

# The uptake of titanium ions by hydroxyapatite particles— structural changes and possible mechanisms

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Received 18 April 2005; accepted 26 September 2005

Available online 26 October 2005

## Abstract

In order to understand the effect of titanium ions on the molecular structure of hydroxyapatite (HAp), HAp powders were incubated in solutions with different titanium concentrations. After incubation, the powders obtained were analysed using different techniques, namely X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), differential thermal analysis (DTA), X-ray photoelectron spectroscopy (XPS), and energy dispersive spectroscopy (EDS). The results suggest that, depending on the concentration of titanium in solution, two different mechanisms of interaction with HAp occur. For concentrations equal to or smaller than 200 ppm, the titanium uptake by the solid seems to be primarily due to incorporation in the lattice. For higher concentrations, a dissolution-precipitation process seems to occur, leading to formation of a titanium phosphate compound.

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**Keywords:** Hydroxyapatite; Titanium; Titanium phosphate

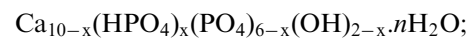
## 1. Introduction

Due to its crystallographic similarity to various calcified tissues of vertebrates, hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (HAp), has been extensively used as a substitute material for damaged teeth or bone over the past three decades, and its compatibility with surrounding tissues has been experimentally proven.

Several methods to prepare HAp have been reported in the literature, including precipitation, conversion of other calcium phosphate salts, solid-state reactions, and sol gel crystallisation [1–3].

Chemically precipitated HAp differs from the apatites obtained by high temperature, hydrothermal and igneous preparations because of its submicroscopic crystal size,

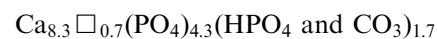
structural distortion and non-stoichiometry, since it is usually calcium and hydroxyl deficient [4]. At present, the following formula is generally suggested [5] for non-stoichiometric (carbonate free) HAp:



$$0 < x < 1, n = 0-2.5.$$

The degree of non-stoichiometry depends on the synthesis method and is usually characterised by the Ca/P ratio. The total electrical charge is assumed to be compensated by the introduction of  $\text{H}^+$ , giving rise to  $\text{H}_2\text{O}$  molecules replacing  $\text{OH}^-$  ions.

Bone mineral is a heterogeneous material, which is in constant evolution. Its composition varies, depending on species, type of bone, diet, etc. However, its chemical composition can be represented approximately by a single chemical formula:



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in which  $\square$  represents a vacancy [6]. With maturation, the bone crystal approaches, but never reaches, the perfect HAp structure.

HAp easily forms solid solutions via chemical reactions with various metal oxides, halides, and carbonates. Apatite is capable of accommodating several substituents, while still maintaining its basic structure.  $\text{Ca}^{2+}$  can be substituted to some extent by monovalent ( $\text{Na}^+$ ,  $\text{K}^+$ ) [7], divalent ( $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ) [8–10] and trivalent ( $\text{Y}^{3+}$ ) cations [11]. Among the anionic substitutions, the significant ones are replacement of  $\text{OH}^-$  by  $\text{CO}_3^{2-}$  [12],  $\text{F}^-$  [13,14],  $\text{Cl}^-$  [14], and  $\text{PO}_4^{3-}$  by  $\text{CO}_3^{2-}$  [15],  $\text{AsO}_4^{3-}$  and  $\text{VO}_4^{3-}$  [16]. Some substitutions are coupled with others [17–20] to maintain charge balance in the apatite, e.g.  $\text{CO}_3^{2-}$  for  $\text{PO}_4^{3-}$  coupled with  $\text{Na}^+$  for  $\text{Ca}^{2+}$ . The trivalent anionic phosphate sites cannot accept vacancies, probably because the trivalent anions are quite large and vacancies would destabilise the lattice [21]. By contrast, the cationic sites can accept vacancies, up to a maximum of 2 sites out of the 10 existing in stoichiometric apatites [21].

Due to its interesting chemical and physical properties, synthetic HAp finds various applications, not only as a biomaterial, but also as an adsorbent for chromatography to separate proteins and enzymes [22], as a catalyst for dehydrogenation and dehydration of alcohols [23], and as an effective means for removing dissolved divalent cations from solution. For instance, it has been regarded as a possible solid for immobilisation of pollutant metals, particularly  $\text{Pb}^{2+}$ , from aqueous solutions [24].

In what concerns HAp applicability in the biomedical field, the capacity of its lattice to act as a host for different chemical species has been explored. The most common example is the preparation of carbonate-substituted HAp [12,15] and fluoride-substituted HAp [13,14]. Another potential method for improving the biological activity of HAp is the incorporation of silicon (or silicate groups) into its lattice [25].

The properties of HAp that are affected by substituents are: lattice parameters ( $a$  and  $c$  axis dimensions), crystal size and shape, crystal strain, crystallinity, infrared absorption spectral properties and thermal stability [26]. When the substituents are present simultaneously, they may have additive, synergistic, or opposite effects on the properties of the apatite crystallites [20,27,28].

The principal constituent of the inorganic part of human and animal bone and teeth is quite similar to HAp. The type and amount of ionic substitutions in the apatite phase of bone vary from the wt% level (e.g. 5 wt%  $\text{CO}_3^{2-}$ ) to the ppm-ppb level (e.g.  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ ) [8,9,15]. Although these levels of substitution are small, the replacement ions play a major role in the biochemistry of hard tissues. Certain metals, such as aluminium, iron, cadmium and lead, are known to cause bone pathologies in humans and animals. Studies have been reported concerning the effects of aluminium in bone disorders in individuals with chronic renal disease subjected to dialysis [29,30]. Lead poisoning [31], also known as “plumbism”, is caused by inhalation of

lead in the form of dust or its absorption through the skin, the mechanism involved being attributed to isomorphous substitution of  $\text{Ca}^{2+}$  by  $\text{Pb}^{2+}$  in bone, leading to formation of solid solutions of HAp and lead HAp. Also, the interaction of cadmium with biological apatites is responsible for an osseous disease with effects similar to osteoporosis [32].

Although titanium is one of the metallic materials more widely used in the biomedical field, its interaction with apatites is not clearly understood. This work aims at contributing to the study of the influence of titanium ions in the structure of HAp.

## 2. Materials and methods

Commercial HAp powders (CAM Implants) pre-heated at 1000 °C were incubated in solutions containing different concentrations of titanium, ranging from 50 to 350 ppm. These samples will be identified as HApXTi throughout the text, X being the amount of Ti, in ppm, that was present in the incubation media. The HAp powder surface area was 76 cm<sup>2</sup>/mg and 90% of the particles were smaller than 20.51  $\mu\text{m}$  with a volume average diameter of 7.96  $\mu\text{m}$ . All the solutions were prepared with de-ionised water and the chemical reagents were of p.a. grade. The dissolution studies were carried out using a saline solution of 0.9% NaCl to which the metal ions were added in the form of a concentrated salt solution (Titrisol Merck Standard - $\text{TiCl}_4$  in 18% HCl). A solid-to-liquid ratio of 500 mg of HAp to 50 ml of solution was used. The samples were tested in polyethylene flasks, maintained at 37 °C ( $\pm 0.2$  °C) for 10 days in a warm air cabinet equipped with an orbital shaker. An agitation speed of 250 r.p.m. was used throughout the experiments.

After incubation, the solid and liquid phase were separated by centrifuging at 4500 r.p.m. and the supernatant liquid was analysed by atomic absorption spectroscopy (AAS) for Ti ions using a GBC 904-AA spectrometer. The solid samples were thoroughly washed with de-ionised water to eliminate  $\text{Cl}^-$  and  $\text{Na}^+$  ions and dried in a stove at 60 °C for 24 h. The solids were then analysed using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, energy dispersive spectroscopy (EDS), differential thermal analysis (DTA) and X-ray photoelectron spectroscopy (XPS).

The phase composition of the as-received HAp and of the powders incubated in solutions containing different concentrations of Ti were determined using a Siemens D5000 diffractometer with  $\text{CuK}_\alpha$  radiation; the X-ray generator operated at 40 kV and 40 mA. A secondary monochromator was used on the diffracted beam side with a scintillation counter detector. Data were collected over the  $2\theta$  range with a step size of 0.02° and a count time of 12 s. Identification of phases was achieved by comparing the diffraction patterns of the ceramic powders with ICDD (JCPDS) standards. Determination of the structural parameters of HAp and the powders incubated in solutions containing different concentrations of Ti was made by Rietveld refinement of the X-ray diffraction data collected for the powders. The refinement software GSAS was used and the refinements were based on the structural data of Kay et al [33] using the space group  $\text{P6}_3/\text{m}$ . The following parameters were refined: background parameters, scale factor, zero point, lattice parameters, and atomic positions. The FT-IR spectra were obtained using a Perkin Elmer 2000 FT-IR spectrometer. All the samples were prepared as KBr discs and were run at a spectral resolution of 4 cm<sup>-1</sup>. Five hundred scans were accumulated in order to obtain a high signal-to-noise level. A nitrogen purge of the sample compartment was performed to minimise artefacts that could arise from residual air bands ( $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapour). The derivative and curve fitting algorithms were performed with the software PeakFit from AISN Software. Initial peak positions were obtained from second derivative spectra of the raw data. Second derivative spectra were calculated based on the Stavitzky and Golay method [34], which provides a combined approach to smoothing and derivatisation. The number and

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