HYDROLYSIS OF CALCITE IN POTASSIUM PHOSPHATE SOLUTIONS

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Abstract: Hydrolysis of calcite was investigated in 0.1 mol/L $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ solutions with various pHs between 4.5 and 8.5 at 60°C by means of solution analyses (pH, Ca and P concentrations), X-ray diffraction, Fourier-transformed infrared spectroscopy and scanning electron microscopy. Calcite was mostly hydrolyzed within several days and the final product was octacalcium phosphate (OCP) or apatite phase depending on their initial pHs. OCP was initially formed in the solution with lower pH and it was transformed into apatite phase with increasing in pH. Calcite was directly transformed into apatite in 0.1 mol/L K_2HPO_4 solution with the highest initial pH. These phenomena were probably related to solubility of apatite, OCP and calcite at pH during hydrolysis. FT-IR analysis showed that the apatite phase formed was B-type carbonated apatite, in which CO_3^{2-} ion substituted for PO_4^{3-} ion.

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INTRODUCTION

Calcium carbonate in aragonite form is a main constituent of marine coral, of which skeleton structure is similar to human cancellous bone. The marine coral has been widely used as a bone filler for the deficient part of hard tissue, because it has an open pore structure suitable for penetration of osteoblast to enable a new bone formation and its resorbability.¹ Marine coral can be converted into hydroxyapatite while preserving its porous skeleton structure by hydrothermal treatment in phosphate solution.²⁻⁴ The product is called coralline apatite⁵ and it has been commercially available, for example, as Pro Osteon (Interpore Cross). In the hydrothermal treatment, calcium carbonate reacts with phosphate ion to form carbonated apatite, that is, hydroxyapatite containing carbonate ion in the lattice structure, though the reaction process has not been fully understood so far. There have been only a few studies on hydrolysis of CaCO_3 itself related to carbonated apatite formation. Ames reported that carbonated apatite was formed by phosphate replacement of calcite in alkaline Na_3PO_4 solution.⁶ Later Simpson reported the effect of pH and phosphate concentration on the carbonated apatite formation from calcite and sodium phosphate solution.⁷ Monma and Takahashi reported carbonated apatite formation through the reaction of calcium hydrogen phosphate in the presence of CaCO_3 .⁸ In the present study, hydrolysis of calcite was investigated in potassium phosphate solutions at different initial pH by X-ray diffraction analysis, Fourier transform infrared spectroscopy and scanning electron microscopy.

MATERIALS AND METHODS

Commercially available calcium carbonate, CaCO_3 was used without further purification. X-ray diffraction analysis showed that calcite was the only phase present and no other phase was found. Four kinds of potassium phosphate solutions were used for the experiment, that is, 0.1 mol/L KH_2PO_4 , 0.1 mol/L K_2HPO_4 and their 2:1 and 1:2 mixed solutions. Measurement of pH was done at 60°C by using a pH meter (TOKO TPX-90, Tokyo, Japan) equipped with a glass electrode calibrated at pH 4, 7 and 9. Initial pHs of the solutions was 4.51 (0.1 mol/L KH_2PO_4), 8.44 (0.1 mol/L K_2HPO_4), 6.44 (2:1 mixed solution) and 7.09 (1:2 mixed solution). About two grams of the calcite powder was put in 200 mL of each solution kept at 60°C. The solution was magnetically stirred at about 300 rpm during the reaction. The overall Ca/P ratio in the system is 1 and the amount of P is about 80% in excess with respect to a Ca/P ratio of 1.67 in stoichiometric hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. After appropriate time intervals, 2 mL of the suspension was picked up from the solution and then filtrated through a 0.2 μm -membrane filter. The solid residue was washed with distilled water several times and finally with ethanol then dried at 80°C. Analysis of the filtrate was also done on pH and concentration of Ca, and P. Calcium ion concentration was determined by an atomic absorption spectroscopy with $\text{C}_2\text{H}_2/\text{N}_2\text{O}$ flame (Aanalyst 300, PERKIN ELMER Co., Ltd., Kanagawa, Japan). Phosphate concentration was spectrophotometrically determined at 830nm using phosphomolybdenum method. On the other hand, the dried residue was characterized by using X-ray diffraction (XRD) analysis, Fourier transform

Matsuya S, Udoh K, Nakagawa M, Ishikawa I
infrared (FT-IR) spectroscopy, and scanning electron microscopic (SEM) observation. The XRD patterns of the specimens were recorded with a vertically mounted diffractometer system (RINT 2500V, Rigaku, Tokyo, Japan) using counter-monochromatized $\text{CuK}\alpha$ radiation generated at 40kV and 100mA. The specimens were scanned from 10° to 60° of 2θ in a continuous mode at a scanning rate of $2^\circ/\text{min}$. Lattice parameter of the final product phase was determined by WPPF (whole-powder-pattern fitting) program installed in the work station attached to the XRD equipment. FT-IR spectra were measured with a KBr disc method by using the FT-IR spectrometer (SPECTRUM 2000LX, PERKIN ELMER Co., Ltd., Norwalk, CT, USA). Scanning electron microscope (JSM 5400LV, JEOL Co., Ltd., Tokyo, Japan) was used for the observation of the morphology at an acceleration voltage of 15kV after gold coating.

RESULTS AND DISCUSSION

Figure 1 shows change in pH of each phosphate solution with time during hydrolysis of calcite. A rapid increase in pH from 4.5 to 7 was observed within 1 h after the start of reaction in 0.1mol/L KH_2PO_4 solution. Then pH began to increase rapidly again after 2 h. Thus an increase in pH seemed to occur in two steps. The pH was kept around 9 between 8 h and 50 h and finally tended to decrease down to 8. Similar changes in pH were also observed with the 2:1 and 1:2 solutions with medium initial pH of 6.5 and 7 though the initial rapid increase was not remarkable. With 0.1mol/L K_2HPO_4 solution, which had the highest initial pH of 8.4, pH increased up to 9.4 within 1 h and was kept constant during the hydrolysis.

Figure 1 Change in pH of each phosphate solution with time during hydrolysis of calcite.

a: 0.1mol/L KH_2PO_4 , b: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$,
c: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$, d: 0.1mol/L K_2HPO_4

Figure 2 shows change in P concentration with time during hydrolysis in the phosphate solutions.

With 0.1mol/L KH_2PO_4 solution, which had the lowest pH, P concentration rapidly decreased within 30 min. The initial rapid increase in P concentration corresponded to the initial pH decrease in the solution, as shown in Fig.1. With the increase in initial pH of the solutions, the rate of decrease in P concentration became smaller. The final P concentration decreased with the decrease in initial pH of the solution. This fact suggests that the amount of P absorbed in calcite was larger in the solution with lower initial pH. This is caused by the difference in final product in those solutions, as described later.

Figure 2 Change in P concentration with time during hydrolysis in the phosphate solutions.

a: 0.1mol/L KH_2PO_4 , b: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$,
c: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$, d: 0.1mol/L K_2HPO_4

Figure 3 shows change in Ca concentration with time during hydrolysis in the phosphate solutions. Calcium concentration showed maximum between 3 and 5 ppm within 30 min and then gradually decreased down to 0.1 - 0.4 ppm in the phosphate solutions except for in 0.1mol/L K_2HPO_4 solution. With the K_2HPO_4 solution, Ca concentration slightly increased up to about 0.4 ppm and was kept below 0.3 ppm through the whole reaction.

Figure 3 Change in Ca concentration with time during hydrolysis in the phosphate solutions.

a: 0.1mol/L KH_2PO_4 , b: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$,
c: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$, d: 0.1mol/L K_2HPO_4

Hydrolysis of Calcite in Potassium Phosphate Solutions

Figure 4 shows X-ray diffraction patterns for the hydrolysis products in 0.1 mol/L KH_2PO_4 solution, which had a lowest pH, at various times. A strong peak around 29° was from 104 reflection of the original calcite. Its intensity decreased with time and the peak had almost disappeared after 48 h. Another strong peak around $4-5^\circ$ showed the formation of octacalcium phosphate(OCP). Apatite (AP) phase also formed together with OCP. The peak intensity of OCP showed a maximum after 4 h and then decreased.

Figure 4 X-ray diffraction patterns for the hydrolysis products in 0.1 mol/L KH_2PO_4 solution at different time.

Figure 5 X-ray diffraction patterns for the hydrolysis products in 0.1 mol/L K_2HPO_4 solution at different time.

With decreasing in intensity of OCP, apatite phase increased. This fact suggested that apatite was partly formed through OCP. Figure 5 shows X-ray diffraction patterns for the hydrolysis products in 0.1 mol/L K_2HPO_4 solution, which had a highest initial pH, at various times. OCP formation was not confirmed and apatite was exclusively formed during the hydrolysis. Thus calcite was directly transformed into apatite without OCP formation.

Figure 6 X-ray diffraction patterns for the final hydrolysis products in the phosphate solutions. a: 0.1 mol/L KH_2PO_4 , b: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$, c: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$, d: 0.1 mol/L K_2HPO_4

Figure 6 shows X-ray diffraction patterns for the final hydrolysis products in the phosphate solutions. With the increase in pH of the solutions, that is, the amount of K_2HPO_4 , OCP formed less and apatite predominantly formed as the final product. It was suggested that the two-step increase in pH corresponded to OCP formation and its transformation to apatite. It was also found that a small amount of unreacted calcite tended to remain in the solutions with medium pH range. Calcite completely disappeared in the solutions with the lowest and the highest pH within 4 days. The overall reaction rate seemed to depend on pH of the phosphate solutions. Lattice parameter of hexagonal apatite crystal in the final products was obtained by WPPF and is shown in Table 1.

Table 1 Lattice parameters of hexagonal apatite crystal and their CO_3 content in the final products

Solution	$\text{CO}_3(\%)$	a (Å)	b (Å)
0.1 mol/L KH_2PO_4	1.2	-	-
$\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$	4.6	9.452	6.887
$\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$	8.5	9.439	6.893
0.1 mol/L K_2HPO_4	8.0	9.426	6.897

Figure 7 shows FT-IR spectra for the final hydrolysis products in the phosphate solutions. As found in X-ray diffraction analysis, the FT-IR spectra (a) showed co-existence of OCP and apatite phase in 0.1 mol/L KH_2PO_4 solution with the lowest initial pH. With the increase in pH of the solutions, the spectra showed only the existence of apatite phase.

Figure 7 FT-IR spectra for the final hydrolysis products in the phosphate solutions.

a: 0.1 mol/L KH_2PO_4 , b: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$,
c: $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$, d: 0.1 mol/L K_2HPO_4

Absorption band around $1400\text{--}1450\text{ cm}^{-1}$, which was assigned to ν_3 stretching vibration of CO_3^{2-} ion, was found in the spectra.^{9,10} This fact suggested that the apatite formed was carbonated apatite. The band reveals formation of B-type carbonated apatite, in which CO_3^{2-} ion substituted for PO_4^{3-} ion in the apatite lattice.^{11, 12} Featherstone et al. reported that CO_3 content in carbonated apatite was calculated from the absorbance ratio of CO_3 band at 1415 cm^{-1} (A_{1415}) and the phosphate band at 575 cm^{-1} (A_{575}) in the FT-IR spectrum by the following equation.¹³

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

Table 1 shows the CO_3 content of the final hydrolysis products calculated from the eq.(1). The CO_3 content increased with increasing in pH of the solutions. This is partly due to difference in the formation ratio of OCP to apatite in the final product phase.

Figure 8 shows the relationship between CO_3 content and a-axis parameter in the apatite phase together with the data reported by LeGeros.^{14, 15} A linear relation holds between a-axis and CO_3 content expressed by the following equation.

$$\text{a-axis (\AA)} = 9.44 - 0.006X (\text{CO}_3 \text{ wt\%}) \quad (2)$$

The lattice parameter (a-axis) obtained in the present study also seems to hold the same relation though the values are slightly larger than those. This fact may suggest that K^+ ion substitutes for Ca^{2+} ion in the apatite lattice because the former has a larger ionic radius than the latter. It was reported that substitution of K^+ ion for Ca^{2+} occurred in the hydrolysis of monetite or OCP to form K^+ -containing carbonated apatite.^{16, 17} Further study will be needed to elucidate the effect of the substitution on lattice parameters.

Figure 8 Relationship between CO_3 content and a-axis parameter in the apatite formed.

Figure 9 shows SEM photographs of the products during hydrolysis in 0.1 mol/L KH_2PO_4 and 0.1 mol/L K_2HPO_4 solutions. Original calcite crystal powder shows a distorted cuboid form. With 0.1 mol/L KH_2PO_4 solution, thin plate-like OCP crystals are

Figure 9 SEM photographs of the original calcite powder (a) and the products during hydrolysis in 0.1 mol/L KH_2PO_4 for 1 h (b) and 120 h (d), in 0.1 mol/L K_2HPO_4 for 1 h (c) and 96 h (e), in $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=2/1$ for 144 h (f) and in $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4=1/2$ for 144 h (g). Bars in the figures show $5\mu\text{m}$.

observed after 1 h. The surface of the plate-like crystals became rough after 4 days. OCP was transformed into carbonated apatite with preserving its original outer shape (Fig9 b,d). This means that the carbonated apatite was formed through the topotactical reaction of OCP. On the other hand, with 0.1 mol/L K_2HPO_4 solution, OCP crystals are not observed as anticipated

by the results of XRD and very fine crystals are found through the reaction (Fig9 c,e). From comparison of SEM photographs for the final hydrolysis products in

the phosphate solutions (Fig9 d-g), it was found that the plate-like crystals of OCP disappeared and fine particulate crystals were seen instead with the increase in pH of the solutions.

Solubility curves of calcite, OCP and hydroxyapatite (OHAp) are very helpful to understand the hydrolysis process. Figure 10 shows solubility curves of Ca plotted against pH for the three compounds calculated from their solubility products.¹⁸ Initial pHs of the solutions are also shown by vertical dashed lines in the figure. OHAp is the most stable phase and OCP phase is a pseudostable phase at pH between 3.5 and 9.5 among them. In the hydrolysis process, calcite first dissolved into the solution and Ca^{2+} ion and CO_3^{2-} ion concentration increased. In the most acidic KH_2PO_4 solution with an initial pH of 4.5, Ca^{2+} ion concentration became high due to high solubility of calcite at the pH. As the reaction proceeded, pH of the solution increased up to 6.8 within 30 min. Equilibrium solubility for Ca^{2+} ion was about 600 ppm at the pH (Fig. 10). As simultaneous precipitation of OCP occurred, the actual concentration was increased only up to around 4.5 ppm at 30 min as shown in Fig. 3. OCP solubility is about 8.3 ppm of Ca^{2+} ion and OHAp solubility is about 1.8 ppm. The solution might have been supersaturated with respect to not only OHAp but also OCP and lead pseudostable OCP formation. As the OCP precipitated, Ca^{2+} ion concentration was further decreased after several hours as shown in Fig. 3. OCP would transform gradually into OHAp (carbonated apatite in this case) as a most stable phase with decreasing in Ca^{2+} ion concentration. With the increase in pH of the solutions, dissolution of calcite was limited and Ca^{2+} ion concentration would not increase to supersaturate with respect to OCP. Thus OCP would not form any more in the solution with high pH and calcite was transformed directly into OHAp without formation of OCP. It was reported that OCP was hydrolyzed to form OHAp in the presence of Ca^{2+} ion according to the following reaction.¹⁹

Figure 10 solubility curves of Ca plotted against pH for OHAp, OCP and $CaCO_3$ (Calcite). Vertical dashed lines show the initial pH of the solutions.

a: 0.1 mol/L KH_2PO_4 , b: $KH_2PO_4/K_2HPO_4=2/1$, c: $KH_2PO_4/K_2HPO_4=1/2$, d: 0.1 mol/L K_2HPO_4

This reaction seemed to occur similarly in the case of carbonated apatite formation. Proton evolution by the above reaction caused a decrease in pH observed at the later stage of the hydrolysis in the solution with low initial pH, as shown in Fig.1. Iijima et al. also reported OCP formation favored instead of AP when the speed of Ca^{2+} ion addition was increased in the solution with initial Ca/P ratio between 0.043-0.14.²⁰ They concluded that an appropriate addition speed was necessary to maintain the degree of supersaturation to OCP. The result of the present study well agrees with their observation.

CONCLUSION

Hydrolysis of calcite was investigated in potassium phosphate solutions with various pHs between 4.5 and 8.4. Calcite was mostly hydrolyzed in the solutions within several days and the final product was OCP or apatite phase depending on their initial pHs. OCP was initially formed in the solution with lower pH and it was transformed into apatite phase with increasing in pH. Calcite was directly transformed into apatite in 0.1 mol/L K_2HPO_4 solution with the highest initial pH. This phenomenon was probably related to solubility of apatite, OCP and calcite at pH during hydrolysis. FT-IR analysis showed that the apatite phase formed was B-type carbonated apatite, in which CO_3^{2-} ion substituted for PO_4^{3-} ion.

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