Comparative study of hydroxyapatite formation from α- and β-tricalcium phosphates under hydrothermal conditions

Tomoyo GOTO, Ill Yong KIM, Koichi KIKUTA and Chikara OHTSUKI
Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan

We investigated the crystal growth of hydroxyapatite (HAp) from α-phase (α-TCP) and β-phase (β-TCP) tricalcium phosphates showing different solubility, under hydrothermal conditions. Samples of α-TCP and β-TCP were treated up to 72 h under hydrothermal conditions at 120°C. The α-TCP sample was completely transformed into HAp crystals within 1 h after the powder was exposed to hydrothermal conditions. In contrast, the β-TCP sample required more than 72 h to achieve complete transformation into HAp crystals. This difference in transformation behavior affected the morphology of the formed HAp crystals, which were observed to form plate- and rod-shaped crystals from α- and β-TCP, respectively. The high dissolution rate of α-TCP led to fine, plate-shaped crystals whose morphology was maintained up to 72 h once they formed. In comparison, the low dissolution rate of β-TCP allowed production of large, well-crystallized HAp crystals through the hydrothermal treatment conditions, even though the chemical composition of the reactant samples were the same. The morphology of the HAp crystals formed as a result of the hydrothermal conditions was controlled by selecting starting materials whose solubility affects an increase in the degree of supersaturation in the solution.

Key-words : Hydrothermal processing, Hydroxyapatite, Tricalcium phosphate, Solubility, Ionic product

1. Introduction

Hydroxyapatite [HAp; Ca10(PO4)6(OH)2] is a calcium orthophosphate compound that is widely used as a biomaterial for bone repair.1) HAp is also applicable as chromatography column fillers2–4) and carrier materials for drug delivery.5)–7) These biological characteristics of HAp depend not only on its composition but also on the morphology of the crystals, which affects the adsorption of biological molecules such as proteins.8–10) HAp has two types of crystal planes, the so-called α- and c-faces. Kawasaki et al. reported that the α-face showed a positive charge due to two Ca2+, while the c-face showed a negative charge due to six O2− belonging to three PO43−.3)–4) Therefore, morphological control of a HAp crystal is an attractive area of research that focuses on the development of HAp-based materials with unique biological functions.

Unique morphology of HAp crystal was prepared by gel growth, molten salt, flux, and hydrothermal methods.10)–13) Hydrothermal processing is one of the popular ways of fabricating HAp crystals with unique and well-crystallized features.13) Many researchers have attempted to synthesize HAp crystals by a hydrothermal treatment of reactants containing calcium and phosphate sources. In 1956, Perloff et al. reported that hydrothermal treatment of dicalcium phosphate anhydrous (DCPA, CaHPO4) allowed production of large HAp crystals approximately 0.3 mm in length.14) Dicalcium phosphate dihydrate (DCPD, CaHPO4·2H2O) has also been used for production of large HAp crystals through hydrothermal processing.15)–17) Hydrothermal treatment of alpha-tricalcium phosphate (α-TCP, Ca3(PO4)2) led to production of rod-shaped HAp crystals approximately 20 µm in length.18) Whiskers of HAp between 20 and 30 µm in length were formed through hydrothermal treatment of beta-tricalcium phosphate [β-TCP; Ca5(PO4)3] with the addition of citric acid.19) The formation of needle-shaped HAp crystals 0.4 µm in length was also reported after hydrothermal treatment of monocalcium phosphate monohydrate [MCPM; Ca(H2PO4)·H2O] combined with Ca(OH)2 and/or lactic acid.20) Plate-shaped HAp crystals have also been synthesized by a hydrothermal method using octacalcium phosphate [OCP, Ca10(HPO4)2(PO4)2·5H2O].21) In addition, a mixture of DCPD and β-TCP was used for hydrothermal synthesis of needle-shaped HAp crystals with a maximum length of 60 µm.22) These reports show that the morphology and composition of HAp crystals varies depending on many parameters, including solubility of the reactant, composition of the starting conditions, and additives to the aqueous solutions, as well as on the temperature and length of time of the hydrothermal processing.

Because previous studies mainly focused on optimization of the hydrothermal processing in order to achieve production of large and well-crystallized HAp with unique morphology, fundamental findings regarding the transformation from simple reactants of calcium phosphates into HAp crystals under hydrothermal condition are still insufficient. In order to provide further development on hydrothermal processing for production of HAp crystals with specifically designed morphology, the present study focuses on the transformation behavior of tricalcium phosphates that are polymorphic with different solubility such as α-TCP and β-TCP. A simple hydrothermal treatment was applied to α-TCP and β-TCP samples for comparison in the formation of HAp crystals.

2. Experimental procedure

2.1 Hydrothermal treatment

α-TCP (Taihei Chemical Industrial Co., Ltd., Japan) and β-TCP (Taihei Chemical Industrial Co., Ltd., Japan) were used as...
starting materials. Samples of \( \alpha \)-TCP or \( \beta \)-TCP powder (0.25 g) were put in a 90 cm\(^3\) polytetrafluoroethylene (PTFE) vessel (Shikokurika Co., Ltd., Japan) with an ammonium solution (20 cm\(^3\)) that had been adjusted to a pH of 9. The sealed vessel was then placed in an oven at 120°C for 30 min of preheating. The samples then remained in the oven for periods ranging from 1 to 72 h, which constituted the hydrothermal treatment of the powders. After the hydrothermal treatment, the vessel was cooled immediately with a fan under room temperature and the samples were taken out of the vessel. The obtained samples were then washed with ethanol and acetone to stop the formation reaction, followed by drying at 40°C for more than 12 h.

2.2 Characterization

The crystalline phases of the samples were identified by powder X-ray diffraction (XRD; RINT2100HL, Rigaku Co., Japan) using Cu K\(\alpha\) radiation at 40 kV and 20 mA. For a quasi-quantitative evaluation of HAp formation, the fraction of HAp detected in the products was determined from the obtained XRD patterns. The fraction of HAp \( f_{\text{HAp}} \) was calculated using the ratio of the integrated intensity of each sample, as shown in the following formula:

\[
f_{\text{HAp}} = \frac{I_{\text{HAp}}}{I_{\text{HAp}} + I_{\alpha\text{-TCP}} + I_{\beta\text{-TCP}}} \times 100 \%
\]

where \( I_{\text{HAp}} \) and \( I_{\alpha\text{-TCP}} \) were calculated by the integrated intensity of the 211 at \( 2\theta = 31.8^\circ \) for HAp, the 132 at \( 2\theta = 24.1^\circ \) for \( \alpha \)-TCP, and the 214 at \( 2\theta = 27.8^\circ \) for \( \beta \)-TCP reflections, respectively. Crystalline phases detected by XRD used for calculation of \( f_{\text{HAp}} \).

The morphology of the products was observed under scanning electron microscope (SEM; JSM-5600, JEOL Ltd., Japan). For SEM observation, the samples were coated with sputtered gold film. The size and aspect ratio of the formed products were determined from the SEM images. The aspect ratio was defined by length with respect to width of the products. Averages of the size and aspect ratio were calculated by measuring 50 particles. Transmission electron microscopy (TEM; JEM-2010F, Hitachi Ltd., Japan) was also used to observe the morphology of the products. For TEM observation, the products were dispersed in ethanol by ultrasonic fragmentation. Fourier transform infrared spectrometry (FT-IR; FT/IR-610, JASCO Co., Japan) was applied after the products were ground and mixed with potassium bromide at a mass ratio of about 1:50. The mixed powder was pressed into pellets for analysis in transmission mode. The atomic ratios of Ca and P of the products were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; Optima 2000DV, PerkinElmer Japan Co., Ltd., Japan) after the samples were dissolved in nitric acid solution.

The concentrations of Ca and P in the ammonium solution were also measured by ICP-AES. The pH values of the ammonium solution before and after the hydrothermal treatment were measured by the glass electrode method using a glass electrode-type pH meter (D-51, Horiba Ltd., Japan).

3. Results

3.1 Characteristics of the synthesized HAp

Figure 1 shows the powder XRD patterns of the starting materials and those of the products after the hydrothermal treatment of \( \alpha \)-TCP [Fig. 1(a)] and \( \beta \)-TCP [Fig. 1(b)] at 120°C for 72 h. Each of the starting materials was confirmed to be \( \alpha \)-TCP [PDF no. 00-009-0348] and \( \beta \)-TCP [whitlockite; PDF no. 00-009-0169] from the powder XRD patterns. After the 72 h hydrothermal treatment, the starting materials were completely transformed into HAp (PDF no. 00-009-0432). The typical characteristics of HAp crystals formed by the treatment of \( \beta \)-TCP showed a higher relative intensity of 300 reflection against that of 002 reflection, compared to the HAp crystals formed by the treatment of \( \alpha \)-TCP.

Figure 2 shows the SEM images of the starting materials [Figs. 2(a) and 2(d)] and products assigned to HAp crystals from the XRD patterns after the hydrothermal treatment of \( \alpha \)-TCP [Figs. 2(b) and 2(c)] and \( \beta \)-TCP [Figs. 2(e) and 2(f)] at 120°C for 72 h. The average particle size of both the \( \alpha \)-TCP [Fig. 2(a)] and \( \beta \)-TCP [Fig. 2(d)] of starting materials ranged from 1 to 3 \( \mu \)m in diameter. Aggregates consisting of needle- and plate-shaped crystals 1–3 \( \mu \)m in length were observed in the product prepared from \( \alpha \)-TCP powder. Rod-shaped crystals approximately 30 \( \mu \)m in length were observed in the product prepared from \( \beta \)-TCP powder. Fibrous crystals were also partially observed. The aspect ratios of the synthesized HAp crystals evaluated from the SEM images and the Ca/P atomic ratios determined by the ICP-AES analysis are summarized in Table 1. Plate-shaped crystal was regarded as a rectangle and defined the aspect ratio by the ratio of length of long side with respect to short side on the rectangle. In addition, calculation of aspect ratio of needle- or rod-shaped crystals were also used long axis and short axis as length and width, respectively. The size and aspect ratio of the HAp crystals prepared by the hydrothermal treatment of \( \beta \)-TCP were larger than those of \( \alpha \)-TCP, although the Ca/P atomic ratio of the HAp synthesized from \( \alpha \)-TCP was 1.51, which was similar to that from \( \beta \)-TCP.

Figure 3 shows the TEM images and electron diffraction patterns of the products after the hydrothermal treatment of \( \alpha \)-TCP [Fig. 3(a)] and \( \beta \)-TCP [Fig. 3(b)] at 120°C for 72 h. The image of HAp crystals formed from \( \alpha \)-TCP [Fig. 3(a)] and its electron diffraction pattern shows that the plate- and needle-like HAp crystals consist of single crystals with a \([-110]\) zone axis, and the unit cell parameters of the HAp phase (hexagonal with the P6\(_3\)/m space group) are consistent with the data for PDF no.00-009-0432. The electron diffraction pattern shows that the formed plate-shaped HAp is a well-crystallized hexagonal single crystal. In contrast, the HAp crystals synthesized from \( \beta \)-TCP had rod-shaped crystals [Fig. 3(b)] and their electron diffraction pattern was the same as that of the product from \( \alpha \)-TCP.
result shows that the HAp crystals synthesized from both \( \alpha \)-TCP and \( \beta \)-TCP grew along the \( c \)-axis.

**Figure 4** shows the FT-IR spectra of the products prepared by the hydrothermal treatment at 120°C for 72 h. (a) and (b) are products prepared from \( \alpha \)-TCP and \( \beta \)-TCP, respectively.
3.2 Transformation of TCP to HAp

From the powder XRD patterns of the products prepared by the hydrothermal treatment of \( \alpha \)-TCP and \( \beta \)-TCP, the fraction of HAp (\( F_{\text{HAp}} \)) in the products was determined as a function of treatment period and is shown in Figure 5. The starting material \( \alpha \)-TCP was transformed into HAp crystals completely within 1 h after the hydrothermal treatment started. In contrast, the fraction of HAp formed in the product prepared from \( \beta \)-TCP showed a gradual increase up to 72 h before completely transforming to HAp crystals.

Figure 6 shows the SEM images of the products after 1, 6, and 24 h of the hydrothermal treatment of \( \alpha \)-TCP and \( \beta \)-TCP. After the hydrothermal treatment for 1 h, fine needle- and plate-shaped crystals 1–3 \( \mu \)m in size [Fig. 6(a)] were formed in the products prepared from \( \alpha \)-TCP. The morphology and size of the HAp crystals formed 6 and 24 h after the hydrothermal treatment of \( \alpha \)-TCP [Figs. 6(b) and 6(c), respectively] were almost the same as those for 1 h [Fig. 6(a)]. Thus, the production of HAp crystals was completed within 1 h and formed crystals were small. In contrast, the morphology of the products formed by hydrothermal treatment of \( \beta \)-TCP for 1 h was almost same as that of the \( \beta \)-TCP starting material [Fig. 6(d)]. Some needle-shaped particles, which were assigned to HAp crystals, were observed in the products prepared by hydrothermal treatment of \( \beta \)-TCP for 6 h, and the amounts and sizes of the needle-shaped crystals increased with increasing treatment period [Fig. 6(e)]. \( \beta \)-TCP, originally of irregular shape, was hardly observed after treatment for 24 h [Fig. 6(f)]. Based on observation of the formed HAp crystals, which appeared needle- and rod-shaped, changes in the length, width, and aspect ratio of the crystals were determined as a function of the treatment period and are shown in Figure 7. The length of the products from \( \beta \)-TCP increased with increasing treatment period [Fig. 7(a)], while the increase in its width was not as significant [Fig. 7(b)]. Meanwhile, the length and width of the HAp crystals in the product prepared from \( \alpha \)-TCP did not change with increasing treatment period. The aspect ratio of the HAp crystals prepared from \( \beta \)-TCP was slightly larger after the treatment for more than 6 h than that of the HAp crystals prepared from \( \alpha \)-TCP.

Figure 8 shows the pH values of the aqueous solutions after the hydrothermal treatment of \( \alpha \)-TCP and \( \beta \)-TCP at 120°C for various treatment periods. The pH value of the aqueous solution was initially adjusted to 9 before exposure of \( \alpha \)-TCP and \( \beta \)-TCP to the treatment. After the treatment of \( \alpha \)-TCP, the pH was approximately 5 within 1 h, followed by a slight decrease in pH with increasing treatment period. In contrast, the pH of the solution after treatment of \( \beta \)-TCP increased to approximately 10 after the hydrothermal treatment of around 6 h, followed by a remarkable decrease, to approximately 5 after 24 h. Changes in Ca and P concentrations of the solutions due to the hydrothermal treatment of \( \alpha \)-TCP and \( \beta \)-TCP at 120°C are shown in Figure 9. In the case of the hydrothermal treatment of \( \alpha \)-TCP, the Ca concentration moderately increased with increasing treatment periods. In contrast, a remarkable increase in the Ca concentration of the solution occurred around 12 h after the hydrothermal treatment of \( \beta \)-TCP began. These trends were also observed in the changes in P concentrations in the solutions after the hydrothermal treatment. After the hydrothermal treatment for more than 12 h, the Ca and P concentrations of the solution in which \( \beta \)-TCP samples were immersed were higher than those of the solution in which \( \alpha \)-TCP samples were immersed. The higher concentrations of Ca and P in the solution after the hydrothermal treatment indicated the reduced amounts of precipitates in the solution during the hydrothermal processing.

4. Discussion

4.1 Composition of synthesized HAp

It is apparent from the results in the present study that both types of tricalcium phosphate were transformed into HAp crystals within 24 h under hydrothermal conditions at 120°C at an initial pH of 9. The resultant HAp crystals had the same Ca/P atomic ratio of around 1.5 but different morphologies, depending on the
4.1 Transformation of TCP to HAp

The transformation and growth of HAp crystals are governed by the dissolution behaviors of α- and β-TCP. The solubility of α-TCP in water is higher than that of β-TCP because α-TCP has a “looser” structure and a higher internal energy than β-TCP. \[ \text{Ca}_3(\text{PO}_4)_2 \rightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \] (2)

The measured Ca/P value of the formed HAp from both tricalcium phosphates was approximately 1.5. In addition, the FT-IR spectra showed that synthesized HAp crystals had substituted HPO$_4^{2-}$. These results indicate possible formation of non-stoichiometric HAp, as generally given by the formula

\[ \text{Ca}_{10-z}((\text{PO}_4)_x(\text{OH})_{2-z})_z \cdot n\text{H}_2\text{O}; z = 0-1, n = 0-2 \]

Supposing that the Ca/P atomic ratio is 1.5 and the other substitutions are included, the calcium-deficient HAp is assumed to be formed by

\[ 9\text{Ca}^{2+} + x\text{HPO}_4^{2-} + (6 - x)\text{PO}_4^{3-} + x\text{OH}^- + n\text{H}_2\text{O} \]
\[ \rightarrow \text{Ca}_9((\text{PO}_4)_{6-x}(\text{OH})_x)_z \cdot n\text{H}_2\text{O}, \]

which results in a decrease in pH following the dissolution of tricalcium phosphate.

4.2 Morphology of synthesized HAp

In the present study, the HAp crystals formed from β-TCP had rod-shaped crystals. The results of TEM indicate that the HAp crystals grew along the c-axis while exposing the a-face, regardless whether the source of the crystal was α-TCP or β-TCP. Many previous studies have reported that HAp crystals grow along the c-axis under hydrothermal conditions, and these crystals are predisposed toward the formation of whiskers or rod- or needle-shaped crystals. This indicates that HAp crystals have a rod-shaped form, with the a-face of the prismatic plane as the equilibrium form under hydrothermal conditions. Since a slow crystal growth rate and driving force generally leads to polyhedral crystals that are close to idiomorphic, formation of rod-shaped HAp crystals from β-TCP is attributed to its low rate of crystal growth. The crystal sizes of HAp formed from α-TCP are smaller than those from β-TCP. Plate-shaped crystals were observed on the HAp crystals synthesized from α-TCP through hydrothermal treatment, in addition to needle-shaped crystals. \[ \text{Ca}_3(\text{PO}_4)_2 \rightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \] α-TCP was transformed into OCP by conventional hydrolysis. Formation of plate-shaped HAp crystals therefore resulted from HAp formation through an intermediate phase such as OCP under hydrothermal conditions. Actually, it has been reported that the plate-shaped crystal morphology of HAp was maintained through transformation of OCP with plate-shaped crystals into HAp under hydrothermal conditions.

4.3 Transformation of TCP to HAp

The transformation and growth of HAp crystals are governed by the dissolution behaviors of α- and β-TCP. The solubility of α-TCP in water is higher than that of β-TCP because α-TCP has a “looser” structure and a higher internal energy than β-TCP. \[ \text{Ca}_3(\text{PO}_4)_2 \rightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \] (2)

The solubility products \( K_{sp} \) of α-TCP and β-TCP at 25°C are reported as \( pK_{sp} = (\log K_{sp}) = 25.5 \) and 28.9 for α-TCP and β-TCP, respectively. The dissolution of α- and β-TCP would increase the degree of supersaturation with respect to HAp, resulting in nucleation of HAp and its subsequent crystal growth. In the case of hydrothermal treatment of α-TCP, the dissolution of α-TCP rapidly proceeded after exposure to the aqueous solution to complete the transform to HAp crystals within 1 h (Fig. 5).
the solution in which the α-TCP was hydrothermally exposed decreased to approximately 5 after the treatment periods around 6 h (Fig. 8). The Ca and P concentrations of the solution appeared to gradually increase after soaking for more than 6 h (Fig. 9). These results indicated that the HAp crystals formed within 1 h, followed by further dissolution and precipitation. In contrast, during the hydrothermal treatment of β-TCP, HAp precipitation was so slow that an increase in the pH of the solution was observed over 3 h, followed by a decrease in pH to 5 for more than 24 h. Moreover, increases in the Ca and P concentrations of the solution were observed at around 12 h, followed by a gradual increase after 24 h or more. The slower reaction rate of the formation of HAp from β-TCP was distinctly confirmed by the fraction of HAp in the products (Fig. 5), which was less than that from α-TCP. Supposing the ionic product ($IP$) with respect to HAp of stoichiometric composition,

$$10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^- \rightarrow \text{Ca}_{10}^{10+}(\text{PO}_4)^{6-}(\text{OH})_2$$

$$IP = [\text{Ca}^{2+}]^{10}[\text{PO}_4^{3-}]^6[\text{OH}^-]^2$$

Here a simplified condition would be applied on comparison between α-TCP and β-TCP.

Fig. 9. Ca and P concentrations of the aqueous solutions after the hydrothermal treatment of α-TCP and β-TCP for various periods. ●: α-TCP, ○: β-TCP.

The high rate of nucleation in the solution is attributed to the high solubility of α-TCP. The values of $\sigma$ of the solution after the treatment of α-TCP were almost equal to those after the treatment for 1 h or more. This means that the nucleation and crystal growth were almost completed. The size of HAp crystals formed from the α-TCP powder was approximately 1 μm after the hydrothermal treatment for 1 h or more. In contrast, the value of $\sigma$ of the solution after the treatment of β-TCP increased up to 3 h, followed by a decrease to zero after treatment for 24 h or more. The size of HAp crystals in the samples prepared by the hydrothermal treatment of β-TCP rapidly increased after hydrothermal treatment for periods between 6 and 12 h. The number of nucleations was quite small for the sample prepared from β-TCP, which means that the initial increase in the degree of supersaturation was low and led to the slow growth of HAp crystals in the solution. These phenomena are consistent with the results of our previous report, in which we reported the formation of HAp crystals from α-TCP under solvothermal conditions in a water-ethanol system.14 Solvothermal treatment of α-TCP in a water-ethanol solution gave varied morphology of HAp crystals, from plate-shaped to needle-shaped, depending on the fraction of ethanol in the water. As the apparent solubility of α-TCP and HAp decreased with increasing fraction of ethanol in solvent, the growth rate of HAp crystals in the water-ethanol solution was slower than that in water alone. In the present study, although $\sigma$ was calculated from the data after the hydrothermal treatment at 120°C, the speculated estimation of the changes in the $IP$ value from the data on the products and the solution after the hydrothermal conditions was worth determining the formation behavior of the HAp crystals.

5. Conclusion

We investigated the difference of HAp formation behavior between two different types of tricalcium phosphate under hydrothermal conditions. The rate of HAp formation from α-TCP was faster than that from β-TCP. The synthesized HAp was grown along the c-axis and led to a calcium-deficient HAp crystal with HPO4 substitution, regardless of the starting materials. The HAp crystals synthesized from α-TCP showed small, plate-shaped crystals, while those from β-TCP showed large, rod-shaped crystals. The differences in crystal size and morphology were attributed mainly to the dissolution rate of TCP and growth rate of HAp crystals. The morphology of HAp crystals could be controlled by the dissolution behavior, which affects the rate of increase in the degree of supersaturation in the solution through careful selection of the starting materials.

<p>| Table 2. Summary of the equilibrium constants at 25°C |</p>
<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$</td>
<td>$7.11 \times 10^{-3}$ mol/L</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$</td>
<td>$6.30 \times 10^{-8}$ mol/L</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$</td>
<td>$4.73 \times 10^{-13}$ mol/L</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- = \text{CaH}_2\text{PO}_4^+$</td>
<td>$25.6$ (mol/L)$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{HPO}_4^{2-} = \text{CaHPO}_4$</td>
<td>$548$ (mol/L)$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{PO}_4^{3-} = \text{CaPO}_4$</td>
<td>$2.9 \times 10^6$ (mol/L)$^{-1}$</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$</td>
<td>$13.8$ (mol/L)$^{-1}$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$</td>
<td>$1.004 \times 10^{-14}$ (mol/L)$^2$</td>
</tr>
</tbody>
</table>
Innovative Areas: (a) by Grant-in-Aid for Scientific Research (Area no. 2206) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). This work was supported (b) by the Hydrothermal Treatment of the Samples.

Fig. 10. Changes in (a) relative supersaturation (σ) with respect to HAp and (b) crystal length, after the hydrothermal treatment of the samples. • α-TCP, ○ β-TCP.

Acknowledgments The authors appreciate support from the G-COE program (Global Center of Excellence Program, Japan Society for the Promotion of Science). This work was supported by Grant-in-Aid for Scientific Research (No. 22107007) on the Innovative Areas: “Fusion Materials” (Area no. 2206) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References