

Topotaxial replacement of chlorapatite by hydroxyapatite during hydrothermal ion exchange

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ABSTRACT

Exchange of Cl⁻ by OH⁻ in synthesized chlorapatite single crystals was investigated under hydrothermal conditions. Hydrothermal treatments were performed at various temperatures from 200 to 500 °C, for intervals between 3 and 96 h in KOH or NaOH solutions. Ion exchange of Cl⁻ in the chlorapatite crystals was completed at low temperature (500 °C) for a short time (12 h) in 6.25 M KOH solution, and resulted in the formation of hydroxyapatite. The rate of ion exchange was accelerated by increasing the reaction temperature and/or concentration of the alkaline solutions. That the converted crystals were single crystals of hydroxyapatite was confirmed by X-ray precession photographs. The hydroxyapatite single crystals that formed from the chlorapatite single crystals by the topotaxial ion exchange under alkaline hydrothermal conditions had a characteristic texture, exhibiting channels on the surfaces and tunnels inside, both along the *c* axis of the crystals. A dissolution and precipitation process is proposed for the ion-exchange reaction conducted under hydrothermal conditions.

INTRODUCTION

Calcium apatites occur in nature both biologically and as minerals. Apatites have found important uses in several industrial applications, such as fertilizer in the agricultural industry and phosphor in the lighting industry. Calcium hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂, hereafter referred to as HAP] is the most important member of the phosphate mineral group, mainly because it is the prototype of the inorganic material in hard tissues such as bone and teeth, and is also regarded as an important implant material with significant clinical potential (e.g., Sanger and Kuhs 1992; Hench 1991). Thus, much research concerned with HAP has been carried out in fields such as crystallography, mineralogy, medical science, and material science.

In recent years, some work has been conducted to evaluate the possibility of employing HAP as a precursor material for the removal of heavy metal ions from waste water (Reichert and Binner 1996; Suzuki et al. 1981). This possibility is based on the apatite structure, which has the ability to undergo a series of isomorphous substitutions involving both cations and anions (Narasaraju and Phebe 1996). According to a review by these authors, Sr²⁺, Ba²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ substitute for Ca²⁺ in HAP, and F⁻, Cl⁻, and I⁻ may substitute for OH⁻. Furthermore CO₃²⁻ may substitute not only for OH⁻ but also for PO₄³⁻ groups (Legeros et al. 1968; Driessens et al. 1983). Studies on the ionic substitutions in HAP are important in medical science, because biological apatite includes various foreign ions.

Because the natural apatite minerals and biological apatite include OH⁻, F⁻, and Cl⁻ in their structure, the solid solutions in the ternary system of HAP, chlorapatite [Ca₁₀(PO₄)₆Cl₂, hereafter referred to as CIAP], and fluorapatite [Ca₁₀(PO₄)₆F₂, hereafter referred to as FAP] have been well studied, both crystallographically (e.g., Sudarsanan et al. 1972; Sudarsanan and Young 1978; Tse et al. 1973; Hughes et al. 1990) and experimentally (e.g., Elliott and Young 1967; Rai et al. 1979, Maiti and Freund 1981; Latil and Maury 1977; Simpson 1968; Stearns and Berndt 1973; Higuchi et al. 1974). As for the HAP-CIAP system, Rai et al. (1979) showed the existence of a homogeneous solid solution series over the entire compositional range. According to the papers mentioned above, these solid solutions were prepared by reactions that did not include an ion exchange.

Elliott and Young (1967) provided the first evidence of the solid-state ion exchange in the apatite structure. They converted CIAP single crystals to HAP single crystals by heating at 1300 °C for 2 weeks in water vapor at atmospheric pressure. Neutron activation analysis and X-ray diffraction (XRD) precession photographs demonstrated that the reaction products were essentially single crystals of HAP, although a small amount of Cl remained in the crystals.

The ion-exchange rate of Cl⁻ in CIAP by OH⁻ must depend on the concentration of OH⁻ in the ion-exchange medium. It is well known that the ion product of water increases with the increase in temperature and pressure (density). Thus, the concentration of OH⁻ must increase under hydrothermal conditions at high temperature and pressure. In fact, Brenan (1994) showed that diffusion coefficients of anions in the apatite structure measured under hydrothermal conditions at 1 GPa were higher

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than those measured at 1 atm. Furthermore, alkaline solutions have high concentration of OH^- . It is expected that the ion-exchange rate of Cl^- in CIAP by OH^- accelerates under alkaline hydrothermal conditions. In this paper, experiments were directed at determining the appropriate experimental conditions for the ion exchange of Cl^- in CIAP single crystals with OH^- , and the mechanism of the ion exchange under alkaline hydrothermal conditions.

EXPERIMENTAL PROCEDURE

Single crystals of CIAP were prepared by means of the flux method using NaCl as a flux (Oishi and Sugiura 1997). 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, respectively, was used as a solute. The solute (0.075 mol%) was heated with the flux in a platinum crucible at 1100 °C for 10 h, followed by cooling down to 500 °C at a rate of 5 °C/h. Hexagonal prismatic CIAP crystals, 2–4 mm long and 0.5–1 mm wide, were grown under these conditions. The CIAP crystals belong to the hexagonal system with the space group $\text{P6}_3/\text{m}$. The hexagonal prism crystals with large dimensions were subsequently selected for hydrothermal treatment. Two different alkaline solutions of KOH (0.01–10 *M*) and NaOH (6.25 and 8.25 *M*) were employed as an ion-exchange media. The experiments were carried out in a platinum capsule (30 mm in length, 3 mm in diameter, and 0.15 mm in thickness) by adding ~20 mg of the single crystals together with an alkaline solution. The volume of the solution added to each run was approximately 40 μL , which corresponds to 35% of the capsule volume. The capsule was welded shut with an electric arc.

The platinum capsule was placed at the bottom of a test tube type vessel made from Stellite 25. In all of the treatments, an internal pressure of 100 MPa was imposed in the vessel by using distilled water as a pressure medium. The vessel was heated to a predetermined temperature (200–500 °C), held at each temperature for several hours (3–96 h), and then cooled to room temperature by removing the furnace from the vessel. During the treatment, temperature was measured on the outside wall of the vessel with a thermocouple at a position corresponding to the bottom of the capsule. After hydrothermal treatment, the capsule was cut open, and the contents washed with deionized distilled water by successive decanting.

Powder XRD was employed for identification and determination of the lattice constants of the treated crystals. Measurements were made on an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 100 mA. Diffraction patterns were taken of the 2θ range from 10 to 80° at a scanning speed of 4 °/min. The lattice parameters were calculated by the least-squares method from the diffraction peaks collected in the 2θ range from 41 to 61° at a scanning speed of 0.5 °/min and step sampling interval of 0.006°, using Si as an internal standard (Cullity 1978). In addition, more accurate characterization of the crystallinity of the treated crystals was carried out using a Weissenberg camera, which was operated at an oscillation angle of 30° with CuK radiation.

Crystal morphologies were evaluated with a scanning electron microscope (SEM, Hitachi, S-530). To determine the reaction process, chlorine mapping and line analyses were conducted, using an energy-dispersive X-ray unit (KeveX). The

samples were prepared by selecting hydrothermally treated crystals, mounting them in epoxy resin, and polishing them to a mirror-like surface. The surfaces observed were perpendicular to the *c* and *a* axes of the crystals.

The compositions of the treated crystals were determined by electron microprobe analysis (Jeol, JXA-8600NX). The following mineral standards (ASTIMEX, MINM25-23) were employed for the quantitative determination: hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] for Ca and P; tugtupite, ($\text{Na}_4\text{BeAlSi}_4\text{O}_{12}\text{Cl}$) for Na and Cl; and sanidine (KAlSi_3O_8) for K, respectively. The analyses were conducted at a constant filament current of 15 nA, and the amount of each element (wt%) was computed using the ZAF correction procedure. The compositions were determined from an average of 20 points on the polished surface of the samples.

RESULTS

Hydrothermal treatment in KOH solutions

Hydrothermal treatments of the CIAP single crystals were conducted by considering the following reaction factors: temperature, reaction interval, alkaline solutions and their concentrations. The experimental conditions are summarized in Table 1 together with the phases identified in the reaction products.

Figure 1a shows XRD patterns of the crystals after the hydrothermal treatments at different temperatures in 6.25 *M* KOH solution. The crystals retained their original CIAP structure after the hydrothermal treatment at 200 °C. In contrast, when the temperature was increased to 300 °C, some HAP was formed. At temperatures above 300 °C, the CIAP crystals were completely transformed to HAP.

The XRD patterns of the crystals treated at 500 °C in 6.25 *M* KOH solution for various intervals are given in Figure 1b. From these results, one can clearly observe a trend with increasing reaction time that is similar to that observed for increasing temperature. The formation of HAP in the CIAP crystals was observed after the treatment for intervals as short as 3 h. The increase in the reaction time to 12 h resulted in the complete transformation of the CIAP to the HAP structure.

The effects of the concentration of the KOH solutions on XRD patterns of the hydrothermally treated crystals are shown in Figure 1c. When the CIAP crystals were treated in the concentrated KOH solutions, they were completely transformed to HAP. However, no transformation took place in the CIAP crystals treated hydrothermally in the dilute KOH solution (0.01 *M*) or in pure water.

SEM photographs of the crystals after the hydrothermal treatment in the KOH solutions of various concentrations, are shown in Figure 2a through 2d. The crystals treated in 0.01 *M* KOH solution (Figs. 2a and 2b) revealed the same flatness on the hexagonal prism faces and sharpness of the edges of fracture surfaces as those found on the original CIAP single crystals. The results suggested that no changes in the crystals were caused by the treatment, which was also supported by the XRD data.

The hydrothermal treatments in the concentrated KOH solutions resulted in reduced transparency of the original crystals, but the treated CIAP crystals macroscopically retained their original morphology with regard to shape and dimensions. In general, hydrothermal treatment, especially with a temperature

TABLE 1. Summary of the hydrothermal treatments of chlorapatite single crystals

Sample ID (M)	Solution (°C)	Concentration (h)	Temperature phases	Duration	Determined	Lattice parameter	
						a (Å)	c (Å)
1	KOH	6.25	500	96	HAP	9.4207	6.8810
3	KOH	6.25	500	48	HAP	9.4215	6.8808
5	KOH	6.25	500	12	HAP	9.4236	6.8802
26	KOH	6.25	500	6	CIAP+HAP		
25	KOH	6.25	500	3	CIAP+HAP		
16	KOH	6.25	400	48	HAP	9.4227	6.8806
17	KOH	6.25	300	48	CIAP+HAP		
36	KOH	6.25	200	48	CIAP		
37	KOH	6.25	200	96	CIAP		
18	KOH	0.01	500	12	CIAP		
27	KOH	0.1	500	12	CIAP+HAP		
19	KOH	1	500	12	HAP	9.4249	6.8778
28	KOH	10	500	12	HAP	9.4226	6.8809
2	NaOH	8.25	500	96	HAP	9.4227	6.8824
4	NaOH	8.25	500	48	HAP	9.4240	6.8822
6	NaOH	8.25	500	12	HAP	9.4249	6.8808
23	NaOH	6.25	500	12	HAP	9.4233	6.8801
10	Water		500	12	CIAP		
11	Water		500	96	CIAP		

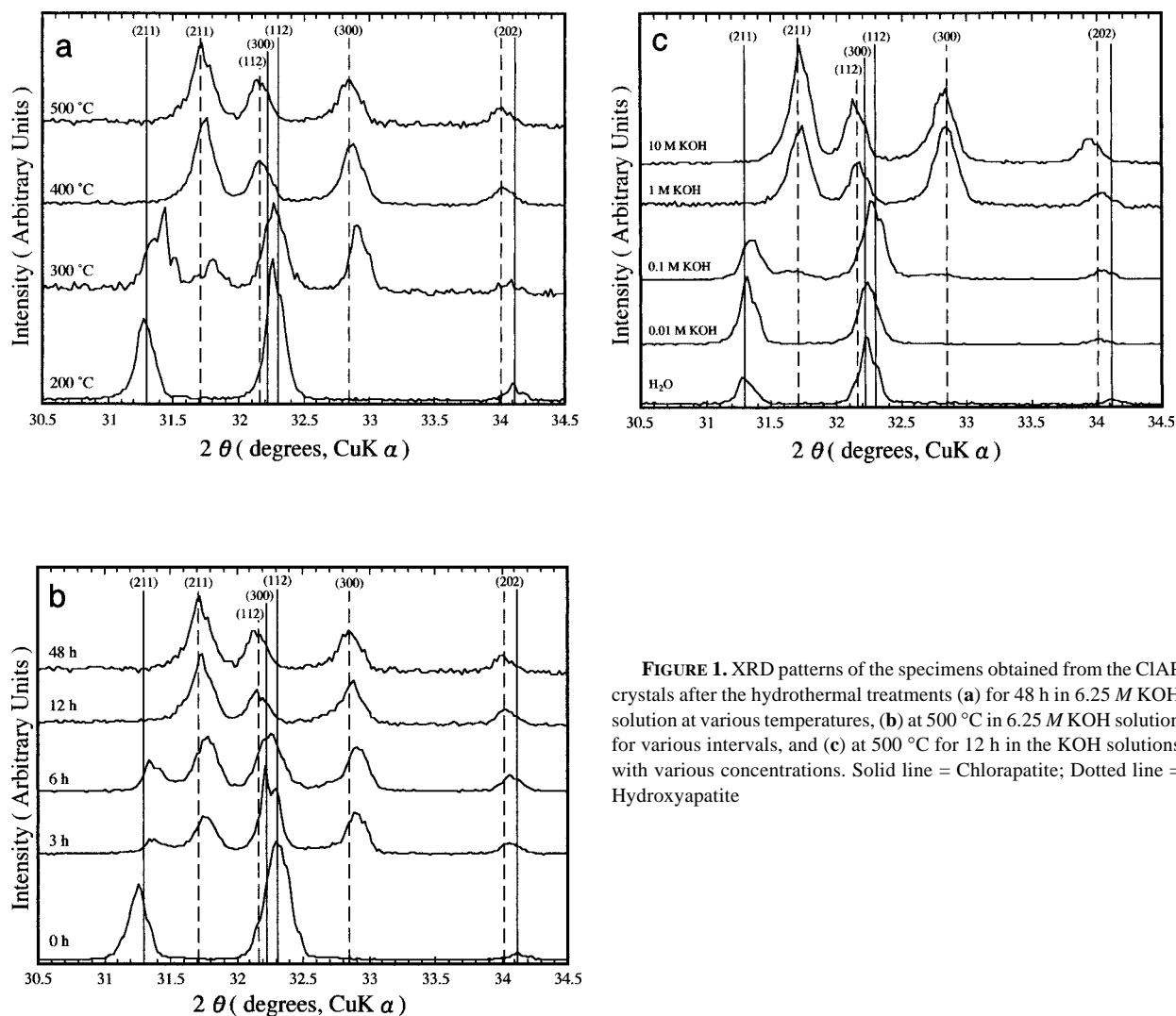


FIGURE 1. XRD patterns of the specimens obtained from the CIAP crystals after the hydrothermal treatments (a) for 48 h in 6.25 M KOH solution at various temperatures, (b) at 500 °C in 6.25 M KOH solution for various intervals, and (c) at 500 °C for 12 h in the KOH solutions with various concentrations. Solid line = Chlorapatite; Dotted line = Hydroxyapatite

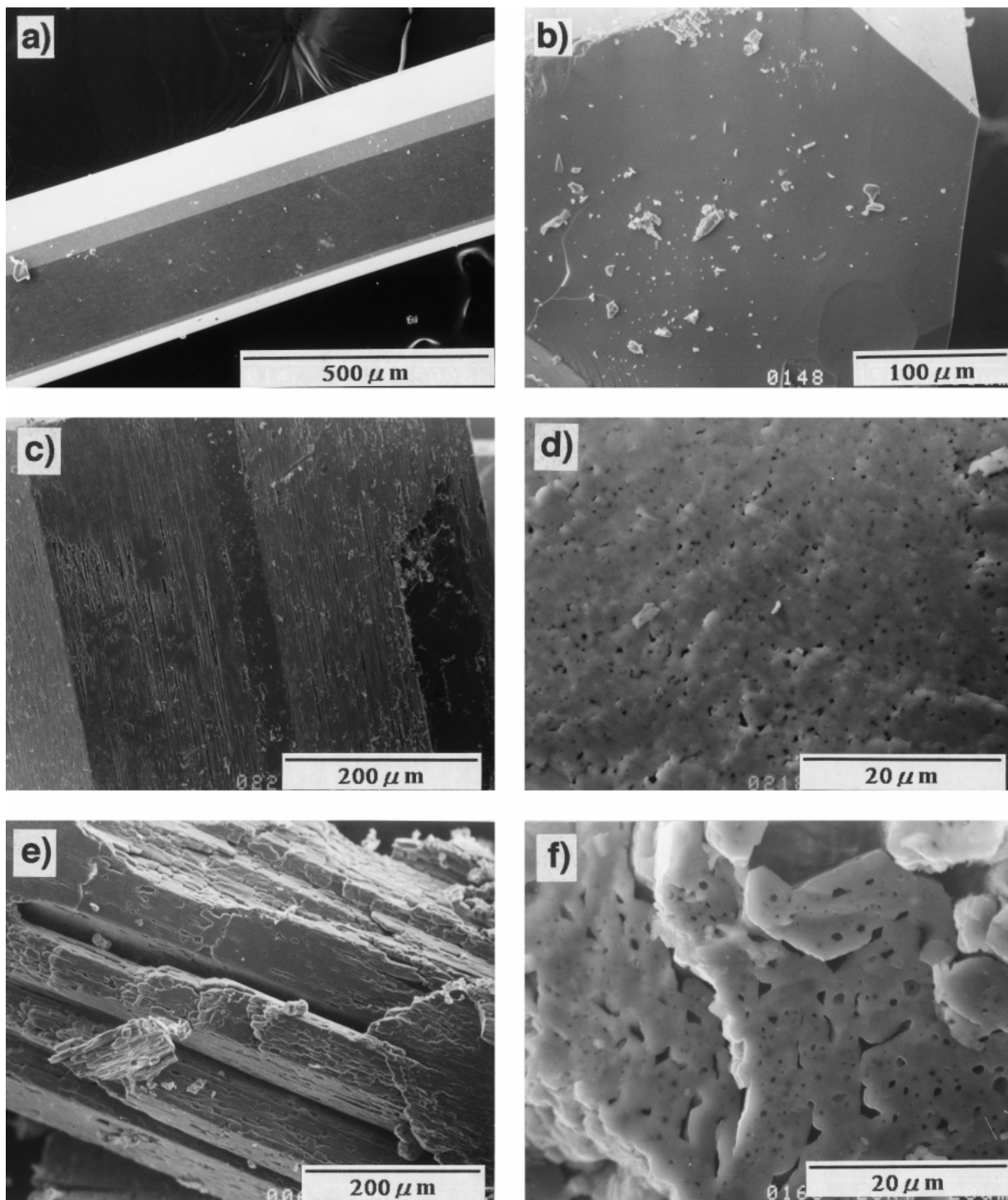


FIGURE 2. SEM images of the prism surfaces and cross sections of the HAP crystals produced by the hydrothermal treatments of the CIAP crystals at 500 °C for 24 h in 0.01 M (a, b) and 10 M KOH solution (c, d), and at 500 °C for 12 h in 6.25 M NaOH solution (e, f).

gradient, produced new crystals from the original ones by means of dissolution and precipitation process. In our study, no extra crystals were formed by the treatment.

The treatments in the concentrated KOH solutions transformed the CIAP crystals to HAP. Tiny elongated channels formed parallel to the c axis on the prism surfaces (Fig. 2c) and tiny holes with a diameter of $<0.5\ \mu\text{m}$ formed in the cross sections of the crystal, perpendicular to the c axis (Fig. 2d). The holes are distributed randomly and seem to be tunnels parallel to the c axis. Based on observation made of the polished surface along the c axis (Figs. 5e and 5g), the length of the tunnels is limited to $10\ \mu\text{m}$. They do not penetrate the crystals, but trace a zigzag course.

Hydrothermal treatment in NaOH solutions

The crystallographic transformation to HAP was also found to occur in the CIAP single crystals exposed to different alkaline solutions. When the CIAP crystals were treated in $6.25\ \text{M}$ NaOH solution at $500\ ^\circ\text{C}$ for 48 h, they were completely transformed to HAP. The treated crystals exhibited more corroded surfaces (Fig. 2e) compared with those found on the crystals treated in the KOH solutions. Irregular, randomly distributed cavities, with a width of $0.5\text{--}2.0\ \mu\text{m}$, were also formed on the fracture surface of the crystal perpendicular to the c axis (Fig. 2f). Some of the cross sections of the cavities were polygonal in shape.

DISCUSSION

Topotaxial ion exchange under hydrothermal conditions

The structural analyses of the CIAP crystals treated under alkaline hydrothermal conditions depict their transformation to HAP crystals without formation of any by-products. The HAP crystals obtained by the hydrothermal treatment retained the original shape of the CIAP single crystals. More crystalline

details were revealed from the oscillation photograph shown in Figure 3. The spots taken by the Weissenberg camera illustrate a geometrical distribution of atoms with respect to the c axis in the crystal hydrothermally transformed to HAP. The pattern showed that the crystal was a single crystal with excellent quality. Although the pattern was similar to that of the hexagonal structure, the converted crystal was indexed to the monoclinic system with the space group $P2_1/b$, because superlattice spots corresponding to the monoclinic structure were found in the pattern. The formation of HAP with the monoclinic structure by the ion exchange of CIAP under hydrothermal conditions, agreed well with the result obtained by solid-state ion exchange (Elliot and Young 1967; Elliot et al. 1973). It is concluded that the CIAP single crystals were converted topotaxially to the HAP single crystals by ion exchange under alkaline hydrothermal conditions.

Texture of the hydrothermally converted HAP single crystals

Elliot and Young (1967) converted CIAP single crystals to HAP single crystals by heating at $1300\ ^\circ\text{C}$ for 2 weeks in water vapor at atmospheric pressure. They described neither the course of the reaction nor the characteristics of the converted crystals except for their crystal structure. On the other hand, Brennan (1994) noted that the interfaces between the crystals of FAP or the CIAP and the fluid remain smooth and show no evidence of pitting or corrosion at $1000\ ^\circ\text{C}$.

We found that the conversion of CIAP to HAP proceeds at much lower temperatures under alkaline hydrothermal conditions. In addition, the HAP crystals converted from the CIAP crystals under hydrothermal conditions had a characteristic texture on their surfaces and inside. The tiny channels and holes parallel to the c axis were formed on the surface and inside of the converted HAP crystals, respectively. The development of

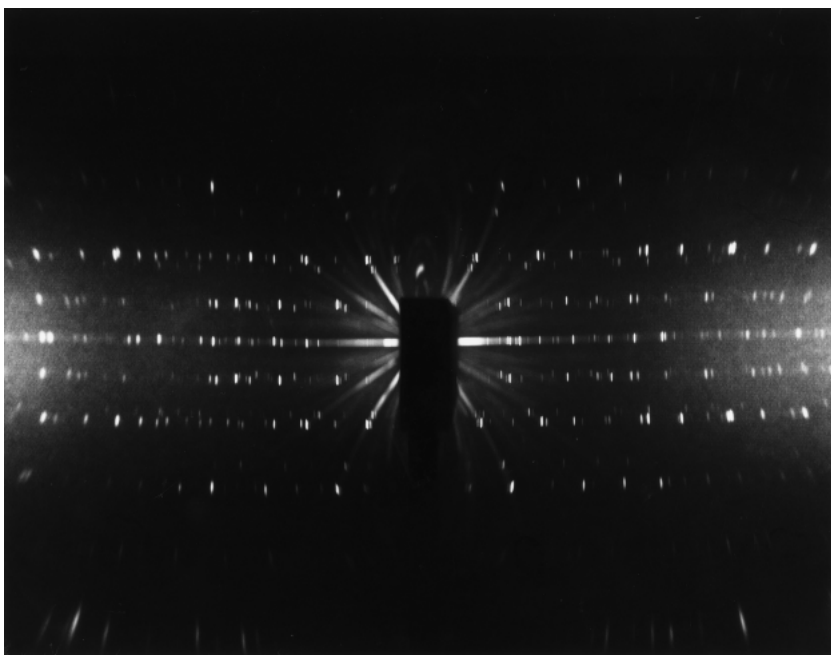


FIGURE 3. X-ray precession photograph of a crystal treated at $500\ ^\circ\text{C}$ for 12 h in $6.25\ \text{M}$ KOH solution. The photograph, taken with a Weissenberg camera with CuK radiation, shows the c axis parallel to the rotation axis.

this texture may be explained by the following two reasons.

Although no information related to the dissolution of CIAP under alkaline hydrothermal conditions had been reported previously, it is likely that the surface features of the converted HAP crystals are due to the dissolution during the hydrothermal treatments in alkaline solutions. This inference is supported by the observation that the texture of the converted HAP crystals formed in KOH solutions is different from that formed in NaOH solutions. Young (1980) reported that acid dissolution of HAP crystals tends to be strongly anisotropic, even to the point of producing tunnels parallel to the c axis. Our results suggest that similar anisotropy may exist under alkaline hydrothermal conditions.

The holes formed in the crystals might not be textures inherited from etch pits developed during dissolution, because they did not penetrate the crystals and the dimension of the holes were homogeneous. If the holes were produced only by dissolution, larger holes should be produced at the surface.

We believe that these holes are formed by an ion-exchange process under hydrothermal conditions. The ion exchange proceeds by replacement of large Cl^- ions having a radius of 1.81 Å by smaller OH^- ions with a radius of 1.68 Å. As a result the conversion of CIAP [$a_0 = 9.641$ Å, $c_0 = 6.771$ Å (JCPDS Card 33-271)] to HAP [$a_0 = 9.418$ Å, $c_0 = 6.884$ Å (JCPDS Card 9-432)] is accompanied by a large shrinkage along the a axis and a small expansion along the c axis. To maintain the single-crystal structure, the dimensional change must be compensated for, which appears to proceed by the formation of the holes along the c axis inside the converted HAP single crystals. This assumption is supported by the fact that such holes were not formed by the ion exchange of F^- in FAP single crystals by OH^- under alkaline hydrothermal conditions, because of this

type of conversion results in an expansion of the crystal lattice along the a axis, as well as along the c axis (Yanagisawa and Rendon-Angeles, unpublished data, 1999).

Lattice parameter of hydrothermally converted HAP single crystals

Previous studies have assigned HAP to the hexagonal system (Young and Holcomb 1982). The lattice parameters of the HAP crystals completely converted by the hydrothermal treatments were determined in the hexagonal form to facilitate comparison with those in the literature. The results are shown in Figure 4 and also summarized in Table 1.

Young and Holcomb (1982) summarized the lattice parameters of hexagonal HAP crystals that had been prepared by various methods and heat treated in nitrogen or steam. According to their analysis HAP prepared by means of hydrolysis of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (by refluxing it in water), has the largest a_0 (9.4389 Å), whereas HAP prepared by precipitation followed by heat treatment at 400 °C in nitrogen gave the smallest a_0 (9.4029 Å). The largest c_0 (6.8933 Å) was found in HAP prepared by direct precipitation, and the smallest c_0 (6.8777 Å) in hydrothermally prepared HAP.

The lattice parameters of our specimens were within those summarized by Young and Holcomb (1982). From Figure 4, one can observe a gradual contraction of a and expansion of c in the HAP crystals, with the increase in reaction time, concentration of the alkaline solution, and the reaction temperature. This behavior agrees with the change in lattice parameters for the conversion of CIAP into the HAP crystal structure. Although no evidence for the replacement of Ca by K has been reported for synthetic HAP crystals (Posner 1961), electron probe microanalyses (Table 2) of the HAP single crystals of

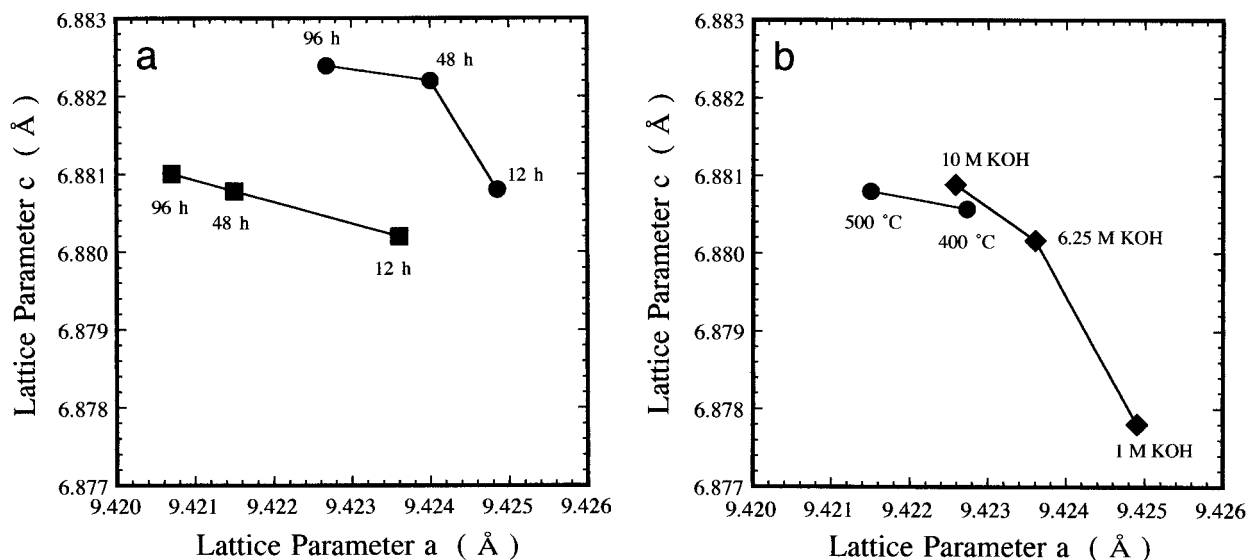


FIGURE 4. Lattice parameters determined for the converted hydroxyapatite single crystals, assigned to the hexagonal system. (a) The crystals were synthesized in 6.25 M KOH solution (box) and 6.25 M NaOH solution (circle) at 500 °C for various intervals. (b) The crystals were synthesized in KOH solutions with various concentrations at 500 °C for 12 h (diamond), and in 6.25 M KOH solution for 48 h at different temperatures (circle).

this study, which had been completely converted using 6.25 M KOH solutions (samples 1 and 5), revealed the presence of a small amount of both K and Cl. These results suggest that the variation of the lattice parameters of the HAP crystals as a function of reaction time, temperature, or concentration of the alkaline solutions, can be attributed mainly to the simultaneous increase and decrease of the amount of K and Cl, respectively, as the reaction proceeds. Moreover, the difference in the lattice parameters between the HAP crystals obtained from 6.25 M KOH and 8.25 M NaOH solutions is associated with a compositional change in the crystals, namely, either the uptake of Na or the loss of Cl in the HAP structure (Table 2).

Ion-exchange mechanism

The details about the course of the ion-exchange reaction in the CIAP single crystals were investigated by observing cross sections of the partly ion exchanged crystals obtained by hydrothermal treatment in 6.25 M KOH solution at 500 °C for 3 h. Figure 5 shows SEM photographs taken on the cross sections of the crystals parallel to the *a* axis (Figs. 5a and 5c) and *c* axis (Figs. 5e and 5g), together with the results of Cl mapping and line analysis on the same area or line indicated in the SEM photograph.

In the SEM photographs, it is easy to identify the presence of two phases: a porous dark part near the crystal surface, and a light part inside the crystal. It is interesting to note that the outer layer developed at this stage contains of holes that are distributed randomly parallel to the *c* axis. The two phases are separated by a sharp boundary in texture as well as composition. Cl X-ray of the same areas (Figs. 5b and 5f), confirmed that the outer part of the crystal corresponds to the HAP structure. From these observations, it is clear that the ion-exchange process begins from the surfaces of the crystals that were in contact with the reaction media.

More details of the concentration profile in the crystals are revealed by the Cl line analyses (Figs. 5d and 5h). The difference in Cl concentration along the direction in which the ion exchange proceeds is clearly indicated by two plateaus separated by a sharp boundary between the converted HAP part and the unreacted CIAP part. This result agrees with the XRD patterns that show CIAP being converted to HAP without the formation of solid solutions between them (Fig. 1). The concentration profiles obtained in this study reveal no diffusion layer, in contrast to the results obtained by Brennan (1994) and Farver and Giletti (1989), who determined that the exchange of the ionic and cationic species in the apatite crystals occurs by solid-state diffusion, even under hydrothermal conditions, provided the solution is saturated in apatite.

Young (1980) suggested that diffusion of OH⁻ in the apatite

structure is essentially parallel to the *c* axis, because a feature of the apatite structure is the *c* axis-oriented column of OH⁻ ions with an associated triangle of calcium ions. Brennan (1994) clearly showed that diffusion coefficients for anions along the *c* axis was much larger than that along the *a* axis. Tse et al. (1973) also suggested that OH⁻ motion along the columns should be relatively easy, whereas motion between adjacent columns should be less likely. They showed that the mechanism of ionic motion is an interchange of ions with vacancies in the solid state.

The ion exchange of Cl⁻ with OH⁻ in the CIAP single crystals, under alkaline hydrothermal conditions, occurred along both the *a* and *c* axes, and it proceeded very fast, even at low temperatures in comparison with that expected for solid-state diffusion. Furthermore, the HAP crystals converted from the CIAP crystals had characteristic textures, exhibiting channels on the surface and tunnels inside. The boundary between the converted and original part was clear without a diffuse (concentration) gradient. All these results cannot be explained by solid-state, ion exchange.

Another possible mechanism for ion exchange observed in this study is a simultaneous dissolution and deposition process (Farver and Giletti 1989). The fact that the HAP crystals obtained by the hydrothermal treatment included alkali metal ions used as a reaction medium might support the dissolution and deposition process. In ordinary hydrothermal treatments, the original crystals are dissolved in a reaction fluid and transported to recrystallize in another place. In our experiments, however, the CIAP crystals were topotaxially converted to the HAP crystals, which suggested that the dissolved species were not transported for a long distance but that they were incorporated into the solid almost at the same place. The converted crystals were essentially single crystals, which suggests that the converted crystals should have some structural relation to that of the original crystals.

We surmise that dissolved species are clusters, much larger than ionic species. The dissolution of the CIAP crystals in alkaline solutions and formation of the clusters must result in the ion exchange of Cl⁻ at the surface of the clusters by OH⁻. Hence, some amount of Cl⁻ must remain in the inside of the clusters. The HAP crystals obtained in 8.25 M NaOH solution included a larger amount of Cl than those in 6.25 M KOH solution, despite of the high concentration of OH⁻ in the reaction medium, and the hydrothermal treatment in 8.25 M NaOH solution made the surfaces of the crystals very rough. These results suggest that larger clusters formed in the NaOH solution had larger clusters than in the KOH solution.

The hydrothermal conversion of the CIAP crystals to HAP occurred along the *a* axis as well as the *c* axis, even at low

TABLE 2. Electron microprobe analyses of the ion exchanged HAP single crystals

Sample ID	Solution and concentration	Time (h)	Chemical composition (wt%)					Chemical formula*
			Ca	P	Cl	Na	K	
2	NaOH 8.25 m	96	38.08 ± 0.30	18.58 ± 0.20	3.90 ± 0.65	1.15 ± 0.10	—	Ca _{9.50} Na _{0.50} (PO ₄) ₆ (OH) _{0.90} Cl _{0.60}
1	KOH 6.25 m	96	39.88 ± 0.30	18.58 ± 0.30	0.78 ± 0.09	—	0.19 ± 0.02	Ca _{9.95} K _{0.05} (PO ₄) ₆ (OH) _{1.78} Cl _{0.17}
5	KOH 6.25 m	12	39.99 ± 0.30	18.58 ± 0.25	0.82 ± 0.10	—	0.08 ± 0.03	Ca _{9.98} K _{0.02} (PO ₄) ₆ (OH) _{1.77} Cl _{0.21}

Note: The crystals were converted under hydrothermal conditions at a temperature of 500 °C.

* Formula proportions based on 10 cations and the amount of OH⁻ was determined by charge balance.

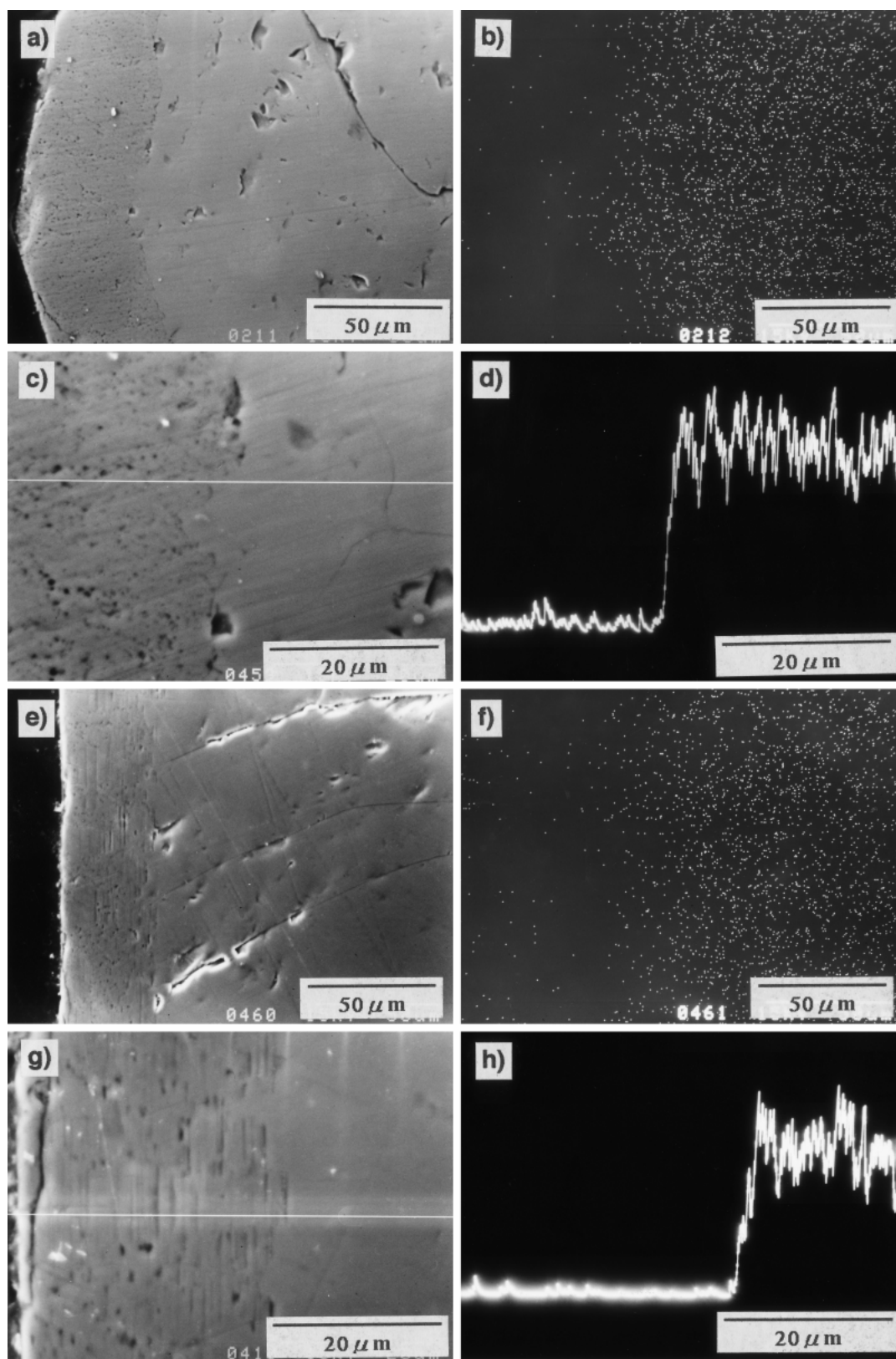


FIGURE 5. SEM images of the cross sections of the crystals parallel to the *a* axis (a, c) and *c* axis (e, g), Cl X-ray maps and line scans of the partially ion-exchanged chlorapatite single crystals treated under hydrothermal conditions at 500 °C in 6.25 M KOH solution for 3 h.

temperatures around 300 °C. In contrast, temperatures above 750 °C were necessary for the conversion of the FAP single crystals to HAP under alkaline hydrothermal conditions; furthermore, this reaction proceeded only along the *c* axis with the formation of large tunnels developed along the *c* axis from the surface by dissolution (Yanagisawa and Rendon-Angeles, unpublished data, 1999). The solubility of CIAP crystals under alkaline hydrothermal conditions might be very high in comparison with that of FAP. In other words, the bonding strength in the CIAP structure along the *a* axis must be reduced by incorporation of large Cl⁻ ions into the structure. Furthermore, the formation of the zigzag tunnels in the crystals by the conversion of CIAP to HAP, might give a path for the reacting fluid to penetrate into the crystals.

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