Acta Biomaterialia 8 (2012) 1180-1189

Contents lists available at SciVerse ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

On the effect of temperature on the insertion of zinc into hydroxyapatite

Sandrine Gomes^{a,b}, Jean-Marie Nedelec^{a,b,*}, Guillaume Renaudin^{a,b}

^a Clermont Université, ENSCCF, Laboratoire des Matériaux Inorganiques, BP 10448, 63000 Clermont-Ferrand, France ^b CNRS, UMR 6002, LMI, 63177 Aubière, France

A R T I C L E I N F O

Article history: Received 12 September 2011 Received in revised form 3 December 2011 Accepted 5 December 2011 Available online 13 December 2011

Keywords: Bioceramics Zinc doping Calcium phosphates Rietveld refinement Thermal treatment

ABSTRACT

Rietveld analysis of X-ray powder diffraction patterns recorded from 28 hydroxyapatite (HAp) samples containing various amounts of zinc (0, 1.6, 3.2 and 6.1 wt.% Zn) and heat treated at various temperatures (between 500 °C and 1100 °C) has enabled the Zn insertion mechanism into the HAp crystal structure to be finely characterized. The formation of Zn-doped HAp was achieved above 900 °C only. Zn-doped HAp has the Ca₁₀Zn_x(PO₄)₆(OH)_{2-2x}O_{2x} (0 < $x \le 0.25$) chemical composition with a constant Ca/P ratio of 1.67 due to the insertion mechanism into the hexagonal channel (partial occupancy of the 2*b* Wyckoff site with the formation of linear O–Zn–O entities). Samples heat treated at 500 °C were almost single phase, HAp did not incorporate Zn and about half of the Zn atoms incorporated during the synthesis are not observable by X-ray powder diffraction (contained in an amorphous compound or physisorbed at the HAp surface). The reversible formation of Zn-doped β -TCP phase was observed at 600 °C, reached its maximum content at 900 °C and had almost vanished at 1100 °C. The results presented here strengthen the recently described mechanism of Zn insertion in the interstitial 2*b* Wyckoff position of the HAp structure, and explain the origin of the contradictory reports in the corresponding literature.

© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Apatites, $Ca_{10}(PO_4)_6(F,CI,OH)_2$, are a complex and diverse class of materials [1] which have gained increasing importance due to their biological role. One of the main constituents of bone and hard tissue in mammals is a calcium phosphate mineral whose structure closely resembles hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$. The socalled biological apatite refers to poorly crystallized non-stoichiometric carbonate-containing HAp. The inorganic content varies from 65% in bone to 90% in dental enamel [2].

Because biological apatites are formed in biological conditions, they usually contain a large variety of doping elements (F, Si, Sr, Mg, etc.) that can also have some specific biological properties. The important role of zinc has been put forward in the recent literature [3–6]. In effect, uptake and release of Zn in the body are strongly mediated by the bone reservoir, where the Zn content ranges from 125 to 250 ppm (against 28–33 ppm for the whole body) [6]. It has been demonstrated that zinc has a stimulatory effect on bone formation and mineralization in vivo and in vitro [7,8], and that Zn incorporation into implants promotes bone formation around the material [9–11], improves biological properties [9,12] decreases the inflammatory response [13,14], and has an antibacterial effect [15].

* Corresponding author at: Clermont Université, ENSCCF, Laboratoire des Matériaux Inorganiques, BP 10448, 63000 Clermont-Ferrand, France. Tel.: +33 4 73 40 71 95; fax: +33 4 73 40 53 28.

In order to understand the mechanisms of incorporation of doping elements in HAp, and to correctly characterize natural and/or pathological nanocrystalline multi-substituted apatite materials, it is of great importance to perform detailed structural characterizations of substituted synthetic HAp. Our previous study has established the Zn location into the HAp structure [16]. For high synthesis temperatures (1100 °C), Zn2+ cations are inserted along the hexagonal channel of the HAp structure at the 2b Wyckoff site forming O-Zn-O linear entities. Zn²⁺ leads to an insertion solid solution with general chemical formula $Ca_{10}Zn_x(PO_4)_6(OH)_{2-2x}O_{2x}$, contrary to β -tricalcium phosphate (β -TCP, β -Ca₃(PO₄)₂) that realizes a substitution solid solution with chemical formula $Ca_{3-x}Zn_x$ $(PO_4)_2$. The present study aims to enlarge the investigation of the Zn²⁺ incorporation in HAp vs. the temperature (heat treatment from 500 °C to 1100 °C). This study was motivated by the contradictory reports in the literature on the Zn²⁺ incorporation in HAp; namely about its solubility, ranging from a few percent to 15 mol.% [17-19], about the Zn atoms' location, sorbed on the HAp surface (either sixfold or fourfold coordinated), or incorporated in one of the two crystallographic Ca sites (the ninefold coordinated Ca1 and the sevenfold coordinated Ca2 sites) of the HAp structure [17,20-28].

2. 2- Materials and methods

2.1. Sol-gel elaboration

The sol-gel route was used to synthesize undoped and Zndoped HAp samples [16]. Briefly, to produce 2 g of pure HAp





E-mail address: j-marie.nedelec@univ-bpclermont.fr (J.-M. Nedelec).