



# Effect of carbonate and phosphate ratios on the transformation of calcium orthophosphates



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## ABSTRACT

Complexes among phosphate, carbonate and calcium have been synthesized by a designed hydrothermal method. Effects of carbonate and phosphate ratios on the transformation of calcium-orthophosphates were investigated. With X-ray diffraction measurement the synthesized product at the low (0.15) and the high (1.8) molar ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  is calcium phosphate hydrate at pH 9.0, and hydroxylapatite (HAp) at pH 8.0, respectively. Fourier transform infrared spectroscopy of product at the high ratio (1.8) of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  shows that the  $\text{CO}_3^{2-}$  peaks disappear, and the strong peaks at 1412 and 1460  $\text{cm}^{-1}$  are assigned to the vibrations of  $\text{PO}_4^{3-}$  in HAp.  $^{31}\text{P}$  nuclear magnetic resonance spectra of products at the low (0.15–0.6) to the high (1.2–1.8) ratios of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  are obtained at 2.9 and 2.7 ppm, respectively. Molar ratios of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  are effective on the reduction of carbonate activity during the formation and infiltration events of calcium-phosphate surface precipitates, and are subsequently enclosed during HAp formation.

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## 1. Introduction

Phosphorus (P) is an essential nutrient for plant growth and it is also defined as ‘the disappearing nutrient’ due, in part, to the potential shortage of phosphate rock resources and a fast growth in demand for phosphate-based fertilizers [1]. Management of soil phosphorus is thus, an important aspect for optimal plant growth. Mismanagement of soil P, however, poses a threat to the quality of both surface- and ground-water. Water eutrophication, which has become a worldwide environmental issue, is one typical example [2]. Only a marginal proportion of soil phosphorus is present as phosphate ions in the soil solution. Although phosphate ions can reach higher concentrations in highly fertilized soils, their concentrations in soil solution range from 0.1 to 1  $\mu\text{M}$  [3]. This range is of particular concern for regions largely dominated by calcareous and alkaline soils [4]. The detailed mechanism for the mobility and bioavailability of inorganic phosphate has been still rather poorly understood and somewhat predicted [5].

Calcium in alkaline conditions is the dominant cation which reacts initially with phosphate radicals.  $\text{Ca}^{2+}$  is not only derives from alkaline soils, but also from sediments. The calcium-phosphates present in the limed acid soils are more soluble than the calcium-phosphates of the calcareous soils. This makes the calcareous soils inferior to the limed acid soils in terms of plant availability of soil P [6]. Different types of minerals such as brushite, are followed by transformation to monetite, continued by a slow transformation to octa-calcium phosphate (OCP), and ultimately HAp. All these incidents depend on temperature [7] and the rate of precipitation [8,9]. Phosphate present as HAp, as well as other solid phases including OCP and TCP, is much less bioavailable to plant uptake than dissolved P species [10]. The recognition that total soil P concentration is a poor predictor of the P bioavailability has led to extensive research on chemical speciation of P in soils with the emphasis on predicting its bioavailability [11]. However, Yoshimura et al. (2004) reported that when the concentration of phosphate was low in the solution containing calcite particles, unreacted particles-identified as calcite phase were not sufficiently converted to HAp. It seems that large grains of calcite were difficult to completely convert to HAp under low concentration of phosphate or at low temperature. When the concentration of phosphate increased, then the calcite particles can be completely transformed to HAp [12]. In high calcium concentration, precipitation of calcium

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phosphates is an important mechanism for phosphorus immobilization [13].

In spectroscopic studies using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), Ronson and McQuillan, (2002) found brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) crystallization in the co-adsorption of calcium and phosphate on  $\text{TiO}_2$  at pH 6.5 [14]. Hunger et al. (2004) have identified the phosphorus speciation in alum-amended poultry litter by  $^{31}\text{P}$  solid state nuclear magnetic resonance (NMR) [15]. Moreover, Barbara et al. (2006) have characterized aquatic phosphorus by using  $^{31}\text{P}$  solution state NMR [16]. And, calcium orthophosphates had similar chemical shifts and relatively broad line shapes in  $^{31}\text{P}$  NMR spectra from 3.5 ppm to 2.6 ppm [17]. Two dimensional  $^{31}\text{P}$  heteronuclear correlation (HetCor) has been successfully applied to study the bio-mineralization of calcium phosphates, allowing identification of OCP prior to HAp according to the literature [18]. Wang et al. (2008) reported that apatite formation was complicated by the possibility of forming several calcium phosphate phases. The HAp is preferentially formed under neutral or basic conditions; in acidic conditions, phases such as DCPD and OCP are often present. These results may occur by the initial precipitation of DCPD or OCP followed by transformation to a more apatitic phase, but if, the calcium/phosphate molar ratio was 1.5, then HAp was formed [19]. Moreover, in other investigation of the co-sorption of phosphate and calcium on boehmite scanning electron-microscopy with energy-dispersive X-ray spectroscopy was employed to examine the morphology of HAp and to estimate the surface Ca/P distribution. In SEM images, only fine particles of boehmite were observed, and HAp was not found probably due to poorly crystallized and smaller in size than the boehmite particles. From EDX analysis the Ca/P ratio in the bright regions was 1.12, which was considerably smaller than that for stoichiometric HAp, it was likely adsorbed phosphate to influence the formation of HAp [20].

Carbonate ( $\text{CO}_3^{2-}$ ) is widely present in alkaline environment. It is a chief carbonate constitution in minerals and is extremely varied and ubiquitous in chemically precipitated sedimentary. The most common carbonate mineral is calcite which could be phosphate super-binder. This makes it interesting to study the role of carbonate in the formation of Ca-P compound-minerals (including the precipitation process as well as type and amount of phosphate). Additionally, to our knowledge, the mechanism of binding ion exchange among phosphate, carbonate and calcium is largely obscured during all the above mentioned types of Ca-P compound-minerals.

The overarching objective of this study was to determine the mechanism for transformation of calcite to calcium orthophosphate under different ratios of phosphate to carbonate. A series of laboratory experiments were conducted to determine the characteristics of synthesized products under the different molar ratios of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  by using X-ray diffraction (XRD), scanning electron-microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX), Fourier transform infrared spectroscopy (FTIR) and magic angle spinning nuclear magnetic resonance (MAS-NMR). The co-precipitates as different components were characterized and the effect of carbonate on growth of calcium orthophosphate (Ca-P) were discussed.

## 2. Experiments

### 2.1. Water and chemicals

Water was de-ionized twice and filtered through an activated carbon column and a micro filter (EASY pure UV); it had a resistance greater than  $18.3 \text{ M}\Omega/\text{cm}$ . The chemicals used were of analytical grade quality from Sinopharm Chemical Reagent Co., Ltd., China.

### 2.2. Sample preparation

All experiments were carried out at  $60.0 \pm 0.1^\circ \text{C}$  in a Pyrex flask, with a total volume of 0.37 L, stirred by a magnetic stirrer. Stock solutions of calcium, carbonate, and phosphate were prepared from  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ . For the preparation of the aqueous solutions, de-ionized twice,  $\text{CO}_2$ -free water was used. The supersaturated solutions were prepared in the Pyrex flask by mixing volumes of  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  and 0.25 L of 13 mM of  $\text{Na}_2\text{CO}_3$ , as the appropriate supernatant solutions were flocculated with adding gradually 0.1 L of 67 mM of  $\text{CaCl}_2$ . The molar ratio of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  was in the order: 0.15, 0.30, 0.60, 1.2, and 1.8. The pH at the low molar ratio (0.15) of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  was 9.0; however, at the high ratio (1.8) of  $\text{PO}_4^{3-}/\text{CO}_3^{2-}$  was decreased to 8.0. The solution was sealed by parafilm with a hole for sparged  $\text{N}_2$  gas to reduce the effect of  $\text{CO}_2$  in aqueous solution on the reaction throughout the experiment. The suspension was taken out at 60 min and centrifuged ( $\times 10,000 \text{ rpm}$ , 6 min) to separate solid from liquid. All the samples were quickly rinsed by using the de-ionized twice,  $\text{CO}_2$ -free water until the electrical conductivity was less than  $30 \mu\text{S}/\text{cm}$ . The purified samples were dried overnight at  $40^\circ \text{C}$  and stored in desiccators for XRD measurement.

### 2.3. Powder X-ray diffraction

Powder XRD measurements were performed on a Bruker D8 Advance diffractometer equipped with a Lynx-Eye detector using Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). The diffractometer was operated at a tube voltage of 40 kV and a tube current of 40 mA with a scanning rate of  $2^\circ/\text{min}$ , and step intervals of  $0.02^\circ 2\theta$ . For the collection of high-resolution digital patterns for Rietveld structure refinements of hureaulite, primary soller slits, secondary soller slits, and divergence slits were set as  $4^\circ$ ,  $4^\circ$ , and 1 mm, respectively. A scan rate of  $1^\circ/\text{min}$  was adopted to attain adequate diffraction intensity. Rietveld structure refinement and quantitative analysis were performed using the total pattern analysis solution (TOPAS) program [21].

### 2.4. SEM and EDX spectroscopy

Scanning electron microscopy (SEM, FEI-QUANTA 200) was employed to investigate the morphology of products after the samples were coated with a thin conductive layer (gold). Energy dispersed X-ray (EDX, 1132-10) spectroscopy (voltage of 30 kV) was used to estimate Ca and P elemental distribution on the surface of synthesized products. Spectroscopic software (Genesis, Version 4.61) was applied for EDX spectra and estimated P/Ca distribution on the surface of synthesized products at selected micro-areas of the SEM images. The EDX (Wt%) of elements (Ca and P) was used for the elemental distribution calculations.

### 2.5. FTIR spectroscopy

The FTIR measurements were performed with a Bruker Vertex 70 model spectrophotometer in the mid infrared area, and a frequency ranges from  $400$  to  $4000 \text{ cm}^{-1}$ . The recording was performed with a resolution of  $4 \text{ cm}^{-1}$  and 32 scans per sample. The spectra were recorded by spectroscopic software (OPUS, Version 6.5). Each spectrum was corrected against pure KBr and/or ambient air as a background spectrum. Then the spectra were fitted and analyzed by Origin 8.0 Pro to identify the location of peaks in the spectra. The spectra were flattened by baseline and followed by multi-peaks Gaussian fitting, respectively.

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