65	197.24	151.58	9.81	4.75
4	6.19	2.83	1.56	1.64	1.64	122.16	142.10	13.92	10.21
5.	7.50	0.54	0.29	0.32	1.68	0.42	9.86	19.73	295.24
6	7.56	0.46	0.26	0.25	1.61	0.36	3.52	22.29	383.06
7	7.76	0.42	0.23	0.23	1.66	0.12	5.05	10.58	500.94
8	7.84	0.38	0.20	0.23	1.70	0.08	2.21	18.22	596.55
9	7.92	0.34	0.19	0.15	1.66	0.05	3.09	16.27	640.64
10	8.00	0.30	0.16	0.11	1.75	0.03	2.07	13.15	622.29

*Conc. in moles/l

Table 3.8 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $\times 10^{+10}$	$H_2AsO_4^-$ $\times 10^{+5}$	$HAsO_4^{2-}$ $\times 10^{+5}$	AsO_4^{3-} $\times 10^{+11}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	844.20	20.81	1.28	2.53	1.3×10^{-104}	103.8
2	745.09	20.15	1.36	2.95	2.8×10^{-104}	103.6
3	397.27	16.26	1.66	5.45	5.6×10^{-103}	102.3
4	229.46	14.22	2.20	10.91	7.7×10^{-101}	100.1
5	0.62	0.78	2.49	252.19	1.3×10^{-96}	95.9
6	0.38	0.54	1.99	231.55	1.2×10^{-96}	95.9
7	0.15	0.34	1.98	363.90	6.5×10^{-96}	95.2
8	0.10	0.29	1.98	439.01	9.4×10^{-96}	95.0
9	0.49	0.16	1.35	361.09	5.5×10^{-96}	95.2
10	0.26	0.10	1.28	329.21	1.6×10^{-96}	95.8
					Average	= 98.3

*Conc. in moles/l.

Table 3.9 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$ (Sample No.3 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax) maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.75 \times 10^{-13}$

(ii) H_3AsO_4: $K_1 = 4.0 \times 10^{-3}$, $K_2 = 1.0 \times 10^{-7}$ and $K_3 = 3.2 \times 10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+4}$	g atom ratio Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times 10^{+9}$	$H_2PO_4^-$ $\times 10^{+5}$	HPO_4^{2-} $\times 10^{+5}$	PO_4^{3-} $\times 10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	5.59	3.09	1.67	1.61	1.69	556.87	162.71	4.01	0.74
2	5.68	3.00	1.61	1.56	1.70	435.73	156.63	4.74	1.07
3	5.86	2.53	1.40	1.42	1.64	245.82	133.74	6.13	2.10
4	5.98	2.03	1.14	1.24	1.61	150.02	107.60	6.50	2.94
5	7.49	0.59	0.30	0.58	1.65	0.43	10.10	19.58	286.30
6	7.56	0.55	0.27	0.56	1.69	0.29	8.15	18.74	322.02
7	7.78	0.51	0.24	0.45	1.78	0.11	5.03	19.18	546.88
8	7.87	0.42	0.22	0.44	1.60	0.07	3.78	17.73	622.24
9	7.94	0.38	0.20	0.40	1.58	0.05	3.05	16.84	694.20
10	8.00	0.34	0.19	0.21	1.61	0.03	2.54	16.67	760.80

*Conc. in moles/l.

Table 3.9 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $X10^{+10}$	$H_2AsO_4^-$ $X10^{+5}$	$HAsO_4^{2-}$ $X10^{+5}$	AsO_4^{3-} $X10^{+11}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	997.04	15.52	0.60	0.75	$1.6x10^{-108}$	107.7
2	775.81	14.85	0.71	1.09	$1.8x10^{-107}$	106.2
3	457.71	13.26	0.96	2.22	$4.5x10^{-106}$	105.3
4	297.17	11.35	1.08	3.31	$6.9x10^{-106}$	105.1
5	1.16	1.14	4.41	436.67	$5.2x10^{-96}$	95.3
6	0.83	1.20	4.36	506.73	$6.3x10^{-96}$	95.2
7	0.27	0.64	3.90	751.08	$1.5x10^{-94}$	93.82
8	0.18	0.53	3.93	932.10	$9.2x10^{-95}$	94.03
9	0.11	0.41	3.58	999.82	$8.0x10^{-95}$	94.05
10	0.05	0.19	1.95	625.28	$2.3x10^{-95}$	94.64
						Average= 97.0

*Conc. in moles/l.

Table 3.10 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$ (Sample No.4 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax) maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.75 \times 10^{-13}$

(ii) H_3AsO_4: $K_1' = 4.0 \times 10^{-3}$, $K_2' = 1.0 \times 10^{-7}$ and $K_3' = 3.2 \times 10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+4}$	g atom ratio Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times 10^{+9}$	$H_2PO_4^-$ $\times 10^{+5}$	HPO_4^{2-} $\times 10^{+5}$	PO_4^{3-} $\times 10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	5.92	3.51	1.82	2.69	1.68	276.99	173.00	9.11	3.58
2	6.13	3.07	1.50	2.12	1.79	136.71	138.50	11.82	7.54
3	6.25	2.19	1.21	1.57	1.60	8.17	109.13	12.28	10.33
4	6.34	1.97	1.07	1.52	1.61	57.19	93.96	13.01	13.46
5	7.42	0.61	0.29	0.66	1.71	0.56	11.05	18.39	228.97
6	7.48	0.57	0.26	0.66	1.74	0.37	9.13	17.45	249.45
7	7.66	0.53	0.25	0.53	1.74	0.19	6.53	18.90	408.90
8	7.78	0.48	0.23	0.43	1.75	0.11	4.80	18.32	522.50
9	7.85	0.44	0.21	0.41	1.75	0.07	3.90	17.48	585.78
10	7.95	0.39	0.19	0.33	1.74	0.04	2.87	16.20	683.45

*Concl. in moles/l.

Table 3.10 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $\times 10^{+10}$	$H_2AsO_4^-$ $\times 10^{+5}$	$HAsO_4^{2-}$ $\times 10^{+5}$	AsO_4^{3-} $\times 10^{+11}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	803.19	26.72	2.22	5.92	8.6×10^{-103}	102.1
2	346.81	18.71	2.52	10.89	4.1×10^{-101}	100.3
3	187.72	13.35	2.37	13.51	3.5×10^{-101}	100.4
4	142.00	12.48	2.73	19.12	4.0×10^{-101}	100.4
5	1.73	1.82	4.78	403.12	1.8×10^{-96}	95.8
6	1.35	1.63	4.94	477.95	2.1×10^{-96}	95.7
7	0.52	0.95	4.32	632.91	2.9×10^{-95}	94.5
8	0.26	0.62	3.71	715.48	7.4×10^{-95}	94.1
9	0.18	0.51	3.60	817.50	8.1×10^{-95}	94.1
10	0.09	0.33	3.01	859.60	9.4×10^{-95}	94.0
						Average = 97.1

*Conc. in moles/l.

Table 3.11 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$ (Sample No.5 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax) maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.75 \times 10^{-13}$

(ii) H_3AsO_4: $K_1' = 4.0 \times 10^{-3}$, $K_2' = 1.0 \times 10^{-7}$ and $K_3' = 3.2 \times 10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+4}$	g atom ratio Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times 10^{+9}$	$H_2PO_4^-$ $\times 10^{+5}$	HPO_4^{2-} $\times 10^{+5}$	PO_4^{3-} $\times 10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	5.84	4.21	1.14	1.49	1.60	210.17	109.19	4.78	1.56
2	6.11	3.47	0.88	1.15	1.71	84.04	81.36	6.63	4.04
3	6.29	3.07	0.79	1.04	1.68	48.16	70.53	8.70	8.03
4	6.48	2.72	0.69	0.91	1.70	25.83	58.58	11.20	16.00
5	7.37	1.09	0.19	0.45	1.70	0.44	7.75	11.49	12.75
6	7.47	1.01	0.17	0.41	1.74	0.27	5.98	11.17	156.07
7	7.65	0.97	0.19	0.40	1.64	0.15	4.89	13.83	292.27
8	7.77	0.79	0.15	0.32	1.68	0.07	3.18	11.86	330.62
9	7.85	0.57	0.11	0.21	1.78	0.04	2.11	9.48	317.67
10	7.95	0.53	0.12	0.20	1.65	0.03	1.79	10.09	425.53

*Conc. in moles/litre.

Table 3.11 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $\times 10^{+10}$	$H_2AsO_4^-$ $\times 10^{+5}$	$HAsO_4^{2-}$ $\times 10^{+5}$	AsO_4^{3-} $\times 10^{+11}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	77.97	40.17	5.17	21.33	7.4×10^{-101}	100.1
2	197.66	101.85	13.12	5.40	1.0×10^{-98}	97.9
3	111.19	86.72	16.91	10.55	4.0×10^{-97}	96.4
4	58.02	70.08	21.16	20.45	1.6×10^{-95}	94.7
5	143.23	13.43	31.48	236.20	1.0×10^{-91}	91.0
6	0.88	10.39	30.68	289.81	2.3×10^{-91}	90.6
7	0.41	7.27	3.24	464.47	8.8×10^{-90}	89.1
8	0.19	4.64	27.33	515.05	4.0×10^{-90}	89.4
9	0.09	2.66	18.88	427.90	1.0×10^{-91}	90.9
10	0.06	2.03	18.17	518.37	3.9×10^{-91}	90.4
					Average =	93.0

* Conc. in moles/litres

Table 3.12 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$ (Sample No.6 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium: 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.75 \times 10^{-13}$

(ii) H_3AsO_4: $K_1' = 4.0 \times 10^{-3}$, $K_2' = 1.0 \times 10^{-7}$ and $K_3' = 3.2 \times 10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	P $\times 10^{+3}$	As $\times 10^{+3}$	g atom ratio Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times 10^{+9}$	$H_2PO_4^-$ $\times 10^{+5}$	HPO_4^{2-} $\times 10^{+5}$	PO_4^{3-} $\times 10^{+11}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	6.14	5.54	1.30	2.09	1.63	115.11	119.34	10.43	6.81
2	6.21	5.34	1.25	2.00	1.64	92.77	113.01	11.60	8.90
3	6.53	4.54	0.96	1.62	1.72	31.15	79.21	16.99	27.25
4	6.70	2.93	0.66	1.06	1.70	13.54	50.37	16.13	38.35
5	7.37	1.04	0.24	0.39	1.65	0.56	9.87	14.65	162.54
6	7.45	1.02	0.23	0.38	1.67	0.40	8.58	15.30	204.16
7	7.62	1.00	0.22	0.36	1.72	0.20	6.20	16.38	323.12
8	7.72	0.83	0.20	0.32	1.60	0.11	4.63	15.38	382.04
9	7.80	0.79	0.17	0.28	1.75	0.07	3.57	14.26	425.84

*Conc. in moles/litre.

Table 3.12 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $x10^{+9}$	$H_2AsO_4^-$ $x10^{+5}$	$HAsO_4^{2-}$ $x10^{+5}$	AsO_4^{3-} $x10^{+10}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	332.22	183.44	25.32	11.18	$5.3x10^{-94}$	93.0
2	266.89	173.13	28.09	14.58	$2.5x10^{-94}$	93.0
3	89.21	120.98	41.02	44.49	$7.2x10^{-91}$	90.1
4	35.36	70.37	35.45	57.00	$2.6x10^{-91}$	90.5
5	1.25	11.80	27.66	207.54	$3.2x10^{-91}$	90.5
6	89.29	10.06	28.37	255.93	$1.4x10^{-90}$	89.9
7	0.42	7.03	29.32	391.23	$3.4x10^{-89}$	88.5
8	0.25	5.15	27.04	454.25	$2.2x10^{-89}$	88.6
9	0.15	3.92	24.75	499.77	$1.8x10^{-89}$	88.7
						Average = 90.3

* Conc. in moles/Litre

Table 3.13 pH-Dependence of the solubility equilibria of a solid solution of strontium phosphate apatite(SPA) and strontium arsenate apatite(SAA).

Solute :0.1g of $Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$ (Sample No.7 of Table 2.4) washed with a solution of 2% EDTA maintained at a pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 50ml of an appropriate buffer combination of potassium acid phthalate-sodium hydroxide or boric acid-borax) maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5C

Dissociation constants of

(i) H_3PO_4: $K_1 = 7.51\times10^{-3}$, $K_2=6.33\times10^{-8}$ and $K_3 = 4.75\times10^{-13}$

(ii) H_3AsO_4: $K_1'=4.0\times10^{-3}$, $K_2'=1.0\times10^{-7}$ and $K_3' = 3.2\times10^{-12}$

PART A

S. No.	Final pH	Measured conc. (g atom/l) Sr $\times10^{+3}$	P $\times10^{+3}$	As $\times10^{+3}$	g atom ratio Sr/(P+As)	Calculated conc. (g ions/l) H_3PO_4* $\times10^{+10}$	$H_2PO_4^-$ $\times10^{+5}$	HPO_4^{2-} $\times10^{+5}$	PO_4^{3-} $\times10^{+10}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	6.49	7.76	0.77	3.97	1.64	279.35	64.77	12.64	1.84
2	6.60	7.40	0.52	3.81	1.70	139.56	41.73	10.51	1.98
3	6.82	6.24	0.34	3.27	1.73	48.38	24.00	10.03	3.13
4	7.08	5.35	0.28	2.96	1.65	17.71	15.99	12.17	6.92
5	7.36	4.81	0.25	2.61	1.68	6.13	10.54	15.28	16.56
6	7.52	3.63	0.17	2.00	1.67	2.28	5.69	11.92	18.67
7	7.56	3.42	0.15	1.82	1.73	1.69	4.26	10.63	18.26
8	7.71	3.48	0.14	1.96	1.66	0.85	3.29	10.70	25.97
9	7.78	2.13	0.18	1.10	1.66	0.83	3.77	14.41	41.09
10	7.85	2.07	0.20	1.04	1.67	0.68	3.63	16.26	54.49
11	7.94	1.75	0.15	0.88	1.69	0.36	2.33	12.83	52.88

*Conc. in moles/litre.

Table 3.13 - PART B

S. No	Calculated conc. (g ions/l)				Ionic product of the solute	
	H_3AsO_4* $x10^{+9}$	$H_2AsO_4^-$ $x10^{+5}$	$HAsO_4^{2-}$ $x10^{+5}$	AsO_4^{3-} $x10^{+9}$	Kip	pKip
(1)	(11)	(12)	(13)	(14)	(15)	(16)
1	245.07	303.55	93.62	9.25	$7.9x10^{-86}$	85.1
2	171.25	272.70	108.58	138.29	$6.5x10^{-85}$	84.2
3	74.52	196. 96	130.14	27.51	$1.6x10^{-83}$	82.8
4	27.95	134.40	161.58	62.16	$1.4x10^{-81}$	80.8
5	23.23	212.89	48.77	357.54	$2.1x10^{-79}$	78.7
6	3.52	46.59	1.54	163.49	$7.9x10^{-79}$	79.1
7	2.70	39.30	142.69	165.79	$5.4x10^{-80}$	79.3
8	1.56	31.98	164.01	269.18	$2.9x10^{-79}$	78.5
9	0.65	15.67	94.43	182.09	$4.8x10^{-81}$	80.3
10	0.45	12.85	91.02	206.21	$1.2x10^{-80}$	79.9
11	0.26	9.04	78.77	219.56	$4.6x10^{-81}$	80.3
						Average = 80.8

*Conc. in moles/l.

Table 3.14 pH-dependence of the solubility equilibria of strontium arsenate apatite(SAA)

Solute : 0.1g of $Sr_{10}(AsO_4)_6(OH)_2$ (Sample No.8, Table 2.4) washed with a solution of 2% EDTA maintained at pH 10 using ammonium chloride-ammonium hydroxide as buffer combination.

Dissolving medium : 50ml of an appropriate buffer combination of Potassium acid phthalate-sodium hydroxide or boric acid-borax maintained at a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C

Dissociation constants of H_3AsO_4 : $K_1' = 4.0 \times 10^{-3}$, $K_2' = 1.0 \times 10^{-7}$ and $K_3' = 3.2 \times 10^{-12}$

PART A

S. No	Final pH	Measured conc. (g atom/l) Sr $\times 10^{+3}$	Measured conc. (g atom/l) As $\times 10^{+3}$	g atom ratio, Sr/As	Calculated conc. (g ions/l) H_3AsO_4* $\times 10^{+4}$	$H_2AsO_4^-$ $\times 10^{+5}$	$HAsO_4^{2-}$ $\times 10^{+5}$	AsO_4^{3-} $\times 10^{+8}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	6.63	6.56	3.79	1.73	155.95	266.10	113.51	1.55
2	6.75	6.06	3.56	1.70	101.43	228.15	128.31	2.30
3	7.01	5.34	3.19	1.67	38.52	157.65	161.33	5.28
4	7.23	4.27	2.54	1.68	13.85	94.13	159.85	8.68
5	7.48	3.10	1.89	1.64	3.89	47.05	142.11	13.73
6	7.53	2.85	1.71	1.66	3.87	39.03	132.36	14.34
7	7.65	2.60	1.62	1.60	1.66	29.63	132.25	18.92
8	7.74	2.49	1.54	1.61	1.07	23.70	130.27	22.90
9	7.82	2.13	1.29	1.65	0.63	18.27	111.33	23.59
10	7.92	3.08	1.25	1.66	0.40	13.41	111.56	29.69

*Conc. in moles/l

Table 3.14 - PART B

S. No	Phases expected to be formed and their ionic products							
	$Sr_{10}(AsO_4)_6(OH)_2$		$Sr(HAsO_4)$		$Sr_2(HAsO_4)(OH)_2$		$Sr(H_2AsO_4)_2$	
	Kip	pKip	Kip	pKip	Kip	pKip	Kip	pKip
(1)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
1	3.10×10^{-83}	82.5	7.4×10^{-6}	5.1	7.4×10^{-22}	21.1	4.6×10^{-8}	7.3
2	2.7×10^{-82}	81.5	7.8×10^{-6}	5.1	1.2×10^{-21}	20.9	3.1×10^{-8}	7.5
3	3.6×10^{-80}	79.4	8.4×10^{-6}	5.0	3.9×10^{-21}	20.4	1.3×10^{-8}	7.8
4	1.6×10^{-77}	76.8	6.8×10^{-6}	5.2	6.9×10^{-21}	20.2	3.8×10^{-9}	8.4
5	4.2×10^{-79}	78.4	4.4×10^{-6}	5.4	1.3×10^{-20}	19.9	6.9×10^{-10}	9.2
6	2.9×10^{-79}	78.5	3.8×10^{-6}	5.4	1.8×10^{-20}	19.8	4.3×10^{-10}	9.4
7	1.1×10^{-78}	78.0	3.4×10^{-6}	5.5	2.2×10^{-20}	19.7	2.3×10^{-10}	9.6
8	3.4×10^{-78}	77.5	3.2×10^{-6}	5.4	2.9×10^{-20}	19.5	1.4×10^{-10}	9.9
9	1.2×10^{-78}	77.9	2.4×10^{-6}	5.6	2.9×10^{-20}	19.5	7.1×10^{-11}	10.1
10	5.9×10^{-78}	77.2	2.3×10^{-6}	5.6	3.6×10^{-21}	20.4	3.7×10^{-11}	10.4
	Average= 78.8							

Table 3.15 Ionic products and Free Energies of solution of SPA and SAA and their solid solutions.

S. No	Molecular Formula	pKip (average)	$G_{soln.}$ K.cals/mole
1	$Sr_{10}(PO_4)_6()^{(OH)_2}$	99.4	141.15
2	$Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$	98.3	139.65
3.	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$	97.1	138.04
4	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$	97.1	138.00
5	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$	93.0	132.20
6	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$	90.0	128.30
7	$Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$	80.8	114.80
8	$Sr_{10}(AsO_4)_6(OH)_2)$	78.8	111.95

Table 3.16 Solubility equilibria of strontium phosphate apatite (SPA) strontium arsenate apatite (SAA) and their solid solutions in 0.165M NaCl solution.

Solute : 0.1g each of SPA, SAA and six of their solid solutions.

Dissolving medium : 50 ml of 0.165M NaCl.

Temperature : 37±0.5°C

Dissociation constants of

(i) H_3PO_4: $K_1=7.51\times10^{-3}$, $K_2=6.33\times10^{-8}$ and $K_3=4.75\times10^{-13}$

(ii) H_3AsO_4: $K_1=4.0\times10^{-13}$, $K_2=1.0\times10^{-7}$ and $K_3=3.2\times10^{-12}$.

S No	Molecular Formula	Final pH	Measured conc.(g atoms/l) Sr $\times10^{+3}$	P 10^{+3}	As 10^{+3}	Calcuated Conc.(g ions/l) PO_4^{3-}	AsO_4^{3-}	g atom ratio, Sr/P+As	Kip	pKip
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	$Sr_{10}(PO_4)_6(OH)_2$	7.20	0.3849	0.2238	-	1.3527×10^{-9}	-	1.72	5.25×10^{102}	101.2
2	$Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$	7.10	0.7150	0.3948	0.0359	1.0429×10^{-9}	8.0536×10^{-10}	1.66	5.08×10^{-99}	98.2
3	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$	7.20	0.5288	0.2727	0.0419	7.2273×10^{-10}	2.5639×10^{-9}	1.68	1.69×10^{-99}	98.2
4	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$	7.20	0.6049	0.2504	0.1252	9.4063×10^{-10}	3.8945×10^{-9}	1.61	1.22×10^{-98}	97.9
5	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$	7.20	0.8525	0.2092	0.3138	7.8564×10^{-10}	9.7578×10^{-9}	1.63	5.22×10^{-95}	94.2
6	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$	7.20	1.0602	0.2321	0.3600	8.7198×10^{-10}	1.1194×10^{-8}	1.78	2.0809×10^{-93}	92.6
7	$Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$	7.20	2.8876	0.2976	1.4672	7.7518×10^{-10}	3.2943×10^{-8}	1.64	1.5979×10^{-85}	84.7
8	$Sr_{10}(AsO_4)_6(OH)_2$	7.30	1.9800	-	1.1578	-	4.9247×10^{-8}	1.71	4.3742×10^{-84}	83.3

3.3 Results

An easy reference to the vertical columns of all the Tables, desired for purposes of explaining the results, was facilitated by numbering them serially, the number being given in brackets at the top of each column.

Table 3.1 to 3.6 deal with the study of dissolution kinetics of SPA and SAA and a representative solid solution. The details of the solute and the dissolving medium were given at the top of each table. In addition, the three dissociation constants of orthophosphoric acid and orthoarsenic acid were given at the top of each table. The final pH of each system was given under column (3) while the measured concentrations of strontium, phosphorus and arsenic expressed as g atoms/litre were given in the subsequent 2-3 columns. The g atom ratios, Sr/(P+As), of the systems calculated from the measured concentrations are given in the subsequent column.

The period of equilibration in all the cases extended up to 24 hours within which a series of convenient time-intervals were chosen for determining the concentrations of the dissolved ions of the solute. From these concentrations the g atom ratio, Sr/(P+As), was calculated and given in the final column of each table. The final pH of all the systems of a given solute were found to be nearly the same as expected from the fact that the same buffer combination was used. As expected, the concentrations of the ionic species going into solution increased with time, the increase being rapid in

the beginning. An equilibration period of about twelve hours was found to lead to saturation in all the cases, the subsequent variations being within the ranges of experimental fluctuations. For all the time-intervals investigated for the given system the g atom ratio, Sr/(P+As), was found to be in close proximity of the stoichiometric value of 1.67 indicating that the dissolution is stoichiometric.

Tables 3.7 to 3.14 deal with the study of pH dependence of solubility equilibria of SPA, SAA and six of their solid solutions spread over the entire compositional range. Out of them, tables 3.7 and 3.14 are concerned with systems containing SPA and SAA as solutes respectively.

For purposes of reducing unwieldiness of the tables caused by a total of 16-17 columns they have been split into two parts such that the first nine columns come under part A while the remaining come under part B. Column (1) is repeated in part B to facilitate an easy reference to the concerned pH.

It is evident that, as given at the top, each table refers to a single sample as solute taken in a total of about ten systems, each system being maintained at a different pH. The pH range chosen in all the cases was found to range between 5.5 and 8.0. While the pH of each system and the strontium content are given under column (2) and (3) respectively, column (4) gives the phosphorus content for the SPA systems and As content for the SAA systems. The g atom ratio, Sr/P or Sr/As calculated is given in column (5). Column (6) to (9) contain

the concentrations in a g ions/litre of the corresponding undissociated orthoacids and of their dissociation products calculated from the measured phosphorus and arsenic contents respectively. The ionic product Kip of SPA and SAA could be calculated and given respectively in Tables 3.7 and 3.14 under column (10). Column (11) of the tables contains the corresponding pKip values calculated from the expression,

$$pKip = - \log Kip.$$

The following aspects were considered relevant in explaining the subdivision of total measured phosphorus and arsenic into the species, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and H_3AsO_4, $H_2AsO_4^-$ and AsO_4^{3-} respectively as given under columns (6) to (9) of the tables. Orthophosphoric[203,215] acid being a tribasic acid exhibits in its solution, when dissociated, the following equilibria:-

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad (3.3)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad (3.4)$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad (3.5)$$

It is evident that H^+ ion mentioned in the above equilibria exists as H_3O^+ ion in aqueous media. The total amount of phosphorus present in a solution of SPA, represented as P in column (4) of Tables 3.7 to 3.13 can be subdivided into (i) the undissociated acid and (ii) its dissociated ionic species ($H_2PO_4^-$), (HPO_4^{2-}) and (PO_4^{3-}), making use of the pH of the system and the three dissociation constants of the acid. Expression for the dissociation constants, K_1, K_2 and K_3

and their values at 37°C are given below:

$$K_1 = \frac{(H_2PO_4^-)\ (H^+)}{(H_3PO_4)} = 7.51 \times 10^{-3} \qquad (3.6)$$

$$K_2 = \frac{(HPO_4^{2-})\ (H^+)}{(H_2PO_4^-)} = 6.33 \times 10^{-8} \qquad (3.7)$$

$$K_3 = \frac{(PO_4^{3-})\ (H^+)}{(HPO_4^{2-})} = 4.73 \times 10^{-13} \qquad (3.8)$$

The quantities in brackets represent the activities of the species involved. The activity coefficients of these ions were considered to be unity in a 0.165M solution of NaCl as suggested by La Mer[191]. The concentration and activity of each ion are therefore considered to be the same, the solubility product, Ksp, and the corresponding ionic product, Kip, of each solute being therefore considered synanymous. The following is the method of calculation adopted for splitting up of the total measured concentration of phosphorus into the corresponding dissociation products, out of which the trivalent ortho ions are needed for calculation of Ksp. The total dissolved phosphorus in g atoms/litre is given by the expression,

$$P_{total} = (H_3PO_4)+(H_2PO_4^-)+(HPO_4^{2-})+(PO_4^{3-}) \qquad (3.9)$$

The quantities on the right hand side are the concentrations of the respective species, the first being expressed in moles/l and the rest in g ions/l. From equation 3-6 to 3-8 it can be shown that

$$H_3PO_4 = \frac{(P) \times (H^+)^3}{q} \qquad (3.10)$$

$$H_2PO_4^- = \frac{(P) \times 7.51\times10^{-3} \times (H^+)^2}{q} \quad (3.11)$$

$$HPO_4^{2-} = \frac{(P) \times 47.53 \times 10^{-11} \times (H^+)}{q} \quad (3.12)$$

$$PO_4^{3-} = \frac{(P) \times 224.9 \times 10^{-24}}{q} \quad (3.13a)$$

where

$$q = (H^+)^3 + 7.51\times10^{-3}(H^+)^2 + 47.53\times10^{-11}(H^+) + 224.9 \times 10^{-24} \quad (3.13b)$$

Table 3.14 contains results of similar calculations done in the case of orthoarsenic acid. Orthoarsenic acid being a tribasic acid exhibits in its aqueous solutions, when dissociated, the following equilibria.

$$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+ \quad (3.14)$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ \quad (3.15)$$

$$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+ \quad (3.16)$$

Analogous to the aspects mentioned in the context of dissociation of orthophosphoric acid the following expression can be arrived at in the case of the above equilibria:-

$$K_1' = \frac{(H_2AsO_4^-)(H^+)}{(H_3AsO_4)} = 4.0\times10^{-3} \quad (3.17)$$

$$K_2' = \frac{(HAsO_4^-)(H^+)}{(H_2AsO_4^-)} = 1.0\times10^{-7} \quad (3.18)$$

$$K_3' = \frac{(AsO_4^{3-})(H^+)}{(HAsO_4^{2-})} = 3.2\times10^{-12} \quad (3.19)$$

$$As_{total} = (H_3AsO_4) + (H_2AsO_4^-) + (HAsO_4^{2-}) + (AsO_4^{3-}) \quad (3.20)$$

$$(H_3AsO_4) = \frac{(As) \times (H^+)^3}{q'} \quad (3.21)$$

$$(H_2AsO_4^-) = \frac{(As) \times 4.0\times10^{-3} \times (H^+)^2}{q'} \quad (3.22)$$

$$(HAsO_4^{2-}) = \frac{(As) \times 4.0\times10^{-10} \times (H^+)}{q'} \quad (3.23)$$

$$(AsO_4^{3-}) = \frac{(As) \times 12.8 \times 10^{-22}}{q'} \quad (3.24)$$

where

$$q' = (H^+)^3 + 4.0\times10^{-3}(H^+)^2 + 4.0\times10^{-10}(H^+) + 12.8\times10^{-22} \quad (3.25)$$

Thus knowing the total phosphorus present in a solution of apatite at a given pH, the concentrations of the undissociated orthophosphoric acid and its three dissociation products can be calculated, since there are four unknown quantities associated with the four equations (3-10) to (3-13). Similar calculations could be made for evaluating the concentrations of orthoarsenic acid and its three dissociation products using equations (3.21) to (3.24). As in the case of the phosphate system, from the measured pH values of the saturated solutions given in column (2) of the Tables, the corresponding OH^- ion concentration could be calculated taking ionic product of water expressed as pKw to be 13.54 at 37°C. The concentrations of OH^- ions were not included in the tables since they could be obtained from the relationship.

$$pH + pOH = pKw = 13.54 \quad (3.26)$$

Having thus obtained the concentrations of all the species present in the solutions of the apatites, the ionic product, Kip, of SPA and SAA could be calculated on the basis of the corresponding molecular formulae. It is evident that since the temperature was maintained constant, a confirmation that the apatite phase was controlling the solubility could be provided by a constancy of its Kip at all the pH values. In the case of SPA the ionic products of all the possible phases likely to control the solubility equilibria such as $SrHPO_4$, $Sr(H_2PO_4)_2$ and the reported surface complex, $Sr_2(HPO_4)(OH)_2$, were calculated using the measured concentrations of strontium and phosphorus. The resulting values are given under column 12-17 of Table 3.7 which include the corresponding pKip values also. A similar set of calculations is made for SAA and the ionic products of $SrHAsO_4$, $Sr(H_2AsO_4)_2$, and the surface complex $Sr_2(HAsO_4)(OH)_2$ were calculated from the measured concentrations of strontium and arsenic and reported under column 12-17 of Table 3.14. These two sets of additional columns given under the two tables are meant to serve as representative sets of calculations to explore the possibility of non-stoichiometric dissolution involving one of these phases as the solute. In spite of the fact that the pKip values of these phases are less divergent than those of apatite at the pH values investigated, the apatite phase is still considered to be controlling the solubility since the g atom ratio of the solutions mainly Sr/P in the case of Table 3.7.and Sr/As in the case of 3.14 are close to what is expected for apatite as the solute phase.

While assessing the relative constancies of the pKip values of the phases likely to be formed in the solution of apatites, it should be kept in mind that for simple phases like $SrHPO_4$, $Sr_2(HPO_4)(OH)_2$, $Sr(H_2PO_4)_2$, $SrHAsO_4$, $Sr_2(HAsO_4)(OH)_2$ and $Sr(H_2AsO_4)_2$, the power to which the measured concentrations of ions such as Sr^{2+}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, AsO_4^{3-}, and OH^- ions were to be raised were low in comparison with those required for the apatite phase. Such a disparity in the value of the indices to which the concentrations were to be raised was likely to magnify the errors involved proportional to the value of the power to which a particular concentration was raised, since the corresponding experimental error involved got simultaneously raised to the same power. In the light of these considerations, it could be concluded that the pKip value of the apatite phase was the most consistent at all the pH values investigated confirming the occurrence of stoichiometric dissolution of the samples. Results on the solubility equilibria of a total of six solid solutions of SPA and SAA were subjected to calculations similar to those of the end-members and incorporated in Tables 3.8 to 3.13. As in the case of the end-members, the g-atom ratio, Sr/(P+As), of the saturated solutions approached stoichiometry at all the pH values investigated. In addition, the Kip's and the pKip's of the samples of the solid solutions calculated as in the case of the end-members on the basis of their molecular formulae exhibited a constancy at all the measured pH values. The average pKip values showed a regular decrease from SPA to SAA while the solid solutions had intermediary values.

For the sake of brevity calculations done to get the Kip values of phases other than those of apatite were deleted from tables 3.8 to 3.13, since representative sets of such calculations were already given in the case of the end-members. In all these cases the proximity of the g atom ratio, Sr/(P+As), to the stoichiometric values of 1.67 suggested the redundancy of inclusion of the Kip values of other possible solid phase controlling the solubility equilibria. Making use of the experimentally determined Kip values of SPA, SAA and their solid solutions, the free energy decrease accompanying the dissolution of each sample was calculated and given in Table 3.15. A systematic decrease in the magnitude of ΔG as one goes from SPA through its solid solutions with SAA to pure SAA confirms the homogeneity of the samples and ensures the formation of the solid solutions.

Table 3.16 contains the solubility data of SPA, SAA and six of their solid solutions with 0.165M NaCl as the exclusive dissolving medium. The solute taken in each system was indicated under column (2) while the final pH is given under column (3). As in the case of the preceeding tables of this chapter the measured concentrations of phosphorus and arsenic were subdivided into all the possible ionic species as described earlier. Out of them only PO_4^{3-} and AsO_4^{3-} are included in column (6) and (8). The rest of the calculated values being deleted. As in earlier cases the Kip and the pKip values of apatite were calculated and included in columns (10) and (11) of the table. The final pH of these systems was found to range

between 7.10 and 7.30 inspite of the fact that use of the buffer combination was deliberately avoided. As indicated by column (11) of the table a systematic decrease of the pKip values occurs as one goes from SPA to SAA the decrease being from 101 to 83. In addition, these pKip values, obtained in the absence of the buffer combination in the dissolving medium, are in agreement with the corresponding values obtained in the presence of the buffer combination, the agreement being more marked with the values obtained in the acidic region using the buffer combination, potassium acid phthalate and phtalic acid. The evidence for stoichiometric dissolution was provided, as in the case of the earlier tables by the proximity of the g atom ratio, Sr/(P+As), to the stoichiometric value 1.67.

In order to establish the fluctuations in the evaluated pKip values of the samples an attempt was made to scrutinize the errors involved in the determination of all the quantities required for such an evaluation. While the determinations of strontium, phosphorus and arsenic were free from errors since they were done using atomic absorption spectroscopy and spectrophotometry the only source of error can be attributed to the measurement of pH of the solution. Based on a series of determinations on the pH of the standard buffer solution the variation in the measured value was found to be fluctuating over a range of values +2% and -3% subjecting the final measured pH of the apatite phase to such corrections and recalculating the pKip values it could be found that the pKip varied by +1.15 and -1.78 from the average of all the values obtained from a given table using a given sample of solute.

3.4 Discussion

3.4.1 Fundamental Aspects

3.4.1.1 Mechanism of Dissolution of Ionic Crystals

A brief mention of fundamental principles[281,282] governing the solubility of ionic crystals in aqueous media was considered desirable in the present context in order to provide an interpretation of the results on solubility of the samples of apatites investigated. A solution is a homogeneous mixture of two or more substances the composition of which is variable within the certain limits beyond which saturation occurs. A crystalline solid is characterized by an orderly arrangement of its constituent ions, the forces holding them in their relative positions being a consequence of its lattice energy which is defined as the minimum energy required for the conversion of its constituent ions from solid to gaseous state. When such a solid enters into solution an attraction between the solvent molecules and the constituents of the lattice of the solute, caused by the existence of solvation energy, occurs. An interplay of lattice and solvation energies controls the dissolution of the solute which is favoured when it is accompanied by a release of energy. It is evident that in polar solvents like water the solvation of the ions constituting the solute is facilitated by the dipolar interaction between the solvent molecules of these ions. The solubility of a crystalline solid is controlled by size, charge and electronic structure of its constituent ions since both the energies mentioned above are, in turn, dependent on these

parameters. In general, charge remaining the same, large ions pack less tightly than small ones resulting in the formation of a solid of a higher solubility. Similarly, it can be expected that increase in the charge of ions constituting a crystal brings about a greater binding leading to a lowering of the solubility.

In the dissolution studies the role of water as a solvent has been explained on the basis of the polarity of its molecules. Water molecules which function as dipoles get oriented in an electrostatic field and exert attractive forces on the charged particles. When the ionic crystals come in contact with water, the molecules of the latter align themselves such that their negative and positive ends are oriented respectively towards the oppositely charged ions of the crystal[281]. The interionic attraction within the crystal is weakened consequent upon the dipolar forces exerted by water. The ions are thus pulled into solution. The detached ions move away from the crystal along with the accompanying water molecules. The dissolution of the ionic compounds in polar solvents like water may thus be explained. Additional factors that greatly influence the dissolution of crystalline solids in polar solvents can be, among others, the proton donating and proton accepting tendencies in acid-base reactions, action of oxidising or reducing agents and formation of complex ions. It is established beyond doubt that water dipoles exist as molecular aggregates due to hydrogen bonding. A prerequisite for a substance to be soluble in water is

its ability to weaken the hydrogen bonding such that its particles may be able to penetrate into the intermolecular spaces of the solvent. Such a weakening is brought about by the orientation of the water dipoles in the electrostatic field of an ion.

3.4.1.2 Thermodynamic Aspects of Dissolution

It is evident that in a saturated solution of an ionic compound an equilibrium is established between the undissociated molecules of the solute and the products of dissociation accompanied by changes in enthalpy as demanded by the laws of thermochemistry. The free energy change, ΔG_{soln}, accompanying such a process at temperature T can be shown to be given by,

$$\Delta G_{soln} = -- RTln\ Ksp \qquad (3.23)$$

where the other terms involved have their usual significance. On the basis of the fundamental thermodynamic expression used for defining the change in free energy, it can be shown that

$$\Delta G_{soln} = \Delta H_{soln} -- T\Delta S_{soln} \qquad (3.24)$$

where ΔH_{soln} and ΔS_{soln} are the changes in heat content and entropy of solution respectively.

In order to evaluate Kip of a given solubility equilibrium making use of equation (3.23), ΔG_{soln} is desired which, in turn, is obtained from ΔH_{soln} and ΔS_{soln} of the process. Visualising dissolution of an ionic compound to be consisting of (i) breaking down of the crystal architecture for which the lattice energy 'U' is operative and (ii) the hydration

of the constituting ions so set free, for which the summation of the individual hydration energies is made use of, it can be shown that the overall heat change involved in the process which is the same as the heat of solution, ΔH_{soln}, is given by:-

$$\Delta H_{soln} = \Sigma \Delta H_{hi} + U \qquad (3.25)$$

where $\Sigma \Delta H_{hi}$ is the sum of heats of hydration of the ions, while ΔH_{hi} is the corresponding value for the i^{th} ion. It is evident that appropriate signs for the quantities involved in the above expression are to be given on the basis of the established conventions. It can be concluded from the above expressions that for a highly soluble compound the absolute value of $\Delta \Sigma H_{hi}$ is greater than that for U while the converse is valid for cases of low solubility. While $\Delta \Sigma H_{hi}$ is the summation of the enthalpy changes involved in the conversion of the products of dissolution to their corresponding hydrated species, U can be shown to be made up of two principal energy terms contributed by columbic attraction and repulsion operative among the constituting ions of the crystal lattice and can be shown to be given in K cals/mole at 0°C by the expression.

$$U = \left(\frac{NAe^2 Z_+ Z_-}{R_o}\right)\left(1 - \frac{1}{n_B}\right) \qquad (3.26a)$$

$$= \left(\frac{332AZ_+ Z_-}{R_o}\right)\left(1 - \frac{1}{n_B}\right) \qquad (3.26b)$$

where N = Avogadro's number, A=Madelung's constant which depends upon the crystal arrangement, e=electronic charge, Z_+ and Z_- are the valancies of the cation and anion respectively

which constitute the crystal lattice, R_o is the minimum cation to anion distance equal, for approximate purposes, to $(r_+ + r_-)$ where r_+ and r_- are respectively the cationic and anionic radii and n_B is the Born exponent which depends upon the electronic configuration of the ions and leads to the evaluation of the repulsive forces operative. Having explained the implications involved in the theoretical evaluation of ΔH_{soln} of equation (3.24), a theoretical evaluation of ΔH_{soln} involved in this equation which is now desired, can be obtained from the expression,

$$\Delta S_{soln} = [(\text{Sum of the entropies of products of dissolution}) - (\text{entropy of solute})] \qquad (3.27)$$

It is evident that the quantities on the right hand side of the above expression can be evaluated using the Latimer expression[283]

$$S^\circ_{298} = [3/2\ R \ln.(\text{at.wt.of the species}) - 0.94] \qquad (3.28)$$

where S°_{298} refers to the entropy contribution of the desired species at 25°C, the expression being valid only for simple salts such as the alkali halides. Further, in the event of participation of gaseous ions, application of the Sackur-Tetrode equation[282]

$$S^\circ_g = 26.0 + [3/2\ R \ln.(\text{at.wt.})] \qquad (3.29)$$

is also desired where S°_g refers to the desired gaseous ions. While the above discussion involves a circuitous evaluation of ΔG_{soln} desired for arriving at a theortical basis for dissolution of ionic compounds, a more direct approach is possible as

shown below starting with (i) $\Sigma\Delta G_{hydration}$, the summation of the free energy changes of hydration of the constituting ions of the solute and (ii) $\Delta G_{lattice}$, the free energy changes of formation of the lattice of the solute,

$$\Delta G_{soln} = \Sigma\Delta G_{hydration} - \Delta G_{lattice} \qquad (3.30)$$

Using a specific example of a solute of general formula, M_mN_n, the quantities of the right hand side of the above expression can be shown to be given by the relationships, (3.31 to 3.35) as given below:-

$$\Delta G_{hydration} = m.\Delta G_{hM} + n.\Delta G_{hN} \qquad (3.31)$$

$$= \frac{-164Z_+^2\ m}{r_+ + 0.85} - \frac{164Z_-^2\ n}{r_- + 0.1} \qquad (3.32)$$

The fundamental expression

$$\Delta G_{lattice} = \Delta H_{lattice} - T\Delta S_{lattice} \qquad (3.33)$$

assumes the form

$$\Delta G_{lattice} = -U - T\Delta S_{lattice} \qquad (3.34)$$

appropriate signs being given to the terms involved. As explained earlier $\Delta S_{lattice}$ desired in the above expression can be evaluated using the Latimer[283] and Sackur-Tetrode[282] equations given; equations (3.28) and (3.29). On substitution of the appropriate values for the quantities involved in equation (3.34), expression for $\Delta G_{lattice}$ assumes the following form:-

$$\Delta G_{lattice} = \frac{332\ AZ_+Z_-(n_B-1)}{R_o\ n_B} - 8.03\ (m+n) \qquad (3.35)$$

Substituting the values of $\Delta G_{hydration}$ and $\Delta G_{lattice}$ obtained from the expressions (3.32) and (3.35) respectively, ΔG_{soln} in K cal/mole at 298° K for such a system is given by the expression,

$$\Delta G_{soln} = -\left\{\frac{(164Z_+^2\, m)}{(r_+ + 0.85)} \quad \frac{(164Z_-^2\, n)}{(r_- + 0.1)}\right\} + \left\{\frac{332\, Az_+\, Z_-}{R_o\, n_B}(n_B - 1) - 8.03\,(m+n)\right\}$$

K cal/mole (3.36)

To emphasize the dependence of ΔG_{soln} on the replacement of an anion of the solute by another of a different ionic radius the above expression can be differentiated with respect to r_- at constant r_+ which leads to the relationship,

$$\left(\frac{\partial \Delta G_{soln}}{\partial r_-}\right)_{r+} = \left\{\frac{-164Z_-^2 n}{(r_- + 0.1)^2} - \frac{332AZ_+Z_-}{R_o^2}\right\} \qquad (3.37)$$

It is evident that the changes ensuing in $\Delta G_{hydration}$ and $\Delta G_{lattice}$ consequent upon such a replacement are given respectively by the first and second terms on the right hand side of the above expression.

3.4.1.3 Discussion of Present Results on Solubility

A. Stoichiometric Dissolution and Attainment of Saturation.

It could be concluded from studies on the dissolution kinetics of SPA, SAA and one of their representative solid solutions that saturation could be attained within a period of about 12 hours of equilibration and that the dissolution is stoichiometric. The duration of equalibration required

for attainment of saturation of solubility of a solute in a given solvent depends on, among others, the particle size of the solute and the rate of shaking. These parameters were maintained the same for all the samples. As expected the period of equilibration required for attainment of saturation was found to be nearly the same for all the samples and was comparable with that reported in the earlier literature[195] for similar experimental conditions. The constancy in the g atom ratio, Sr/(P+As), indicates that the dissolution is stoichiometric. This is expected since the samples of apatites prepared are of a high order of parity as indicated by their chemical analyses and other methods of characterization. The non-stoichiometric dissolution of apatites reported in the earlier literature[190] can be attributed to the presence of trace impurities of highly soluble phases associated normally with the solute phase.

B. Dependence of Solubility on pH of Medium of Dissolution and Constancy of Solubility Products.

It is evident from the results reported that for a set of experimental conditions adopted the solubility products of SPA, SAA and their solid solutions remained constant within the limits of experimental error. With a decrease in the pH of the dissolving medium it is found that, inspite of the fact the amounts of strontium, phosphorus and arsenic going into solution increased markedly, the solubility product remained unaltered within the limits of experimental error.

The solubilities of all the samples studied as a function of pH of the dissolving medium showed a marked increase with a decrease in pH. An interpretation of this observation was provided by the simultaneous equilibria established in systems involving dissolution of apatites. With SPA as solute, the equilibrium which is relevant in the present context is the following:-

$$Sr_{10}(PO_4)_6(OH)_2 \rightleftharpoons 10Sr^{2+} + 6PO_4^{3-} + 2OH^- \quad (3.38)$$

Among the products of dissolution PO_4^{3-} and OH^- ions are capable of participating in a few more simultaneous equilibria characteristic of a saturated aqueous solution of an apatite. The presence of PO_4^{3-} in aqueous medium initiates establishment of the following equilibria which are all pH dependent.

$$PO_4^{3-} + H_3O^+ \rightleftharpoons HPO_4^{2-} + H_2O \quad (3.39)$$

$$HPO_4^{2-} + H_3O^+ \rightleftharpoons H_2PO_4^- + H_2O \quad (3.40)$$

$$H_2PO_4^- + H_3O^+ \rightleftharpoons H_3PO_4 + H_2O \quad (3.41)$$

The OH^- ion on the other hand, takes part in an additional equilibrium characteristic of all aqueous media as shown below:-

$$H_3O^+ + OH^- \rightleftharpoons H_2O \quad (3.42)$$

which is also pH dependent. A shift from left to right occurs in all the above equilibria when H_3O^+ ion concentration is increased. All these equilibria are collectively responsible for influencing the equilibrium concentrations of the participants of equation (3.38). Since the concentration of PO_4^{3-}

ion is influenced by the equations (3.39) to (3.41), which in turn are dependent on equation (3.42).

It is evident from an examination of the above mentioned equilibria that an increase in the hydrogen ion concentration brings about a decrease in the PO_4^{3-} and OH^- ion concentration participating in equation (3.38). Since the Ksp of apatite at 37°C is to maintain a constancy more of the solute goes into solution to achieve this objective. Consequently the solubility of SPA increases with a decrease in pH of the medium of dissolution. A similar argument is valid for systems containing SAA and the solid solutions of SPA and SAA as solutes, since the AsO_4^{3-} ion concentration is also likewise affected by a decrease in pH. The foregoing arguments are substantiated by the observed fact that the calculated proportions of PO_4^{3-} or AsO_4^{3-} ions of the saturated solutions of the samples decreased with an increase in the hydrogen ion concentration of the medium of dissolution (Tables 3.7 to 3.14).

Based on the concept of ionic equilibria prevalent in such systems and the role of dissociation constants of the polybasic acids, H_3PO_4 and H_3AsO_4, in controlling these equilibria, the higher solubility with an increase in arsenic content of the samples could be attributed to the higher dissociation constants of H_3AsO_4 over those of H_3PO_4. It is evident that the repression in the equilibria involving the dissociation products of H_3AsO_4 with an increase in the

H_3O^+ ion concentration demands a higher dissolution of the corresponding apatite phase to compensate for the depletion of the AsO_4^{3-} ion. In addition, a convincing basis for the higher dissolution of SAA over that of SPA, as mentioned earlier, could be provided by the theoretical considerations leading to the derivation of equation (3.37) which gives variation in ΔG_{soln} with a change in the ionic radius of the replacing anion involved.

A saturated solution is characterized by the existence of an equilibrium between the dissolved and undissolved parts of a solute. It can be shown from considerations of chemical potential that when the dissolved fraction dissociates compeletely in a saturated solution, the product of the activities of the constituent ions raised to appropriate powers is a constant at a given temperature, known as the activity solubility product, Ksp. It is convenient to express the solubility in terms of the solubility product since the latter enables the former to be evaluated even in media containing complexing and common ions. Polymorphism, particle size, degree of hydration, occurrence of chemical reactions leading to either hydrolysis or complex formation and surface exchange may be considered as some of the important characteristics of the solute phase which influence its solubility and hence the solubility product. The ionic strength μ, of the dissolving medium given by half of the summation of the products of molality and square of the charge of all the ionic species

present, is another important factor influencing the solubility product. The following expression which can be derived on the basis of the Debye-Hückel theory gives the solubility of a salt as a function of the ionic strength, μ at 25°C.

$$\log S = \log S_o + \frac{0.509\ (Z_+)(Z_-)\ \sqrt{\mu}}{1+\ 0.329\ \ a\ \sqrt{\mu}} \qquad (3.43)$$

Where S_0 is the solubility at zero ionic strength, a = distance of closest approach of the ions and Z_+ and Z_- are the respective valancies of the positive and negative ions of the salt.

In the present investigations the medium of dissolution adopted was constituted by buffer combinations of desired pH maintained at a molarity of 0.165 with respect to sodium chloride. The ionic strength of the dissolving medium thereby remained virtually constant over the entire compositional range of the buffer combinations. The role of the ionic strength of the medium of dissolution as a parameter of the solubilities of apatites could thus be avoided.

It has been suggested by La Mer[191] that it is complicated to calculate the activity coefficients when ions of high and opposite charge are involved as in the case with solutions of SPA and SAA; the use of the Debye-Hückel equation for the precise calculation of such ions has been found to be inadequate. It was therefore recommended by him that an aqueous solution of 0.165M sodium chloride is considered as a solvent of reference in which all the activity coefficients may be assigned a value of unity. In the light of

such a consideration the ionic product of the solute Kip is calculated instead of the solubility product, Ksp. The concentrations of the ionic species were used instead of their activities for purposes of calculations of Kip values reported in the present section.

It may be relevant to mention in this context an important concept advanced by Bronsted[285,286] even before the enunciation of the Debye-Hückel theory. Based on an extensive series of investigations he could show that a constant ionic environment contributed by a large excess of an inert neutral salt can ensure a constancy of the activity coefficients of ions present in relatively low concentrations. When such a condition is fulfilled, the ionic product, Kip, of a solute is related to the corresponding activity product, Ksp, by a constant factor enabling thereby the use of the former for purposes of comparison.

C. Variation in the solubility Product of Strontium Apatites due to the Replacement of PO_4^{3-} by AsO_4^{3-}

The overall change in the solubility of an ionic compound depends exclusively on the relative variations in $\Delta G_{hydration}$ and $\Delta G_{lattice}$ terms as discussed earlier. The latter becomes more dominant for sparingly soluble salts like apatites. This can be justified by the fact that the alterations in hydration energies[284] for the pair of anions involved, namely, PO_4^{3-} and AsO_4^{3-}, in the substitution investigated, are of very small magnitude and consequently

thelattice energy becomes more dominant in controlling the solubility. These conclusions can be substantiated by examining the terms involved in the expressions (3.40) and (3.41). The covalent radius of AsO_4^{3-} (1.18Å) being higher than than of PO_4^{3-} (1.10Å) contributes to a relatively more loose packing, since the cation, Sr^{2+} is the same in all the cases involved. That SAA is relatively less stable than SPA is evident from the experimental ΔG_{soln} values, the values being 141.15 and 111.95 K cal/mole respectively for SPA and SAA. The reported[282] increase in the solubilities of sodium halides in the order NaF, NaCl, NaBr and NaI with an increase in the anionic radii[285], (F^-, Cl^-, Br^- and I^- being 1.34, 1.81, 1.95 and 2.17Å respectively) cation remaining the same, could substantiate the above observations. The observed increase in the solubility of apatites with an increase in the arsenic content of the samples, pH and temperature remaining the same, can thus be accounted for exclusively on the basis of a decrease in the lattice energy with an increase in the arsenic content. That the lattice energies of the samples decrease with an increase in arsenate content is further substantiated by the fact that the Gibbs function of solution of the samples calculated from corresponding Ksp values using the conventional thermodynamic expression shows a systematic decrease with an increase in the arsenate content. As mentioned earlier the replacement of phosphate by a relatively bigger ion such as arsenate (covalent radii of PO_4^{3-} and AsO_4^{3-} are 1.10Å and 1.18Å respectively) brings about a decrease in the lattice energy due to the consequent loose packing.

D. Explanation of the Absence of Extraneous phases functioning as Solutes during the Dissolution of Apatites.

The present investigations on solubility of apatites prove that the apatite phase is exclusively controlling its dissolution, the extraneous phases being absent. The observed deviations in the experimental values of pKip can be explained as follows:

The pKip values of the samples were calculated from the measured concentrations of the dissolved species of SPA, SAA and their solid solutions at a constant temperature. It is clear from the procedure adopted for such calculations that the principal factors which contribute to a deviation of these computed values from those expected are the experimental errors involved in the microanalytical determinations of the dissolved species. Out of these ions, OH^-, with its dominant accompanying effect on the calculated values of the PO_4^{3-} or AsO_4^{3-} ion from the measured P_{total} or As_{total} value, as indicated by equations (3.9) and (3.20) is of significance. It is evident that an error in its measurement effects not only its own concentration term used directly in the calculation of Kip but also that of PO_4^{3-} or AsO_4^{3-} which are computed from the P_{total} or As_{total} and the measured pH values. These errors get accentuated in the pKip calculations of apatites, the molecular formulae of which involve, ten, six and two g ions respectively of Sr^{2+}, PO_4^{3-} or AsO_4^{3-} and OH^-. Such computations involve large powers to which the corresponding concentrations are to be raised to get the

pKip values. In order to scrutinize the validity of the concepts advanced earlier, suggesting the role of other solid phase such as the secondary salts, $SrHPO_4$ or $SrHAsO_4$, a surface complex, $Sr_2(HPO_4)(OH)_2$ or $Sr_2(AsO_4)(OH)_2$, in controlling the solubility equilibria of apatite systems, the ionic product of these and other solid phases were calculated following the procedures adopted for the apatites.

In general, the errors involved in the measurements of the concentrations of the dissolving species of apatites are likely to magnify the fluctuations in the calculated values of the ionic products since the latter were of a very low order of magnitude involving powers of the ionic concentrations. Since the powers to which ionic concentrations were to be raised to get the Kip values were much lower in the case of the secondary salt and the surface complex than that for apatite, as is evident from the molecular formulae, the errors of the former were supposed to be lower. The g atom ratio, Sr/(P+As), in the case of additional phases is not stoichiometric. For apatite phase the ratio was found to be close to the stoichiometric value. These considerations could exclusively eliminate the possibility of phases other than apatites in controlling the solubility equilibria of the systems. Though the observed constancy in Kip values of the apatite phase was not very striking, it could still be concluded that their solubility equilibria were characterized by stoichiometric dissolution.

3.5 Summary

The solubility equilibria of strontium phosphate apatite, strontium arsenate apatite and a total of six of their solid solutions spread over the entire compositional range were investigated with the intention of studying their dependence on the extent of isomorphous substitution of PO_4^{3-} by AsO_4^{3-}. The studies carried out at 37°C were extended to a few chosen buffered dissolving media spread over a pH range, 5.50 to 8.0. The minimum duration of equilibration required for the attainment of saturation was established through studies on the dissolution kinetics. Equilibrating powdered samples of the solutes with appropriate buffer solutions, the colloidal component was separated from the saturated solutions by filtration through $1G_4$ sintered glass crucibles and the filtrates were subjected to micro-analytical determinations of the concentrations of the dissolved ions. The proportion of H_3PO_4 and H_3AsO_4 and the corresponding dissociation products were calculated respectively from the experimentally determined phosphorus and arsenic contents of the solutions using the dissociation constants and the pH of the medium.

Taking into consideration the possible ionic equilibria which can be established in such systems, the ionic products of primary and secondary phosphates, a complex, $Sr_2(HPO_4((OH)_2$ and SPA were calculated for systems having the latter as solute. Similar calculations were carried out for the ionic products of the arsenic counterparts in SAA systems. A

combination of these two sets of calculations was brought about in the case of systems having the solid solutions of the end-members as solutes. The medium of dissolution was kept at a molarity of 0.165M with respect to sodium chloride in order to maintain the ionic strength constant. This enabled the solubility product of the solute, Ksp, to be considered as its ionic product, Kip, in its saturated solution assuming the activity coefficients of each one of products of dissolution to be unity in such systems.

Based on the molecular formulae of the solutes the corresponding ionic products of the saturated solution were calculated making use of the sets of concentrations of the products of dissolution.

For each sample, the Kip value was found to be constant within the limits of experimental errors as was to be expected from the constancy of the temperature of equilibration. The Kip values were in addition found to increase systematically with an increase in the arsenate content. A theoretical interpretation was given in terms of a decrease in lattice energy consequent upon a replacement of PO_4^{3-} by AsO_4^{3-}, covalent radii of P and As being 1.10 and 1.18 Å respectively.

SYNOPSIS

Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of substances known as apatites. It has been the subject of extensive investigations because of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. Among such diverse exchange reactions a few have attained significance during the recent past consequent upon the toxicity of the elements involved, such an exchange being the mechanism of their incorporation into human skeletal system

Based on the contemporary importance given to the toxicity to the human system by arsenic and β-active Sr-90, a product of atomic explosions, studies on the replacement of calcium by strontium (ionic radii 0.99 and 1.13Å respectively) and of phosphate by arsenate covalent radii (1.10 and 1.18Å respectively) have been chosen for the present investigations. Among heteroionic cationic substitutions on calcium hydroxylapatite replacement of Ca^{2+} by Sr^{2+} is significant since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90. Such an incorporation even in trace amounts, can be fatal because

of the long half-life period of Sr-90 (28.5 years). It is evident that a complete replacement of Ca^{2+} ions by Sr^{2+} ions leads to the formation of strontium phosphate apatite, $Sr_{10}(PO_4)_6(OH)_2$, while that of PO_4^{3-} by AsO_4^{3-} on strontium phosphate apatite leads to strontium arsenate apatite $Sr_{10}(AsO_4)_6(OH)_2$, both being iosmorphs of calcium hydroxylapatite. A partial replacement in either case leads to formation of solid solutions of the concerned end-members.

The toxicity of elemental arsenic and its salts is well known. There is prevalence of arsenic poisoning among workers employed in the manufacture of insecticides, paints and dyes containing the element. Inhalation of arsenic through nose and mouth and exposure of the skin to it are supposed to be responsible for the ailment. In spite of the fact that arsenic is distributed primarily throughout the soft tissues in living organisms its incorporation in the human skeletal system through $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ exchange on calcium hydroxylapatite of bone is probable.

It could be unambiguously established that ions incorporated in the human skeletal system through exchange reactions on calcium hydroxylapatite of bones play a significant role in two principal bone processes, namely, calcification and resorption, the deposition and dissolution respectively of calcium hydroxylapatite at the interface of bone and body fluids. Consequently, any attempt in the direction of elimination or minimization of such a toxicity is associated with a study of the solubility of calcium hydroxylapatite

as well as of 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 strontium phosphate apatite, strontium arsenate apatite and a series of six of their solid solutions spread over the entire compositional range, was undertaken. Adopting co-precipitation of the end-members in aqueous media through a judicious modification of the existing methods, the samples were prepared at 37°C to simulate biological conditions.

Characterization of these samples was brought about through sophisticated instrumental techniques such as x-ray diffraction, electronmicroscopy, i.r. and Laser Raman Spectral studies in addition to the conventional chemical analyses. Vegard's law demands that the unit cell volume of a homogeneous series of solid solutions varies linearly with the composition and offers a convenient method of scrutinizing their homogeneity. As is to be expected from the bigger size of the arsenate ion, a replacement of phosphate by it brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of arsenate ion replacing phosphate ion, observed in the present series of solid solutions, confirmed their homogeneity. The electronmicrographs of a few representative samples revealed the hexagonal pattern of the crystals confirming the absence

of extraneous phases and enabling approximate calculation of the specific surface areas from the measured average dimensions of the individual crystals.

The i.r. and Laser Raman spectra could confirm the identity of the samples. The predominant absorption peaks recorded in the traces of the samples were found to be due to the PO_4^{3-}, AsO_4^{3-} and OH^- ions.

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-} ion by AsO_4^{3-} ion on strontium phosphate apatite. Since it was intended to determine the solubility product of each sample from data resulting from the chemical analyses of the saturated solutions, 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 product so determined, the studies in each case were extended to a few chosen pH values, the range being restricted to the limits, 5.5 and 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 coefficients of polyvalent ions could be avoided by assuming all of them to be unity without foregoing accuracy. It is evident that such calculations make the solubility product, Ksp, and the ionic product, Kip, synanymous.

Each one of the powdered samples was equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature-shakerbath. 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 $1G_4$ sintered glass crucible before the solutions were analyzed for the products of dissolution. A separate experiment could prove the suitability of such crucibles for colloidal separation.

While phosphorus and arsenic were determined spectrophotometrically, atomic absorption spectroscopy was adopted for the determination of strontium, the attainable accuracy in all the cases being scrutinized by analyses of solutions of known compositions.

A scrutiny of attainment of saturation and the minimum period of equilibration required for the purpose were determined through dissolution kinetics of a couple of representative samples. From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric-acid and its three 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. Similar calculations were done with ortho arsenic acid in the case of systems having arsenate -

containing samples as solutes.

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 be unambiguously 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. It is evident that for the phosphate containing apatites such phases are the primary and secondary phosphates of the metal concerned in addition to the apatite phase. By analogy with a double salt, $Ca_2(HPO_4)(OH)_2$, a phase reported to control the solubility product of calcium hydroxyl apatite by functioning as a surface coating, the ionic product of its strontium counterpart, $Sr_2(HPO_4)(OH)_2$, was also calculated for the present systems. Examination of the data on solubility of all the phases mentioned above reveals that the ionic product of apatite showed a constancy over the entire pH range investigated and the calculated set of values were found to lie within the error limits. It is evident that the corresponding arsenate phases are relevant for strontium arsenateapatite while the phases of both phosphate and arsenate are to be considered for the systems involving the solid solutions. Such calculations were done on the data of solubility of all these samples. That the apatite phase

controlled the solubility was further supplemented by the fact that the g atom ratio, Sr/(P+As), of the saturated solutions of all the samples was in the proximity of the theoretical value (1.67) confirming unambiguously the occurrence of stoichiometric dissolution of apatites.

It could be established further that the solubility product of each sample of the series while remaining constant at all the pH values investigated, decreased systematically with an increase in the extent of replacement of PO_4^{3-} by AsO_4^{3-}. An interpretation of these results could be provided by the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.

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APPENDIX

List of Publications

1. S.K. Gupta, P.V.R. Rao, G. George, T.S.B. Narasaraju, Determination of Solubility Products of Phosphate and Vanadate Apatites of Calcium and their Solid Solutions, J. Mat. Sci., **22** 1286-1290, 1987.

2. G. George, S.K. Gupta, P.V.R. Rao, T.S.B. Narasaraju, Preparation and Characterization of Phosphate and Arsenate Apatites of Strontium and their Solid Solutions, J. Met. Sci., **22** 2274-2276, 1987.

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Determination of solubility products of phosphate and vanadate apatites of calcium and their solid solutions

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To understand the toxic effects of vanadium on the human skeletal system, the solubility products of phosphate and vanadate apatites of calcium and eight of their solid solutions, spread over the entire compositional range, were investigated at 37° C in 0.165 M sodium chloride solution. They were found to increase with increase in the vanadium content, the dissolution being found to be stoichiometric. A theoretical interpretation based on changes in lattice and hydration energies resulting from isomorphous ionic substitution is advanced.

1. Introduction

By virtue of its biological significance and its remarkable ability to undergo several isomorphous cationic and anionic substitutions involving toxic ions, calcium phosphate apatite, $Ca_{10}(PO_4)_6(OH)_2$ (CPA), the principal inorganic constituent [1] of human bones and teeth, has been the subject of extensive investigations to throw light on the mechanism of incorporation of such ions into the human skeletal system. It was established that the toxicity is controlled by the dependence of the principal bone processes, calcification and resorption, on the extent of incorporation of toxic ions. The present work dealing with the replacement of PO_4^{3-} by VO_4^{3-} resulting in the formation of its isomorph, calcium vanadate apatite, $Ca_{10}(VO_4)_6(OH)_2$ (CVA), was undertaken because the mechanism of occurrence of toxic effects [2, 3] of vanadium and its salts, such as paralysis, convulsions and sleepiness leading to bronchitis and bronchopneumonia caused when their proportion exceeds 1 mg kg^{-1} body weight, were not investigated earlier. In addition, these studies were intended to clarify a few ambiguities associated with the available results on the solubilities of apatites, especially in the context of its reported non-stoichiometric [4–6] dissolution.

2. Experimental details

CPA, CVA and a series of eight of their solid solutions, prepared through appropriate modifications of a wet method [7–9], were characterized through X-ray, infrared, electron microscopic and thermal analyses, in addition to conventional chemical analyses [8–11]. Their solubility products were determined in buffered 0.165 M sodium chloride solution at the biologically significant temperature of 37° C by analyses of their saturated solutions. Each system was set up by adding 0.2 g of apatite to potassium acid phthalate–sodium hydroxide or boric acid–borax buffer of required pH prepared in 200 ml of 0.165 M sodium chloride, the latter being needed to maintain the ionic strength during dissolution effectively constant [12]. The ionic strengths of the systems were found to range between 0.20 and 0.24. Further, an aqueous solution of 0.165 M sodium chloride, a solvent of biological importance, may be considered as a standard solution [13] of reference in which all activity coefficients of dissolved ionic species could be taken as unity. This avoids inaccuracies involved in the calculations of activity coefficients needed for the evaluation of solubility products of solutes containing polyvalent ions, and enables ionic products of saturated solutions of such substance to be taken as their solubility products. Equilibration took place in a thermally insulated cabin maintained at 37 ± 0.5° C for about 12 h, in air-tight polyethylene containers shaken at a regulated speed using a mechanical shaker. Attainment of saturation was confirmed separately by carrying out investigations on the dissolution kinetics of CPA, CVA and a representative solid solution of them as solutes at pH 5.2 and pH 7.5. The systems were equilibrated as above and the studies could be extended in each case to a total duration of 24 h by setting up ten identical systems, equilibration of each system being interrupted at convenient time-intervals. The equilibration time required for the attainment of saturation in each case was found to be 4 h. In order to be doubly sure about the attainment of saturation, a duration of 12 h was chosen for equilibration throughout the investigations. The colloidal component [14] of the solute was separated from the solution by filtration through a G4 sintered glass crucible under suction at the temperature of equilibration. From the saturated solutions thus obtained calcium was determined volumetrically [9] while phosphate [15] and vanadate [9, 16] were determined spectrophotometrically, a separate aliquot being taken each time. The effect of common ions on pK_{sp} of CPA and CVA was also investigated at convenient pH values.

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TABLE I Solubility products of phosphate and vanadate apatites* of calcium and their solid solutions in 0.165 M sodium chloride solution

Serial no.	Final pH	Measured conc. (10^3 mol l^{-1})			Calculated activities (mol l^{-1})			Mole ratio, Ca/(P + V)	pK_{sp}	Average pK_{sp}
		Ca	P	V	$a_{(OH^-)}$† $\times 10^8$	$a_{(PO_4^{3-})}$ $\times 10^{12}$	$a_{(VO_4^{3-})}$ $\times 10^{13}$			
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Solute:	*calcium phosphate apatite,* $Ca_{10}(PO_4)_6(OH)_2$									
1	4.77	3.36	2.06	–	0.16	0.21	–	1.62	118	
2	4.94	3.17	1.87	–	0.25	0.42	–	1.69	116	114
3	5.20	2.67	1.53	–	0.46	1.14	–	1.74	114	
4	5.65	2.30	1.29	–	1.28	7.50	–	1.78	109	
Solute:	*solid solution no. 1,* $Ca_{10}(PO_4)_{5.7}(VO_4)_{0.3}(OH)_2$									
5	5.48	1.03	0.55	0.06	0.87	1.47	0.08	1.69	118	
6	5.85	0.71	0.38	0.05	2.04	5.56	0.36	1.60	115	114
7	7.01	0.14	0.05	0.03	29.5	107.0	39.7	1.65	112	
8	7.20	0.12	0.04	0.03	45.7	164.0	76.7	1.65	111	
Solute:	*solid solution no. 2,* $Ca_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$									
9	5.54	1.17	0.56	0.14	1.00	1.89	0.23	1.64	116	
10	5.90	0.82	0.42	0.10	2.29	7.55	0.84	1.58	114	113
11	7.01	0.18	0.06	0.05	29.5	120.0	59.7	1.64	111	
12	7.20	0.15	0.05	0.04	45.7	182.0	123.0	1.66	110	
Solute:	*solid solution no. 3,* $Ca_{10}(PO_4)_{4.9}(VO_4)_{1.1}(OH)_2$									
13	5.22	2.60	1.24	0.37	0.48	1.01	0.13	1.60	116	
14	5.62	1.84	0.80	0.34	1.20	4.01	0.78	1.62	113	
15	6.05	1.10	0.37	0.31	3.23	13.2	5.12	1.61	112	113
16	7.01	0.36	0.05	0.02	29.5	95.2	21.5	1.62	109	
Solute:	*solid solution no. 4,* $Ca_{10}(PO_4)_{3.7}(VO_4)_{2.3}(OH)_2$									
17	5.03	5.32	1.64	1.57	0.31	0.56	0.23	1.72	116	
18	5.17	5.09	1.34	1.47	0.43	0.87	0.41	1.80	115	
19	5.40	4.47	1.16	1.37	0.72	2.16	1.13	1.76	112	112
20	6.03	3.42	0.71	1.29	3.09	22.8	19.3	1.70	106	
Solute:	*solid solution no. 5,* $Ca_{10}(PO_4)_{3.1}(VO_4)_{2.9}(OH)_2$									
21	5.08	5.89	1.16	2.25	0.35	0.49	0.42	1.72	116	
22	5.27	5.52	0.96	2.11	0.54	0.99	0.95	1.79	114	
23	5.57	4.75	0.79	1.96	1.07	3.21	3.53	1.72	111	111
24	6.17	4.19	0.47	1.88	4.26	28.3	53.2	1.77	104	
Solute:	*solid solution no. 6,* $Ca_{10}(PO_4)_{2.3}(VO_4)_{3.7}(OH)_2$									
25	5.19	6.73	0.96	2.94	0.45	0.69	0.91	1.72	115	
26	5.39	6.24	0.87	2.61	0.71	1.55	2.05	1.79	112	
27	5.65	5.46	0.56	2.48	1.29	3.26	6.46	1.79	110	111
28	6.61	1.99	0.07	1.17	11.7	28.5	244.0	1.59	106	
Solute:	*solid solution no. 7,* $Ca_{10}(PO_4)_{1.6}(VO_4)_{4.4}(OH)_2$									
29	5.27	7.21	0.78	3.43	0.54	0.81	1.54	1.71	115	
30	5.40	6.73	0.64	3.14	0.72	1.20	2.58	1.77	112	
31	5.79	6.01	0.42	2.98	1.77	4.67	14.8	1.76	108	109
32	6.42	5.07	0.19	2.75	7.58	33.7	242.0	1.72	101	
Solute:	*solid solution no. 8,* $Ca_{10}(PO_4)_{0.8}(VO_4)_{5.2}(OH)_2$									
33	5.33	7.78	4.52	3.92	0.62	0.61	2.33	1.78	113	
34	5.52	7.45	3.55	3.83	0.95	1.14	5.46	1.78	111	
35	6.14	6.78	2.01	3.76	3.98	10.5	9.28	1.70	103	107
36	6.65	2.95	0.12	1.72	12.8	6.02	429.0	1.69	102	
Solute:	*calcium vanadate apatite,* $Ca_{10}(VO_4)_6(OH)_2$									
37	5.33	8.27	–	5.15	0.62	–	3.06	1.60	112	
38	5.53	7.88	–	4.41	0.98	–	6.60	1.78	110	107
39	5.90	7.12	–	3.92	2.29	–	32.2	1.64	106	
40	6.60	3.78	–	2.25	10.9	–	448.0	1.68	100	

*0.2 g apatite, washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide, is taken in 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide or boric acid and borax brought to a molarity of 0.165 M with respect to sodium chloride.

†Calculated from the measured final pH of the equilibrated system.

TABLE II Studies on the effect of common ions on the solubility equilibria of calcium phosphate apatite

Serial no.	Common ion added ($mg l^{-1}$)		Final pH	Measured conc. (10^3 mol l^{-1})		Mole ratio: Ca/P	Calculated activity (10^{12} mol l^{-1})	Solubility product of solute,
	Ca	P		Ca	P		$a_{(PO_4^{3-})}$	pK_{sp}
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	10	–	5.62	3.23	1.19	2.71	6.03	108
2	30	–	5.62	4.44	0.79	2.46	4.01	108
3	–	10	5.48	2.49	1.59	6.87	4.26	110
4	–	30	5.48	1.75	2.58	11.1	6.91	110
							Average	109

$K_{sp} = (Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$.
Solute: 0.2 g $Ca_{10}(PO_4)_6(OH)_2$ washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.
Dissolving medium: 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 M with respect to sodium chloride.
Temperature: 37 ± 0.5° C; $pK_w = 13.54$.

3. Results

A few representative sets of results on the determination of the solubility products of CPA, CVA and eight of their solid solutions are given in Table I. Experimentally determined concentrations of calcium, phosphorus and vanadium for each sample at a measured pH are given in columns 3 to 5. While the activities of OH^- and Ca^{2+} ions were thus available directly from the measured pH and concentrations of Ca^{2+}, respectively, those of PO_4^{3-} and VO_4^{3-} could be calculated from the total concentrations of phosphorus and vanadium given in columns 4 and 5, the details of the calculations being given later.

The activities of PO_4^{3-} and VO_4^{3-} thus calculated for each sample at the chosen pH values are given in columns 7 and 8, respectively, the corresponding activities on the other ionic species shown in Equation 7 being omitted.

Results on the determination of solubility products of CPA, CVA and their solid solutions involving microanalytical determination of their constituent ions, known for their mutual interference [8], are vulnerable to errors. In addition, these errors become magnified in the evaluation of solubility products because of the high powers to which the activities of some of the constituting ions are to be raised. Keeping these limitations in view, the activity products of all the possible solute phases likely to control the solubility equilibria of CPA and CVA and their solid solutions such as $CaHPO_4$, $Ca_2HPO_4(OH)_2$, $Ca(H_2PO_4)_2$, $CaHVO_4$, $Ca_2HVO_4(OH)_2$ and $Ca(H_2VO_4)_2$ were calculated in the light of their hydrolytic dissolution. For the sake of brevity the calculated data of phases other than CPA, CVA and their solid solutions are not given in the present communication, because the divergence of the K_{sp} values calculated was much more for them in comparison with those of the above phases. Consequent upon the errors involved, the divergence in K_{sp} of CPA, CVA and their solid solutions is still considerable, although it is found to be lower than the values for the other phases. The pK_{sp} values of the phases are given in column 10 of Table I.

Results of the effect of common ions on the solubility equilibria of CPA and CVA are given in Tables II and III respectively. It was found from these results that the pK_{sp} values (column 9, Tables II and III) of the apatite phase exhibited a constancy proving the response of the solubility of apatites to the common-ion effect. As expected, the mole ratios, Ca/P (column 7, Table II) and Ca/V (column 7, Table III) in these cases were found to diverge from the stoichiometric values in accordance with the principle of solubility product.

4. Discussion

It is evident that the solubility product, K_{sp}, of CPA is equal to the product of the concentrations of the

TABLE III Studies on the effect of common ions on the solubility equilibria of calcium vanadate apatite

Serial no.	Common ion added ($mg l^{-1}$)		Final pH	Measured conc. (10^3 mol l^{-1})		Mole ratio: Ca/V	Calculated activity (10^{13} mol l^{-1})	Solubility product of solute,
	Ca	V		Ca	V		$a_{(VO_4^{3-})}$	pK_{sp}
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	10	–	5.70	8.41	2.94	2.85	9.63	107
2	30	–	5.70	10.7	1.76	6.07	5.78	109
3	–	10	5.79	6.42	4.22	1.52	20.90	107
4	–	30	5.79	4.71	5.69	0.83	28.20	108
							Average	108

$K_{sp} = (Ca^{2+})^{10}(VO_4^{3-})^6(OH^-)^2$.
Solute: 0.2 g $Ca_{10}(VO_4)_6(OH)_2$ washed with a 2% solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.
Dissolving medium: 200 ml of an appropriate buffer combination of potassium acid phthalate and sodium hydroxide brought to a molarity of 0.165 M with respect to sodium chloride.
Temperature: 37 ± 0.5° C; $pK_w = 13.54$.

dissolved ions raised to appropriate powers, as given by the products $(Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$. While the concentrations of Ca^{2+} and OH^- were available directly from the measurements, that of PO_4^{3-} was calculated as shown below from the overall analytical concentration of PO_4^{3-} represented as P_{total}.

Orthophosphoric acid, being a tribasic acid, dissociates as shown below:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad (1)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad (2)$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad (3)$$

It is evident that the H^+ ion in the above equilibria exists as H_3O^+ ion in aqueous media. The total amount of phosphorus present in a solution of CPA, represented as P in the tables, can be subdivided as shown below into (i) the undissociated acid, and (ii) its dissociated ionic species $(H_2PO_4^-)$, (HPO_4^{2-}) and (PO_4^{3-}), making use of the pH of the system and three dissociation constants [17, 18], K_1, K_2 and K_3 of the acid:

$$K_1 = \frac{a_{(H_2PO_4^-)}a_{(H^+)}}{a_{(H_3PO_4)}} = 7.51 \times 10^{-3} \quad (4)$$

$$K_2 = \frac{a_{(HPO_4^{2-})}a_{(H^+)}}{a_{(H_2PO_4^-)}} = 6.33 \times 10^{-8} \quad (5)$$

and

$$K_3 = \frac{a_{(PO_4^{3-})}a_{(H^+)}}{a_{(HPO_4^{2-})}} = 4.73 \times 10^{-13} \quad (6)$$

The activity coefficients of all these ions were considered to be unity in a 0.165 M sodium chloride solution as suggested by La Mer [13]. Thus the total dissolved phosphorus is given by the expression,

$$a_{(P_{total})} = a_{(H_3PO_4)} + a_{(H_2PO_4^-)} + a_{(HPO_4^{2-})} + a_{(PO_4^{3-})} \quad (7)$$

where the activities are expressed in moles/litre.

From Equations 4 to 6 it can be shown that

$$a_{(H_3PO_4)} = \frac{a_{(P_{total})}a_{(H^+)^3}}{q} \quad (8)$$

$$a_{(H_2PO_4^-)} = \frac{a_{(P_{total})}K_1 a_{(H^+)^2}}{q} \quad (9)$$

$$a_{(HPO_4^{2-})} = \frac{a_{(P_{total})}K_1 K_2 a_{(H^+)}}{q} \quad (10)$$

$$a_{(PO_4^{3-})} = \frac{a_{(P_{total})}K_1 K_2 K_3}{q} \quad (11)$$

where $q = a_{(H^+)^3} + K_1 a_{(H^+)^2} + K_1 K_2 a_{(H^+)} + K_1 K_2 K_3$. A similar set of calculations [19] could be done to obtain the activity of the vanadate ion, $a_{(VO_4^{3-})}$, from its ionization constants [9], K_1, K_2 and K_3 taken, respectively, as 3.98×10^{-4}, 1.32×10^{-8} and 1.00×10^{-13}. A combination of these two sets of calculations could be made for the solid solutions.

The pK_{sp} values of the phases given are only a few among a total of about ten determinations made in each case, the individual values being found to differ from the average by about $\pm 7\%$. Within these limitations it could be concluded that the samples exhibited stoichiometric dissolution [9, 10, 20–24] contrary to the results reported in the earlier literature [4–6]. This is further substantiated by the proximity of the observed mole ratios, Ca/(P + V), of the systems with the stoichiometric value of 1.67. An additional substantiation of the stoichiometric dissolution of apatites could be provided by the remarkable regularity with which the end-members responded to the common-ion effect.

While the pK_{sp} of a given solute is supposed to be independent of the pH of the dissolving medium at a given temperature, it was found to decrease systematically with an increase in pH in all the solutes reported in this work. Substantiation of such results in the case of apatite systems was provided by Larsen [25, 26]. Based on an established fact that an apatite exists as a colloidal component in its saturated solution, Larsen supposed it to behave like an amphoteric colloid such that in highly acidic media the observed pK_{sp} is lower than expected while in alkaline media the converse is the case. The reason suggested by him was the occurrence of negative and positive adsorption of anions, respectively above and below the isoelectric point which is supposed to be in the vicinity of pH 5. However, further clarification can be provided by subsequent investigation.

A theoretical interpretation of the dependence of solubility of an ionic crystal on anionic replacement is possible through thermodynamic considerations [27]. For an ionic compound, change in the Gibbs energy accompanying dissolution, ΔG_{soln}, is related to K_{sp} as shown below, at a given temperature, T, and can be calculated by the expression

$$\Delta G_{soln} = -RT \ln K_{sp} \quad (12)$$

using the experimental value of K_{sp}. Alternatively, it can be evaluated by considering dissolution of an ionic compound to consist of (i) breaking down of its crystal architecture, and (ii) the hydration of the constituent ions thus set free, resulting in the expression

$$\Delta G_{soln} = \Sigma \Delta G_{hi} - \Delta G_{lattice} \quad (13)$$

where $\Sigma \Delta G_{hi}$ is the sum of the Gibbs energy changes of hydration of the constituting ions of the solute, while $\Delta G_{lattice}$ is the Gibbs energy change of formation of the lattice. The terms on the right-hand side of Equation 13 can be calculated [27] for an ionic crystal and can be shown to be dependent on the replacement of a given anion by another of a divergent ionic radius, as is the case with PO_4^{3-} and VO_4^{3-} ions.

It can be concluded that while the overall change in the solubility of an ionic compound depends exclusively on the relative variations in $\Delta G_{hydration}$ and $\Delta G_{lattice}$ terms, as mentioned above, the latter becomes more dominant for sparingly soluble salts such as apatites. This can be justified by the fact that the alterations in hydration energies [28] for the pair of anions involved, i.e. PO_4^{3-} and VO_4^{3-} in the substitution investigated, are of a very small magnitude [29]. That CVA is more soluble than CPA under a given set of experimental conditions could be

substantiated by the fact that the lattice energy of CVA is expected to be lower than that of CPA because the covalent radius of VO_4^{3-} (0.122 nm) is greater than that of PO_4^{3-} (0.110 nm). The decomposition temperature from thermogravimetric analysis [9, 30] was of the order of 1000 and 1300° C, respectively, for CVA and CPA. These theoretical considerations are adequate to explain qualitatively the dependence of solubility of ionic crystals on ionic replacement.

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Preparation and characterization of phosphate and arsenate apatites of strontium and their solid solutions

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Samples of phosphate and arsenate apatites of strontium and six of their solid solutions, spread over the entire compositional range, were prepared by a wet method. They were characterized by chemical, X-ray, electron microscopic and infrared analyses. The validity of Vegard's law established the homogeneity of the solid solutions.

1. Introduction

Calcium hydroxylapatite, $3Ca_3(PO_4)_2 . Ca(OH)_2$, the principal inorganic constituent [1] of animal bones and teeth, provides structural stability to skeletal and dental systems while storing calcium and phosphorus to maintain their biologically required levels in the body fluids. In addition, it acts as a detoxifying depository to store unwanted ions consequent upon its ability to undergo a series of cationic and anionic isomorphous substitutions [2]. Principal among such substitutions have been the replacement of Ca^{2+} by Sr^{2+} and of PO_4^{3-} by AsO_4^{3-} which constitute, respectively, the mechanisms of incorporation of strontium and arsenic in the human skeletal system, the former leading to radiation damage [3, 4] if β-active ^{90}Sr is involved, and the latter to toxicity [5, 6]. While $Ca^{2+} \rightleftharpoons Sr^{2+}$ exchange was investigated extensively [3, 7], studies on substitution of phosphate by arsenate on strontium hydroxylapatite were not undertaken earlier. In order to throw light on the influence of $PO_4^{3-} \rightleftharpoons AsO_4^{3-}$ exchange on the principal bone processes, a series of six solid solutions of phosphate and arsenate apatites of strontium, (SPA and SAA, respectively) spread over the entire compositional range, were prepared and characterized. The details of these investigations are reported in the present paper.

2. Experimental details

The experimental details for the preparation of the samples by precipitation were based on the following equation:

$$10\ Sr^{2+} + 6\ XO_4^{3-} + 2\ OH^- \rightarrow Sr_{10}(XO_4)_6(OH)_2$$

where X = phosphorus or arsenic for the end-members and (P + As) for the solid solutions. Stock solutions of Sr^{2+}, PO_4^{3-} and AsO_4^{3-} were prepared respectively from strontium nitrate, diammonium hydrogen phosphate and arsenic pentoxide, the latter being converted to AsO_4^{3-} by the addition of an appropriate amount of sodium hydroxide. From these solutions, preserved in polyethylene containers, the amounts of Sr^{2+}, PO_4^{3-} and AsO_4^{3-} were determined by appropriate analytical methods [8].

For preparation of each sample, calculated volumes of solutions of the starting materials containing stoichiometric quantities required for a yield of ~ 30 g were used. An appropriate volume of strontium nitrate solution treated with a required volume of ethylene diamine [2, 3] to maintain a pH of ~ 12 on dilution to 1000 ml was taken in a 3 litre round-bottomed flask. Diammonium hydrogen phosphate and/or sodium orthoarsenate solutions, stoichiometric with that of the Sr^{2+} solution used, were likewise treated with ethylene diamine and diluted to 1000 ml such that the pH of the resulting solution was ~ 12. This solution was added dropwise to that of Sr^{2+}, the precipitation being done at 37 ± 0.5° C to simulate biological conditions. Air free of CO_2 was bubbled through the precipitation medium to prevent the formation of carbonate apatite and also to keep the medium well stirred. The produce was refluxed for about 2 h in contact with the mother-liquor, left overnight, filtered through a G4 sintered glass crucible and washed with water until the washings were neutral. The samples were then washed with acetone and air-dried to 800° C for ~ 6 h and cooled in a desiccated atmosphere, for use in chemical, X-ray and infrared analyses, the experimental details of which are the same as those described elsewhere [8, 9]. The air-dried samples were used for electron microscopic analysis [10].

3. Results and discussion

3.1. Chemical analysis

The weight per cents of strontium, phosphorus and arsenic of the samples were determined by analytical procedures specially worked out for the purpose [8, 9]. These results are given in columns 3, 4 and 5 of Table I. The g atom ratios, Sr/P + As, and molecular formulae of the samples were calculated from these results and are given in column 6 of the table. The results indicated that these ratios vary between 1.63 and 1.69, the theoretical value being 1.67. A striking

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TABLE I Chemical analysis of solid solutions of phosphate and arsenate apatites of strontium

Sample number	Sample	Sr (wt %)	P (wt %)	As (wt %)	g atom ratio, Sr/P + As	Molecular formula
1	2	3	4	5	6	7
1.	Strontium phosphate apatite	58.96	12.38	–	1.68	$Sr_{10}(PO_4)_6(OH)_2$
2.	Solid solution: I	58.13	11.09	3.14	1.66	$Sr_{10}(PO_4)_{5.4}(AsO_4)_{0.6}(OH)_2$
3.	Solid solution: II	56.47	8.83	8.11	1.64	$Sr_{10}(PO_4)_{4.4}(AsO_4)_{1.6}(OH)_2$
4.	Solid solution: III	56.44	8.44	8.54	1.67	$Sr_{10}(PO_4)_{4.2}(AsO_4)_{1.8}(OH)_2$
5.	Solid solution: IV	54.05	5.10	15.69	1.65	$Sr_{10}(PO_4)_{2.6}(AsO_4)_{3.4}(OH)_2$
6.	Solid solution: V	58.55	4.37	16.58	1.69	$Sr_{10}(PO_4)_{2.3}(AsO_4)_{3.7}(OH)_2$
7.	Solid solution: VI	51.59	1.85	21.97	1.66	$Sr_{10}(PO_4)_{1.0}(AsO_4)_{5.0}(OH)_2$
8.	Strontium arsenate apatite	50.26	–	25.77	1.66	$Sr_{10}(AsO_4)_6(OH)_2$

TABLE II X-ray and infrared analyses of solid solutions of phosphate and arsenate apatites of strontium

Sample number	Lattice parameters (nm)		Unit cell volume, V_{uc}, $\sqrt{3}/2\ a^2c$ (nm)^3	Molar volume $V_{uc}N$ (ml mol^{-1})	Wave numbers of peaks (cm^{-1})		
	a	c			PO_4^{3-}	AsO_4^{3-}	OH^-
1	2	3	4	5	6	7	8
1.	0.976	0.726	0.598	360	1075 (s),* 1030 (s), 948 (m)	–	3572 (w)
2.	0.982	0.728	0.608	366	1072 (s), 1028 (s), 947 (m)	851 (s)	3564 (w)
3.	0.993	0.734	0.627	378	1068 (s), 1017 (s), 946 (m)	850 (s)	3564 (w)
4.	0.996	0.736	0.632	381	1018 (s), 945 (m),	852 (s)	3564 (w)
5.	1.013	0.744	0.662	399	1025 (s), 942 (m)	833 (s)	3562 (w)
6.	1.016	0.746	0.667	402	1028 (s), 941 (w)	830 (s)	3562 (w)
7.	1.031	0.754	0.694	418	1028 (s), 973 (m)	821 (s)	3556 (w)
8.	1.043	0.760	0.716	431	–	863 (s), 841 (s), 825 (s)	3556 (w)

*s = strong, m = medium, w = weak.

agreement between the experimental g atom ratios with the stoichiometric value justifies the suitability of the methods adopted for preparation and chemical analysis of the samples.

3.2. X-ray data

The lattice parameters a and c of the samples given in columns 2 and 3 of Table II were found to increase in the ranges 0.976 to 1.043 nm and 0.726 to 0.760 nm, respectively, with an increase in the proportion of arsenate. The unit cell and molar volumes of the samples given in columns 4 and 5, respectively, of Table II increase in the ranges, 0.598 to 0.716 nm^3 and 360 to 431 ml, respectively. Such a systematic increase in the lattice parameters as well as in the unit cell volumes with an increase in the proportion of AsO_4^{3-}, as indicated in Figs 1 and 2, confirms the homogeneity of the solid solutions, since a dilation of the unit cell is expected by the replacement of phosphate by arsenate (covalent radii, 0.110 and 0.118 nm, respectively). In addition, Fig. 2 substantiates the validity of Vegard's law which states that the unit cell volume is a linear function of the composition in the case of homogeneous solid solutions.

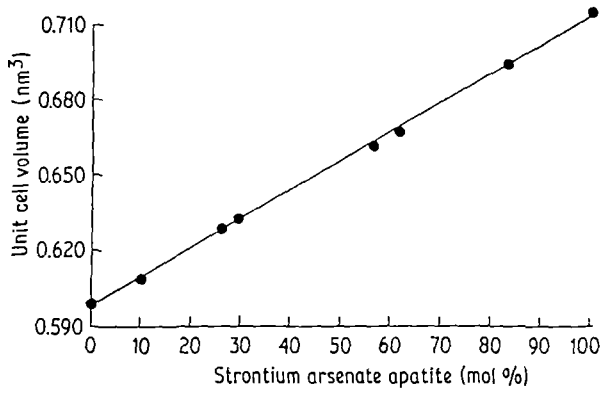

Figure 1 Dependence of unit cell volume of solid solutions of phosphate and arsenate apatites of strontium on the mol % strontium arsenate apatite.

3.3. Infrared data

The infrared absorption spectra of the samples [11, 12] exhibited characteristics OH-stretching mode of apatite in the vicinity of 3560 cm^{-1}. The characteristic phosphate peaks observed close to 1075, 1030 and 950 cm^{-1} and those of arsenate observed in the vicinity

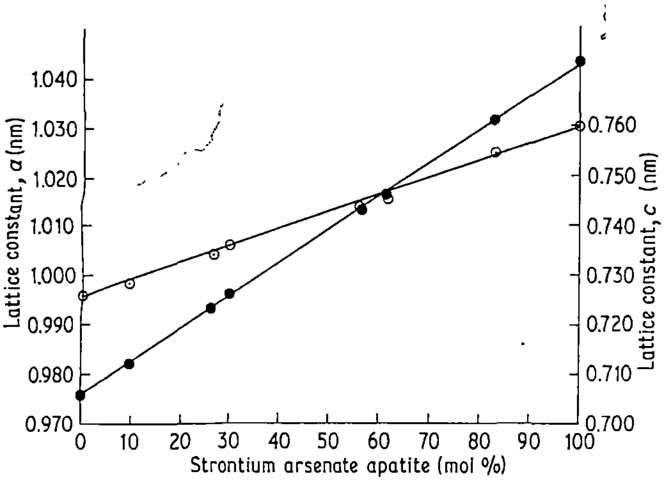

Figure 2 Dependence of lattice parameters of solid solutions of phosphate and arsenate apatites of strontium on the mol % strontium arsenate apatite. (●) Value of lattice parameter 'a'; (⊙) value of lattice parameter 'e'.

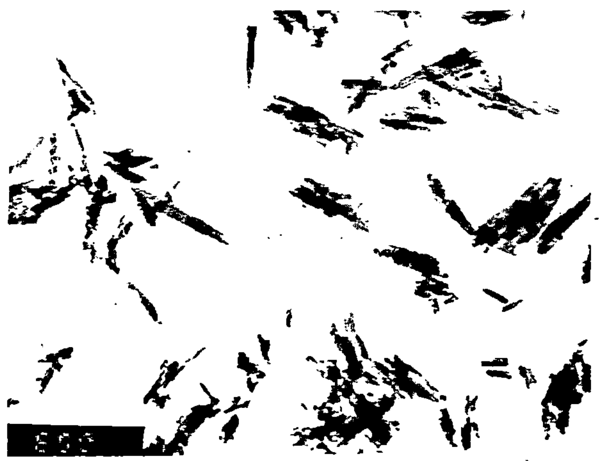

Figure 3 Electron micrograph of the solid solution of phosphate and arsenate apatite of strontium (sample 4 of Table I) × 35 000.

of 850 cm^{-1} also substantiate the homogeneity of the samples, the area under the phosphate peak being gradually suppressed and that under the arsenate peak increased as the proportion of the latter increased.

3.4. Electron microscopic studies

A representative electron micrograph of one of the samples (no. 4 of Table I) given in Fig. 3 shows the hexagonal shape of the crystals characteristic of apatites [13, 14].

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