



# Effects of trace elements in fish bones on crystal characteristics of hydroxyapatite obtained by calcination

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## Abstract

Hydroxyapatite (HAp) which has ion-exchange properties is a useful sorbent for heavy metals and radionuclides. Ion-exchange capacity is influenced by the composition and crystallinity of HAp. In this study, synthesis of HAp from calcined fish bones was investigated, focusing on the effects of major trace elements. The HAp formed by calcination of fish bones is most likely B-type carbonated HAp. Even when we include the Na, K and Mg contents, the molar ratio of (Ca+substituted cation)/P of fish bones was about ~5% lower than the theoretical one (Ca/P=1.67). X-ray diffraction and EXAFS analysis results indicated that the crystallinity of Horse mackerel bones (Hm) is the lowest. Calcined Hm had the highest Mg content, accompanied with the formation of  $\beta$ -tricalcium phosphate and the least crystalline HAp of the fish bones studied. In calcination of Tuna bones (Tn), which had a high Ca/P ratio and low Mg content, highly crystalline HAp and calcium oxide were formed at temperatures above 800 °C. The findings are useful for application of calcined fish bones as green materials for water remediation, because these factors strongly affect the efficiency of ion exchange in HAp and the pH changes in solutions after HAp immersion. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** A. Calcination; B. X-ray methods; D. Apatite; Trace elements

## 1. Introduction

Hydroxyapatite (HAp;  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is an apatite mineral which is the inorganic component of bones and teeth. It has useful characteristics, including ion-exchange and sorption capacity; thus HAp is widely investigated as a sorbent in permeable reactive barriers for radionuclides and heavy metal ions [1]. Bone meal and charcoal have been used as permeable reactive barrier materials for  $\text{UO}_2^{2+}$  in groundwater [2]. Removal of contaminants such as  $\text{Co}^{2+}$  [3],  $\text{Sr}^{2+}$  [4,5],  $\text{Zn}^{2+}$  [6],  $\text{Cr}^{3+}$  [7] and  $\text{SeO}_3^{2-}$  [8] using HAp derived from animal bones has been attempted over the years. HAp is typically synthesized from chemical reagents by solid-state synthesis [9], co-precipitation [10], or hydrothermal treatment [11]. However, chemical synthesis has some drawbacks such as impurity incorporation and relatively high cost. On another front, naturally-derived HAp has been also investigated. HAp

syntheses from waste products, including egg-shells [12], coral [13], and animal bones [3–5,14–23] have been reported. As described above, this HAp is expected to be an excellent sorbent for heavy metals and radionuclides in waters and soils [1–7].

In most cases, naturally-derived HAp is readily obtained from waste animal bone by calcination [3–5,14–22]. Studies have shown that calcination of animal bone results in two types of decomposition in which CaO or  $\beta$ -tricalcium phosphate ( $\beta$ -TCP;  $\text{Ca}_3(\text{PO}_4)_2$ ) are formed, instead of, or as well as, HAp. Several researchers mentioned that CaO is formed in calcined bone minerals when the Ca/P ratio is higher than the stoichiometric one (1.67) [17,18], and that  $\beta$ -TCP is formed when Ca/P is lower than 1.67 [14–16]. In case of the fish bone, calcined HAp used various fish species with some trace elements were reported such as tuna [16], sword fish [17], Brazilian river fish [21], cod fish [22], and so on [5,14–16]. Many researchers have reported also formation of HAp and bi-phase includes  $\beta$ -TCP. In addition, Hamada et al. investigated crystal phase and elemental composition of 18 fish bone

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ashes [14]. They reported that the formed crystal phases can be classified into three groups: HAp type, HAp/ $\beta$ -TCP type and  $\beta$ -TCP type, depending on the Ca/P atomic ratio of the bones [14].

However, from the point of view of application as sorbents, these impurities contribute no ion-exchange reaction. Additionally, CaO promotes precipitation by increasing the pH. Therefore investigation of the resulting HAp powder is important for applications as materials for environmental remediation. Especially, trace elements such as Na, K and Mg in bone might influence the formation of calcium phosphate after calcination, as suggested by previous researches. The present study focuses on the effects of trace elements in fish bone on formation of HAp (in particular its crystallographic structure) and by-products. The relationship between trace elements and HAp crystal characteristics was investigated by comparison of four kinds of fish bones from which composition differs.

## 2. Materials and methods

### 2.1. Calcination of fish bones

Four types of fish bones prepared from: Tuna (Tn), Yellow tail (Yt), Greater amberjack (Ga), and Horse mackerel (Hm) from Japan were used as starting materials. Fish bones were boiled and washed to remove the soft tissues, such as cartilage, and dried at room temperature for 1 week. The dried bones were cut into 2–3 cm pieces, and then calcined at 400, 600, 800, or 1000 °C for 2 h in air using an electronic furnace (EYELA TMF-2200, Tokyo, Japan).

### 2.2. Characterization

The thermal decomposition of uncalcined fish bones was investigated by thermogravimetric-differential thermal analysis (TG-DTA; TG-DTA2000SA, Bruker AXS, Yokohama, Japan). Samples were heated from 25 to 1000 °C at a heating rate of 20 °C/min under an air flow rate of 10 cm<sup>3</sup>/min. Fourier transform infrared spectra were also collected using a FT-IR (FT/IR-670plus, Jasco, Tokyo, Japan) in transmission mode to characterize the functional groups in HAp. The samples were ground and mixed at 2% in potassium bromide (KBr). The crystalline phases of the samples was identified by powder X-ray diffraction (XRD: Ultima IV, Rigaku, Tokyo, Japan) using CuK $\alpha$  radiation at 40 kV and 40 mA. XRD patterns were recorded in the range  $2\theta=10\text{--}60^\circ$  with a step of  $0.01^\circ$  and a scanning rate of  $2.0^\circ/\text{min}$ . The crystallite diameters were calculated from the XRD data for the 002 peaks using the Scherrer equation for rods:

$$D_{hkl} = K\lambda/\beta \cos \theta \quad (1)$$

where  $D_{hkl}$  is the crystallite diameter,  $\beta$  is an integral breadth,  $K$  is the Scherrer constant (we took  $K=1.05$ ),  $\lambda$  is the wavelength of the CuK $\alpha$  radiation ( $\lambda=0.15418$  nm), and  $\theta$  is the Bragg angle. The morphology was observed under a scanning electron microscope (SEM; VE-9800, KEYENCE, Japan), at an accelerating voltage of 20 kV. Transmission

electron microscopy (TEM; TECNAI-20, Phillips, Netherlands) was also used at an accelerating voltage of 200 kV. The specific surface areas (SSA) were determined by the seven point N<sub>2</sub>-adsorption BET method (AUTOSORB-1, YUASA, Osaka Japan). The elemental composition of calcined fish bones was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; VISTA-MPX, SII Nano-Technology Inc., Chiba, Japan) after decomposition in 6 M HNO<sub>3</sub>. Determination was conducted in triplicate. Extended X-ray absorption fine structure (EXAFS) spectra of the Ca K-edge were collected on BL06 at the Kyushu Synchrotron Light Research Center (SAGA-LS; Saga, Japan). The spectra of samples were measured using an ionization chamber in transmission mode. The photon energy was scanned in the range 3.7–5.6 keV for the Ca K-edge. The samples were mixed with boron nitride (BN) and pressed into pellets. The oscillation was multiplied by  $k^3$  and filtered using the “HANNING” method before Fourier transformation using REX2000 software (Rigaku, Tokyo, Japan). Reference samples for comparison with the calcined fish bones were: HAP-200 (Taihei Chemical Industrial Co., Ltd., Osaka, Japan), a chemically produced hydroxyapatite (ChemHAp);  $\beta$ -tricalcium phosphate (Taihei Chemical Industrial Co., Ltd., Osaka, Japan); calcium carbonate (CaCO<sub>3</sub>, Wako Pure Chemical Industries, Ltd., Osaka, Japan); and CaO (obtained by calcination of CaCO<sub>3</sub> at 1000 °C for 3 h).

## 3. Results and discussion

### 3.1. Chemical composition and organic content ratio in fish bones

The elemental compositions of fish bones calcined at 600 °C are listed in Table 1. The Ca/P atomic ratios of calcined fish bones are lower than the ratio in stoichiometric HAp, Ca/P=1.67. The Ca content in calcined Hm was about 4% lower than that in the other calcined bones. The trace elements, such as Na, K, Mg and Sr, are also listed; the Mg content in calcined Hm is about 60% higher than that in the other samples. Additionally, the contents of Zn, Mn and Si were less than the ICP-AES detection limits. Previously reported compositions of calcined bone included not only Ca and P, but also Na, Mg, K and other minor elements [14–20,22,23].

Fig. 1 shows the TG-DTA plots of four fish-bone samples. These data show three stages of decomposition behavior, as previously reported [18,19]. At the first stage (100–300 °C) release of water molecules from fish bone was observed, and the corresponding mass loss was about 30%. From 300–600 °C, a further 30–40% of mass was lost, because of decomposition of organic compounds such as protein and fat in bone. The small mass loss of 1–2% above 600 °C was caused by decarbonation [18,19]. These results imply that the total organic content of Yt bones was higher (by 5–10%) than those of the other bones. The organic contents are in the order: Yt > Ga > Tn ~ Hm. Additionally, the position of the maximum of the exothermic peak around 500 °C varied, with Tn bones showing a significantly lower peak position than the

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