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Observation of fluorapatite formation under hydrolysis of tetracalcium phosphate in the presence of KF by means of soft X-ray emission and absorption spectroscopy

E. Z. KURMAEV[1], S. MATSUYA[2*], S. SHIN[3], M. WATANABE[4], R. EGUCHI[3], Y. ISHIWATA[3], T. TAKEUCHI[3], M. IWAMI[4]
[1]Institute of Metal Physics, Russian Academy of Sciences – Ural Division, 620219 Yekaterinburg GSP-170, Russia
[2]Section of Biomaterials Engineering, Faculty of Dental Science, Kyushu University, Fukuoka 812-8582, Japan
[3]Institute for Solid State Physics, Tokyo University, Roppongi, Minato-ku, Tokyo 106-8666, Japan
[4]Institute of Materials Structure Science, Tsukuba, Ibaraki 305-0801, Japan
[5]Research Laboratory for Surface Science, Faculty of Science, Okayama University, Okayama 700-8530, Japan
E-mail: smatsuya@dent.kyushu-u.ac.jp

The effect of fluoride on the hydrolysis of tetracalcium phosphate (TTCP; $Ca_4(PO_4)_2O$) in 0.1 mol/l KH_2PO_4 containing 62–83 mmol/l KF was studied with the help of X-ray fluorescence measurements. Fluorine X-ray emission and absorption spectra of the final product of hydrolysis and reference samples (CaF_2 and $Ca_5(PO_4)_3F$) were measured at Beamline BL-2C of Photon Factory (PF, Tsukuba). Based on these measurements we concluded that hydrolysis of TTCP in the presence of KF converts it into fluorapatite. Formation of CaF_2, which is often found in the hydrolysis of hydroxyapatite at high fluoride concentration, was not observed.

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1. Introduction

Fluoride has been found effective for the prevention of dental caries in various forms and concentrations in dentifrices and mouthwashes and in prescribed gels, varnishes and lacquers [1]. Jenkins reviewed fluoride research related to a mechanism of caries prevention for the past 40 years and concluded that fluoride in plaque fluid favored remineralization of dental tissue [2]. Demineralization and remineralization of a tooth may occur simultaneously and caries would form if the former were predominant. Fluoride in plaque fluid promotes remineralization and reduces the caries formation. Increase in fluoride concentration in the plaque fluid favors the remineralization. Topically applied fluoride may promote the increase in fluoride concentration due to the formation of CaF_2-like deposits. Despite extensive studies of enamel (or dentin)-fluoride interactions, it is not clear what kind of fluoride incorporation takes place: in the form of fluorapatite ($Ca_5(PO_4)_3F$) or calcium difluoride (CaF_2) [3–4]. It has been supposed that CaF_2 may form a ''reservoir'' for fluoride to subsequently react with the mineral component of teeth [5–6]. Therefore, the further investigations of fluoride/mineral interactions are necessary which will be helpful in efforts to develop improved-efficacy anticaries compositions. Tanizawa *et al.* [7] concluded from their X-ray photoelectron spectroscopic (XPS) study that OH^- ion in hydoxyapatite was exchanged for F^- ion to form exclusively fluorapatite in a neutral solution even at high concentration of F up to 10 000 ppm (526 mmol/l). It was reported that a magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy enabled distinguishing between CaF_2 and $Ca_5(PO_4)_3F$ at an extremely fast spinning rate of 15.5 kHz [8]. Besides the two methods, XPS and MAS NMR, X-ray emission and absorption spectroscopy also give us a valuable information of the chemical state of fluoride ion incorporated into hydroxyapatite ($Ca_5(PO_4)_3OH$), because the spectroscopy is very sensitive to chemical bonding and local surrounding of emitting and absorbing atoms [9].

Tetracalcium phosphate (TTCP; $Ca_4(PO_4)_2O$), which is a main component of calcium phosphate cement as an alternative of hard tissues, hydrolyzes to form a calcium deficient hydroxyapatite in 0.1 mol/l KH_2PO_4 solution [10]. When the hydrolysis was done in the presence of

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*Author to whom all correspondence should be addressed.

potassium fluoride (KF), fluoride ion is incorporated into the hydroxyapatite [11].

In this paper we have investigated the fluorine X-ray emission and absorption spectra of the final product of hydrolysis of TTCP in 0.1 mol/l KH_2PO_4 solutions containing various concentration of KF. Based on these measurements and their comparison with spectra of the reference samples (CaF_2 and $Ca_3(PO_4)_3F$), we concluded that TTCP is transformed into fluorapatite.

2. Experimental

The X-ray fluorescence measurements were performed at undulator Beamline BL-2C of the Photon Factory (PF, Tsukuba) consisting of a grazing incidence soft X-ray monochromator with a varied space plane grating [12]. The end station is equipped with a soft X-ray emission spectrometer [13] and a commercially available photoelectron spectrometer (VG-CLAM2), which enables calibration of the incident photon energy. The spectrometer uses the Rowland circle geometry, on which an incident slit, gratings and a detector are located. The detector is numerically positioned tangentially on the Rowland circle by the three-axis control of two translations and one rotation using pulse motors. In order to compensate the distortion of the slit image, a multichannel detector is used. To increase the quantum efficiency of the detector, a surface of the microchannel plate is coated with CsI.

We have measured F Kα X-ray emission spectra (XES) ($2p \rightarrow 1s$ transition) using a laminar-type holographic spherical grating ($R = 7$ m, $N = 2400$ lines/mm). A 20 μm incident slit width was used which provided an energy resolution of 0.4 eV according to the ray-trace simulation. The excitation energy was selected far from the F 1s threshold at $E = 750$ eV to measure nonresonant F Kα XES. The time of exposure was 4200 s for CaF_2 and 6500–6900 s for fluorapatite and samples under investigation.

TTCP ($Ca_4(PO_4)_2O$) was prepared by heating an equimolar mixture of dicalcium phosphate ($CaHPO_4$) and calcium carbonate at 1500 °C for 6 h. An X-ray diffraction pattern (XRD) showed no phase other than TTCP. The hydrolysis experiment was done in 0.1 mol/l KH_2PO_4 solutions containing various initial concentrations of KF, from 83 (sample 1) to 62 mmol/l (sample 2). TTCP (2 g) was placed into 100 ml solution kept at 37 °C and under constant stirring. CO_2-free nitrogen gas was passed through the solution during the experiment. The solution pH was continuously monitored with a glass reference electrode connected to a pH meter (F-7ss, Hitachi-Horiba, Kyoto, Japan). The pH was between 6 and 7 during hydrolysis and tended to increase with time. The solution was filtrated after the hydrolysis for 10 days and the product was washed several times with distilled water and then with ethanol. In our previous study [11], final concentration of fluoride in the filtrate was about 29 mmol/l and 0.1 mmol/l for the initial concentration of 83 and 62 mmol/l, respectively, which corresponded approximately to F-uptake of 5.4 and 6.2 mmol. If 2 g of TTCP fully convert to fluorapatite, F-uptake will be 4.37 mmol. The uptake in samples 1 and 2 was slightly larger than the theoretical F-uptake. This fact suggests that other phase but fluorapatite formed. Fig. 1 shows the XRD patterns for the hydrolysis product and the reference samples of commercial CaF_2 and fluorapatite (Wako Pure Chemical Ind., Osaka, Japan). The XRD patterns of the products showed a similarity to the commercial fluorapatite though the diffraction peaks were slightly broadened due to a difference in crystallinity [11]. CaF_2 seemed not to be formed in both of the samples.

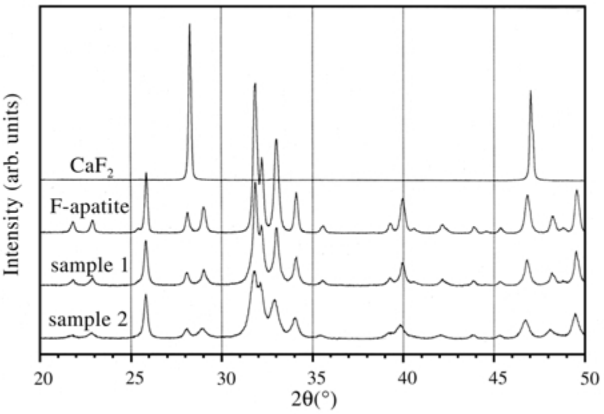

Figure 1 X-ray diffraction patterns of the final product after hydrolysis of TTCP in 0.1 mol/l KH_2PO_4 containing 83 (sample 1) and 62 (sample 2) mmol/l KF and reference samples, CaF_2 and F-apatite.

3. Results and discussion

The nonresonant fluorescent X-ray emission spectroscopy with samples excited far from an absorption threshold can be considered a two step process. The first step corresponds to an electron transition from a core level to an empty valence level when the sample absorbs an incident photon. The second step is the emission of a photon when an electron makes a transition from an occupied valence level to fill the core hole created by the incident photon absorption. Both steps are governed by the dipole selection rule, $\Delta l = \pm 1$, which means that the 1s holes in fluorine can only be filled by 2p-valence electrons. F 1s total electron yield spectra measure the X-ray absorption cross-section as a function of incident photon energy and probe unoccupied p-states.

As the core holes are localized to their particular atoms, the transition matrix elements are dominated by fluorine 2p contributions from these particular atoms, and as a result all non-local contributions to the transition matrix element can be neglected. This provides a high sensitivity of F Kα XES and F 1s TEY to the local surrounding of emitting and absorbing atoms, respectively. A conclusion about the chemical state of fluorine atoms in the reacted products can be obtained by comparison of their X-ray emission and absorption spectra with spectra of reference samples CaF_2 and $Ca_5(PO_4)_3F$ (F-apatite).

Fig. 2 shows F Kα XES of samples 1 and 2 that are compared with spectra of reference samples CaF_2 and F-apatite. F Kα XES of CaF_2 is found to be very similar to that reported by Sugiura [14]. It consists of a prominent peak around 677.2 eV and high-energy K^1L^1-satellites at

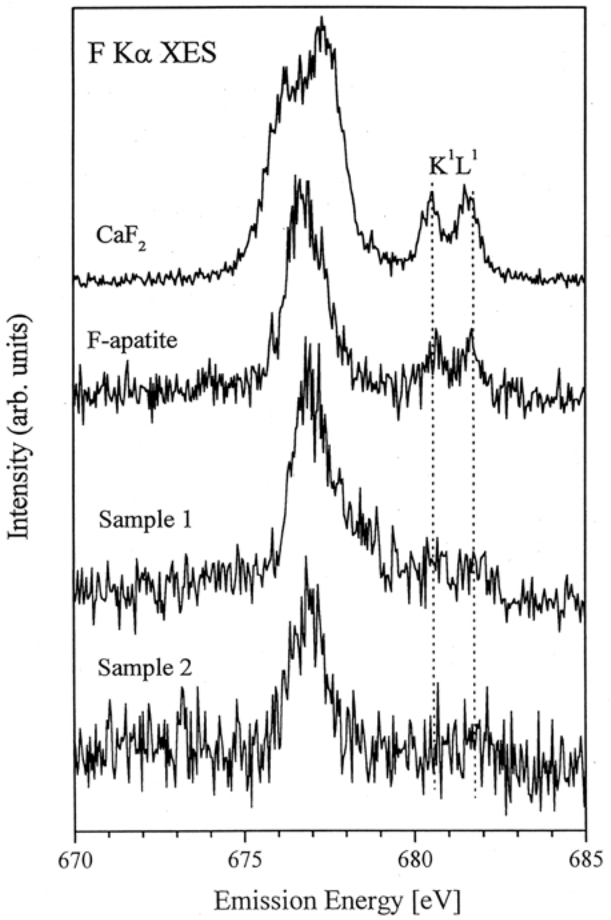

Figure 2 F Kα XES of the final product after hydrolysis of TTCP in 0.1 mol/l KH_2PO_4 containing 83 (sample 1) and 62 (sample 2) mmol/l KF and reference samples, CaF_2 and F-apatite.

680.0–681.5 eV. According to Sugiura *et al.* [14], before the actual emission of the K^1L^1 satellites takes place, the vacancy in the F^- 2p valence shell is filled by an electron from the calcium ion by leakage through a potential barrier between adjacent calcium and fluorine ions (in CaF_2 the fluorine atom is tetrahedrally coordinated by 4 Ca atoms at a distance of 2.3655 Å). Then the doubly ionized state $1s^{-1}2p^{-1}$ is deexcited and the F Kα XES is emitted and the K^1L^1 satellites are quenched. The similar satellites are also found in F Kα XES of F-apatite because a fluorine atom in this compound has also Ca atoms in the first coordination sphere (3 Ca atoms at the distance of 2.302 Å) [15] and the same mechanism can explain the origin of high-energy K^1L^1 satellites in CaF_2 and F-apatite. The high-energy K^1L^1 satellites are present in F Kα XES of samples 1 and 2 (in F Kα XES of sample 2 the splitting of satellite is not seen because of low intensity of spectrum) and their appearance can serve as some indication of F-Ca bonding in the final product of hydrolysis of tetracalcium phosphate in the presence of KF.

The full width at half of maximum (FWHM) of F Kα XES is found to be different for CaF_2 and F-apatite because in the first case F atom is coordinated by 4 Ca atoms at the distance of 2.366 Å and 6 F atoms at the distance of 2.731 Å, whereas in the second case a F atom has three neighboring Ca atoms at a distance of 2.302 Å and no fluorine atoms in the first coordination sphere.

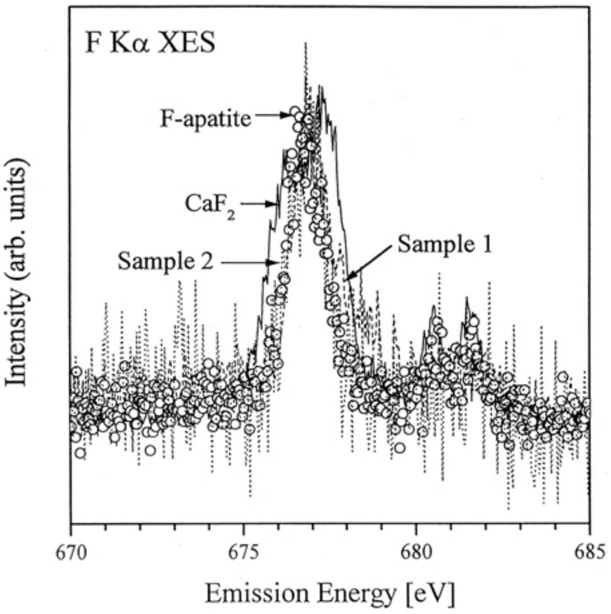

Figure 3 Comparison of F Kα XES of CaF_2, F-apatite and samples 1 and 2 normalized to intensity maximum.

Therefore we do not have strong F-F interactions for F-apatite and corresponding overlapping of F 2p-wave functions which results in less FWHM of F Kα XES than for CaF_2. As seen, F Kα XES of samples 1 and 2 (Fig. 3) are very similar in energy position and FWHM to that of F-apatite and quite different with respect to that of CaF_2. This suggests that the hydrolysis process of TTCP in the presence of KF converts it into F-apatite for both fluoride concentrations. Fluoride concentration for CaF_2 to be precipitated from solutions saturated with respect to hydroxyapatite is 6 mmol/l at pH 7.5 [16], which is close to the pH value during hydrolysis in this study. In the preparation of sample 1, final fluoride concentration was about 29 mmol/l and pH was around 7. Therefore, it is quite reasonable for CaF_2 to precipitate during hydrolysis. However, our experimental findings allowed us to conclude that the formation of CaF_2 in the hydrolysis product is completely excluded which is in agreement with our XRD data according to which in samples 1 and 2 only an apatite phase was found (Fig. 1). This finding agrees with a conclusion of Tanizawa *et al.*, in which hydroxyapatite transformed into F-apatite in neutral solution containing a high concentration of fluoride ion [7]. As already described in an experimental section, F-uptake was in excess regarding to a stoichiometric F-apatite formation from 2 g of TTCP. The excess fluoride seemed not to precipitate as CaF_2 as shown in our XES study. It is not clear now why CaF_2 was not formed in samples 1 and 2. However, as the hydrolysis of TTCP was carried out in 0.1 mol/l KH_2PO_4 solution, CaF_2 may react with phosphate ion to form fluorapatite. Ca/P ratios in sample 1 and 2 was about 1.61 and 1.63, respectively [11]. Those values are slightly smaller than a stoichiometric value of 1.67. So fluoride in this sample should be incorporated into an apatite structure as a calcium-deficient fluorohydroxyapatite. Further study will be needed to investigate the formation condition of CaF_2.

The results of the studies of X-ray emission spectra are also confirmed by X-ray absorption measurements. Fig. 4

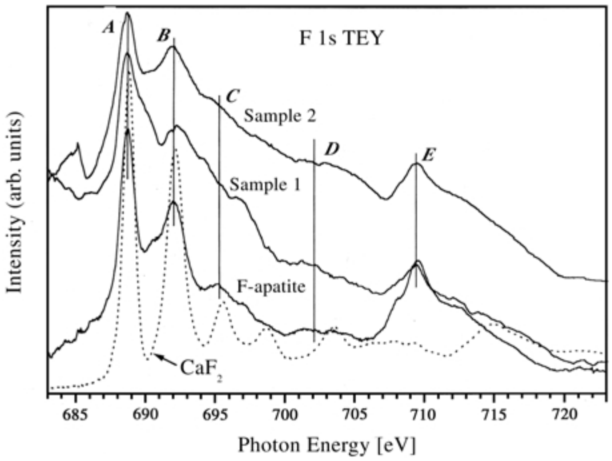

Figure 4 F 1s TEY of the F-apatite phase formed by hydrolysis of TTCP in 0.1 mol/l KH_2PO_4 containing 83 (sample 1) and 62 (sample 2) mmol/l KF and reference samples, CaF_2 and F-apatite.

shows that the main absorption peaks (*A–E*) of F 1 s TEY of samples 1 and 2 are very similar to those of F-apatite. On the other hand, the fine structure of F 1s TEY of CaF_2 is quite different. Therefore, based on these measurements, one can also conclude that fluoride promoted TTCP hydrolysis to form F-apatite.

4. Conclusion

The effect of fluoride on apatite formation under hydrolysis of TTCP in 0.1 mol/l KH_2PO_4 containing 62–83 mmol/l KF was studied by means of X-ray emission and absorption spectroscopy. It has been found that fluorine spectra of the final product of hydrolysis are very similar to that of F-apatite and quite different with respect to that of CaF_2. Based on these findings we have concluded that fluoride only promoted TTCP hydrolysis to form F-apatite.

Acknowledgments

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