Enhancement of HPO$_4$–OH layered structure in octacalcium phosphate and its morphological evolution by acetic acid

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We show that acetic acid enhances the HPO$_4$–OH layer structure of octacalcium phosphate (OCP) and hypothesize that the presence of acetic acid is essential for obtaining large-sized highly crystalline OCP with relatively high-temperature (~65°C) aqueous-solution synthesis methods. The OCP crystal consists of three types of layer structures (apatite-like, transition, and HPO$_4$–OH). X-ray diffraction (XRD) analysis indicates that increasing acetic acid concentration leads to the development of their greater structure. Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic measurements indicated development of the highly HPO$_4$–OH layer-structure. The enhanced layer structure development caused by acetic acid is in contrast to the generally observed decrease in HPO$_4$–OH layer structure in the presence of –COOH-containing molecules such as citrate and succinate.

1 Introduction

Octacalcium phosphate (OCP) is a well-known metastable crystalline phase of calcium phosphate that has been employed as a precursor for hydroxyapatite (HAP) formation through specific solid–solid transformation.1–6 OCP is preferentially formed in solutions with slightly acidic to neutral pH (5.0–7.0).7–9 Previous studies have reported that the ideal OCP forms in the P$1$ triclinic space group with the Ca$_9$(HPO$_4$)$_2$(PO$_4$)$_4$·5H$_2$O (Ca/Po$_4$ ratio 1.33, Ca:PO$_4$ = 8:6) chemical formula.1,2,9,10 The OCP crystal structure consists of three sublayer structures along the a-axis, namely, a HAP-like layer structure (Apa: Ca/Po$_4$ ratio 2.00, Ca:Po$_4$ = 4:2), a transition structure (Tra: Ca/Po$_4$ ratio 1.33, Ca:Po$_4$ = 4:3), and a HPO$_4$–OH layered structure (Lay: Ca/Po$_4$ ratio 0.00, Ca:Po$_4$ = 0:2).2,9,10 The OCP crystal exhibits a layered structure with Apa–Tra–Lay–Tra–Apa stacking along the a-axis (Fig. 1). Therefore, the a-axis parameter (18.3 Å) in OCP crystals is much larger than the b-axis (9.63 Å) and c-axis (6.87 Å) parameters. Because of the large a-axis parameter and low symmetry, a strong reflection at a low angle (2θ = ~4.7°) is observed in the typical OCP X-ray diffraction (XRD) patterns; this reflection can be used as a signature of the OCP structure.2,5

Previous studies have reported that the OCP crystal structure can be easily altered by thermal fluctuations and incorporation of different –COOH-containing molecules.2,6,11–14 This effect was described as a combination of molecular intercalation and the release of the Lay phosphate ions. Momma and Goto12 showed that succinate incorporation into CPO crystals leads to an elongation of the a-axis to 21.5 Å, demonstrating that the interactions between the –COOH-containing molecules and Lay in OCP can significantly modify the OCP lattice parameters, especially the a-axis parameter. Recently, high-resolution (HR) NMR experiments provided direct evidence on the existence of molecular intercalation in OCP crystals that maintain the overall OCP crystal structure.11,13,16 Markovic et al.12,17 investigated the changes in the lattice parameter of OCP formed in the presence of various –COOH-containing molecules in slightly acidic aqueous solutions. For acetic acid, one of the simplest –COOH-containing molecules, no evidence of a change in lattice parameters and the formation of –COOH-containing OCP was found.

Following the work of Newesely et al.13 demonstrating the synthesis of large (~1 mm) OCP single crystals using acetic acid, Mathew et al.15 reported the formation of large OCP single crystals through the hydrolysis of dihydrate CaHPO$_4$·2H$_2$O [dicalcium phosphate dihydrate (DCPD)] crystals in a solution containing 100 mM acetic acid. These findings contrast with the lack of the effect on the crystal lattice axis parameters found by

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Fig. 1. Unit cell of OCP, with regions commonly described as the Apa, Tra and Lay indicated drawn by VESTA3 program.43) Blue: Ca, Purple grey: P, Red: O.
Markovic et al.\textsuperscript{12,17} While the presence of -COOH-containing molecules in aqueous solutions during OCP synthesis generally leads to a decrease in the structure and degree of order in the resulting OCP materials, ordering have been shown to be enhanced by synthesis in the presence of acetic acid.

Therefore, the understanding of how acetic acid molecules affect OCP mineralization would generate further interest into the OCP mineralization process. Previous studies mainly focused on the changes of lattice parameters, especially on the change of the in the a-axis parameter and the c-axis parameter.\textsuperscript{15,17} However, it has been suggested that in addition to affecting the c-axis structure, -COOH-containing molecules affect the a axis structure, according to previous reports indicating that the presence of -COOH-containing molecules can strongly affect HAp formation and structures.\textsuperscript{18-20} Such an influence on HAp formation naturally suggests that -COOH-containing molecules affect the OCP Apa structure as well; however, this hypothesis has not been confirmed. Therefore, the effects of acetic acid on the OCP crystal structure mineralization process, especially on the Apa structures is investigated in this study.

2. Experimental section

2.1 Preparation of solutions for crystalline OCP synthesis

All reagents were reagent grade or mass analysis grade and were dissolved in double-distilled water (resistance at 18.2 MΩ cm) and <5 ppb in total organic content). The reaction solutions were prepared using 1 M CaCl\textsubscript{2}, 1 M CH\textsubscript{3}COONa, 1 M CH\textsubscript{3}COOH, 0.5 M KH\textsubscript{2}PO\textsubscript{4}, and 0.5 M K\textsubscript{2}HPO\textsubscript{4}. CH\textsubscript{3}COONa and CH\textsubscript{3}COOH solutions were mixed in the prepared solution with a pH of 5.7 at 25°C.

2.2 Synthesis of DCPD by solution chemistry processes

DCPD was used as the OCP precursor. Twenty-five milliliters of 0.5 M KH\textsubscript{2}PO\textsubscript{4} and 5 mL of 0.5 M K\textsubscript{2}HPO\textsubscript{4} were mixed with a magnetic stirrer in a glass beaker. After thorough mixing, 15 mL of 1 M CaCl\textsubscript{2} was added immediately into the solution with stirring. The total P\textsubscript{2}O\textsubscript{5} and Ca\textsuperscript{2+} ion concentration in the prepared solution was 0.33 M. This supersaturated calcium phosphate solution was stirred at 400–600 Hz for 1 h at room temperature and pressure.

The precipitated materials were separated by centrifugation for 30 s, and then washed five times with 2 mL of H\textsubscript{2}O. The solid phases were then immediately rewarshed several times with 2 mM of a mixed alcohol solution (ethanol:isopropanol = 1:1 v/v) in order to remove any residual water and subsequently dried at room temperature.

2.3 OCP synthesis methods in various COOH-containing solutions from DCPD

Acetic buffer solutions with different concentrations (0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, 20.0, 50.0, 100, 200, and 500 mM) were prepared at 65°C in 2 mL polypropylene tubes. Fifty milligrams of DCPD was added to the acetic buffer solutions with the solutions mixed using a vibrational mixer. After mixing, all vessels were capped to avoid evaporation and then placed in a zirconia sand (\(\phi = 0.2 \text{ mm}\)) bath at 65°C. For each solution, the pH was monitored using a pH electrode (LAQUA standard TousH electrode 9615-10D, Horiba Co., Kyoto, Japan) connected to a multimeter (D-51AC, Horiba Co., Kyoto, Japan) with the electrode soaked in acetic buffer solutions for a few minutes to stabilize the electrode condition. The mixed solution pH values were recorded every 2 s. After reacting for 15 h, the precipitates were separated by centrifuging, washed five times with 2 mL double-distilled water and well ejected water using micropipettes, and then were dried at 65°C for 1 h.

2.4 Material characterization methods

The precipitates with a mixture of ethanol and isopropyl alcohol with 1:1 weight ratio were then dropped on a transmission electron microscopy (TEM) Cu microgrid covered with holey carbon films and air dried on KimWipes\textsuperscript{®} for TEM observation at an acceleration voltage of 200 kV (JEOL-2200, JEOL Co., Tokyo). The treated precipitates were also mounted on nine pure Si plates and examined through field emission scanning electron microscopy with energy dispersive X-ray spectroscopy at an acceleration voltage of 15 kV and amplitude of 70 µA (FE-SEM/EDX, FE-SEM: FEI40, FEI Co., the Netherland, EDX: EDAX GENESIS, EDAX Japan Co., Japan). For each condition, at least 15 samples were used for the FE-SEM/EDX measurement. The auto calibration mode was used.

Chemical shifts were measured using an attenuated total reflection (ATR) type of FT-IR spectrometer (FT-IR: Nicolet 6300, ThermoScientific Co., USA) equipped with a triglycine sulfate (TGS) detector (32 scans, resolution 2 cm\textsuperscript{-1}). The background of measurements was atmosphere.

The 31P chemical shifts in the CaPO\textsubscript{4}\textsubscript{5} were determined using a solid-state NMR spectrometer (NMR: JNM-ECX400 JEOL Co., Japan and AVANCE III HD 600WB, Bruker AXS Co., USA) with a resonance frequency of 400.0 MHz (JNM-ECX400) and 600 MHz (AVANCE III HD 600WB). For all measurements, magic-angle spinning (MAS) with a single pulse mode for 31P was applied at frequencies of 10000 or 15000 rpm in 4 or 5 mm zirconia rotors. The sample weight was ~0.2 g, and the contact time for the 31P MAS measurements was 36 ms with relaxation delays of 60 s or 5 ms with relaxation delays of 10 s in each measurement interval. Each measurement was repeated 1400 times. The 31P chemical shift was calibrated as 0.0 ppm using a 0.5 M K\textsubscript{2}HPO\textsubscript{4}–KH\textsubscript{2}PO\textsubscript{4} solution with a pH of 6.5.

XRD (RINT-40, Rigaku Co., Japan, J\textsubscript{00} = 0.15406 nm) measurements were performed at an acceleration voltage of 50 kV and a magnitude of 100 mA using a Cu target. The 2θ value was varied from 3 to 60° in 0.01° increments with 0.5 s used for each step. The entrance slit size was 5 mm × 10 mm.

3. Results and discussions

3.1 Characterization of DCPD for OCP synthesis

Figure 2(a) shows an FE-SEM micrograph of the precipitate formed in 0.33 M Ca and PO\textsubscript{4} solution after 1 h of reaction time. The length and width of the rhombohedral plate-like crystals were as high as 50 and 10 µm respectively; spherical aggregates of the crystals were also observed. The precipitate consisted mostly of single-phase crystals. Figure 2(b) shows the XRD pattern of the rhombohedral plate-like crystal precipitate. Four strong peaks were observed at 2θ = 11.8, 21.2, 23.4, and 29.2°, corresponding to the (020), (12-1), (040), and (14-1) reflections of DCPD, respectively.\textsuperscript{29} The precipitates were therefore determined to be DCPD.

3.2 pH monitoring during OCP formation for various concentrations of acetic acid in solution

Figure 3 shows the pH curves obtained during OCP formation in various concentrations of acetic acid. In solutions with low concentration of acetic acid (<100 mM), pH values increased in
the initial mixing stage because of the DCPD dissolution process. In the control solution (acetic acid free solution), the pH reached 7.5 and then rapidly decreased to around 5.4. This rapid pH decrease was followed by a gradual (0.025/h) pH decrease until the final pH of 5.1 was reached after 15 h. By contrast, no obvious pH maxima were found for solutions with high acetic acid concentrations (>200 mM). However, as in the case of the low acetic acid concentration solutions, the final pH values were around 5.1. Thus, irrespective of acetic acid concentration, all materials were synthesized under acidic conditions (pH 5.0–5.7).

3.3 Microscopy observation of the precipitates formed in various acetic-acid-containing solutions

Figure 4 shows the micrograph of the precipitates formed in various acetic acid containing solutions. Figure 4(a) shows FE-SEM micrographs of the OCP crystal precipitates formed in the control solution. The OCP crystals showed a typical elongated ribbon-like morphology with length, width, and thickness of 10–20 μm, ~2 μm, and 200 nm, respectively. The edges of the single crystals were often rectangular [inset; Fig. 4(a)], sometimes forming blade-like morphologies, and sometimes forming spheritic aggregates. Figure 4(b) shows optical micrographs of the OCP crystal precipitated formed in the 50 mM acetic acid containing solution. The whole morphology is as same as the OCP formed in the control solution. However, the size of crystals were much larger than those formed in the control solution. The length, width and thickness of the single crystals were approximately 30–80 μm, 2–5 μm, and 0.2–5 μm, respectively. Figure 4(c) shows a transmission optical micrograph of the OCP crystals formed in 100 mM acetic-acid-containing solution. The OCP crystals exhibit a rigid plate-like morphology with length, width, and thickness of 50–100 μm, 10–20 μm, and 0.2–5 μm, respectively. The OCP crystals sometimes also formed polycrystalline spherulites. The edges had a sword-like shape, not a rectangular shape. When OCP crystals synthesized in above 100 mM acetic acid-containing solution, there were no significantly changing toward to that formed in 100 mM acetic-acid-containing solution [Fig. 4(d)].

3.4 XRD, Fourier transform infrared spectroscopy (FT-IR), NMR, and FE-SEM/EDX analysis of OCPs formed in various acetic-acid-containing solutions

Figure 5(a) shows the XRD patterns of the precipitates formed at 15 h in solutions with various acetic acid concentrations. In all cases, the signature (100) OCP reflection at 2θ = 4.7° indicated the presence of the OCP phase. The peaks at the other 2θ were also similar to the standard OCP peaks. The relative intensity ratios of the (100) peaks increased, and the relative intensity ratios of the strongest peak of OCP [(100) peak, 2θ = 4.7°] to the second strongest peak [(4-1-2) peak, 2θ = ~26°] were approximately 100:90, 100:50, 100:25, and 100:3 for the control and 5, 10, and 100 mM acetic acid solutions, respectively. The integrated intensity of the diffraction peaks was taken into account the measurement accuracy and the preferred orientation of the samples. This suggests that the layered structure of OCP along
the a-axis became more crystalline in the presence of acetic acid. The typical HAP peak at 2θ = 10.8° was not observed in XRD pattern of precipitates formed in various acetic-acid-containing solutions.

Figure 5(b) shows a magnified view of the XRD patterns of the precipitates formed at 15 h using solutions with various acetic acid concentrations. The pattern of the control precipitate shows a single peak at 2θ = 26.3°, a broad single peak at 2θ = 26.5°, and overlapping peaks around 2θ = 30.4–35.5°. For the precipitates formed in low acetic acid concentration (<5 mM), the overlapping peaks around 2θ = 30.4–35.5° showed typical HAP diffraction band reflections. This indicates that the presence of layer stacking defects along the precipitate a-axis direction.

Figure 6 shows FT-IR spectra of the precipitates formed with various concentrations of acetic acid. The OCP FT-IR spectra exhibited monomodal strong absorption corresponding to \( v_1' \) (PO\(_4\) stretching at 1025 cm\(^{-1}\)) and many weak OCP sub-absorptions bands at 864, 917, 936, 963, 1058, and 1080 cm\(^{-1}\) and at 1105, 1123, 1130, and 1185 cm\(^{-1}\) due to PO\(_4\) and HPO\(_4\) vibrations, respectively. The spectra of the precipitates formed in acetic acid solutions showed an extra OCP absorption band at 1005 cm\(^{-1}\) corresponding to the HPO\(_4\) \( v_1'' \) mode, which is the most intense OCP absorption mode. The intensity of the band at 1005 cm\(^{-1}\) was enhanced with increasing acetic acid concentration. Thus, the obtained FT-IR results indicate that acetic acid enhances the \( \text{Apa} \) structure of OCP.

Figure 7 shows solid-state \(^{31}\text{P}\) NMR spectra of the precipitates formed in the control and 5 and 100 mM acetic acid solutions measured at 15 h. Previous work has shown that four chemical shifts, denoted as \( P1 \) (PO\(_4\) from \( \text{Apa} \)), \( P2/P4 \) (PO\(_4\) from \( \text{Apa} \)), \( P3 \) (PO\(_4\) from \( \text{Tra} \)), and \( P5/P6 \) (HPO\(_4\) from \( \text{Lay} \)) are present in the OCP NMR spectrum at 3.6, 3.1, 1.9, and -0.4 ppm, respectively. The spectrum of the precipitate formed in the control solution shows a strong \( P3 \) shift and weak and broad \( P1 \) and \( P2/P4 \) shifts. Chemical shifts corresponding to \( P3/P6 \) were not obvious in the control precipitate.

On the other hand, the spectrum of the precipitate formed in 5 mM acetic acid solution showed a bimodal shift arising from \( P1 \) and \( P2/P4 \) and monomodal shifts arising for \( P5/P6 \) and \( P3 \), as found in typical OCP NMR spectra. Furthermore, the spectrum of the precipitate formed in 100 mM acetic acid solution showed a strong \( P1 \) shift, indicating a well-developed HAP structure in the OCP phase. The obtained NMR results indicate that the presence of acetic acid led to changes in the \( \text{Apa} \) and \( \text{Lay} \) OCP structures.

Figure 8 shows the Ca/PO\(_4\) ratios obtained by FE-SEM/EDX for the materials formed with various acetic acid concentrations. The Ca/PO\(_4\) ratio for the material formed in the control solution was 1.45 ± 0.07 (N = 15). As acetic acid concentration was increased, the Ca/PO\(_4\) ratio first rapidly decreased in the low acetic acid concentration range (<20 mM), reaching 1.15 ± 0.03 at 20 mM, and then stabilized at approximately 1.15 for concentrations greater than 20 mM. Thus, it was found that OCP Ca/PO\(_4\) ratios decreased with increasing acetic acid concentration.
3.5 Electron microscopy observation of the precipitates formed in various acetic-acid-containing solutions

The average sizes of OCP crystals formed in acetic-acid-containing solutions increased with increasing acetic acid concentration but remained below 200 μm. For example, in acetic acid free conditions, precipitates mainly comprised crystals with length and thickness of 10 μm and 200 nm, respectively. In 50 mM acetic-acid-containing solutions, precipitates mainly comprised rigid crystals with length and thickness of 200 μm and 20 μm, respectively. For concentrations above 100 mM, the average sizes of OCP crystals and acetic acid concentration were only weakly correlated. However, even for solutions with high acetic acid concentrations, a few of the formed crystals exhibited the same size as the crystals formed in low acetic acid concentrations.

Figure 9(a) shows TEM photographs of typical single OCP crystals perpendicular to the plate-like plane. The selected area electron diffraction (SAED) image of Fig. 9(a) shows the positions of the (010) and (001) OCP diffraction spots [Fig. 9(b)], indicating that the bc plane is the plate-like plane in OCP. HR-TEM showed well-ordered lattice fringes with a moiré pattern along the bc plane [Fig. 9(c)], indicating that atomic disorder is present along the a-axis of the crystal. Furthermore, small regions of OCP crystals showed poor lattice fringes [Fig. 9(d)]. Figure 8(e) shows a low-resolution TEM micrograph of an ultrathin section of OCP large-scale plate-like crystals in the vertical direction along the a-axis. Examination of HR-TEM image shows that the structure of the OCP crystals formed in the control solution consisted of well-ordered lattice fringes [Fig. 9(c)] with a few poorly crystalline [Fig. 9(d)] and polycrystalline regions [Fig. 9(f)]. The surface of crystalline was covered amorphous like regions ranging 10 nm in thickness [Fig. 9(h)].

Figure 10(a) shows a TEM image and an SAED pattern of the OCP crystals. The SAED pattern of the plate-like OCP crystals along the a-axis exhibits clear Laue spots corresponding to the single crystal. HR-TEM image exhibited well-ordered lattice fringes [Fig. 10(b)]. Examination of the ultrathin section of the large-scale plate-like OCP crystals [Fig. 10(c)] revealed that they mainly consisted of well-ordered lattices in the vertical direction along the a-axis with a lattice spacing of 2.47 Å [Fig. 10(d)]. The surface of OCP crystals were also covered with amorphous like structures. Poor lattice was found the edge of amorphous regions [Fig. 10(e)].

To summarize, EDX, NMR and FT-IR spectroscopic measurements similarly showed that acetic acid plays an important role in the formation of the OCP Lay structure. XRD analysis and TEM observation indicated that OCP crystals formed in acetic acid containing solution were highly crystallinity and well-ordered layered structured along to a-axis.

Kamitakahara and his colleagues demonstrated the use of hydrothermal synthesis for obtaining HAP from OCP. According to their results, heating at 65°C for 1 h is not sufficient to transform OCP into HAP during drying processes. We therefore conclude that the results obtained in the present study originated from the modification of OCP structures by acetic acid.

NMR and FT-IR measurements showed that Apa and Lay OCP...
While the mechanism for the generation of highly crystalline plate-like crystals showing well-ordered lattice fringes along the HR-TEM image of OCP surface in the vertical direction along the section in the vertical direction along the section.

Lay formation is how enhance the other hands, when OCP synthesized with high concentration of acetic acid solution. (a) Bright-field image of plate-like crystals showing well-ordered lattice fringes along the a-axis with SAED pattern. (b) HR-TEM image and FFT pattern of plate-like crystals along the a-axis. (c) Low-resolution bright-field image of the same sample in the ultrathin field image of plate-like crystals along the a-axis. (d) HR-TEM image of plate-like crystals showing well-ordered lattice fringes along the a-axis. (e) HR-TEM image of OCP surface in the vertical direction along the a-axis.

Fig. 10. Electron micrograph data for the precipitate formed in 100 mM acetic acid solution. (a) Bright-field image of plate-like crystals along the a-axis with SAED pattern. (b) HR-TEM image and FFT pattern of plate-like crystals showing well-ordered lattice fringes along the a-axis. Low-resolution bright-field image of the same sample in the ultrathin field image of plate-like crystals along the a-axis. (d) HR-TEM image of plate-like crystals showing well-ordered lattice fringes along the a-axis. (e) HR-TEM image of OCP surface in the vertical direction along the a-axis.

structures were more crystalline at increasing acetic acid concentration. The attenuation of hk diffraction band structures found by XRD measurements and it indicated that acetic acid enhance OCP coherent domain sizes. These results imply that the development of highly ordered Apa structure by acetic acid is one of the main factors responsible for the formation of highly crystalline OCP. Considering the OCP Apa-Tra-Lay-Tra-Apa layer crystal structure, it is suggested that an ordered highly crystalline Apa structure enables the existence of the highly ordered Lay structure because the Apa structure acts as a connector of Lay bridge structures. This relationship was also confirmed by microtome HR-TEM observations. Furthermore, the decreasing of Ca/Po ratio as acetic acid concentration increasing is also indicated this tendency. In short, when OCP synthesized without or with low concentration of acetic acid, low-crystallinity and small OCP crystals with relatively high Ca/Po ratio were formed. On the other hands, when OCP synthesized with high concentration of acetic acid, the tendency was completely opponent. Therefore, we are considering the key of well-crystallized OCP large crystal formation is how enhance the Lay of OCP.

We now discuss the reason for the generation of the enhanced order in Lay and Apa OCP obtained by the use of acetic acid. While the mechanism for the generation of highly crystalline Apa structure in the precursor phase was not observed and no evidence for acetic acid incorporation into OCP lattices was found, a hint for the mechanism can be derived from the results of Mathew et al.18) who obtained large OCP crystals formed in 100 mM acetic acid at 40°C and showed that amorphous calcium phosphate (ACP) phases formed as an initial phase during the OCP formation process.24,25) ACP phases have been shown to play an essential role in the formation of crystalline calcium carbonate through cluster-based phase transformation.25,26) In our study, despite the relatively high synthesis temperature of 65°C, OCP crystals were also synthesized from ACP in aqueous solutions due to the formation of OCP in aqueous solutions. Furthermore, HR-TEM observation showed that OCP crystals were covered by amorphous layer structure. Thus, we can conclude that ACP was formed as a precursor phase of the OCP.

The formation of OCP crystals from ACP particles suggests that alterations of the physicochemical properties of ACP or of the clusters that are the components of ACP by –COOH-containing molecules control the energetics and the reaction path of OCP formation. Such alteration therefore also controls the final OCP structure. Thus, even though acetic acid was not incorporated in the final OCP structure, its presence can affect the final OCP structure by affecting the early stages of OCP formation. Habraken et al.32) showed that OCP (Ca-deficient OCP) formation proceeded via several ACP precursor stages, described as an ionic pairs and clusters in aqueous solutions. The low Ca/Po ratio of our specimens were also supported this tendency. Using ab initio calculations and X-ray adsorption near edge spectroscopy, Kanzaki et al.33) and Du et al.34) also reported the presence of different Ca–Po4 cluster structures in aqueous solutions or vacuum conditions. Some of the Ca–Po4 cluster components of ACP particles were not structurally similar to those of the crystalline phases, and we infer that such isomer clusters subsequently attenuate the structure of the final solid.33,35)

Based on these results, we propose that acetic acid reduces the formation of Ca–Po4 isomer clusters during OCP formation, leading to the development of highly crystalline Apa structures. Previous research suggested that multiple structures are present in minerals formed by cluster-based mineralization.38,39) For example, vaterite, a metastable phase of calcium carbonate, formed several different structures through cluster-based mineralization. Using ab initio calculation, Demichelis et al.38) showed that vaterite exhibits multiple types of crystal structures with essentially the same Ca+ ions locations but different CO32− ions locations. Analysis of XRD patterns for the crystals obtained by cluster-based mineralization showed that while the main peaks of these crystals coincided well with the standard vaterite peaks and were identified as vaterite, worse agreement was observed for the minor peaks. Similarly, we conclude that OCP investigated in this study also has multiple structures that show a typical OCP peak at 2θ = 4.7° despite the slight differences between their structures. Previous studies1,4,11,18,21,23) reported a variety of lattice parameters for OCP; thus, we infer that the OCP phase can be categorized as an OCP group structure which has called as “multiplied polytype” rather than a strictly single structure such as those of calcite and NaCl describing as rigid crystals.

4. Conclusion

We investigated how acetic acid affects the formation of the OCP crystal structure and found that acetic acid enhanced the Apa and Lay structures, which is important for obtaining well-crystallized and large-size OCP crystals. Analysis of the results and their comparison with the results obtained in previous work suggested that formation of highly crystalline OCP by acetic acid
can be explained by the elimination of the isomers that decrease the development of Apa structures during the ACP precursor stage. The hypothesized existence of Ca–P₃O₃ clusters in several different forms that include the isomers can explain the results of the previous calculation. This investigation shows that the process through which the Apa structure is formed has a cumulative effect on the structure of the final OCP materials and is related to the entire OCP formation process.

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