

# Simultaneous incorporation of carbonate and fluoride in synthetic apatites: Effect on crystallographic and physico-chemical properties

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## Abstract

The mineral in bone is an impure hydroxyapatite, with carbonate as the chief minor substituent. Fluoride has been shown to stimulate osteoblastic activity and inhibit osteoclastic resorption *in vitro*. CO<sub>3</sub>- and F-substituted apatite (CFA) has been considered as potential bone graft material for orthopedic and dental applications. The objective of this study was to determine the effects of simultaneously incorporated CO<sub>3</sub> and F on the crystallographic physico-chemical properties of apatite. The results showed that increasing CO<sub>3</sub> and Na content in apatites with relatively constant F concentration caused a decrease in crystallite size and an increase in the extent of calcium release; increasing F content in apatites with relatively constant CO<sub>3</sub> concentration caused an increase in crystallite size and a decrease in the extent of Ca release. These findings suggest that CFAs as bone graft materials of desired solubility can be prepared by manipulating the relative concentrations of CO<sub>3</sub> and F incorporated in the apatite.

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## 1. Introduction

Bone consists of the mineral and organic (mostly collagen) components. The bone mineral is a calcium phosphate idealized as hydroxyapatite (HA; Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) [1,2]. However, comprehensive studies on bone and synthetic apatites have led to the conclusion that bone mineral is not a pure HA, but is associated with minor elements (e.g. CO<sub>3</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) and trace elements (e.g. Sr<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and F<sup>-</sup>). Carbonate is the chief minor substituent in bone apatite (6.0–8.0 wt.%). Bone apatite can be more accurately described as CO<sub>3</sub>-substituted apatite (CHA) [3,4].

Fluoride therapy (as NaF) for osteoporosis has attracted attention due to its ability to increase bone mass [5,6]. *In vitro*, F added in cell culture media was shown to directly stimulate proliferation and alkaline phosphatase activity of bone forming cells or osteoblasts

[7–12]. F ions released from F-substituted apatite (FA) did not significantly stimulate proliferation but significantly increased collagen syntheses and alkaline phosphatase activity of osteoblast-like cells [13]. F ions released from synthetic FA powder caused higher expression of osteocalcin from human osteoblasts [14]. An *in vitro* study also showed inhibition of the proliferation of osteoclasts and a lower number of resorption pits in CO<sub>3</sub>- and F-substituted apatite (CFA) compared to HA and CHA [15].

Apatites containing both CO<sub>3</sub>- and F ions have been considered as potential bone graft material for orthopedic and dental applications [16,17]. In an *in vivo* study, autoradiographic data showed a higher level of osteoblastic activity at the bone/CFA interface compared to that at the bone/coralline HA (Interpore™) interface [16]. A study comparing the *in vivo* performance of HA, CHA and CFA implanted in dog mandible showed that CFA induced faster bone remodeling, and a more completely formed Haversian system was obtained with CFA compared to HA or CHA [17].

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In previous studies, the individual effects of CO<sub>3</sub> or F substitution on the crystallographic dimensions, crystallite size, morphology and dissolution properties of apatite have been well documented [3,4,18–22]. However, systematic studies on the effect of the simultaneous substitution of CO<sub>3</sub> and F in apatites (CFAs) have not been presented. The purpose of this study was to determine the effects of simultaneously incorporated CO<sub>3</sub> and F on the crystallographic and physico-chemical properties of apatites. The results obtained from this study may provide a better understanding for designing CFAs with desired solubility as bone graft material.

## 2. Materials and methods

### 2.1. Preparation of CFAs

For the preparation of CFAs for this study we used the precipitation method previously described by LeGeros [4,23,24]. Briefly, the precipitation method consisted of the dropwise addition of 250 ml of 0.05 M Ca(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> solution to 750 ml of stirring solution containing various concentrations of sodium phosphate (molar ratio: Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> = 1:1), NaHCO<sub>3</sub> or NaF (Table 1), reacted for 3 h at 100 °C under an air atmosphere. Precipitates were filtered by No. 5 Whatman filter paper, washed with double distilled water and dried at 100 °C for two days. Dry CFAs powder was ground and sieved to particle sizes ranging from 63 to 90 μm.

The CO<sub>3</sub> concentration (3C) used was the same as that used in a previous study showing fast biodegradation [17]. F ions released from FA discs with *F* = 0.98 or 2.23 wt.% significantly increased collagen syntheses and alkaline phosphatase activity of osteoblast-like cells compared to an FA disc with *F* = 0.48 wt.% [13]. F ions released from synthetic FA powders (0.08, 2.01 and 3.34 wt.% F) all showed higher expression of osteocalcin from human osteoblasts compared to F-free apatite powder [14]. Based on the results reported in previous in vivo and in vitro studies, 3C or lower CO<sub>3</sub> concentration and 0F–0.3F concentration were chosen and prepared for this study.

Table 1  
CFAs preparation recipe, for a final volume of 1 l of solution.

Apatite type	Solution compositions (M)			
	Ca(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	Sodium phosphate (molar ratio: Na <sub>2</sub> HPO <sub>4</sub> /NaH <sub>2</sub> PO <sub>4</sub> = 1:1)	NaHCO <sub>3</sub>	NaF
0C/1P/0F	0.0125	0.01	0	0
0C/1P/0.2F	0.0125	0.01	0	0.002
1C/1P/0.2F	0.0125	0.01	0.01	0.002
2C/1P/0.2F	0.0125	0.01	0.02	0.002
3C/1P/0.2F	0.0125	0.01	0.03	0.002
3C/1P/0F	0.0125	0.01	0.03	0
3C/1P/0.05F	0.0125	0.01	0.03	0.0005
3C/1P/0.1F	0.0125	0.01	0.03	0.001
3C/1P/0.3F	0.0125	0.01	0.03	0.003

### 2.2. Crystallographic properties

#### 2.2.1. Lattice parameters

CFAs powder was characterized using a Philips X'Pert X-ray diffractometer with a curved crystal monochromator and Cu K<sub>α</sub> radiation, operating at 45 kV and 45 mA, scanning in a 2θ range of 20–40 °, at a step size of 0.02 ° (2θ) and 3 s per step. Apatite lattice parameters (hexagonal system) were calculated from formula

$$d = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2 + k^2 + hk) + \frac{l^2}{c^2}}}$$

where *d* is the spacing between reflecting planes,  $d = \frac{\lambda}{2 \sin \theta}$ , *h*, *k* and *l* are the Miller indices of reflecting plane, λ (wavelength) = 1.545 Å and θ is the diffraction angle [18]. The *a*-axis dimension was determined from the [300] plane and *c*-axis dimension was determined from the [002] plane.

#### 2.2.2. Crystallite size

In the [002] and [300] directions crystallite sizes were determined from the broadening at half height width ( $\beta_{1/2}$ ) of the diffraction peaks using the Debye–Scherrer formula

$$t = \frac{0.9\lambda}{\beta_{1/2} \cos \theta}$$

where *t* is crystallite size,  $\beta_{1/2}$  is the difference of sample and instrumental broadening,  $\beta_{1/2} = \sqrt{B^2 - b^2}$ , *B* is the observed broadening from the X-ray diffractometry (XRD) pattern and *b* is the instrumental broadening.

#### 2.2.3. Crystal morphology

CFAs powder was mounted on aluminum stubs with graphite adhesive and sputter coated with gold before observation using scanning electron microscopy (SEM) (Hitachi S-3500N).

### 2.3. Physico-chemical properties

#### 2.3.1. Composition

Ca, P and Na concentrations were determined using inductive coupled plasma (ICP) (Thermo Jarrell Ash, Trace Scan Advantage). A 10 mg quantity of CFAs powder was dissolved in 17% HCl and made up to 100 ml in a volumetric flask with double distilled water. The specimens in solutions were pumped through argon plasma excited by a 2 kW/27.12 MHz radiofrequency generator. The concentrations of each element were determined using their characteristic wavelengths (Ca, 317.9 Å; P, 213.6 Å; Na, 588.9 Å).

The F concentration was determined using an F-ion-selective electrode (Orion, 940900) attached to a pH Stat system (Metrohm, Brinkmann, 692 pH/ion meter). 10 ml samples of the CFAs solutions, prepared for ICP, were added to 10 ml of Tisab2. A standard curve was derived from the F standards (0, 1 and 4 ppm).

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