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Topotaxial Conversion of Chlorapatite and Hydroxyapatite to Fluorapatite by Hydrothermal Ion Exchange

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The ion exchange of Cl^- and OH^- with F^- in synthetic calcium chlorapatite and calcium hydroxyapatite single crystals was investigated under hydrothermal conditions. The hydrothermal treatments were conducted using 5 and 10 M KF solutions, at temperatures of 500 and 600 °C under a constant internal pressure of 100 MPa, for intervals between 6 and 336 h. The ion exchange of Cl^- in the chlorapatite crystals proceeded faster than that of OH^- in the hydroxyapatite crystals during hydrothermal treatments at 500 °C in 5 M KF solution. Under these conditions, the chlorapatite crystals were completely converted to fluorapatite crystals. In contrast, the hydroxyapatite crystals were only partially converted to fluorapatite. In both cases, the topotaxial ion-exchange reaction was achieved by a mechanism of dissolution–precipitation of clusters. The partially and completely converted fluorapatite crystals had a characteristic texture, exhibiting tiny tunnels along the c axis of the crystals, and a thin layer of CaF_2 was also produced on the surface of the converted crystals. The influence of the reactivity of the individual apatites on the control of the ion exchange rate is discussed.

Introduction

Biological apatites, geological apatites, and related calcium phosphates have been a research subject for compositional and structural evaluations, since all these apatite species are apt to uptake or incorporate several foreign cations or anions in their sublattices.^{1–4} Replacement of OH^- ions by F^- ions has been mainly investigated on calcium hydroxyapatite (hereafter referred to as HAP), the main constituent of enamels, due to the preventive action of fluoride in the occurrence of dental cavities.^{5–8} Furthermore, the existence of homogeneous solid solutions in the binary system of HAP and calcium fluorapatite (hereafter referred to as FAP) was experimentally determined over the entire compositional range.^{9,10} According to the experimental proce-

dures, all of the solid solutions were produced by chemical reactions that did not involve an ion-exchange mechanism.

The first evidence of ion exchange in the apatite structure was reported to occur in calcium chlorapatite single crystals (hereafter referred to as CIAP), which were converted to HAP single crystals under solid-state conditions by heating the CIAP crystals at 1000 °C for 2 weeks in water vapor at atmospheric pressure.¹¹ On the other hand, Brennan¹² has demonstrated that the ion-exchange rate is further accelerated under hydrothermal conditions at high temperature and pressure. Thus, under hydrothermal conditions at high pressure (1 GPa), the diffusion coefficients of anions measured in the apatite structure indicate that the mobility of anions is greater than that observed at low pressure (1 atm).

Recently, Yanagisawa et al.¹³ have found a different mechanism that achieves faster ion exchange at low temperatures than the solid-state mechanism. The exchange of Cl^- ions with OH^- in the synthetic CIAP single crystals was conducted under alkaline hydrothermal conditions at temperatures as low as 300 °C for 12 h in 6.25 M KOH solution. The ion exchange under alkaline hydrothermal conditions is promoted homogeneously along the a - and c -axes of the CIAP crystals by a topotaxial dissolution–precipitation process. The CIAP crystals are expected to dissolve as

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Table 1. Summary of the Hydrothermal Treatments of Chlorapatite and Hydroxyapatite Single Crystals Treated in KF Solutions

sample ID	KF solution conc (M)	temp (°C)	duration (h)	observed phases	lattice parameter	
					a (Å)	c (Å)
CIAP 1	5	500	6	CIAP + SSFAP ^a		
CIAP 2	5	500	9	SSFAP		
CIAP 3	5	500	12	SSFAP	9.3860	6.8844
CIAP 4	5	500	48	SSFAP	9.3814	6.8840
CIAP 5	5	500	96	SSFAP	9.3804	6.8830
HAP 1	5	500	48	SSFAP	9.4182	6.8805
HAP 2	5	500	96	SSFAP	9.4141	6.8782
HAP 3	5	500	168	SSFAP	9.4088	6.8795
HAP 4	5	500	336	SSFAP	9.3968	6.8783
HAP 6	5	600	24	SSFAP	9.4072	6.8809
HAP 7	5	600	48	SSFAP	9.4030	6.8820
HAP 8	5	600	96	SSFAP	9.3960	6.8800

^a SSFAP = solid solution of fluorapatite–hydroxyapatite.

clusters, much larger than ionic species, and the exchange of Cl^- by OH^- takes place at the surface of the clusters. The ion-exchange reaction, however, is restricted by the reactivity of the different apatite species under alkaline hydrothermal conditions. The conversion of FAP to HAP under hydrothermal conditions begins at temperatures beyond 700 °C in a concentrated solution of KOH (10 M) and proceeds heterogeneously along the *c*-axis from the prismatic ends of the FAP crystals.¹⁴

On the other hand, Higuchi et al.¹⁵ have investigated the mechanism of the formation of FAP on the surface of human tooth enamels. The formation of a thin layer of FAP coating the enamel was obtained by exposing the enamel to a solution of high fluoride concentration at room temperature. In addition, in acidic solutions at low temperature, the HAP exhibits a higher solubility than that of the FAP.⁷ According to the former information, it is expected that the ion exchange of Cl^- or OH^- ions with F^- is likely to occur under hydrothermal conditions. The differences between the hydrothermal conversion rate from CIAP to FAP and that from HAP to FAP are addressed in this study.

Experimental Procedure

Preparation of Chlorapatite and Hydroxyapatite Single Crystals. Single crystals of chlorapatite were prepared by means of the flux method using NaCl as a flux medium.¹⁶ The solute was a mixture of reagent grade $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3 and CaCl_2 at a molar ratio of 6:3:1. The solute concentration was 0.075 mol %. Gem quality, hexagonal prismatic crystals, 4–12 mm long and 0.5–2 mm wide, were synthesized at 1100 °C for 10 h, followed by cooling to 500 °C at a constant rate of 5 °C h⁻¹. On the other hand, the single crystals of hydroxyapatite were prepared from the CIAP crystals by hydrothermal ion-exchange reaction using a KOH solution as an ion-exchange media. The ion-exchange reaction was carried out at 500 °C for 48 h, using 500 mg of gem quality CIAP single crystals placed in a platinum capsule (50 mm length, 5.0 mm outer diameter with 0.2 mm thick wall) together with a 6.25 M KOH solution (0.25 mL). The chemical composition of the CIAP and HAP single crystals, determined by electron microprobe analyses, is given in Table 2.

The surfaces and cross sections of both original single crystals are shown in Figure 1. The as-prepared CIAP single crystals exhibit smooth prismatic surfaces (Figure 1a), and smooth surfaces are also observed on the fracture surfaces (Figure 1b). In contrast, as a result of the hydrothermal treatment, small channels (Figure 1c) and a great number of tiny tunnels oriented parallel to the *c*-axis (Figure 1d) were produced on the surface and inside the converted HAP single crystals. The structures of the CIAP and HAP single crystals are hexagonal (space group $P6_3/m$) and monoclinic (space group $P2_1/b$), respectively.

Hydrothermal Treatments. Two different concentrations of KF solutions (5 and 10 M) were employed as a reaction media. For each run, the CIAP or HAP single crystals (20 mg) were placed at the bottom of a platinum capsule (30 mm length, 3.0 mm outer diameter, and 0.15 mm thickness), and the KF solution (0.04 mL) was subsequently added. The volume of the solution corresponds to 35% of the capsule inner volume. The capsule was then welded shut with an electric arc.

A test tube type vessel made from Stellite 25 was employed for the hydrothermal treatments. The platinum capsule was placed at the bottom of the vessel. During all of the experiments an internal pressure of 100 MPa was imposed inside the vessel using distilled water as a pressure medium. The vessel was heated to a predetermined temperature, 500 °C or 600 °C, holding at each temperature for an interval between 2 and 96 h for CIAP and between 24 and 336 h for HAP crystals. After the treatment the vessel was cooled to room temperature by removing the furnace. During the treatment, the temperature was measured on the outside wall of the vessel with a thermocouple at the position corresponding to the bottom of the capsule. After the hydrothermal treatment, the capsule was cut open, and the contents were washed with deionized distilled water by successive decanting.

Characterization. Powder X-ray diffraction analyses were employed to determine the phases and the lattice constants of the treated crystals. Measurements were made on a Rigaku X-ray diffractometer with graphite-monochromatized Cu K α radiation. For lattice parameter determination, diffraction patterns were taken in the range 41° to 61° 2 θ at a scanning speed of 0.5° min⁻¹ and a step sampling of 0.006°. The lattice parameters were calculated by the least-squares method, using silicon as an internal standard.¹⁷

Morphological aspects of the crystals were examined by SEM (Hitachi S-530). To determine the reaction process, some crystals were selected, mounted in epoxy resin, and then polished to a mirrorlike surface. Chlorine line analyses were conducted on the polished surfaces using an X-ray energy dispersive unit (EDX; Kevex). The compositions of the products were determined by electron microprobe analysis (JEOL, JXA-8600NX). The standards (ASTIMEX) employed and the elements determined are as follows: synthetic fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}_2$] for Ca, P, and F; sanidine (KAlSi_3O_8) for K; and tugtupite ($\text{Na}_2\text{BeAlSi}_4\text{O}_{12}\text{Cl}$) for Cl, respectively. The analyses were conducted at a constant filament current of 15 nA. The ZAF correction procedure was employed to calculate the amount of each element (wt %). Each composition was determined from an average of 40 points on the polished surface of the sample. In addition, infrared absorption spectra were recorded with a Perkin-Elmer 1600 spectrometer, over a range of 3500–3600 cm⁻¹, using 2 mg of powdered samples mixed with 200 mg of KBr in an alumina mortar. Prior to analysis the mixture was dried overnight at 120 °C and then pelletized in a 13 mm diameter die in a vacuum.

Results and Discussion

Hydrothermal Treatments of Chlorapatite in KF Solutions. We focused our attention on the ion-exchange reaction of Cl^- or OH^- ions with F^- in the

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Table 2. Summary of the Electron Microprobe Analyses^a

sample ID	solution and conc	time (h)	chemical composition ^b (wt %)					chemical formula ^c
			Ca	P	Cl	F	K	
CIAP			38.45 ± 0.20	17.58 ± 0.15	6.20 ± 0.10			Ca ₁₀ (PO ₄) ₆ Cl ₂
CIAP 1 ^d	KF 5 M	6	39.57 ± 0.30	18.39 ± 0.30	0.64 ± 0.10	2.61 ± 0.20	0.08 ± 0.05	Ca _{9.98} K _{0.02} (PO ₄) ₆ F _{1.39} Cl _{0.16} (OH) _{0.43}
CIAP 3	KF 5 M	9	39.48 ± 0.35	18.40 ± 0.20	0.56 ± 0.20	2.84 ± 0.20	0.15 ± 0.05	Ca _{9.96} K _{0.04} (PO ₄) ₆ F _{1.51} Cl _{0.12} (OH) _{0.33}
CIAP 6	KF 5 M	96	39.35 ± 0.30	18.38 ± 0.15	0.35 ± 0.10	3.48 ± 0.20	0.27 ± 0.10	Ca _{9.93} K _{0.07} (PO ₄) ₆ F _{1.85} Cl _{0.03} (OH) _{0.05}
HAP			39.88 ± 0.30	18.58 ± 0.30	0.78 ± 0.10		0.19 ± 0.02	Ca _{9.95} K _{0.05} (PO ₄) ₆ Cl _{0.22} (OH) _{1.73}
HAP 2	KF 5 M	96	39.40 ± 0.30	18.42 ± 0.15	0.54 ± 0.25	1.22 ± 0.15	0.33 ± 0.15	Ca _{9.91} K _{0.09} (PO ₄) ₆ F _{0.68} Cl _{0.16} (OH) _{1.07}
HAP 3	KF 5 M	168	39.29 ± 0.30	18.41 ± 0.30	0.56 ± 0.10	2.06 ± 0.20	0.39 ± 0.10	Ca _{9.90} K _{0.10} (PO ₄) ₆ F _{1.09} Cl _{0.16} (OH) _{0.65}
HAP 4	KF 5 M	336	39.14 ± 0.20	18.41 ± 0.35	0.54 ± 0.15	2.17 ± 0.20	0.54 ± 0.10	Ca _{9.86} K _{0.14} (PO ₄) ₆ F _{1.16} Cl _{0.16} (OH) _{0.54}

^a Note: The crystals were converted under hydrothermal conditions at a temperature of 500 °C. ^b The error of the composition depicts the standard deviation of the average value, which was taken from 40 analyses. ^c Formula proportions based on 10 cations and the amount of OH⁻ were determined by charge balance. ^d Analyses conducted in the reacted part of the crystal, which corresponds to the solid solution of FAP.

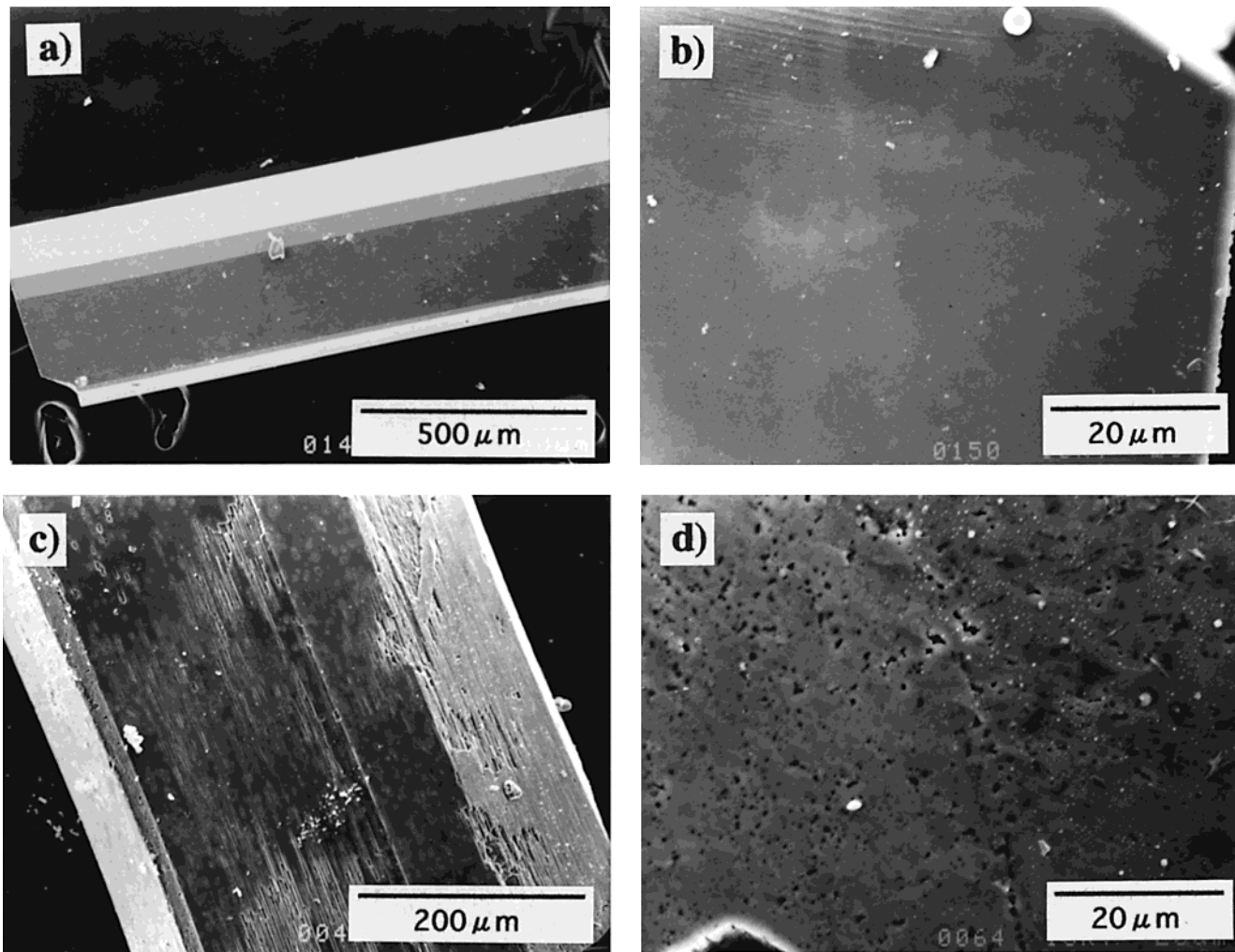


Figure 1. SEM micrographs of the prism surfaces and cross sections of the original (a) chlorapatite single crystals and (b) hydroxyapatite single crystals used for hydrothermal treatments in KF solutions.

CIAP and HAP single crystals, to evaluate the effect of the following factors: reaction interval and concentration of the KF solutions. The conditions of the hydrothermal treatments are summarized in Table 1, as well as the phases identified in the reaction products.

Morphological observations of the remaining products are shown in Figure 2. When the CIAP crystals were treated under hydrothermal conditions at 500 °C in a 5 M KF solution even for a long interval, the aspect of the crystals remained unchanged, in comparison with the original shape and dimensions of the raw CIAP crystals (Figure 2a). However, tiny holes with a diam-

eter < 0.25 μm were formed in the crystals, along the *c*-axis of the crystals (Figure 2b) and a CaF₂ layer (Figure 2c) was also produced on the surface of the crystals. The holes are randomly distributed and seem to be tunnels oriented along the *c*-axis. Observations conducted on the polished surface along the *c*-axis show that the length of these tunnels is < 15 μm (Figure 5c). During the treatment, CaF₂ was precipitated as tiny crystals which were agglomerated to form a layer on the surface of the treated crystals. The formation of the CaF₂ layer was more marked on the crystals treated in a 10 M KF solution.

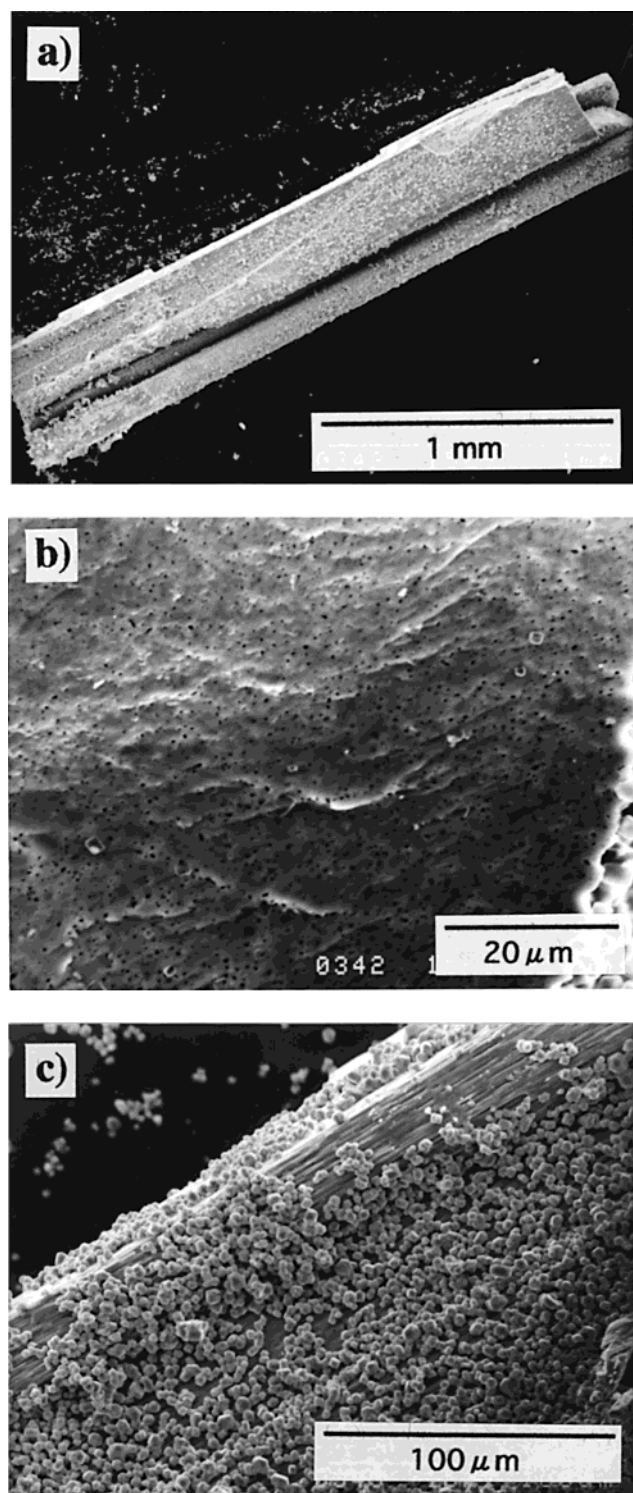


Figure 2. Morphological aspects of the converted crystals under hydrothermal conditions of 500 °C for 96 h in a 5 M KF solution: (a) prism surfaces; (b) cross section normal to the basal plane of the crystals; (c) CaF_2 crystals on the prism surfaces.

Figure 3 shows the X-ray diffraction patterns of the CIAP crystals treated at 500 °C in a 5 M KF solution for various intervals. After 6 h of treatment, two phases were observed in the reaction products. One of these phases corresponded to the original CIAP, and the new phase was considered to be an apatite solid solution in the system FAP–CIAP–HAP. The result of the compositional analysis of this new phase is shown in Table 2.

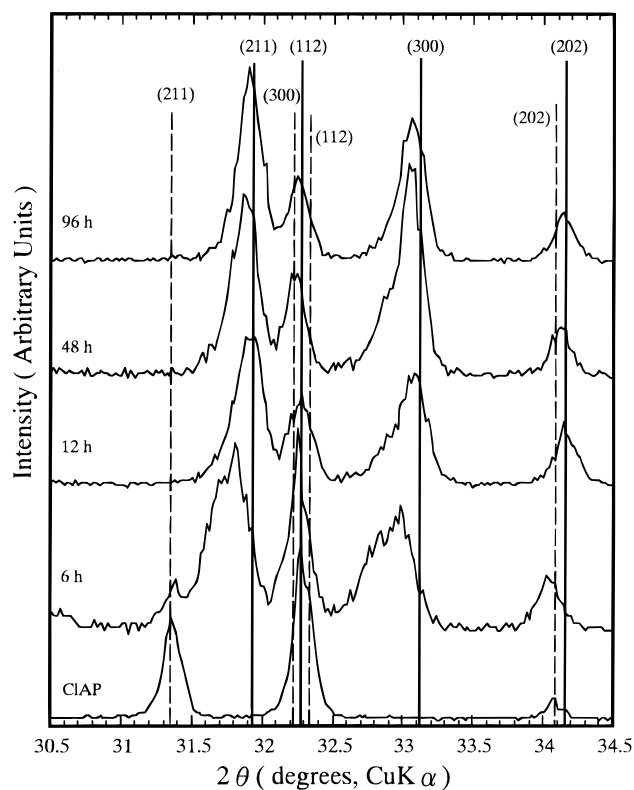


Figure 3. X-ray diffraction patterns of the specimens obtained from the CIAP crystals, after hydrothermal treatments in a 5 M KF solution at 500 °C for different intervals: dotted line = chlorapatite; solid line = fluorapatite.

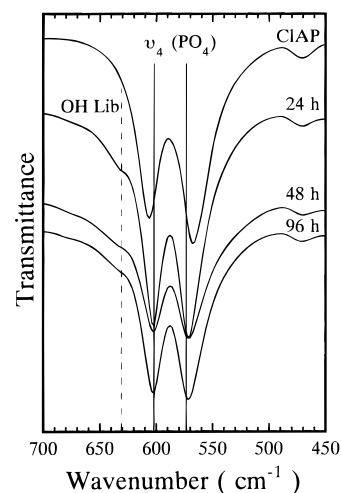


Figure 4. Infrared spectra of the OH librational and $\nu_4(\text{PO}_4)$ bands determined on the specimens synthesized from CIAP crystals, during hydrothermal treatments in a 5 M KF solution at 500 °C for different intervals: dotted line = OH librational band; solid line = $\nu_4(\text{PO}_4)$ bands.

The increase of the reaction interval to 12 h led to the complete conversion of the residual CIAP phase and the formation of a F^- rich solid solution. Over 12 h, the diffraction peaks corresponding to the F^- rich solid solution phase had a slight shift to higher angle in comparison with those obtained by the treatment for 12 h. This shifting may be caused by a gradual incorporation of F^- in the solid solution.^{7,9,10} The compositional analyses (Table 2) clearly showed that the content of F^- increased with the increase in the reaction interval, but that of Cl^- and OH^- decreased.

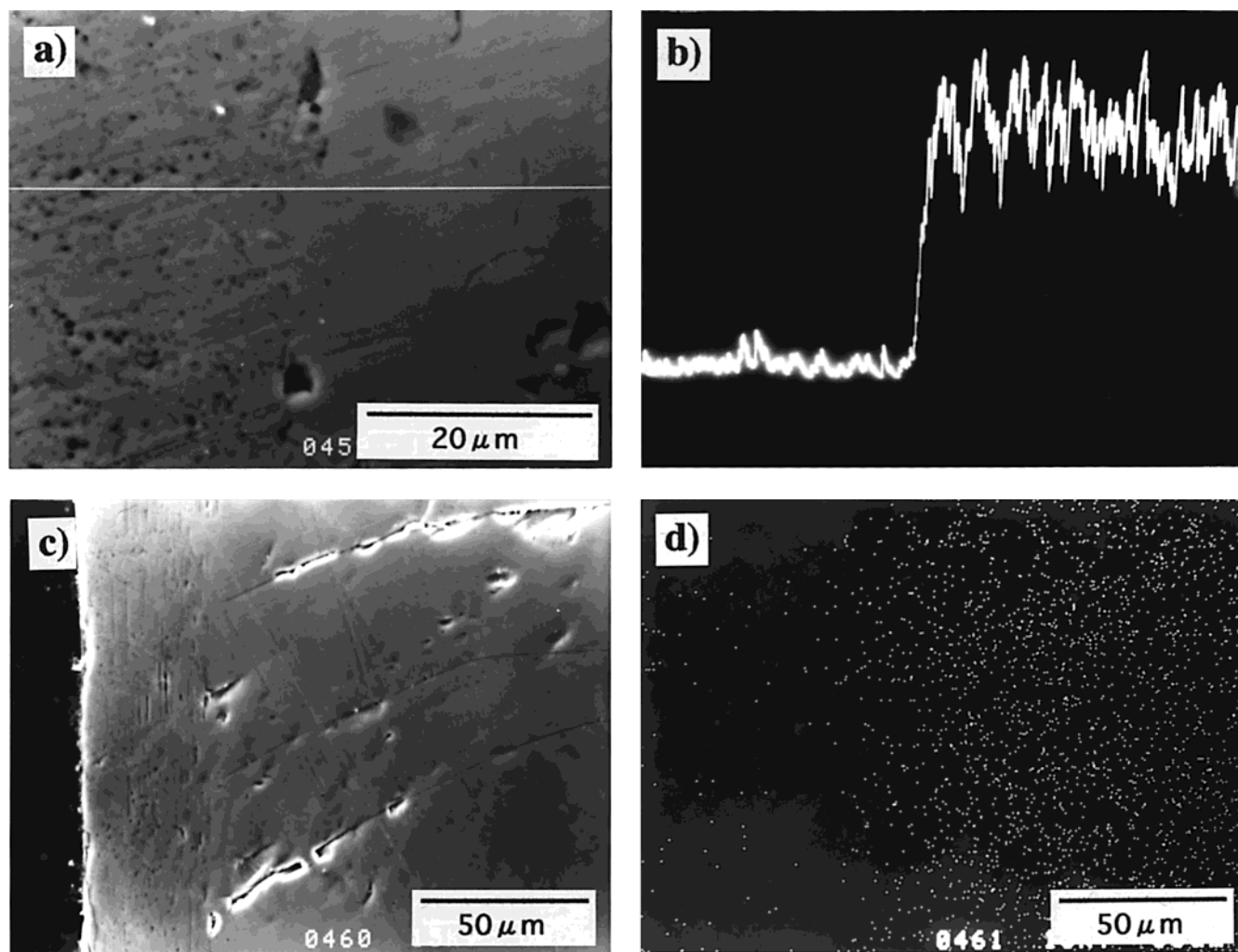


Figure 5. SEM images of the cross sections of the CIAP crystals parallel to the *c*-axis (a, c), and Cl^- X-ray line scanning (b) and mapping (d) of the partially converted CIAP single crystals hydrothermally treated at 500 °C for 6 h in a 5 M KF solution.

The structural changes observed in the CIAP crystals by the hydrothermal treatments are attributed to compositional variations. A simultaneous incorporation of a small amount of OH^- ions in the apatite obtained by the hydrothermal treatment at 500 °C for 24 h is clearly depicted by the presence of the OH librational band at 631 cm^{-1} (refs 18 and 19) in the IR spectra shown in Figure 4. The release of the OH^- content was achieved by increasing the reaction interval to >48 h. The formation of FAP solid solutions containing OH^- ions in their lattice at earlier stages of the ion exchange reaction is due to a simultaneous exchange of Cl^- ions with OH^- ions, as well as F^- . This reaction may proceed due to the high concentration of OH^- ions produced by the dissociation of water under hydrothermal conditions.¹³

Figure 5 shows SEM images and both Cl^- mapping and line analysis of partially converted crystals obtained by the hydrothermal treatment at 500 °C for 6 h in a 5 M KF solution. At an earlier stage of the reaction, the crystal exhibits two parts, a porous layer and a continuous part. The outer layer consists of a series of tiny holes randomly distributed parallel to the *c*-axis (Figure 5a).

These phases are separated by a sharp boundary in the SEM image and in the Cl^- distribution (Figure 5b) as well. The reaction occurred along both the *a*- and *c*-directions. These results suggest that the ion-exchange reaction begins from the surfaces of the crystals without a Cl^- diffusion layer. In addition, the above results indicate that the CIAP crystals were topotaxially converted to FAP solid solution crystals by the ion exchange under hydrothermal conditions.

Hydrothermal Treatments of Hydroxyapatite in KF Solutions. SEM images of the HAP crystals hydrothermally treated at 500 °C in a 5 M KF solution are shown in Figure 6. Even by the treatment conducted for 336 h, no significant changes in the dimensions and shapes of the original HAP crystals were observed (Figure 6a). In contrast, the images of the cross section perpendicular to the *c*-axis of the hydrothermally treated crystals suggest a redistribution and increase of the size (>1 μm) of the tiny holes in the original crystals (Figure 6b). Furthermore, a layer of CaF_2 crystals was produced on the surface of the crystals (Figure 6c). Typical X-ray diffraction patterns of the HAP crystals treated at 500 °C in 5 M KF solutions for several intervals are shown in Figure 7. The evidence that the ion exchange of OH^- with F^- proceeds in the HAP crystals is depicted by the slight shifting of the X-ray diffraction peaks to higher

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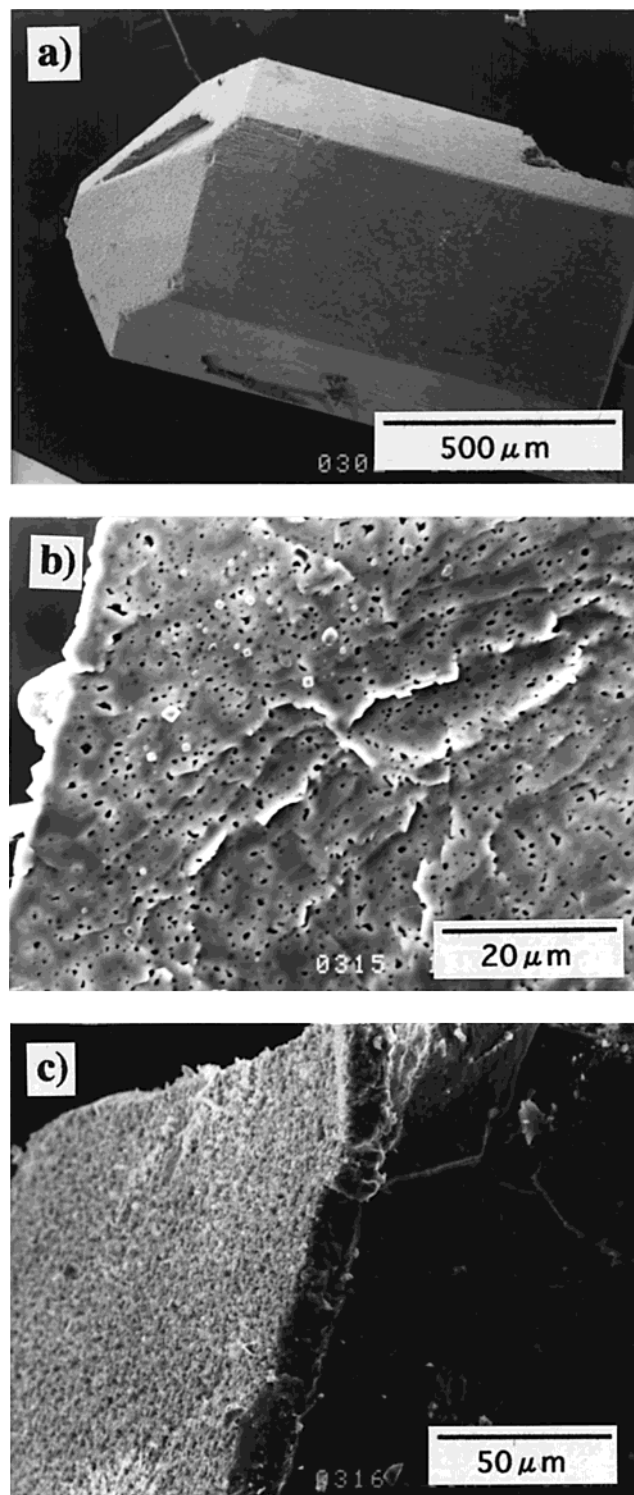


Figure 6. SEM images of the aspects of specimens of partially converted FAP under hydrothermal conditions of 500 °C for 336 h in a 5 M KF solution: (a) prism surfaces; (b) cross section normal to the basal plane of the crystals; (c) CaF_2 crystals on the prism surfaces.

angle. However, the reaction rate is extremely slow in comparison with that of CIAP crystals.

Figure 8 shows the IR spectra of HAP crystals hydrothermally treated at 500 °C in a 5 M KF solution. A progressive reduction of the amplitude of the OH librational band at (631 cm^{-1}) and a slight shifting of the $\nu_4(\text{PO}_4)$ bands (571 and 601 cm^{-1}) to high frequency were noted with increasing reaction interval (Figure 8).

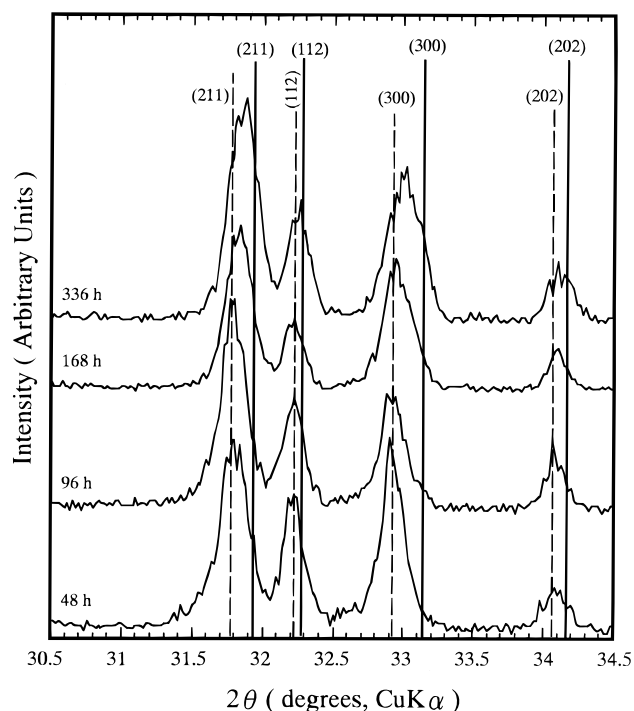


Figure 7. X-ray diffraction patterns of the specimens obtained from the HAP crystals, after hydrothermal treatments in a 5 M KF solution at 500 °C for different intervals: dotted line = hydroxyapatite; solid line = fluorapatite.

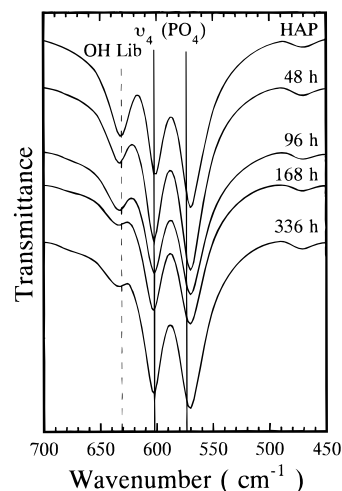


Figure 8. Infrared spectra of the OH librational and $\nu_4(\text{PO}_4)$ bands determined on the specimens synthesized from HAP crystals, during hydrothermal treatments in a 5 M KF solution at 500 °C for different intervals: dotted line = OH librational band; solid line = $\nu_4(\text{PO}_4)$ bands.

In general, the variations observed on both the OH librational and the ν_4 mode PO_4 tetrahedra bands are attributed to the contraction of the Ca_{II} sixfold screw along the a -axis,²⁰ which may result from the progressive incorporation of smaller F^- ions in the X-channels. The content of F^- incorporated during the hydrothermal treatments in the HAP crystals is clearly shown by the compositional analyses in Table 2. These results determined by EPMA analyses are in good agreement with the structural variations determined by both X-ray and IR analyses.

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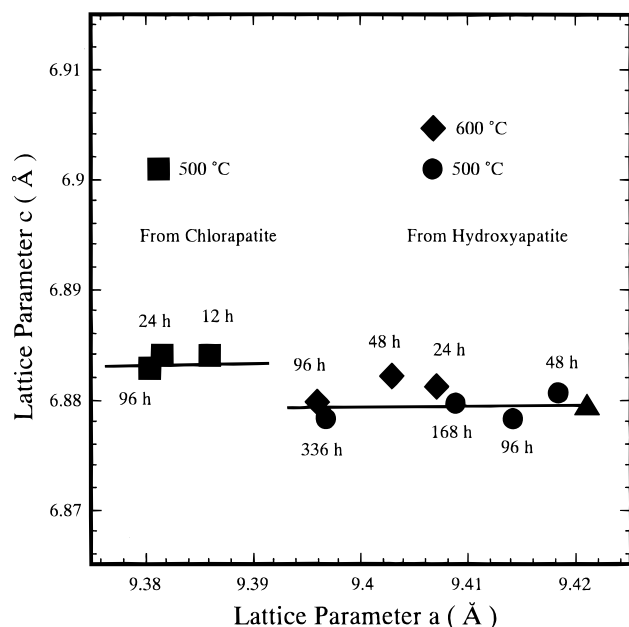


Figure 9. Change of the lattice parameters of the reaction products obtained under hydrothermal conditions using a 5 M KF solution for various intervals. The lattice constants were assigned to the hexagonal system. The triangle shows the lattice parameter of the starting HAP.

The HAP crystals did not exhibit any peculiar patterns of reaction, except for the increase of the dimensions of the small holes inside the crystals. Concentration gradients of F^- were not detected by microprobe electron analyses conducted on the cross section of the partially converted FAP crystals. We surmise that the texture of the raw HAP crystals must affect the conversion process to FAP, because the network of zigzag tiny tunnels along the c -axis allows the reacting fluid to penetrate into the crystals. Thus, the solid solutions in the system HAP–FAP were topotaxially formed by the hydrothermal ion exchange.

Lattice Parameters of the Hydrothermally Converted FAP Crystals. The values of the lattice parameters determined for the converted products from CIAP or HAP are shown in Figure 9 and summarized in Table 1. During the conversion of HAP to FAP, a gradual contraction of the constant a is visible with the increase of the reaction time, and this phenomenon is further accelerated with increasing temperature (Figure 9). Our results are in accordance with those previously reported by Schaecken et al.¹⁰ They determined a linear decrease of the lattice constant a from FAP to HAP in a series of solid solutions. In contrast, for the conversion of CIAP to FAP, the initial reaction even for a short time (12 h) gave a large change of the lattice parameters from the original CIAP ($a = 9.6410$ Å, $c = 6.7710$ Å; JCPDS card 33-271) to the reaction products ($a = 9.3860$ Å, $c = 6.8844$ Å). After that, even with treatment for a long time, only a slight variation of the lattice constant a was detected. The lattice parameters of the reaction products ($a = 9.3804$ Å, $c = 6.8830$ Å) obtained by the treatment of CIAP crystals at 500 °C for 96 h are in better agreement with those of the pure FAP ($a = 9.3684$ Å, $c = 6.8841$ Å; JCPDS card 15-876) than those obtained from HAP. It is concluded that the variation of the lattice constants involved in the structural conversion of CIAP or HAP to FAP against the reaction time and

temperature is mainly attributed to the gradual uptake of F^- and K^+ and the release of Cl^- and OH^- (Table 2) as the reaction proceeds.

Characterization of Texture and Structure of the Hydrothermal Ion-Exchanged Products. The dissolution of HAP crystals in acid solutions is normally anisotropic and produces a series of holes parallel to the c -axis.¹⁹ On the other hand, the conversion of CIAP and HAP to FAP homogeneously proceeded under hydrothermal conditions in KF solutions. When the CIAP crystals were treated in KF solution, tiny tunnels were randomly obtained normal to the c -axis (Figure 2b). A plausible explanation for the development of this texture is based on the changes of the apatite structure by the replacement of large ions (Cl^- 1.81 Å, or OH^- 1.68 Å) by small ions (F^- 1.32 Å).¹³ The apatite structure must undergo a contraction along the a -axis and slight expansion on the c -axis. Thus, for the conversion of CIAP to FAP, a contraction of 0.259 Å along the a -axis and an expansion of 0.116 Å must occur as a result of the ion-exchange reaction. These structural changes must be compensated for, which appears to proceed by the formation of the tiny tunnels inside the converted crystals. In contrast, only a contraction of 0.036 Å is expected along the a -axis by the replacement of HAP into FAP. Therefore, only a slight enlargement and redistribution of the initial tunnels (Figure 6b) in the HAP crystals is expected to occur in order to compensate for the slight contraction.

Mechanism of Fluorine Ion Exchange under Hydrothermal Conditions. Hitherto, in apatite crystals, the exchange of anions (OH^- , Cl^- , or F^-) has been reported to proceed by a mechanism of solid-state diffusion.^{12,21} Brennan¹² confirmed that the anion motion along the c -axis in FAP and CIAP single crystals is faster than that along the a -axis. In the solid-state ion exchange, the apatite structure with X-channels plays an important role in leading the reaction, because the motion of ions along the c -axis in the X-channels is faster by a mechanism of interchange of ions and vacancies²² than that through the sixfold screw (6_3) axis. The conversion investigated in the present study cannot be associated with a solid-state ion-exchange mechanism, because it proceeded at much lower temperatures than that necessary to achieve ion diffusion in the solid state.

The formation of CaF_2 showed that the original crystals were partially dissolved in the KF solution. The hydrothermal conversion proceeded fast along both axes (a and c) even at low temperatures, and the converted crystals included the alkali metal ion (K) used as a reaction medium (Table 2). In addition, the ion exchange topotaxially proceeded without a diffusion layer. Similar results have been obtained by the conversion of CIAP to HAP under alkaline hydrothermal conditions.¹³ One possible mechanism for the ion exchange of anions in CIAP and HAP observed in this study is a simultaneous dissolution–precipitation process.¹³ In ordinary hydrothermal treatments, the process of recrystallization proceeds by the dissolution and transportation of the

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raw species in the reaction medium, and new crystals recrystallize in a different place. Our results, however, suggest that the dissolved species were not transported to a long distance, and those were incorporated into the solid almost at the same place, which allows CIAP and HAP to be topotaxially converted to FAP and SSFAP, respectively. In accordance with the mentioned facts, we point out that during the hydrothermal treatments the crystals are dissolved as clusters, much larger than ionic species. The dissolution of the crystals in the reaction medium and the formation of the clusters must result in the ion exchange at the surface of the clusters. Hence, some amount of the original ions must remain inside the clusters, and the alkaline metal ion in the reaction medium must incorporate into the converted crystals.

The differences between the conversion rate from CIAP to FAP and that from HAP to FAP are mainly associated with the reactivity of the CIAP and HAP under hydrothermal conditions in KF solutions. The

results obtained in the present work clearly show that the reactivity of CIAP crystals is very high in comparison with that of HAP crystals. This reactivity difference might essentially depend on the size of the ions sited in the X-channels. Thus, the presence of large ions, that is, Cl^- , reduces the bonding strength along the a -axis, which results in the increase in the reactivity of the CIAP structure.¹³

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