Transformation of dicalcium phosphate dihydrate into octacalcium phosphate with incorporated dicarboxylate ions

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Octacalcium phosphate (OCP) has a layered structure consisting of apatitic and hydrated layers. The hydrogen phosphate ions in the hydrated layer can be replaced by dicarboxylate ions resulting in the formation of OCP with incorporated dicarboxylate ions. We herein report the transformation behaviour of dicalcium phosphate dihydrate (DCPD), which is used as starting material for the synthesis of OCP in acetic acid (Ace), succinic acid (Suc), suberic acid (Sub), and isophthalic acid (Isp) solutions at a pH of approximately 5.5 at 60°C. We found that DCPD with a small crystal size (specific surface area: 4.9 m²·g⁻¹) completely transformed into OCP within 1 h in Ace solution, whereas DCPD with a large crystal size (specific surface area: 0.62 m²·g⁻¹) did not form the OCP phase even when treated for 3 h. OCP incorporating Suc and Isp was formed from DCPD with a small crystal size in solutions of these dicarboxylic acids. On the other hand, Sub was not incorporated into OCP although Sub is a typical dicarboxylic acid that could be incorporated into the OCP structure. We concluded that although the dicarboxylic acids that are adaptable to these experimental conditions are limited, DCPD can be used as a starting material for OCP with incorporated dicarboxylate ions.

Key-words : Octacalcium phosphate, Dicalcium phosphate dihydrate, Transformation, Dicarboxylic acid, Wet process

1. Introduction

Octacalcium phosphate (OCP) is a member of the group of calcium orthophosphate compounds. OCP has a layered structure composed of an apatitic layer and hydrated layers. The interplanar spacing of the (100), d_{100}, (010), d_{010}, and (001) values of OCP are 18.7, 9.36, and 3.42 Å, respectively.1) The hydrogen phosphate ions located in the hydrated layer can be substituted by dicarboxylate ions. The succinate ion is a representative guest molecule that can be incorporated into the OCP crystal structure. The d_{100}, d_{010}, and d_{001} values of OCP with incorporated succinate ions are 21.4, 9.39, and 3.42 Å, respectively. The d_{100} value of OCP is increased by incorporation of a succinate ion, whereas the changes in the d_{010} and d_{001} values are small because the incorporated succinic acid (Suc) is parallel to the c-axis direction. In addition to Suc, various dicarboxylic acids, such as suberic acid (Sub) and isophthalic acid (Isp), are also incorporated into OCP.2)

The process for synthesising OCP with incorporated dicarboxylate ions has been investigated. Hydrolysis of α-tricalcium phosphate in dicarboxylic acid solution was a representative process for the synthesis of OCP with incorporated dicarboxylate ions and various dicarboxylic ions were incorporated into the OCP crystal structure through this process.3)–5) The other synthetic processes are the gel-mediated growth process6) and homogeneous precipitation using urea.7) The reaction of calcium carbonate and phosphoric acid in dicarboxylic acid solution is another method for synthesising OCP with incorporated dicarboxylate ions.8) OCP with incorporated Suc, Sub, mercaptosuccinic acid, methylsuccinic acid, phthalic acid, and Isp has been synthesised by using this process.9)–13) The molar ratio of CaCO₃/H₃PO₄ used in these reaction systems was 1.6. The reaction whereby OCP is formed with an incorporated dicarboxylate ion is as follows:8)

$$\text{CaCO}_3 + \text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2$$

(1)

$$6\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} + 2\text{Ca}^{2+} + x\text{DCI}$$

$$\rightarrow \text{Ca}_x(\text{HPO}_4)_2 \cdot (\text{DCI})_x(\text{PO}_4)_x \cdot m\text{H}_2\text{O}$$

$$\quad + (12 - m)\text{H}_2\text{O} + 4\text{H}^+ + x\text{HPO}_4^{2-}$$

(2)

where DCI denotes the dicarboxylate ion. According to Eq. (2), dicalcium phosphate dihydrate (DCPD, CaHPO₄·2H₂O) transformed into OCP with incorporated dicarboxylate ions. In other words, the precursor phase of OCP with incorporated dicarboxylate ion is DCPD in this process, although the starting materials were calcium carbonate and phosphoric acid.
DCPD can be transformed into OCP under appropriate conditions, namely in acetate buffer solution,\(^1\)\(^{14}\) hence, the use of DCPD as starting material for OCP with incorporated dicarboxylate ions is reasonable. The synthesis of OCP with incorporated succinate ion using DCPD as the starting material was recently reported.\(^1\)^{15} However, it is not clear whether DCPD is a suitable starting material for OCP with incorporated dicarboxylate ions other than the succinate ion. Since OCP with incorporated dicarboxylate ions has potential as bone repairing materials and adsorbents based on the previous reports,\(^1\)^{16,17} refinement of the synthetic technique and establishing a novel synthetic route to OCP with incorporated dicarboxylate ions are certainly both worthwhile for the creation of novel materials for these applications.

Since OCP is a metastable substance in aqueous solution,\(^1\)^{18} if the transformation rate of DCPD is low, there is a concern that the initially formed OCP will transform into thermodynamically stable hydroxyapatite before the DCPD transformation reaction is completed. Therefore, in this study, DCPD having an appropriate reaction rate was first selected by investigating the transformation behaviour of two kinds of DCPD (with different surface areas) into OCP in acetate buffer solution. Then, we investigated the transformation behaviour of the selected DCPD type in solutions containing the typical dicarboxylic acids, namely Suc, Sub, and Isp.

### 2. Experimental procedures

#### 2.1 Chemicals

DCPD (98%) was purchased from Nacalai Tesque Inc., Kyoto, Japan (product code: 06904-74). The commercial DCPD is abbreviated as c-DCPD. Calcium nitrate tetrahydrate [Ca(NO\(_3\)]\(_2\)·4H\(_2\)O, 98%], diammonium hydrogen phosphate [(NH\(_4\)]\(_2\)HPO\(_4\), 98%], acetic acid (Ace, 99.7%), sodium hydroxide (NaOH, 97%) were purchased from Wako Pure Chemical Ind., Osaka, Japan. Sub (99%) and ISP (99%) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. All chemicals were used without further purification.

#### 2.2 Synthesis of DCPD

A solution of calcium nitrate (100 cm\(^3\), 0.2 mol dm\(^{-3}\)) was stirred at 30°C at 500 rpm in a glass beaker by a magnetic stirrer. Then, 100 cm\(^3\) of a 0.2 mol dm\(^{-3}\) diammonium hydrogen phosphate solution was added to the calcium nitrate solution. A white precipitate was immediately formed after the two solutions were mixed. After 10 min, the formed precipitate was collected by vacuum filtration using filter paper having a pore size of 1 micrometre and washed with distilled water and ethanol, and then dried at 40°C overnight. The synthesized DCPD is hereafter denoted as s-DCPD.

#### 2.3 Transformation of DCPD in carboxylic acid solutions

Seven kinds of carboxylic acid solutions were used as the reaction solutions, the abbreviations of which are defined in Table 1 together with their compositions. Additionally, molecular structures of Suc, Sub and Isp are shown in Fig. 1. The initial pH value of the respective reaction solutions was adjusted to 5.5 at 60°C by using sodium hydroxide solution. The ACE solution was used as standard solution for the transformation of DCPD into OCP without incorporated dicarboxylate ions, which is hereafter denoted as Pure-OCP. The SUC, SUB, and ISP reaction solutions were used for the incorporation of Suc, Sub, and Isp into OCP, respectively. Since OCP with incorporated dicarboxylate ions were sometimes synthesised in a co-buffer system comprising Ace and the target dicarboxylic acid,\(^1\)^{19,20} we investigated the transformation behaviour of DCPD in a solution containing Ace and Suc, Sub, or Isp to investigate the effect of the co-presence of Ace and the dicarboxylic acids on the transformation behaviour of DCPD and on the effect of incorporating the dicarboxylate ion into OCP.

c- and s-DCPD (4.13 g) were added to 300 cm\(^3\) of ACE solution in a glass beaker at 60°C stirred at 500 rpm using a magnetic stirrer. After 5, 10, 30 min, 1, 1.5, 2, and 3 h, 10 cm\(^3\) of calcium phosphate slurry was pipetted. The precipitate was collected by vacuum filtration using a mixed cellulose ester membrane filter having a pore size of 1 micrometre, washed with distilled water and ethanol, and then dried at 40°C overnight. Since transformation of c-DCPD was not observed by 3 h, the reaction period was extended to 24 h. The crystalline phases of the precipitate were characterised to investigate the dependence of the transformation rate of DCPD on the specific surface area of the starting materials.

s-DCPD (1.38 g) was added to 100 cm\(^3\) of ACE, Suc, SUB, ISP, SUC-ACE, SUB-ACE, and ISP-ACE solution, respectively, in a glass beaker at 60°C stirred at 500 rpm using a magnetic stirrer. After 1 h, the precipitate was collected by vacuum filtration using filter paper having a pore size of 1 micrometre, washed with distilled water and ethanol, and then dried at 40°C overnight. The changes in the pH values of the reaction solutions were measured by a

| Table 1. Compositions of the reaction solutions |
|-----------------------------------------------|
| Name of reaction solution | Concentration/mol dm\(^{-3}\) |
|---------------------------|-----------------|
| ACE                       | 0.2             |
| SUC                       | 0.2             |
| SUB                       | 0.2             |
| ISP                       | 0.2             |
| SUC-ACE                   | 0.02            |
| SUB-ACE                   | 0.02            |
| ISP-ACE                   | 0.02            |

![Fig. 1](image-url) Molecular structures of (a) succinic acid (Suc), (b) suberic acid (Sub), and (c) isophthalic acid (Isp).
glass-electrode-type pH meter (electrode model number: 9625-10D, Horiba Ltd., Kyoto, Japan).

2.4 Characterisation

The crystalline phases of the samples were characterised by powder X-ray diffraction (XRD; RINT-2000, Rigaku Co., Tokyo, Japan) using Cu-Kα radiation. The carbon content of the samples was determined using a carbon/sulfur analyser (EMIA-920V, Horiba, Ltd.).

The morphologies of the s- and c-DCPD starting materials were observed by scanning electron microscopy (SEM; SU-8000, Hitachi, Ltd., Tokyo, Japan). Additionally, the specific surface areas of the starting materials were measured using the Brunauer–Emmett–Teller (BET) method with N2 gas as the adsorbate by a surface area measurement instrument (Autosorb-I, Quantachrome Instruments, FL, USA). The samples were heat-treated at 60°C for 14 h under vacuum as a pre-treatment for the specific surface area measurements.

3. Results

3.1 Effects of specific surface area of DCPD on transformation rate

Figure 2 shows the XRD patterns of c- and s-DCPD. All the reflection peaks of c- and s-DCPD were assignable to DCPD, based on the powder diffraction file (PDF) #00-011-0293. The other crystalline phase was not detected in these samples. Figure 3 shows the SEM images of s- and c-DCPD. The s-DCPD platelets had an elongated shape and were approximately 10–20 μm in length. c-DCPD consisted of a mixture of large and small plate-shaped crystals. The sizes of these crystals ranged from approximately 200 μm to several tens of μm, respectively. The specific surface areas of s- and c-DCPD evaluated by the BET method were 4.9 and 0.62 m²·g⁻¹, respectively. We confirmed that the crystalline phase of the DCPD remained after the specific surface area measurement (data not shown).

Figure 4 shows the time-dependent crystalline phase change of (a) s-DCPD and (b) c-DCPD in ACE solution. In the case of s-DCPD, the reflection peak intensities derived from DCPD decreased when the reaction period increased and the reflection peak of DCPD disappeared at 1 h. The reflection peaks of OCP (PDF #01-074-1301) appeared at 5 min and their intensities increased as the reaction periods increased. Only the OCP phase was detected at 1 and 3 h. In the case of c-DCPD, all reflection peaks detected in samples up to 3 h were assignable to DCPD. The other crystalline phase was not detected, although a decrease in DCPD reflection peak intensity was observed at 3 h. Only the OCP phase was detected at 24 h. Thus, s-DCPD is more suitable than c-DCPD to investigate the transformation behaviour of DCPD to OCP, because it showed a moderate transformation rate, which is more appropriate. Hence, s-DCPD was used in subsequent experiments.

3.2 Transformation of DCPD in solutions containing dicarboxylic acids

The XRD patterns of s-DCPD stirred in ACE, SUC, SUB, and ISP solutions for 1 h are shown in Fig. 5. As expected, the transformation of DCPD into OCP was more evident in the solutions containing dicarboxylic acids. The reflection peaks of OCP were observed in the XRD patterns of the s-DCPD samples stirred in these solutions, indicating the transformation of DCPD to OCP. The transformation rate was dependent on the type of dicarboxylic acid present in the solution.
shown in Fig. 4, the crystalline phase of s-DCPD treated with the ACE solution for 1 h corresponded to OCP, more specifically Pure-OCP. The 100 reflection peak of Pure-OCP is detected at 2θ = 4.7°. The crystalline phase obtained when s-DCPD was treated with the SUC solution corresponded to the crystalline phase of OCP. The 100 reflection peak of this sample was detected at a lower angle, namely 2θ = 4.1°, than that of Pure-OCP. Additionally, the 100 reflection peak position corresponded to that of OCP with incorporated Suc ion based on the previous report.12) Hence the observed d_100 expansion indicates incorporation of the Suc ion into OCP. Only the reflection peaks assignable to OCP were detected in a sample of s-DCPD treated with SUB solution. The position of the 100 reflection peak of this sample corresponded to that of Pure-OCP; hence, the Sub ion was not incorporated into OCP. OCP and DCPD were detected in s-DCPD treated with an ISP solution. The 100 reflection peak of this sample was detected at 2θ = 4.4°, indicating that OCP incorporating the Isp ion was formed. The carbon content of s-DCPD treated with ACE, SUC, SUB, and ISP was 0.22, 2.25, 0.99, and 3.79 mass %, respectively. The carbon content of s-DCPD treated with SUC and ISP was larger than that of the other samples because of incorporation of the dicarboxylate ions, based on the XRD results (Fig. 5).

The XRD patterns of s-DCPD treated with ACE, SUC-ACE, SUB-ACE, and ISP-ACE solutions for 1 h are shown in Fig. 6. The broken line indicates the position of the 100 reflection peak of Pure-OCP.
ed at $2\theta = 4.1^\circ$; hence, the Suc ion was incorporated into OCP. The crystalline phase of s-DCPD treated with SUB-ACE solution was OCP. The 100 reflection peak of this sample appeared at the same position as that of Pure-OCP; thus, the Sub ion was not incorporated into OCP. OCP was detected in s-DCPD treated with ISP solution. The 100 reflection peak of this sample was detected at $2\theta = 4.4^\circ$, indicating that the OCP incorporated the Isp ion.

3.3 Time dependent changes of reaction solutions

The time dependent pH changes of the ACE, SUC, and SUC-ACE solutions are shown in Fig. 7. The initial pH of the reaction solution was 5.5. The pH levels of the reaction solutions were increased by addition of s-DCPD into the reaction solution and reached the maximum value of approximately 5.6 within 5 min. Subsequently, the pH of the ACE, SUC, and SUC-ACE solutions gradually decreased to finally reach 5.2, 5.4, and 5.5 at 1 h, respectively. The changes in the pH over time were also examined for the other samples. As in the above-mentioned samples, the pH value increased after the addition of DCPD and then decreased.

The initial, maximum, and final pH values of the reaction solutions are summarised in Table 2. The initial pH value of all reaction solutions was 5.5. The maximum pH value of the reaction solutions was 5.6, with the exception of ISP which had a maximum pH value of 5.9. The final pH values of the reaction solutions were in the range 5.2–5.5, depending on the pH buffering properties of the carboxylic acids in these solutions.

4. Discussion

Based on SEM observation, s-DCPD had a larger specific surface area than c-DCPD because the crystal size of s-DCPD was smaller than that of c-DCPD. According to the XRD patterns shown in Fig. 4, s-DCPD with a smaller crystal size and a larger specific surface area was completely transformed into OCP within 1 h, whereas the transformation of c-DCPD with a larger crystal size and a smaller specific surface area was not confirmed by 3 h. Commercially available DCPD, namely c-DCPD, presents concerns about changes in chemical reactivity due to dehydration during storage and impurities. However, these results likely indicate that the reactivity of DCPD greatly increased as the specific surface area of DCPD increased and that the rate-determining step of the transformation of DCPD into OCP is the dissolution of DCPD.

From the viewpoint of OCP synthesis, it is beneficial that the synthesis reaction is completed in a short time. This is because OCP is a metastable substance in aqueous systems with transformation into hydroxyapatite,21 which would occur if the reaction time was prolonged. Hence, the transformation reaction of DCPD with a large specific surface area is a useful starting point for the synthesis of OCP.

According to Fig. 5 and carbon content analysis, the Suc and Isp ions were incorporated into OCP. Hence, DCPD is usable as a starting material for OCP with the incorporation of dicarboxylate ions other than the succinate ion. As for Isp, the interlayer expansion of OCP formed in the ISP solution was small as compared with OCP with incorporated Isp ion reported in the previous paper.11 This would result from a small amount of Isp ion being incorporated into OCP, and/or incorporated Isp ions not being parallel to the a-axis direction in the hydrated layer of OCP. In contrast, the Sub ion was not incorporated into OCP. A likely cause of this result is that the residual phosphate ions inhibited incorporation of the Sub ion into OCP. The transformation reaction of DCPD into OCP with incorporated dicarboxylate ions [Eq. (2)] would need to be modified to the following chemical equation to fit our experimental systems, because the Ca/P molar ratio of our reaction system was one and the transformation reaction proceeded under calcium-ion-deficient conditions, in other words phosphate-ion-rich conditions.

$$8\text{CaHPO}_4\cdot2\text{H}_2\text{O} + y\text{DCI} \rightarrow \text{Ca}_8(\text{HPO}_4)_2\cdoty(\text{DCI})y(\text{PO}_4)_4\cdoty\text{H}_2\text{O}$$
$$+ (16 - n)\text{H}_2\text{O} + 4\text{H}^+ + (2 + y)\text{HPO}_4^{2-} \quad (3)$$

$(0 \leq y \leq 1)$

The reaction involving the incorporation of the dicarboxylate ion competes with the reaction to incorporate hydrogen phosphate ions. Since our reaction system was rich in phosphate ions, hydrogen phosphate ions were preferentially incorporated into OCP instead of the Sub ion, although Suc and Isp ions were successfully incorpo-
rated into OCP under the same conditions. The adsorption stability of the dicarboxylate ions on the crystal surface of OCP is likely one of the factors that governs the incorporation of dicarboxylate ions into OCP, because the dicarboxylate ions are incorporated into the hydrated layer of OCP during crystal growth. If the dicarboxylate ion adsorbed on the OCP crystal surface is unstable, the dicarboxylate ion is substituted by hydrogen phosphate ion and the dicarboxylate ion is prevented from being incorporated into OCP. The adsorption stabilities of Suc and Isp would be higher than that of Sub and would result in the incorporation of these dicarboxylate ions into OCP under conditions rich in phosphate ions. The dissociation state of dicarboxylic acids in the reaction system can be a controlling factor for the incorporation of dicarboxylate ions into OCP. The dissociation constants of Ace, Suc, Sub, and Isp are summarised in Table 3,\(^2\) based on which the dissociation states of Suc, Sub, and Isp, depending on pH, were calculated (Fig. 8). According to the pH of the reaction systems during transformation (Table 2), the fractions of the di-valent anions of Suc, Sub, and Isp are 43–52, 41–59, and 83–95\%, respectively. Although the fractions of the di-valent anions of Suc and Sub are almost the same in the reaction systems, Suc was incorporated into OCP while Sub was not. In addition, Suc and Isp were incorporated into OCP despite large differences in the fractions of the di-valent anions of Suc and Isp. Hence, the dissociation state of dicarboxylic acids in the reaction system was not a dominant factor for the incorporation of dicarboxylate ions into OCP in this reaction system.

The 100 reflection peak of OCP with incorporated Suc ion was detected at \(2\theta = 4.1^\circ\) regardless of the presence or absence of Ace in the reaction systems (Figs. 5 and 6). Similarly, the 100 reflection peak of OCP with incorporated Isp ion was detected at \(2\theta = 4.4^\circ\) regardless of the presence or absence of Ace in the reaction systems (Figs. 5 and 6). These results indicate that Ace hardly affects the incorporation of dicarboxylate ion into OCP. Although Ace did not affect the incorporation of dicarboxylate ion into OCP, Ace affected the rate of DCPD transformation into OCP. Ace decreased the transformation rate of DCPD in the Suc-Ace system, whereas it accelerated the rate in Isp-Ace systems. The mechanism of the acceleration and deceleration of DCPD transformation is unclear. Further research would be required to clarify this mechanism.

According to Fig. 7, the pH of the reaction solutions first increased and then decreased. Such a pH change due to the reaction of DCPD was precisely discussed by Tafu et al.\(^2\) According to their report, the pH of the reaction solution was increased by DCPD dissolution. The main reactions causing pH to increase are shown below.

\[
\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O} \quad (4)
\]

\[
\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_4^- + \text{OH}^- \quad (5)
\]

The pH of the reaction solution decreased because of OCP formation [Eq. (3)]. The increase and decrease of the pH of the reaction systems depended on the buffering properties of the dicarboxylate ions. According to the \(pK_{a1}\) and \(pK_{a2}\) values (Table 3), the pH buffering capabilities at approximately pH = 5.5 are expected to be in the order Suc > Sub > Ace > Isp. This order corresponds to the smallness of the pH fluctuation during the transformation reaction of DCPD. The pH fluctuations of our reaction system were relatively small compared to the synthetic reaction of OCP with incorporated dicarboxylate ions using calcium carbonate and phosphoric acid.\(^1\) This reaction system has potential as a precisely-controlled synthetic process of OCP with incorporated dicarboxylate ions because the dissociation state of the dicarboxylate ions in the reaction system is almost constant.

### Table 3. Dissociation constants of Ace, Suc, Sub and Isp

| Carboxylic acid | Dissociation constant | \(pK_{a1}\) | \(pK_{a2}\) |
|----------------|------------------------|-------------|-------------|
| Ace            | 4.8                    | \(-^\ast\)  |             |
| Suc            | 4.2                    | 5.5         |             |
| Sub            | 4.5                    | 5.4         |             |
| Isp            | 3.5                    | 4.6         |             |

\(^\ast\): Ace does not have a \(pK_{a2}\) value.

### Conclusion

We investigated the transformation behaviour of DCPD in solutions of various dicarboxylic acids. The transformation rate is likely determined by the specific surface area of DCPD. DCPD with a small crystal size and a large specific surface area was transformed into OCP in Ace solution within 1 h. OCP with incorporated Suc and Isp ions was formed in these dicarboxylic acid solutions. The co-presence of Ace in the reaction system containing Suc and

Fig. 8. Dissociation states of Suc, Sub and Isp depending on pH. H2A, HA− and A2− indicate dicarboxylic acid, mono-valent dicarboxylate ion and di-valent dicarboxylate ion, respectively.
Isp did not inhibit the incorporation of these dicarboxylate ions into OCP. Sub was not incorporated into OCP. This is likely due to the low adsorption stability of the Sub ion on the surface of OCP crystals. Our results indicate that DCPD could be used as the starting material to produce OCP with incorporated dicarboxylate ions, but the dicarboxylic acids that are adaptable to these experimental conditions are limited.

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