Reaction characteristics of a tooth-bleaching agent containing H_2O_2 and NaF: *In vitro* study of crystal structure change in treated hydroxyapatite and chemical states of incorporated fluorine

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Synopsis

This *in vitro* study was performed to elucidate the reaction mechanism of sodium fluoride (NaF), which is added to tooth-bleaching agents to lessen the adverse effect of hydrogen peroxide (H_2O_2) on teeth. Both hydroxyapatite (HAP) and dihydrated dicalcium phosphate (DCPD), model substances for dental hard tissues, dissolved easily in a simple H_2O_2 solution. In the H_2O_2/NaF solutions, however, fluorine compounds that could not be identified by X-ray diffraction (XRD) due to the smallness of the products were formed on the surface of the HAP. X-ray photoelectron spectroscopy (XPS) studies demonstrated that fluoridated hydroxyapatite (FHAP) was formed on HAP, and that calcium fluoride (CaF_2) formation was accelerated by increasing the concentrations of fluorine and H_2O_2 along with the partial dissolution of HAP. In H_2O_2/NaF solution, DCPD also transformed easily to FHAP and CaF_2, which are favorable to the remineralization process on the tooth surface. Thus, the mechanism of NaF was elucidated, and its use together with H_2O_2 for tooth bleaching was proved to be effective. Methodologically, the XPS two-dimensional plot made it possible for the first time to directly estimate the ratio of FHAP and CaF_2 in the reaction products, in contrast to the conventional wet-analytical method, which is simply based on the difference in solubility of the two components.

INTRODUCTION

White teeth are preferable from a cosmetic point of view, and tooth whitening is of interest to dentists and their patients. Toothpastes remove external discoloration, which is localized mainly in the pellicle on the surface of teeth, commonly through the polishing effect of abrasives (1–3). In our previous work (4), attention was directed to the mechanism of pellicle formation. Internal discoloration, however, is a result of defects in the tooth development process, and is also acquired through the use of medicines like tetracycline. Those kinds of discolorations cannot be removed by toothpaste, and therefore dental bleaching has been used to reach this objective. The development of bleaching agents and their formulation have been important goals for oral care researchers and dental product manufacturers. To attain these goals, an understanding of the reaction characteristics between the tooth surface and the bleaching agents is required.

Tooth bleaching became an accepted routine treatment in dental offices in the 1970s (5). The use of liquid hydrogen peroxide (H_2O_2) in dentistry, described as early as 1884, is currently the most common procedure (6–13). Several dentifrices containing H_2O_2 are also currently being marketed (14). Generally, tooth bleaching has been found to be effective on discolored teeth. On the other hand, the use of such strong oxidizing agents has raised questions as to adverse side effects on tooth structure and restorative materials. Tooth sensitivity is a potential side effect of dentist-dispensed home tooth-whitening systems (15). In the past decade, numerous studies have evaluated the effects of peroxide-containing bleaching agents on tooth hard tissue. Most of the studies found insignificant alterations of the enamel surface (16–24). Some researchers, however, actually observed enamel surface alterations by surface analysis techniques (25,26). Especially when patients had enamel cracks or other damage, careful treatment has been proposed to be necessary, and fluoride treatment has been recommended to lessen discomfort (27).

The manufacturers of the in-home bleaching systems generally provide these products with various extras such as fluoride rinses and pre- and post-bleaching treatments. The mechanism of H_2O_2 or fluoride has been individually investigated and described as follows: H_2O_2-containing bleaching agents remove tooth discolorations, where H_2O_2 acts as an oxygenator and an oxidant and then affects the organic phases in the dental enamel (11,28). The caries-preventive effect of fluoride has been well known for many years, and the mechanism has also been proposed (29–37). According to the current concepts on the action mechanism of fluoride (38–40), the caries-preventive effect is mainly attributed to the enhancement of remineralization at the interface of the tooth and oral fluids. Although the individual mechanisms of H_2O_2 and fluoride are fairly well known, the combined use of both H_2O_2 and fluoride complicates the action mechanism, and the problem of how these two components react all at once with the enamel surface has not been fully understood. The use of fluoride for reducing the discomfort caused by H_2O_2 has been recommended without an understanding of the detailed mechanism. Thus, this study was undertaken to examine the mechanism of NaF added to lessen the adverse side effects of H_2O_2 using hydroxyapatite (HAP) as a model material of tooth enamel. X-ray photoelectron spectroscopy (XPS) studies have made it possible for the first time to observe directly the successive change in the ratio of fluoridated hydroxyapatite (FHAP) and calcium fluoride (CaF_2) formed on the surface of the HAP. We also have clarified the reaction mechanism, discovering that FHAP or CaF_2 is produced not simply by depending on the fluoride concentration as shown elsewhere (35), but also by depending on the H_2O_2 concentration. The information about the mechanism and the methodology should be useful in developing bleaching agents.

METHODS

MATERIALS

Hydroxyapatite (HAP; Ca/P molar ratio = 1.65; surface area = 8 m^2g^{-1}), dehydrated dicalcium phosphate (DCPD), sodium fluoride (NaF), and hydrogen peroxide (H_2O_2, 30%) were purchased from Wako Pure Chemicals Co., Japan. Fluorapatite (FAP) crystal from Mexico was powdered, and used as XPS standard material. Calcium fluoride (CaF_2), purchased from Kanto Chemicals Co., Japan, was also used as XPS standard material. NaF and H_2O_2 were diluted with distilled water to given concentrations. The powder

samples of HAP and DCPD, substitute minerals for dental hard tissue, were dispersed in NaF and/or H$_2$O$_2$ aqueous solutions to investigate the reaction characteristics. A stained anterior tooth, which was offered from a forty-year-old male, was used for analysis of its amino acid composition.

REACTION OF HAP AND DCPD NAF AND H$_2$O$_2$ SOLUTIONS

The typical experimental procedure was as follows: NaF was dissolved in 20 cm^3 of H$_2$O$_2$ solutions (15%, pH 5.0; and 30%, pH 4.7) such that the NaF concentrations were 0.0526–0.526 mol/dm^{-3}, i.e., 1,000–10,000 ppm of fluorine. To these solutions, HAP or DCPD (0.5 g) was added, then stirred in a water bath at 25°C for given times. The HAP or DCPD solids were separated from the solutions by filtration (Advantec Co., filter #2), rinsed with 50 cm^3 of deionized water, dried at 105°C, and then examined by X-ray diffraction (XRD) and XPS as shown in the next paragraph. The solutions were analyzed for dissolved Ca^{2+} and PO$_4$$^{3-}$ by ICP-AES (Seiko Instruments Inc., SPS 1500).

CHARACTERIZATION OF REACTION PRODUCTS BY XRD AND XPS

The treated HAP and DCPD samples were examined by XRD (Rigaku Co., RINT 2000) and XPS (ULVAC-PHI Co., ESCA 5100; Mgk α = 1253.6 eV). The XPS studies were carried out in order to examine the chemical states of elements in the HAP, following our previous work (36,37). The powder samples were dusted on polymer film tapes that were mounted on a sample holder. First wide-scan spectra, then narrow-scan spectra for all detected elements were obtained. For characterization of fluorine, an Auger parameter (41), defined as the sum of the binding energy (Eb) for the F1s line and the kinetic energy (Ek) for the F(KLL) Auger line, was utilized. The Ek of the Auger line was plotted against the Eb of the photoelectron line, where the Ek of the Auger line was calculated by subtracting energy at the corrected Auger line position on the spectrum from the photon energy (1253.6 eV), as shown in the equations below. The Auger parameter grids were drawn as a family of lines with slopes of 45 degrees, where all the points on a line had the same value for the Auger parameter because the static charges were rationally cancelled. In the present work, however, the C1s line from adventitious hydrocarbon, which nearly always appears at 284.6 eV, was used for charge correction; thus, each chemical state was supposed to occupy not only a whole Auger parameter line but also a unique point on the line: Auger parameter = Eb of F1s line + Ek of F(KLL) Auger line. (Ek of F(KLL) Auger line = 1253.6 – energy at Auger line position on the spectrum.)
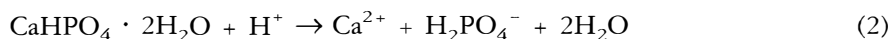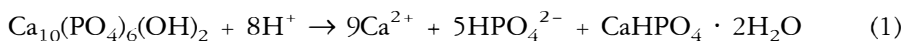
RESULTS

DISSOLUTION OF HAP AND THE FOLLOWING STRUCTURAL CHANGES IN H$_2$O$_2$ SOLUTION

The dissolved Ca^{2+} and H$_2$PO$_4$$^-$ ions from powdered HAP in H$_2$O$_2$ solution (15%, pH 5.0; and 30%, pH 4.7) were analyzed; results are listed in Table I. The dissolution of HAP was accelerated by H$_2$O$_2$ addition, where the driving force was the acidity of the solution as shown, for example, by equations 1 and 2, though the differences due to the concentration of H$_2$O$_2$ were not significant. The pH values in the solutions changed to

Table I
Dissolution of Calcium and Phosphate Ions from HAP, and the Subsequent Crystal Structure Changes
in Hydrogen Peroxide (H_2O_2) Solutions

No.	H_2O_2 (%)	Ca ($\times 10^{-5}$ mol)	P ($\times 10^{-5}$ mol)	Ca/P ratio	XRD pattern of product
1	0	0.6	1.1	0.55	HAP
2	15	1.3	1.9	0.68	HAP
3	30	1.4	2.0	0.70	HAP

around 6.0 after these reactions. From the dissolution data, surface alterations on the HAP were evident. The released Ca/P molar ratios, which differed from the stoichiometric ratio for HAP, indicated so-called incongruent dissolution (42). X-ray diffraction patterns of the untreated HAP and the HAP treated in H_2O_2 (15%, 30%) for two hours are shown in Figure 1. There were no apparent changes in crystal structure, and all these patterns were characteristic of the HAP structure, suggesting that the changes were limited to the outermost surface of the HAP.

$$Ca_{10}(PO_4)_6(OH)_2 + 8H^+ \rightarrow 9Ca^{2+} + 5HPO_4^{2-} + CaHPO_4 \cdot 2H_2O \qquad (1)$$

$$CaHPO_4 \cdot 2H_2O + H^+ \rightarrow Ca^{2+} + H_2PO_4^- + 2H_2O \qquad (2)$$

XRD AND XPS ANALYSES OF STRUCTURAL CHANGE ON HAP TREATED IN H_2O_2/NAF SOLUTION

XRD patterns of HAP treated in the NaF solution and in the solution containing both H_2O_2 and NaF (H_2O_2/NaF solution) are shown in Figure 2. XRD patterns in Figure 2(1) reveal no substantial differences among the differently treated HAP samples. These results are in accordance with the work previously done by us (36,37): partly substituted fluoridated hydroxyapatite (FHAP) forms by the ion exchange between HAP and fluoride as shown by equation 3. In contrast, the results in Figure 2(2) show that HAP was partially transformed to CaF_2, as shown by equation 4, especially in high fluoride solutions.

$$Ca_{10}(PO_4)_6(OH)_2 + nF^- \rightarrow Ca_{10}(PO_4)_6(OH)_{2-n}F_n + nOH^- \qquad (3)$$

$$Ca_{10}(PO_4)_6(OH)_{2-n}F_n + (20 \cdot n)F^- \rightarrow 10CaF_2 + 6PO_4^{3-} + (2 \cdot n)OH^- \qquad (4)$$

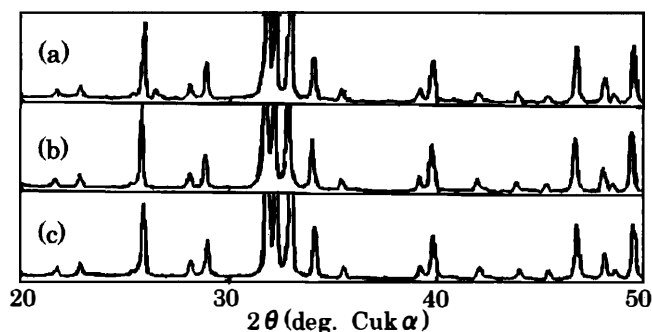The fluoride ions were considered to react only with the surface atomic layers in low-

Figure 1. XRD patterns of HAP power: (a) untreated; (b) treated in 15% H_2O_2 solution; (c) treated in 30% H_2O_2 solution.
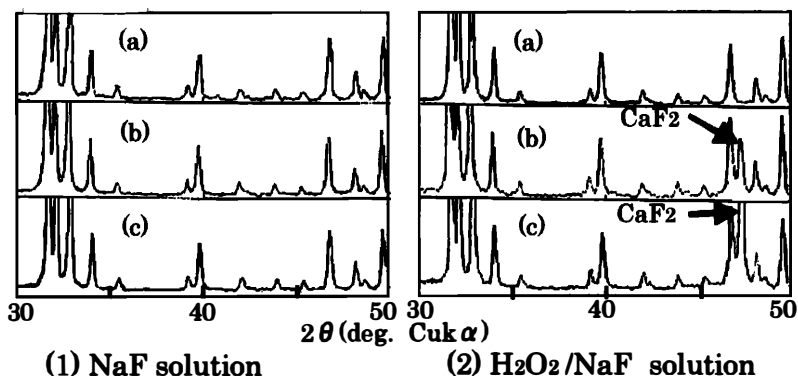
Figure 2. XRD patterns of HAP powder treated in NaF solution and H$_2$O$_2$/NaF solution: (a) F = 1,000 ppm; (b) 5,000 ppm; (c) 10,000 ppm.

fluoride solutions. Hence, XPS was utilized because XRD analysis provides little information about the outermost surface of the HAP. The two representative wide-scan spectra obtained from a series of HAP samples treated in NaF solution and in H$_2$O$_2$/NaF solution are shown in Figure 3. The comparison of the two spectra revealed no significant differences between the two HAP samples, simply showing the presence of C, O, Ca, P, and F. Then, the peak area was calculated to estimate the relative concentrations of the detected elements. The results in Figure 4 show the effect of fluoride concentration on the changes in surface composition (Ca/P and F/Ca molar ratios) of the HAP. The use of fluoride without H$_2$O$_2$ caused a small increase both in Ca/P and in F/Ca, which reached approximately 1.60 and 0.2, respectively. After that, no changes occurred to any measurable degree in the concentration range of fluoride between 1,000–10,000 ppm, confirming FHAP formation. The use of fluoride in the presence of H$_2$O$_2$, however, induced a different behavior, in sharp contrast to that in the absence of H$_2$O$_2$. With an increase in fluoride concentration, Ca/P and F/Ca drastically increased, suggesting that CaF$_2$ formed on the HAP surface besides FHAP.
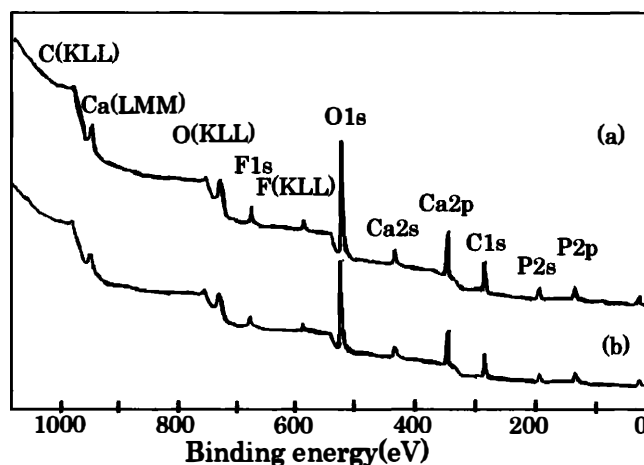

Figure 3. XPS wide-scan spectra of HAP treated in NaF solution (a) and H$_2$O$_2$/NaF solution (b).
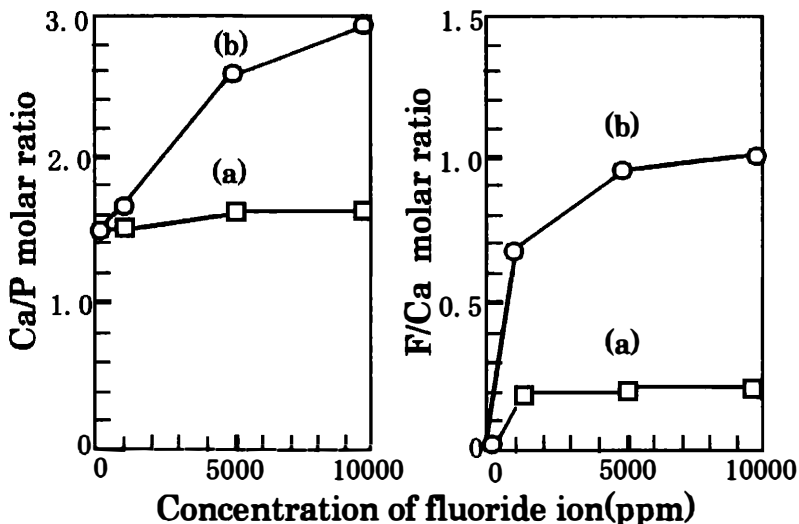
Figure 4. Changes of composition on HAP surface as a function of fluoride concentration in NaF solutions (a) and H_2O_2/NaF solutions (b).

XPS STUDY ON THE CHEMICAL STATES OF THE ELEMENTS ON THE HAP SURFACE TREATED IN H_2O_2/NAF SOLUTION

Spectral shifts for all detected elements such as F, Ca, P, and C were measured. The representative F(KLL) Auger narrow-scan spectra for the HAP treated in NaF solution are shown in Figure 5(1) and for that treated in H_2O_2/NaF solution in Figure 5(2). In both cases, the spectra shifted from the lower-energy position toward the higher-energy positions with increasing fluoride concentration. This result suggests that the products became less FHAP-like and more CaF_2-like as the fluoride concentration increased. The possibility of other new phases besides FHAP or CaF_2 will be discussed later. Especially in H_2O_2/NaF solutions, the chemical shifts were larger and the spectra approached
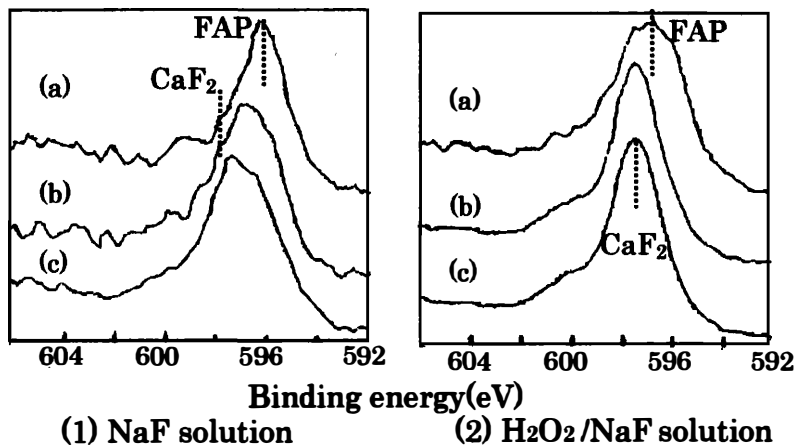

Figure 5. XPS narrow scan spectra (F(KLL)) of HAP powder treated in NaF solution and H_2O_2/NaF solution: (a) F = 1,000 ppm; (b) 5,000 ppm; (c) 10,000 ppm. The vertical dotted lines indicate the energy positions of standard CaF_2 and FAP.

that of CaF_2. This was consistent with the XRD results in Figure 2 showing the diffraction peaks of CaF_2. These findings show that the formation of CaF_2 is dependent on both the pH and the fluoride concentration of the solutions. In addition, the Ca2p spectra were examined, and the representative narrow-scan spectra are shown in Figure 6. A distinct difference was detected in the spectra among the three samples: HAP treated with H_2O_2/NaF, HAP treated with NaF, and untreated HAP. The binding-energy values of the spectra were in good accordance with those of CaF_2, FAP, and HAP, respectively. Thus, the analysis of Ca2p spectra was also useful in identifying the reaction products on the HAP surface, and provided evidence for the formation of CaF_2 when treated with H_2O_2/NaF.

The chemical shifts generally occur on both the photoelectron lines and the Auger lines; thus, the combined use of both lines is considered to be useful. Two-dimensional chemical-state plots are shown in Figure 7, where the Ek of the F(KLL) Auger line is plotted against the Eb of the F1s photoelectron line. The observed energy values were charge-corrected using the C1s line at 284.6 eV; thus, each chemical state occupied a unique point on the two-dimensional grid. The fluoride compounds FAP, CaF_2, and NaF were also analyzed and plotted as reference materials. FAP is shown in the upper right-hand corner, CaF_2 in the lower left-hand corner, and NaF in the lowest position. The chemical states of fluorine from HAP treated in NaF (F = 1,000 ppm) and in H_2O_2/NaF (F = 10,000 ppm) were positively assigned to FAP and CaF_2, respectively. In both NaF and H_2O_2/NaF, the shifts from the FAP position became larger with increasing fluoride concentrations. Thus, the two-dimensional chemical-state plots have shown that both F1s and F(KLL) spectra shifted either with H_2O_2 addition or with the increase in fluoride concentration.

STRUCTURAL CHANGE OF DCPD IN H_2O_2 AND H_2O_2/NAF SOLUTIONS

DCPD has been known as a precursor phase to HAP in the remineralization process, and also as one of the constituents found in dental calculus and precarious lesions (43). Therefore, DCP often coexists with HAP in the dental hard tissues and interacts with
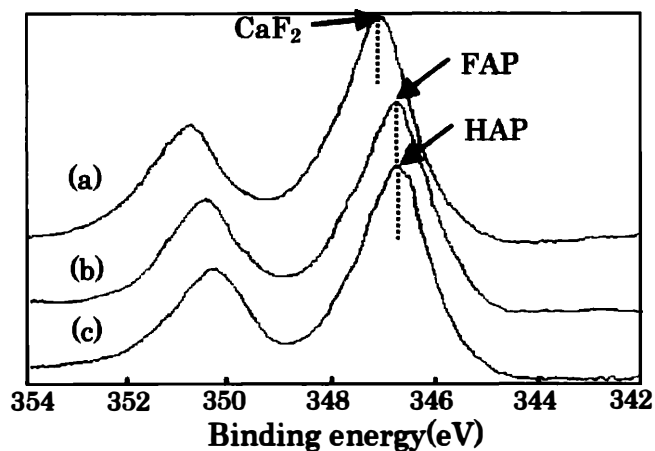

Figure 6. XPS narrow-scan spectra (Ca2p) of HAP: (a) treated in H_2O_2/NaF; (b) treated in NaF; (c) untreated. The vertical dotted lines indicate the energy positions of standard CaF_2, FAP, and HAP.
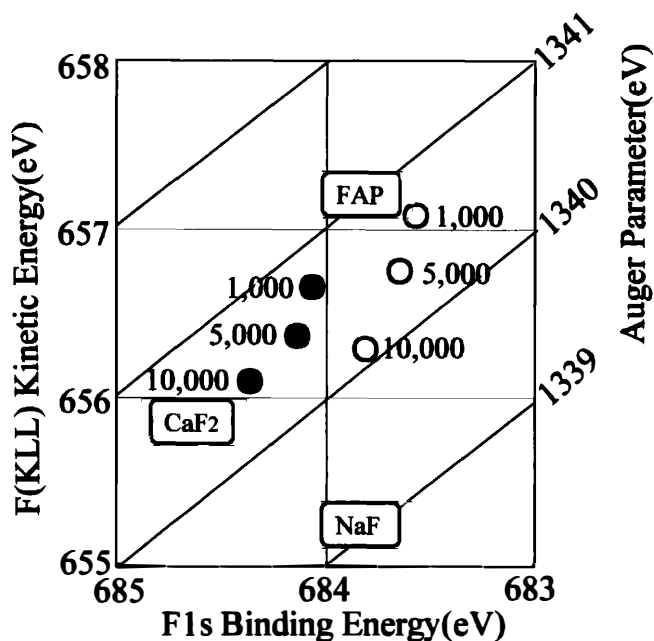
Figure 7. XPS two-dimensional chemical-state plot of fluorine for HAP treated in NaF (○) and H$_2$O$_2$/NaF (●) solutions. The numbers (1,000–10,000) are concentrations of fluoride in solutions (in ppm).

saliva in the oral cavity at the same time. In the tooth-bleaching process by H$_2$O$_2$/NaF, DCPD in the precarious lesion is assumed to play an important role; thus, attention was paid to the behavior of DCPD. Typical X-ray diffraction patterns of DCPD treated in H$_2$O$_2$ and H$_2$O$_2$/NaF are shown in Figure 8. No crystal structure change occurred to DCPD treated with H$_2$O$_2$ alone. In contrast, DCPD was transformed totally to a low-crystallized apatite structure in H$_2$O$_2$/NaF, suggesting that fluoride ions were incorporated to form FHAP, and interestingly, that the growth of FHAP was enhanced by the fluoride even in an H$_2$O$_2$-coexisting system.
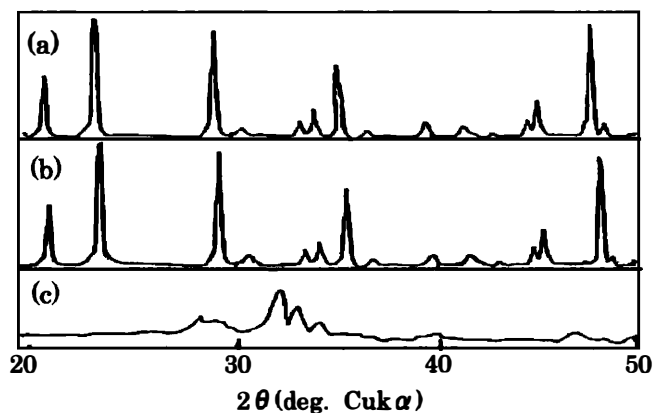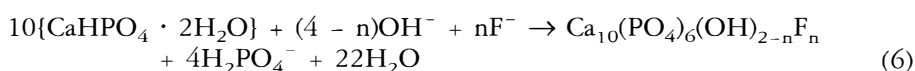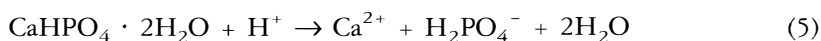

Figure 8. Typical XRD patterns of untreated DCPD (a), treated DCPD in H$_2$O$_2$ solution (b), and in H$_2$O$_2$/NaF solution (c).

The dissolved Ca^{2+} and PO$_4^{3-}$ ions in H$_2$O$_2$ solutions and in H$_2$O$_2$/NaF solutions were analyzed, and the results are shown in Table II. The dissolved Ca^{2+} and PO$_4^{3-}$ ions increased in H$_2$O$_2$ solutions and were also enhanced by increasing the concentration. The molar ratios of released Ca^{2+} and PO$_4^{3-}$ ions from the DCPD were approximately 1.0, and in good accordance with the stoichiometric ratio for DCPD itself. This result indicates that no transformation from DCPD to any other phase occurred. In the H$_2$O$_2$/NaF solutions, however, an increase in the dissolved PO$_4^{3-}$ ions was more pronounced. Judging from the ratio of dissolved Ca^{2+} and PO$_4^{3-}$ ions (Ca/P), a Ca-rich layer like FHAP definitely formed, and this was in accordance with the XRD results in Figure 8, which show the formation of an apatite structure. To sum up these results: in H$_2$O$_2$ solutions, DCPD, unlike HAP, dissolved congruently; when fluoride was present, FHAP was formed. These mechanisms are shown in equations 5 and 6, respectively:

$$CaHPO_4 \cdot 2H_2O + H^+ \rightarrow Ca^{2+} + H_2PO_4^- + 2H_2O \tag{5}$$

$$10\{CaHPO_4 \cdot 2H_2O\} + (4-n)OH^- + nF^- \rightarrow Ca_{10}(PO_4)_6(OH)_{2-n}F_n$$
$$+ 4H_2PO_4^- + 22H_2O \tag{6}$$

DISCUSSION

The use of fluoride has been recommended to lessen the discomfort caused by the H$_2$O$_2$ bleaching of teeth (27). We also have been investigating the bleaching effects of an H$_2$O$_2$/NaF system on the stained teeth. The extrinsic dental stains are often associated with calculus, plaque (44), and adsorbed salivary film materials known as the acquired enamel pellicle (45). The stains on tooth surfaces are composed of various materials such as the inherent colors produced by incorporated tea and coffee and aged proteins (44–47). These kinds of colored materials can be removed comparatively easily by mechanical means. In the present work, the colored materials were actually separated from the stained tooth by scrubbing. The materials were hydrolyzed by heating at 110°C for two hours under decompression in a glass cell containing 2% hydrochloric acid, and the amino acid composition was analyzed with the Amino-Acid Analyzer System (Shimadzu Co., Japan). The results in Figure 9 show a different composition from that of saliva. Most of the stained materials were removed by scrubbing; nevertheless, the colored stain still remained in the subsurface of the tooth. After bleaching with H$_2$O$_2$/NaF (H$_2$O$_2$ = 15%; F = 1000 ppm), however, the stain was removed and the tooth surface became clean. An example of XPS analysis of the teeth before and after bleaching is shown in Figure 10. Nitrogen (N), which originated probably from proteins, disappeared after

Table II
Dissolution of Calcium and Phosphate Ions from DCP Treated in H$_2$O$_2$ and H$_2$O$_2$/NaF Solutions, and the Subsequent Crystal Structure Changes

No.	H$_2$O$_2$ (%)	F (ppm)	Ca ($\times 10^{-5}$ mol)	P ($\times 10^{-5}$ mol)	Ca/P ratio	XRD pattern of product
1	0	0	1.8	1.9	0.95	DCPD
2	15	0	3.4	3.4	1.00	DCPD
3	30	0	5.5	6.1	0.90	DCPD
4	0	1000	0.5	90.0	0.006	HAP
5	15	1000	3.2	97.0	0.033	HAP
6	30	1000	7.5	130.0	0.058	HAP
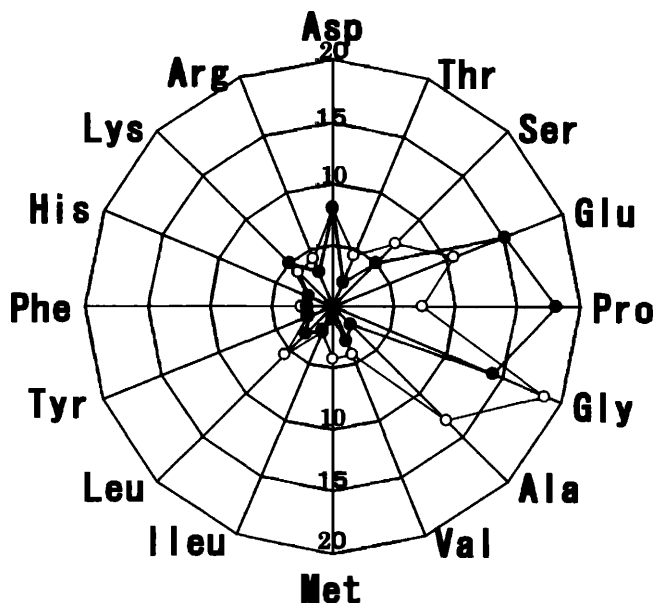
Figure 9. Amino acid compositions in human saliva (●) and in stain separated from human teeth (○). The radii of the circles represent the molar percent of amino acid.
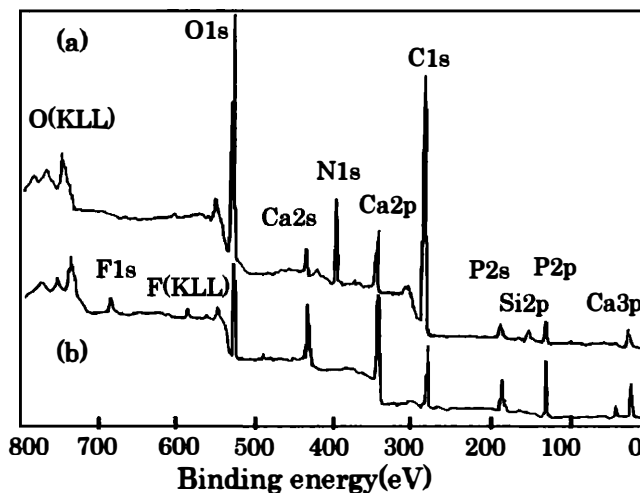
Figure 10. XPS wide-scan spectra of human teeth with stain: (a) before and (b) after bleaching with H_2O_2/NaF.

bleaching, and a small amount of fluorine (F) was detected instead. This result has suggested that the H_2O_2/NaF agent not only bleaches the stained teeth, but also enhances the remineralization accompanied by FHAP formation.

The individual reaction mechanism of H_2O_2 and NaF are well understood, and so we have focused our attention on an investigation of the mixed system. In this work, the preventive effect by the NaF/H_2O_2 agent on discomfort was found to be mainly due to the remineralization at the tooth enamel surface. FHAP was apt to form favorably in

low-level fluoride and H$_2$O$_2$ solutions, and CaF$_2$ in high-level fluoride and H$_2$O$_2$ solutions. These mineral phases probably constitute reservoir sources of the fluoride in the solution during the periods of bleaching, and are proposed to be effective eventually for caries prevention. It should also be pointed out that DCPD, one of the initial caries products, was transformed to FHAP even in the presence of H$_2$O$_2$, when fluoride ions were present. This suggests that the H$_2$O$_2$/NaF agent is also effective for recovering from initial caries.

XPS results have shown that both F1s and F(KLL) lines gradually shift either by H$_2$O$_2$ addition or with the increase in fluoride concentration. It was of interest to know whether the reaction products were new intermediate products other than FHAP or CaF$_2$. To clarify the origin of the spectral shift, the prescribed amount of the two reaction products (a and f in Figure 11) mostly corresponding to FHAP and CaF$_2$, respectively, were uniformly mixed, and the mixture was investigated by XPS. Then, some spectra of the mixtures were mostly identical to each spectrum of the reaction product. A representative spectrum obtained from the mixture is shown in Figure 11(g). Hence, the coexistence of FHAP and CaF$_2$ on the outermost surface might explain the chemical shift and the line broadening. As mentioned above, FHAP comprises a series of solid solutions formed from two end members of FAP and HAP. The intermediate solid solutions between FAP and CaF$_2$, however, are unlikely to form because there is no similarity between these two chemical structures.
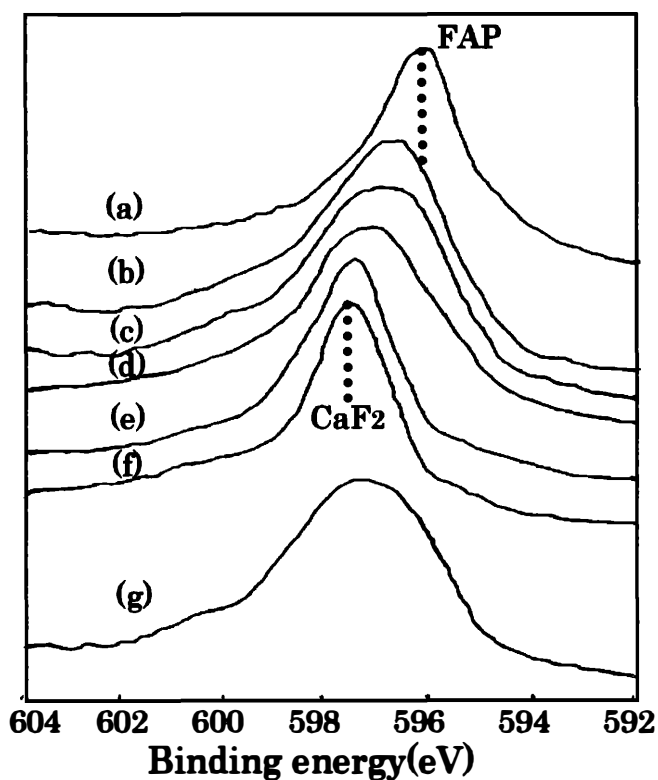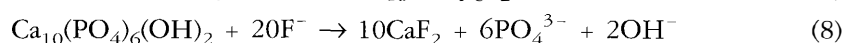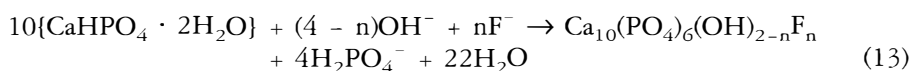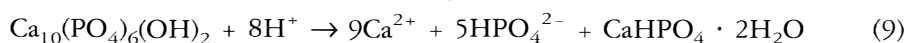

Figure 11. Comparison of F(KLL) spectra from treated HAP (a–f) with a spectrum from the mixture (g). HAP (a–f) is the same as shown in Figure 5. The mixture (g) was prepared by mixing HAP (a) and HAP (f).

The two-dimensional chemical-state plot is methodologically useful because this method makes it possible to estimate the amount of coexisting CaF_2 in the FHAP, instead of the potassium hydroxide (KOH)-soluble fluoride method (48), which is based on the assumption that CaF_2 is soluble only in KOH. For a long time, FHAP and CaF_2 were believed to form dependent on the fluoride concentration of the solutions, and the consequent mechanisms (33) shown by equations 7 and 8 have been often cited, with the condition that CaF_2 formed only with a fluoride concentration of 500 ppm or more. The present results, however, have pointed out that the fluoride concentration is not the only factor determining the type of product and that other mechanisms coexist. A series of fluoride-substituted HAP expressed as FHAP is initially formed by an ion-exchange reaction; then an excess of fluoride converts the FHAP little by little to CaF_2 by a decomposition reaction. The amount of produced CaF_2 is also increased by the addition of H_2O_2. Thus, there is no clear critical pH value or H_2O_2 concentration for determining which product, FHAP or CaF_2, will be formed.

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \tag{7}$$

$$Ca_{10}(PO_4)_6(OH)_2 + 20F^- \rightarrow 10CaF_2 + 6PO_4^{3-} + 2OH^- \tag{8}$$

H_2O_2 is considered to cause the partial incongruent dissolution of HAP and the formation of DCPD as an intermediate product, as shown by equation 9, followed by dissolution of DCPD, shown by equation 10. If fluoride ions exist under this situation, CaF_2 or FHAP would form by equations 11, 12, and 13 below. It should also be pointed out that DCPD, one of the initial caries products, could be transformed to FHAP even in H_2O_2 solution, as long as fluoride ions are present.

$$Ca_{10}(PO_4)_6(OH)_2 + 8H^+ \rightarrow 9Ca^{2+} + 5HPO_4^{2-} + CaHPO_4 \cdot 2H_2O \tag{9}$$

$$CaHPO_4 \cdot 2H_2O + H^+ \rightarrow Ca^{2+} + H_2PO_4^- + 2H_2O \tag{10}$$

$$CaHPO_4 \cdot 2H_2O + 2F^- \rightarrow CaF_2 + HPO_4^{3-} + 2H_2O \tag{11}$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \tag{12}$$

$$10\{CaHPO_4 \cdot 2H_2O\} + (4-n)OH^- + nF^- \rightarrow Ca_{10}(PO_4)_6(OH)_{2-n}F_n$$
$$+ 4H_2PO_4^- + 22H_2O \tag{13}$$

CONCLUSIONS

The reaction mechanisms in an H_2O_2/NaF system of HAP and DCPD, the constituents of teeth and dental caries respectively, were elucidated. The HAP and DCPD dissolved easily in a simple H_2O_2 solution. In the H_2O_2/NaF solution, fluoride compounds formed on the outermost surface of HAP, but the chemical states of fluorine were not possible to identify by XRD due to the smallness of the products. XPS studies, however, demonstrated that FHAP and CaF_2 formed on the HAP, and that CaF_2 formation was, moreover, enhanced along with the partial dissolution of HAP by the increase in NaF and H_2O_2. DCPD also transformed easily to FHAP and CaF_2 by NaF, even under the coexistence of H_2O_2. Both FHAP and CaF_2 were considered to enhance the remineralization, and to be responsible for lessening the discomfort in teeth caused by the bleaching agent containing H_2O_2.

Methodologically, the XPS two-dimensional plot was found to be a powerful means to determine the chemical states of fluoride. Furthermore, this method also made it pos-

sible to estimate directly the ratio of FHAP and CaF$_2$ in the reaction products without separating out the KOH-soluble CaF$_2$.

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