EFFECTS OF FLUORIDE ON THE HYDROLYSIS OF CALCITE IN POTASSIUM DIHYDROGEN PHOSPHATE SOLUTION

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Abstract : Hydrolysis of calcite was investigated in 0.1M KH₂PO₄ solution containing potassium fluoride (0 and 1005 ppm as F) at 37°C by means of solution analyses (pH, Ca, P and F concentrations), X-ray diffraction, ³¹P magic angle spinning nuclear magnetic spectroscopy (MAS NMR), Fourier-transformed infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). With the non-fluoride solution, octacalcium phosphate (OCP) was a main product of the hydrolysis for 10 days though some amount of calcite still remained. With increasing in fluoride concentration in the solution, OCP formed less and apatite phase formed instead. Remaining calcite was also decreased with fluoride concentration. Fluoride in the solution was completely absorbed in the product after hydrolysis for 10 days except for the highest fluoride concentration of 1000 ppm. FT-IR analysis showed that the apatite phase formed was fluoridated B-type carbonated apatite, in which CO₃²⁻ ion substituted for PO₄³⁻ ion. Fluoride ion was found to promote fluoridated carbonated apatite formation directly and/or through OCP transformation.

INTRODUCTION

Calcium carbonate has three well-known modifications, that is, calcite, aragonite and vaterite. Calcite is the most stable phase at ordinary pressure and temperature. Aragonite is a main constituent of marine coral. Its skeleton structure is similar to bone and therefore it has been applied as a bone-substitute in orthopedic field. Marine coral can be converted into hydroxyapatite while preserving its porous skeleton structure by hydrothermal treatment in phosphate solution. The product is called coralline apatite and has an open pore structure suitable for penetration of osteoblast to enable a new bone formation. In the hydrothermal treatment, calcium carbonate reacts with phosphate ion to form carbonated apatite, that is, hydroxyapatite containing carbonate ion in the lattice structure. In our previous study, we investigated the hydrolysis of calcite in potassium phosphate solutions with various initial pHs between 4.5 and 8.4. It was found that calcite was hydrolyzed to carbonated apatite through OCP at lower pH and directly at higher pH. On the other hand, it is well known that fluoride promoted apatite formation in the hydrolysis of various calcium phosphates. Absorbed fluoride usually formed fluorapatite, which was more stable than hydroxyapatite. It is very interesting to know how coexistence of carbonate ion and fluoride ion affected the hydrolysis process and crystallographic features of the apatite phase obtained. There are several reports on the crystallinity and chemical stability of fluoridated carbonated apatite. Generally fluoridation of carbonated apatite improved its crystallinity and chemical stability. In the present study, the effect of fluoride on the hydrolysis product of calcite was investigated in the potassium dihydrogen phosphate solution.

MATERIALS AND METHODs

Commercially available calcium carbonate, CaCO₃ was used without purification. X-ray diffraction analysis showed calcite was the only phase present and no other phase was found. Potassium dihydrogen phosphate solution was prepared from the commercial reagent and its concentration was 0.1 mol/L. Fluoride concentration of the solution was adjusted between 0 and 1000 ppm by adding a known amount of potassium fluoride, KF. Initial pH of the solution was between 4.5 and 5.1 at 60°C depending on the fluoride concentration. Thirty mL of those solution were put in polyethylene bottle and 0.5 g of calcite powder was immersed in the solution. The overall Ca/P ratio in the system is 1.67, which corresponds to the stoichiometry in hydroxyapatite, Ca₅(PO₄)₃OH. The bottle was kept in a water bath incubator at 37°C and under gentle shaking. After immersion for 10 days, the suspension was filtrated and washed with distilled water several times and finally with ethanol. The solid phase was dried at 80°C and its characterization was done by using X-ray diffraction analysis (RINT 2500V, Rigaku, Tokyo, Japan), Fourier transform infrared spectroscopy (SPECTRUM 2000LX, PERKIN ELMER Co., Ltd., Norwalk, CT, USA), magic-angle spinning nuclear magnetic resonance spectroscopy (AM400, Bruker, Germany) and scanning electron microscopic...
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observation (JSM 5400LV, JEOL Co., Ltd., Tokyo, Japan). Analysis of the filtrate was also done on pH and concentration of Ca, F and P. The pH measurement was done by using glass electrode equipped with a pH meter which was calibrated at pH 4, 7 and 9. Calcium ion concentration was determined by an atomic absorption spectrometer (Analyst 300, PERKIN ELMER Co., Ltd., Norwalk, CT, USA) at 422.7 nm with C2H2/N2O flame. Phosphate concentration was spectrophotometrically determined at 830 nm using phospho-molybdenum method. (U-best 50, Jasco, Tokyo Japan) Fluoride ion concentration was determined by F selective electrode attached to an ion meter (720A plus, Orion Research, Cambridge, MA) after adding TISAB to the analyzing solution.

RESULTS

Table 1 shows pH and fluoride concentration of the solutions before and after hydrolysis at various initial fluoride concentrations. The initial pH of 0.1 M KH2PO4 solution (solution 1) was 4.53 and it slightly increased up to 5.1 with the highest fluoride concentration (solution 9). On the other hand, pH increased after the hydrolysis in all of the solutions, but it was between 8.57 and 9.14 and no correlation was found among the solutions containing different amounts of fluoride.

Fluoride ion concentration before and after hydrolysis showed that most of fluoride was absorbed during the hydrolysis with solutions 1 and 8 containing initial fluoride of 500 ppm or less. Figure 1 shows variation of final calcium or phosphate concentration with initial fluoride concentration. Below 200 ppm of fluoride concentration, calcium concentration was between 0.08 and 0.09 mmol/L, and above the concentration it decreased with fluoride concentration. On the other hand, phosphate concentration once decreased with increasing in fluoride concentration and then increased again over 200 ppm of fluoride concentration.

Figure 2 shows X-ray diffraction patterns for the hydrolysis product in the solutions with various fluoride concentrations. Final hydrolysis product was mainly octacalcium phosphate (OCP, Ca8H2(PO4)6(2-)(OH)2) and a small amount of apatite (AP) was also formed in the solution containing no fluoride. With increasing fluoride concentration, OCP phase decreased and instead apatite phase increased. Fluoride promoted fluoridated apatite formation and/or transformation of OCP to fluoridated apatite. It was reported that OCP easily transformed into fluoridated apatite in NaF solutions. Even after the hydrolysis for 10 days, 104 peak of calcite was still observed around 2θ of 29° in the solution containing no fluoride. Above 500 ppm of the initial concentration of fluoride, only fluorapatite

| Table 1 Initial and final pH and fluoride concentration of 0.1 mol/L KH2PO4 solutions |
|-----------------|--------|---------|--------|--------|
| Solution        | pH     | F (ppm) |
|                 | Initial| Final   | Initial| Final  |
| 1               | 4.53   | 9.09    | 0      | 0      |
| 2               | 4.45   | 9.04    | 1.2    | 0      |
| 3               | 4.54   | 8.76    | 6.0    | 0      |
| 4               | 4.43   | 8.63    | 20.7   | 0      |
| 5               | 4.47   | 8.58    | 49.0   | 0      |
| 6               | 4.70   | 9.07    | 95.6   | 0      |
| 7               | 4.59   | 8.68    | 204    | 0      |
| 8               | 4.79   | 8.57    | 502    | 0.07   |
| 9               | 5.10   | 9.14    | 1005   | 228    |

![Figure 1 Variation of final Ca or P concentration with initial fluoride concentration.](image1)

![Figure 2 X-ray diffraction patterns for the hydrolysis product in the solutions with various fluoride concentrations. Number in the left side on each curve corresponds to solution in Table 1.](image2)
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was the final product.

Figure 3 shows change in relative intensity of AP(001)/[OCP (020,110) + AP(001)] and the peak intensity of calcite (104) peak with fluoride concentration. The amount of calcite decreased with increasing fluoride concentration and it completely disappeared at the highest concentration of fluoride (1005 ppm). The X-ray diffraction peaks became well separated and had narrower half width at higher fluoride concentration.

Figure 4 shows $^{31}\text{P}$ MAS NMR spectra of the hydrolysis products in the solution with various fluoride concentrations. The spectrum of the product with no fluoride consisted of two peaks with maximum around 3.2 ppm and -0.3 ppm. With increasing fluoride concentration, a peak around -0.3 ppm of OCP decreased and the maximum around 3.2 ppm shifted to lower chemical shift. Iijima et al. reported MAS NMR spectrum of OCP, in which four separated peaks appeared at 3.5, 3, 1.8 and -0.3 ppm. In the spectrum shown in Fig.5, the first three peaks merge into a peak around 3.2 ppm. OCP crystal has 6 different crystallographic sites in its triclinic unit lattice. Four of the six sites have similar environment to hydroxyapatite or fluorapatite. However, the rest of two sites are quite different from the apatite and related to HPO$_4^{2-}$. The ratio corresponded to that of PO$_4^{3-}$ to HPO$_4^{2-}$ in a chemical formula of OCP, Ca$_8$H$_2$(PO$_4$)$_6$(OH)$_2$. Total area of the three peaks at 3.5, 3 and 1.8 ppm is almost twice as the one at -0.3 ppm. The ratio corresponds to the two different sites in the OCP lattice. At higher fluoride concentration, a broad single peak was observed at 2.7 ppm, which corresponded to PO$_4^{3-}$ ion in the apatite lattice. Hydroxyapatite and fluorapatite has only one crystallographic site in the unit lattice and their $^{31}\text{P}$ MAS NMR spectra show a single broad peak around 3 ppm. The results from MAS NMR well agreed to those from X-ray diffraction analysis as already described.

Figure 5 shows FT-IR spectra for the final products in the solutions with various fluoride concentrations. A strong broad absorption and two weak absorption peaks were seen around 1420, 875 and 700 cm$^{-1}$ in the spectrum of calcite. After the hydrolysis in the phosphate solutions, v3 and v4 absorption bands of PO$_4^{3-}$ ion were found in the regions of 1200-900 cm$^{-1}$ and 650-500 cm$^{-1}$, respectively. With KH$_2$PO$_4$ solution containing non-fluoride, the spectra showed existence of OCP as expected from X-ray diffraction analysis. With increasing in fluoride concentration, the spectra also show co-existence of apatite phase and finally coincide with a spectrum of apatite. Absorption band around 1400-1450 cm$^{-1}$, which was assigned to v3 stretching vibration of CO$_3^{2-}$ ion, was also found in the

Figure 3 Change in relative intensity of AP(001)/[OCP (020,110) + AP(001)] and the peak intensity of calcite (104) peak with fluoride concentration.

Figure 4 $^{31}\text{P}$ MAS NMR spectra for the hydrolysis products in the solutions with various initial fluoride concentrations.

Figure 5 FT-IR spectra for the hydrolysis products in the solutions with various fluoride concentrations.
Matsuya S, Udoh K, Nakagawa M, Ishikawa K spectra. This fact suggested that the apatite formed was fluor-carbonated apatite. The band reveals formation of B-type carbonated apatite, in which $\text{PO}_4^{3-}$ ion in the apatite lattice was substituted with $\text{CO}_3^{2-}$ ion.

Figure 6 shows SEM photographs of original calcite and the final products in the solutions with fluoride concentrations of 0, 49 and 1005 ppm. Original calcite powder (a) shows a distorted rectangular shape with several micron in size. The product in the solution containing no fluoride consists of small needle-like and thin plate-like OCP crystals (b). With increasing fluoride concentration, the crystal shape was gradually altered and finally showed a different spherical shape at the highest fluoride concentration of 1005 ppm (d).

**FIGURE 6** SEM photographs of original calcite (a) and the final products in the solutions with fluoride concentrations of 0 (b), 49 (c) and 1005 ppm (d). Bar in the figure shows 5μm

**FIGURE 7** Change in molar ratios of Ca/P and F/Ca in the hydrolysis products with initial fluoride concentrations. The measured amount of fluoride lies on the line up to 500ppm of fluoride, that is, it means that all of the fluoride ions were absorbed by the solid phase. If calcite completely converted into a stoichiometric fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ by absorbing all of the fluoride, F/Ca molar ratio should be 0.2 and the initial fluoride concentration would be 633 ppm. At an initial concentration of fluoride of 1005 ppm, the absorbed fluoride was about 1.2 mM. The solution contained 0.5 g of calcite, which corresponds to 5 mM of Ca. The actual F/Ca ratio was 0.24 after the hydrolysis and it may suggest formation of other phase like CaF$_2$ though it was not confirmed by X-ray diffraction analysis.

Featherstone et al. reported that CO$_3$ content in carbonated apatite could be calculated from the absorbance ratio of $\nu_3$ CO$_3^{2-}$ band at 1415 cm$^{-1}$ and $\nu_4$ PO$_4^{3-}$ band at 575 cm$^{-1}$ ($A_{1415}/A_{575}$) in the FT-IR spectrum according to eq. (1).

$$\text{CO}_3 \text{ content (wt %)} = 16.1 \times (A_{1415}/A_{575}) - 0.2 \quad (1)$$

We also obtained the CO$_3$ content of the final hydrolysis products from the IR spectra according to eq. (1). Figure 8 shows change in CO$_3$ content with initial fluoride concentrations. As unreacted calcite remained with the lower fluoride concentration, the quantitative equation (1) may not be valid for the evaluation of the CO$_3$ content. However, it would be enough for semi-quantitative purpose. The CO$_3$ content was very
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It was reported that incorporation of fluoride and/or CO$_3^{2-}$ into the hydroxyapatite lattice caused a decrease in a-axis and a slight increase in c-axis.\textsuperscript{11,12} Change in the lattice parameter shown in Table 2 agreed with those previous studies.

Thus fluoride addition largely affects the final hydrolysis product of calcite in potassium dihydrogen phosphate solution. However, the exact mechanism is still uncertain and the further study will be needed to understand the detail hydrolysis process under the presence of fluoride.

**CONCLUSION**

Hydrolysis of calcite in 0.1 mol/L KH$_2$PO$_4$ solution was largely affected by the fluoride ion concentration between 0 and 1005 ppm. OCP was a main product of the hydrolysis for 10 days with the non-fluoride solution. With increasing in fluoride concentration in the solution, OCP formed less and fluoridated B-type carbonated apatite phase formed instead. Calcite remained after the hydrolysis at lower fluoride concentration and decreased with fluoride. Fluoride in the solution was completely absorbed in the product after hydrolysis for 10 days except for at the highest fluoride concentration of 1005 ppm. It was concluded that fluoride ion was found to promote fluoridated carbonated apatite formation directly and/or through OCP transformation.

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