



# Effect of thermal treatment on carbonated hydroxyapatite: Morphology, composition, crystal characteristics and solubility

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Received 30 September 2014; accepted 11 November 2014

## Abstract

Thermal treatment is one of the common methods used in the recovery of biological apatite from bones and teeth. However, the effect of this on its physicochemical and biological properties has not yet been given full consideration. As a simplified research model with characteristics assumed to be similar to biological apatite, carbonated hydroxyapatite was used to study the effect of thermal treatment on its physicochemical properties. Carbonated hydroxyapatite was prepared and heated at 600–1000 °C. The morphology, chemical composition, crystal characteristics, functional groups and solubility of the as-prepared and heated samples were determined. Crystal growth and aggregation were observed for materials heated at 800 °C and above. With increase of heating temperature, carbonate and water content decreased, while the crystallinity increased. The solubility of as-prepared material and those heated at 600 and 700 °C was higher than the reference curve for hydroxyapatite, while that of the rest overlapped the latter. Such changes indicate that the preparation approaches involving high temperature may not be appropriate for the recovery of ‘biological’ apatite; and that the importance of carbonate to the apparent solubility of calcium phosphate must be taken into account in all such work.

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**Keywords:** Biological apatite; Calcium phosphate; Hydroxyapatite; Solubility

## 1. Introduction

Biological apatite (BAp) is the label applied to the calcium phosphate-based material that is the principal inorganic component of calcified tissues such as bones and teeth. It has drawn much attention because of its importance in clinical medicine (e.g. osteoporosis, bone reconstruction) and dentistry

(e.g. caries, bonding chemistry). There have been numerous studies of the preparation, identification and characterization of BAp [1–13]. Nevertheless, there is some inconsistency in the described ultra-structure and chemical composition, perhaps due to the variety of sources and the differences and limitations in the methods of recovery and treatment [14]. There has been some clarification; for example, crystals from bone have been verified to be long platelets rather than rods, while the hydroxyl content is far less than expected [15]. However, consistent solubility data for BAp derived from bone is still lacking [16], despite all previous efforts, even for dental enamel which contains much less organic component than

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dentine and bone [17–21]. This could be ascribed in part to the complexity of BAp's physicochemical properties, the dissolution behavior especially, and in turn this may be due to the drawbacks of the determination method, which has been discussed extensively elsewhere [22]. This situation has then been exacerbated by the thermal treatment used to eliminate the organic matter in preparing BAp from dentine and bone. For example, some compositional, structural and phase changes have been reported for laser-irradiated enamel that had been exposed to a temperature gradient [23]. Similar alterations of BAp were found for human and animal bones on calcination [24]. A heat treatment-induced reduction in the apparent solubility of human dental enamel has been reported [25], but the use of the 'excess solid' method may mean that the results are unreliable [22].

As a less complicated analog of BAp, carbonated hydroxyapatite (CHAp) has been found to be a much closer model than stoichiometric hydroxyapatite (HAp), for dissolution behavior especially [25]. Knowledge of the effect of thermal treatment on the physicochemical properties of CHAp may then be helpful for the interpretation of such effects in the case of BAp. In thermal analysis of a B-type CHAp (in which carbonate substitutes for phosphate), Ivanova et al. [26] found two types of lattice water which were lost at 250–300 °C and 300–400 °C respectively, causing reduction in the values of lattice constants  $c$  and  $a$ . In addition, carbonate loss was said to start at around 400 °C, which was also reported elsewhere for both A-type CHAp (in which carbonate substitutes for hydroxyl) [27] and AB-type (with both substitutions) [28]. In contrast, Lafon et al. [29] reported a two-step decarbonation of an AB-type CHAp to start at about 600 °C. Increase in degree of crystallinity and crystal size was observed for both synthetic CHAp [27] and BAp [24] on heating, as would be expected. However, there appears to have been no study reported of the effect of thermal treatment on the dissolution behavior and solubility of CHAp. Hence, an intention now was to examine the effect of thermal treatment on CHAp in terms of morphology, chemical composition, crystal characteristics and solubility.

A further consideration is of the effect of accidental carbonate contamination of HAp intended for various studies, and most especially of solubility. Such concerns are commonly raised in discussion of the meaning of solid-titration results. It was therefore a second purpose to check formally on such effects.

## 2. Materials and methods

### 2.1. Sample preparation

A modification of the ordinary procedure for preparing HAp was followed [30]. That is, HAp was precipitated by adding 0.1 mol/L  $(\text{NH}_4)_2\text{HPO}_4$  (AnalaR grade, BDH, Poole, UK) dropwise ( $\sim 1/\text{s}$ ) into 0.167 mol/L  $\text{Ca}(\text{NO}_3)_2$  (AnalaR, BDH) to the ideal stoichiometric Ca/P ratio of 1.667. The reaction pH was controlled to within the range 10–11 by the dropwise addition as necessary of 30% ammonia solution (AnalaR,

BDH) whilst being stirred magnetically at  $5 \text{ s}^{-1}$ , stirring being continued for 2 h after the addition of  $(\text{NH}_4)_2\text{HPO}_4$  was completed. The key departure from the usual process is that this reaction was performed in an open beaker, i.e. exposed to the air, and therefore that  $\text{CO}_2$  absorption was allowed to occur. The reaction vessel was then sealed in a stainless steel pressure vessel and heated to 150 °C for 8 h in an electric furnace (Vulcan 3-550, Dentsply, York, PA, USA), then quenched by immersion in cold water for about 15 min. The bulk of the supernatant was discarded and the precipitate ( $\sim 12 \text{ g}$ ) collected by centrifugation (4800 rpm, 3600g, 10 min). This solid was then washed with 30 mL deionized water (Milli-Q RG ultrapure water system, Millipore, Billerica, MA, USA) three times for no more than 1 min each, to minimize dissolution. The resultant solid was dried at 70 °C overnight, pulverized manually with an agate mortar and pestle, passed through a 200-mesh sieve (0.075 mm), and divided into six portions: control, and heated in air at 600, 700, 800, 900 and 1000 °C for 2 h (heating rate:  $10 \text{ K min}^{-1}$ ) in an electric furnace (Vulcan 3-550, Dentsply), cooled to room temperature ( $10 \text{ K min}^{-1}$ ). All samples were stored in a desiccator over silica gel.

### 2.2. Characterization

#### 2.2.1. Morphology and chemical composition

Crystal morphology was examined with scanning electron microscopy (SEM) (S-4800, Hitachi Science Systems, Tokyo, Japan). Powder samples were cemented on copper stubs with a conductive tape and sputter-coated with gold for 40 s (SCD 005, BAL-TEC, Austin, TX, USA) before observation at 5 kV. Calcium (Ca) and phosphorus (P) contents were determined in triplicate using inductively-coupled plasma optical-emission spectrometry (Varian ICP-OES 720-ES, Agilent Technologies, Santa Clara, CA, USA):  $10.0 \pm 0.1 \text{ mg}$  of powder was dissolved in 30 mL 0.1 mol/L hydrochloric acid (AnalaR, BDH), and diluted 1:100 by volume. Thermogravimetric analysis (TGA) (TG 209 F1 Iris, Netzsch, Selb, Germany) of the powders over 35–910 °C (the maximum for the machine) was at  $10 \text{ K min}^{-1}$ ;  $\text{Al}_2\text{O}_3$  was used as the reference. Differential TGA data were smoothed (Loess, sampling proportion: 0.2, polynomial degree: 4, outliers rejected) (Sigmaplot v. 13, Systat Software, San Jose, CA, USA).

#### 2.2.2. Crystal characteristics and functional groups

The crystal characteristics were determined by X-ray diffraction (XRD) (D/max III 2200V/PC, Rigaku, Tokyo, Japan) with packed powder samples mounted on glass stubs, using  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with a graphite-diffracted beam monochromator, over the range  $4\text{--}60^\circ$  ( $2\theta$ ), step size  $0.02^\circ$ , scanning speed  $4^\circ \text{ min}^{-1}$ . Phase identification was by comparison with the standard HAp powder diffraction file (JCPDS File no.72-1243, International Center for Diffraction Data (ICDD), Newton Square, PA, USA). The diffraction data were further analysed for crystallinity and crystal size in software (Jade v.5, MDI, Livermore, CA, USA). Functional groups were identified using Fourier-transform infrared spectroscopy

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