Inorganica Chimica Acta, 67 (1982) 183–187

A Method of Preparation and Characterization of Magnesium-Apatites

S. V. CHIRANJEEVIRAO, J. HEMMERLE, J. C. VOEGEL and R. M. FRANK

Unité de Recherches INSERM U 157, Faculté de Chirurgie Dentaire, Université Louis Pasteur, 4 Rue Kirschleger, 67000 Strasbourg, France

Received May 20, 1982

Isomorphous magnesium cation can be introduced into the lattice of calcium hydroxyapatite at the calcium site by the replacement mechanism. In the present paper a successful preparation of magnesium apatites in aqueous media is reported, and the samples have been characterized by microanalyses, infrared spectroscopy and X-ray diffraction techniques. The crystallinity of the specimens has been observed by scanning electron microscopy. The substitution of magnesium in the lattice of calcium hydroxyapatite is possible due to the closeness of the ionic radius of the divalent cations involved in the substitution reaction.

Introduction

Calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, (HA) is an important inorganic crystalline constituent of human calcified tissues (bones and teeth). It undergoes a series of cationic and anionic isomorphous replacement reaction [1] resulting in the formation of solid solutions with substituted ions. The replacement of calcium by magnesium in HA is of extreme biological significance as it explains the mechanism of incorporation of magnesium in teeth and bones [2, 3]. The exchange process results in the formation of a series of solid solutions of magnesium-apatites, and when made to progress till completion it results in the formation of pure magnesium apatite, $Mg_{10}(PO_4)_6(OH)_2$ according to the following scheme.

$$Ca_{10}(PO_4)_6(OH)_2 + nMg^{2+} \rightarrow Ca_{10-n}Mg_n(PO_4)_6(OH)_2 + nCa^{2+}$$

In biological apatites the presence of many inorganic cations and anions has been detected [4]. Several ions such as F^-, Cl^-, Zn^{2+} *etc.* were found at higher concentrations near the surface whereas other ions such as CO_3^{2-}, Na^+, Mg^{2+} were detected in the deeper parts of the enamel [2, 3]. Therefore it appears clearly that the preparation of synthetic apatites with varying quantities of magnesium in the form of solid solutions is necessary to study the influence of incorporation of magnesium ions in biological apatites. All the methods used earlier for the preparation of solid solutions of calcium hydroxyapatite with varying quantities of divalent cations are by solid state reaction using high temperature or pressure, and sometimes both [5]. The samples prepared by those methods were found however to be discontinuous and non-homogeneous. Little work has been done on the preparation of solid solutions of calcium hydroxyapatite with varying quantities of magnesium, and hence it is desirable to prepare synthetic samples of calcium hydroxyapatite with varying quantities of magnesium. In this paper a successful attempt to elaborate a new method of preparation of homogeneous solid solutions over the entire compositional range by the novel method of co-precipitation in aqueous media is reported. The purity and homogeneity of the samples obtained have been confirmed by chemical analyses, X-ray diffraction and infrared techniques.

Experimental

Material and Methods

All the chemicals used in this work were of analytical grade (Merck or Fluka) and deionised water was used in order to eliminate undesirable ions of water since the samples have been synthesized in aqueous media. To a two necked 2L Pyrex flask separating funnels A and B were fitted with one holed rubber stoppers. In the funnel A stoichiometric quantity of a mixture of calcium nitrate and magnesium nitrate solutions and in the funnel B stoichiometric quantity of ammonium dihydrogen phosphate solutions was added. The pH of the solutions were scrupulously maintained above 9, otherwise it results in the formation of calcium-deficient apatites [6]. Care was taken to avoid the absorption of atmospheric carbon dioxide by fixing guard tubes to the funnels filled with lime. The solutions were carefully added into the flask which contained a dilute solution of ammonium hydroxide in order to maintain the pH of the

0020-1693/82/0000-0000/$02.75

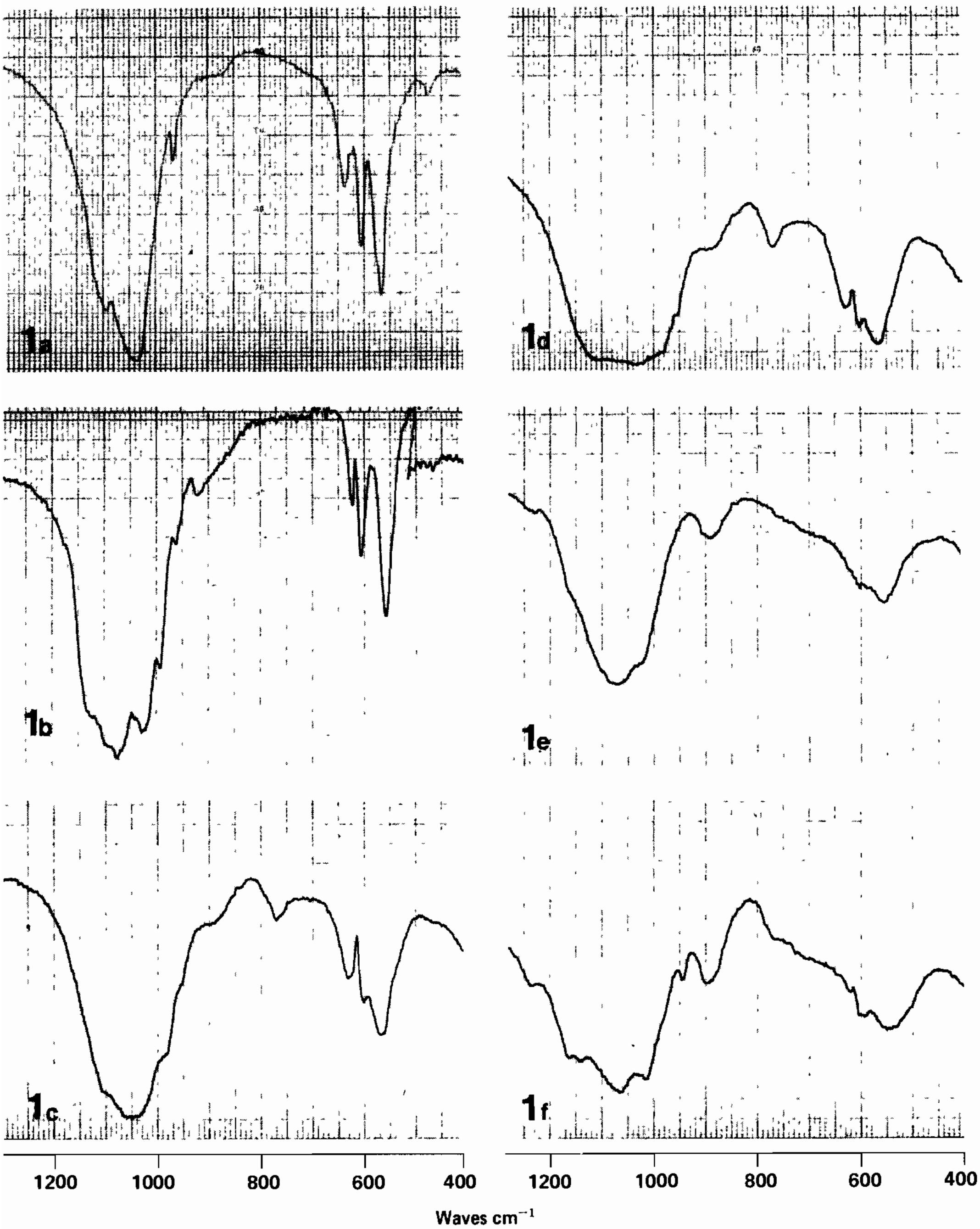

Fig 1. Infrared spectra of the synthesized compounds. (a) $Ca_{10}(PO_4)_6(OH)_2$; (b) $Ca_{8.1}Mg_{1.9}(PO_4)_6(OH)_2$; (c) $Ca_{6.0}Mg_{4.0}(PO_4)_6(OH)_2$; (d) $Ca_{4.0}Mg_{6.0}(PO_4)_6(OH)_2$; (e) $Ca_{1.8}Mg_{8.2}(PO_4)_6(OH)_2$; (f) $Mg_{10}(PO_4)_6(OH)_2$.

medium above 9 during precipitation, and the medium of precipitation was well stirred by means of a magnetic stirrer.

After the precipitation, the contents of the flask were refluxed for about 1 h in order to improve the homogeneity and crystallinity of the samples. The latter were filtered. The precipitate was washed till free from adsorbed ions, dried at 105 °C for 6 h, powdered to 200 mesh (BSS) and analysed for its chemical composition. The density of the samples were determined by means of specific gravity bottles using toluene as a solvent.

Infrared spectra of the samples have been recorded by using a KBr pellet technique with the help of a

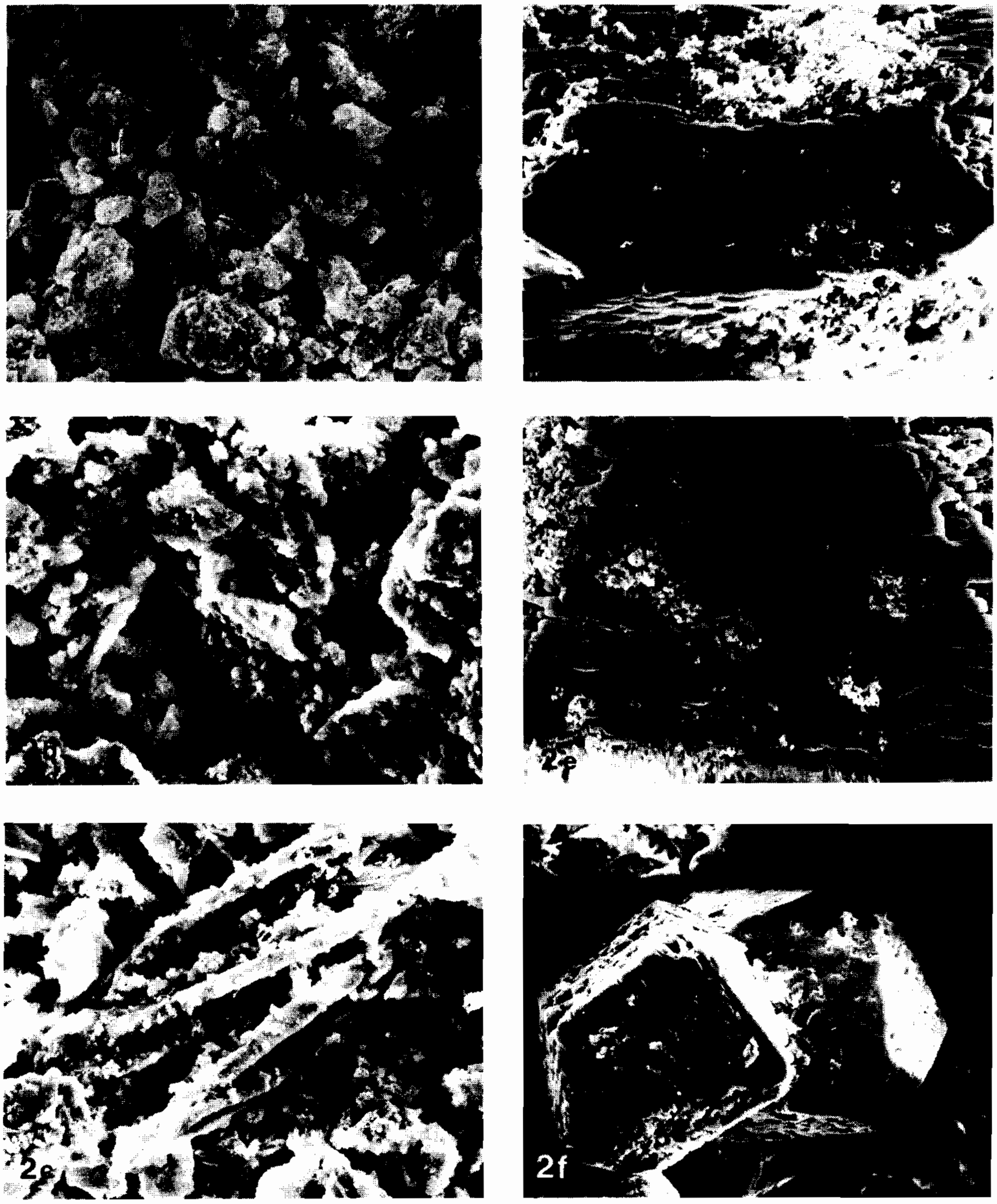

Fig. 2. Scanning electron micrographs of the synthesized compounds. (a) Tiny crystals of $Ca_{10}(PO_4)_6(OH)_2$ × 3300; (b) Presence of needle shaped crystals of $Ca_{8.1}Mg_{1.9}(PO_4)_6(OH)_2$ × 3300; (c) Presence of needle shaped crystals of $Ca_6Mg_4(PO_4)_6(OH)_2$ × 1000; (d) Presence of hexagonal shaped crystals of $Ca_4Mg_6(PO_4)_6(OH)_2$ × 3000; (e) Presence of hexagonal shaped crystals of $Ca_{1.8}Mg_{8.2}(PO_4)_6(OH)_2$ × 3300; (f) Presence of large crystals of $Mg_{10}(PO_4)_6(OH)_2$ × 1600.

Perkin-Elmer 396 double grating spectrophotometer. X-ray diffraction analyses were made on a Philips generator PW1130 equipment using Ni filtered CuK_α radiation generated at 40 KV and 25 mA, scanning speed of $1/2^\circ$ per minute. Scanning electron micrographs were taken on selected areas of the samples using a Jeol 35C SEM operating at 15 KV. The details of the specimen preparation are as follows. A small quantity of the powdered sample (200 mesh BSS) was added to about 100 ml of deionized water taken in a beaker, stirred well and filtered through Millipore filters (Millipore Corporation Bedford, Mass. U.S.A., 8 μm size) under suction so that the powdered material is fixed tightly to the filter paper, then the filter paper was air dried, and a portion carefully cut to the size of the specimen mounting block

TABLE I. Chemic Analyses and X-ray Data of Synthetic Apatite and Its Solid Solutions with Varied Amounts of Magnesium.

Sample No.	Wt. %			Molecular Formula	g atom ratio Ca + Mg/p	Molecular volumes (ml/mol)	X-ray data in Å	
	Ca	p	Mg				*a*	*c*
1	39.95	18.61	–	$Ca_{10}(PO_4)_6(OH)_2$	1.67	338.6	9.429	6.884
2	33.31	19.07	4.73	$Ca_{8.1}Mg_{1.9}(PO_4)_6(OH)_2$	1.68	343.2	9.366	6.887
3	25.54	19.74	10.33	$Ca_{6.0}Mg_{4.0}(PO_4)_6(OH)_2$	1.67	348.7	9.353	6.886
4	17.62	20.43	16.28	$Ca_{4.0}Mg_{6.0}(PO_4)_6(OH)_2$	1.67	352.7	9.329	6.886
5	8.24	21.22	22.59	$Ca_{1.8}Mg_{8.2}(PO_4)_6(OH)_2$	1.67	357.5	9.317	6.884
6	–	21.95	28.71	$Mg_{10}(PO_4)_6(OH)_2$	1.68	363.5	9.298	6.886

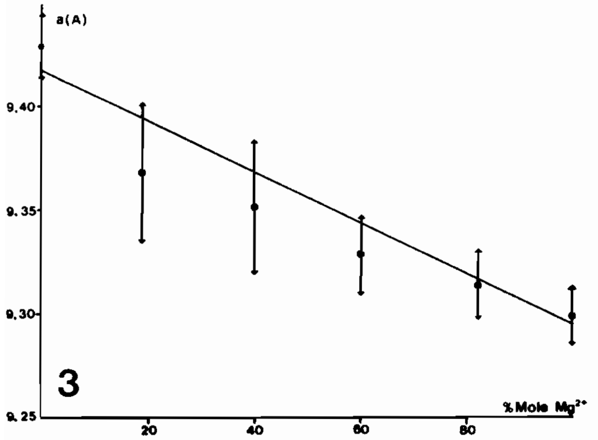

Fig. 3. *a* Parameter evolution *versus* mol percentage of magnesium content.

(10 mm diameter, 5 mm height, brass metal block) and fixed with a conductive paint (Electro conductives Dotite, Japan) air dried and the specimen surface sputtered with Au–Pd alloy with the help of Hummer Jr. evaporator (Siemens, Karlsruhe). Using high voltage and sputtering time of 3 minutes, the thickness of the coating of the metal is approximately 300 Å.

Results

The samples were analysed for calcium, magnesium and phosphate by means of complexometric and spectrophotometric techniques [7, 8] and the experimental Wt.% errors of the determination of calcium, magnesium and phosphate when present together were 0.1, 0.1 and 0.05 respectively. Based on the fact that a molecule of each sample has a total of 10 g atoms of Ca and/or Mg, the molecular formula of the samples were determined and from them the atomic ratio of (Ca + Mg)/P in a mol of each sample was calculated and the results given in Table I. From the density of the samples, the atomic volumes have been determined. The infrared spectra in the range from 1400–400 cm^{-1} have been included in Fig. 1a–f. The scanning electron micrographs have been included in Fig. 2a–f. The micrographs indicated the presence of crystallites. In the absence of Mg^{2+}, the inorganic compound is found to be tiny agglomerated crystals (Fig. 2a) whereas in the compounds with 4.7 to 22.6% of magnesium the individual crystallites are distinctly visible (Fig. 2b–e) while in the compound with 28.7% of magnesium large crystals are clearly seen (Fig. 2f).

To obtain lattice parameters and the unit cell volumes of the crystals from the 2θ values of the X-ray diffraction spectra, the equidistances were determined and the corresponding d_{hkl} values were obtained by comparing them to the values given for hydroxyapatite [9]. The *a*-axis was calculated from the (200), (213) and (222) reflections and the *c*-axis from the (002) and (004) reflections. A graphical representation of the *a* parameter evolution with the mol percent content of magnesium in the samples as given in Fig. 3. The *c* parameter is constant for the while range of Mg substituted compounds with a mean value of $\bar{c}$ = 6.886 Å where it appears that *a* decreases linearly with the Mg content of the apatite.

Discussion

The observed values of the molar atomic ratio (theoretical 1.66) of Ca/P and Mg/P for the extreme members and (Ca + Mg)/P for the intermediates and the closeness of the values of molar volumes of the end members and those intermediate samples which lie within the range of end members is to indicate the formation of homogeneous solid solutions [10]. This interpretation can further be substantiated with the infrared spectral data in which shifts of the ν_3 and ν_4 frequencies due to $(PO_4)^{3-}$ are clearly observed and this is in accordance with the earlier observation on the formation of homogeneous solid solutions [10]. Barnes equation gives a relationship between frequency atomic mass of the participating atoms and the restoring forces between atoms [11]. The ν_3 and ν_4 frequencies of $(PO_4)^{3-}$ (at about 560 and 1050 cm^{-1} respectively) are clearly observed and the shifts in their respective positions can easily be spotted out from the spectra given in Fig. 1a–f which reveals the formation of homogeneous solid solutions. Hydroxyapatite has a hexagonal crystalline structure of the class $P_{6\ 3/m}$ space group with the unit cell dimensions $a = 9.432$ and $c = 6.881$ [12]. It is seen from X-ray diffraction analysis that with the increase of magnesium content in the solid solutions the lattice parameter a is decreasing while that of c has no distinct change, resulting in the contraction of the unit cell. This is understandable since Ca^{2+} (ionic radius 0.99 Å) in the apatite lattice is isomorphously substituted by Mg^{2+} (0.72 Å) which has smaller ionic radius resulting in the formation of homogeneous solid solutions. The scanning electron micrographs showed clearly crystallites characteristic of apatites. The absence of extraneous phases in the micrographs indicated the presence of a single phase of apatite in the samples.

References

1 J. R. Vanwazer, 'Phosphorous and Its Compounds', Vol. 1, p. 530. Interscience, London, 1964.
2 J. A. Weatherell and C. Robinson, 'Biological Mineralization', p. 43–74, Wiley, New York, 1973.
3 I. Zipkin, 'Biological Calcification', p. 69–103. Appenton–Century–Crofies, New York, 1970.
4 E. D. Eanes, *J. Dent. Res., 58,* 829 (1979).
5 G. Engel and W. E. Klee, *J. Solid State Chemistry, 5,* 28 (1972).
6 E. E. Berry, *J. Inorg. Nucl. Chem., 29,* 317 (1967).
7 S. V. Chiranjeevirao, *Current Science, 43,* 309 (1974).
8 S. V. Chiranjeevirao, *Z. Anal. Chem., 284,* 45 (1977).
9 A.S.T.M. File No 9 – 432 (1967).
10 J. R. Partington, 'An Advanced Treatise on Physical Chemistry', Vol. 3, Longmans–Green, London, 1952.
11 R. B. Barnes, R. C. Gore, V. Liddel and V. Z Williams, 'Infrared Spectroscopy', Reinhold, New York, 1944.
12 A. S. Posner, A. Perloff and A. F. Diorio, *Acta Cryst., 11,* 308 (1958).