DEHYDRATION OF WATER MOLECULE IN AMORPHOUS CALCIUM PHOSPHATE

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Abstract Amorphous calcium phosphate (ACP) was synthesized by dropping rapidly aqueous ammonia into calcium dihydrogenphosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, MCP) solution. The composition of ACP was given within the wide range of Ca/P atomic ratio 1.25 ~ 1.55 and was distinguished to three kinds (H-ACP, M-ACP and L-ACP) by different Ca/P atomic ratios. Thermal behavior of water molecule in three types of ACP was investigated by X-ray diffraction, thermal analysis (TG-DTA) and Fourier transformation infrared spectroscopy (FT-IR). Two kinds, the water molecule in ACP existed adsorbed water and bound water. Distinction of these water molecules was possible from Arrhenius plot by relating between heating rates (β) and upper temperature of endothermic peaks (T_m) with thermal analysis (TG-DTA). The activation energy for dehydration of adsorbed water and bound water until about 125 °C was able to determine from the gradient of Arrhenius plot. For example, the activation energy for dehydration of bound water in H-ACP of high calcium type (Ca/P atomic ratio 1.55) was 26.4 kcal/mol. It was considered that bound water was stabilized by increasing Ca/P atomic ratio in ACP.

INTRODUCTION

The authors have been conducting a series of studies on synthesis of amorphous calcium compound and its characteristics¹⁾⁻⁸⁾. Amorphous calcium phosphate (ACP) forms a part unstable precursor of biomineral *in vivo*, and it has been known finally crystallizing to hydroxyapatite (HAp) of low crystalline⁹⁾⁻¹³⁾. The synthesis of ACP was already achieved by liquid phase reactions of rapid mixture method¹⁴⁾ and sol-gel method¹⁵⁾. The

composition and structure of ACP have been reported until now. That is, ACP was constituted of spherical cluster of 9.5Å in diameter with composition of $\text{Ca}_9(\text{PO}_4)_6$ by X-ray reduced radial distribution technique^{16)~18)}. However, thermal behavior of water molecule in three types ACP was still involved many problems to be solved.

The authors have been conducting a series of studies on synthesis of ACP by dropping rapidly aqueous ammonia into calcium dihydrogenphosphate monohydrate (MCP) solution^{6)~8)}. As a previous result, ACP, obtained by controlling condition of hydrolysis reaction of MCP, was distinguished to two kinds by different Ca/P atomic ratios⁷⁾. Furthermore, this paper was investigated in detail on the kind of ACP. ACP could be distinguished into three types from crystallization of ACP in mother liquor, L-ACP (low calcium type, Ca/P atomic ratio: 1.25 ~ 1.32), M-ACP (medium calcium type, Ca/P atomic ratio: 1.34 ~ 1.40) and H-ACP (high calcium type, Ca/P atomic ratio: 1.43 ~ 1.55) for convenience.

Studies were made to investigate synthetic conditions of the above three types ACP, distinction of adsorbed water and bound water in ACP and activation energy for dehydration of these water molecules.

EXPERIMENTAL

MATERIALS

MCP ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) and aqueous ammonia (NH_4OH) used for synthesizing ACP, were special-grade reagents supplied by Kanto Chemical Co., Ltd. The purity was about 98% for MCP and 29% NH_3 for aqueous ammonia.

EXPERIMENTAL METHOD

The MCP solution ($0.005 \sim 0.07 \text{ mol} \cdot \text{dm}^{-3}$) was kept at 0°C, and aqueous ammonia (0.1 ~ 15N NH_4OH) was added quickly to the solution in the specified volume ratio (MCP/ NH_4OH : 80/1 ~ 2/1, addition rate: $40 \text{ cm}^3 \cdot \text{min}^{-1}$) ranging from pH 6 to 12, and gelatinous precipitate formed. The gel was separated from the mother liquor by filtering through a G5 glass filter and it was washed with cold aqueous ammonia and acetone. ACP was given by drying under reduced pressure for 30 min with air passing through silica gel.

Thermal behavior of water molecule in three types ACP was determined by using X-ray diffraction, thermal analysis (TG-DTA), FT-IR and chemical analysis. The quantity of Ca and P were measured with ion chromatography (Toa Denpa Kogyo Co., Ltd.) with a column (PCI-305S).

RESULTS AND DISCUSSION

FORMATION REGIONS OF AMORPHOUS CALCIUM PHOSPHATE

ACP was synthesized at 0 °C and Ca/P atomic ratio in the ACP was affected remarkably by concentration of MCP solution and pH. ACP was distinguished into three types by different Ca/P atomic ratios.

That is, L-ACP was crystallized to dicalcium hydrogenphosphate dihydrate (DCPD) by aging in mother liquor for long time, while M-ACP and H-ACP were crystallized to octacalcium phosphate (OCP) and HAp, respectively.

Figure 1 illustrates the effect of concentration of MCP solution and pH on formation regions of three types ACP by different Ca/P atomic ratios. L-ACP was formed at pH 6~8 under high concentration of MCP solution. M-ACP was obtained at pH 7~10, but concentration of MCP solution did not take part in the formation region and H-ACP was formed at high pH 8~12 and low concentration of MCP solution. The border of three types ACP were indicated mixture regions of two types ACP.

INFRARED ABSORPTION SPECTRA OF AMORPHOUS CALCIUM PHOSPHATE

When the atomic structure analysis of three types ACP was carried out by X-ray reduced radial distribution technique, the patterns of ACP's were indicated regular intervals at interatomic distance below 10Å but was irregular intervals at the above 10Å. These results were characterized by property of amorphous substance^{(6)~(18)}. However, the difference of three types ACP was not

Fig.1 Effect of concentration of MCP solution and pH on composition of amorphous calcium phosphate. Temperature(°C): 0
MCP/NH₄OH volume ratio :100/0.5 ~ 100/20

Fig.2 Infrared absorption spectrum of amorphous calcium phosphate. L-ACP(Ca/P atomic ratio: 1.27)
M-ACP(Ca/P atomic ratio: 1.34)
H-ACP(Ca/P atomic ratio: 1.51)

confirmed from X-ray reduced radial distribution technique. Infrared absorption spectra of these ACP were also compared.

Figure 2 illustrates infrared absorption spectra of three types ACP. Only H-ACP in three types was observed spectrum at around 3860 cm^{-1} assigned to stretching vibration of the O-H group. The peak spectrum at 860 cm^{-1} assigned to HPO_4^{2-} group increased with decreasing Ca/P atomic ratio in ACP. However, the spectrum of adsorbed water assigned to bending vibration of H-O-H and bound water assigned to stretching vibration of O-H were not observed clear difference. So that thermal behavior of water molecule in ACP was investigated by thermal analysis (TG-DTA).

ACTIVATION ENERGY FOR DEHYDRATION OF AMORPHOUS CALCIUM PHOSPHATE

TG-DTA curves of three types ACP are shown in Figure 3. It was observed that a large endothermic peak with upper temperature at around 115°C was resulted from dehydration of water molecule in ACP. The weight loss for dehydration in TG curve slowly

Fig.3 TG-DTA curve of amorphous calcium phosphate.
 L-ACP(Ca/P atomic ratio: 1.27)
 M-ACP(Ca/P atomic ratio: 1.34)
 H-ACP(Ca/P atomic ratio: 1.51)
 Heating rate ($^\circ\text{C}/\text{min}$) : 10

Fig.4 Arrhenius plot for dehydration of amorphous calcium phosphate.
 β : Heating rate, T_m : Temperature of dehydration peak
 L-ACP(Ca/P atomic ratio: 1.27)
 H-ACP(Ca/P atomic ratio: 1.51)

continued until about 600 °C and increased with increasing Ca/P atomic ratio. For example, that of H-ACP was about 24.5 %. But this endothermic peak was considered to overlap adsorbed water and bound water in ACP. Also an exothermic peak at 700 °C was resulted from crystallization ACP to β -TCP.

The water molecule in ACP was known to exist two kinds of adsorbed water and bound water¹⁹⁾. Distinction of these water molecules were possible from Arrhenius plot by relating between heating rate (β) and upper temperature (T_m) of the endothermic peak at about 120 °C with thermal analysis¹⁹⁾. The activation energy for dehydration of bound water in three types ACP was changed by condition of bonding strength. As shown in Figure 4, Arrhenius plot presented by two straight line segments. Although two types of water molecule was often confused, they should be distinguished. The straight line of the large gradient means the dehydration of bound water and small gradient was that of adsorbed water. The adjoining point of two straight lines was indicated starting temperature for dehydration of bound water. That is, the dehydration of bound water was started at above the adjoining point. For example, the temperature of adjoining point was higher H-ACP than L-ACP. The gradient of adsorbed water segment against the point was much the same both L-ACP and H-ACP, but the gradient of slope in bound water segment was bigger H-ACP than L-ACP. The activation energy was determined from this gradient¹⁹⁾.

From the above results, Table 1 shows temperature, quantity and activation energy for dehydration of adsorbed water and bound water. The starting temperature for dehydration of bound water shifted toward high temperature with increasing Ca/P atomic ratio and quantity of bound water increased. For example, the activation energy for dehydration of bound water were 26.4 kcal/mol for H-ACP (Ca/P atomic ratio 1.55) and 10.5 kcal/mol for L-ACP (Ca/P atomic ratio 1.25), respectively. It was considered that bound water was stabilized by increasing Ca/P atomic ratio.

Table 1 Activation energy for dehydration of amorphous calcium phosphate.

	H-ACP	M-ACP	L-ACP
Starting temperature for dehydration of bound water (°C)	100.6±6.0	96.4±1.8	89.5±3.5
Adsorbed water (wt%)*	8.0~11.0	5.0~8.0	5.0~7.0
Bound water (wt%)**	13.0~16.0	13.0~14.0	11.0~13.0
Activation energy for dehydration	{ Adsorbed water (kcal/mol)*	10.3~10.5	8.6~10.5
	{ Bound water (kcal/mol)***	22.0~26.4	15.8~25.2
		10.5~13.7	

*:25~94°C, **:94~600°C, ***:94~125°C

Therefore, the border temperature of adsorbed water and bound water in ACP were possible to determine from Arrhenius plot by relating between β and T_m . It was confirmed that quantity of water molecule and stability of bound water by increasing Ca/P atomic ratio in ACP were differed.

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