Structural, morphological and surface characteristics of two types of octacalcium phosphate-derived fluoride-containing apatitic calcium phosphates

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1. Introduction

Recent studies using synthetic octacalcium phosphate (OCP) in vivo and in vitro have suggested that the hydrolysis process from OCP to hydroxyapatite (HA) is involved in increasing the stimulatory capacity of OCP to activate osteoblastic cells [1–3]. This may explain why new deposition of apatite on various biomaterial surfaces exhibits a higher osteoconductive property, at least with regard to inorganic biominaler formation [4]. OCP has been advocated as a precursor to HA crystals [5,6]. The OCP structure alternately stacks apatitic layers with hydrated layers [6]. The hydrolysis of OCP to HA is thermodynamically favored and, once initiated, is likely to be spontaneous and irreversible [7,8]. Thermodynamic studies have further indicated that soluble amorphous calcium phosphate (ACP) is formed from highly supersaturated solution first and then transformed into HA through an OCP-like intermediate phase [9–11]. Thus, OCP is considered to be a direct precursor in HA formation [12].

Several lines of evidence have confirmed that implanted biomaterials, including OCP material, encounter biomolecules in vivo, including serum proteins [12–15]. Therefore, it is of great interest to understand the transition of physicochemical properties, including chemical composition, crystal perfection and crystal–protein interactions during the precursor hydrolysis in relation to acquiring the stimulatory capacity that enhances bone regeneration. The physicochemical properties, such as chemical composition and specific surface area, undergo substantial changes progressively with the advancement of the hydrolysis of OCP into HA [1,16]. Adsorption of serum protein on OCP and its hydrolyzed apatite products in vitro can be regulated by the degree of hydrolysis a hydroxyapatite (HA). The present study was designed to characterize structural, morphological and surface properties of fluoride-containing apatitic calcium phosphates (CaP) obtained through OCP hydrolysis or direct precipitation of OCP in the presence of 12–230 ppm of fluoride (F). The products were characterized by chemical analysis, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and Fourier transform infrared spectroscopy (FTIR) as well as measurements of surface area, solubility, osteoelastic activities and bovine serum albumin (BSA) adsorption. XRD analysis reconfirmed that both preparations yielded more apatitic CaP with a higher concentration of F. However, the co-precipitated products (CF-CaP) maintained the properties of OCP, in particular the solubility, whereas the hydrolysis products (HF-CaP) had the characteristics of fluoridated apatite. The crystals of plate-like OCP were changed to the crystals of rod-like CF-CaP and small irregular HF-CaP with the advance of the hydrolysis. The SAED analysis detected both OCP and apatite crystals even in the most hydrolyzed CF-CaP. Mouse bone marrow stromal ST-2 cells grew better on CF-CaP compared with HF-CaP. BSA adsorption was inhibited on HF-CaP more than on CF-CaP. These results show that OCP produces physicochemically distinct apatitic fluoridated CaP during hydrolysis, regarding the structure, the crystal morphology and the protein adsorption, depending on the fluoride introduction route, which provides biologically interesting material.

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