JOURNAL OF MATERIALS SCIENCE 31 (1996) 3263–3269

Hydrolysis of tetracalcium phosphate in H_3PO_4 and KH_2PO_4

S. MATSUYA
Department of Dental Materials Engineering, Faculty of Dentistry, Kyushu University, Fukuoka 812, Japan
S. TAKAGI, L.C. CHOW
Paffenbarger Research Center, American Dental Association Health Foundation, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

The activity product of tetracalcium phosphate (TTCP, $Ca_4(PO_4)_2O$), was determined at 37 °C, and the hydrolysis of TTCP was investigated in 0.01–0.1 $mol\,l^{-1}$ H_3PO_4 and KH_2PO_4 solutions by means of calcium and phosphorus analyses, X-ray diffraction and infrared analysis. The activity product, defined as $K_{sp} = (Ca^{2+})^4\ (PO_4^{3-})^2\ (OH^-)^2$, was 37.36 as pK_{sp}, which was smaller than that previously reported (42.4). TTCP easily hydrolysed to form calcium-deficient apatite (Ca-def OHAp, $Ca_{5-x}(HPO_4)_x(PO_4)_{3-x}(OH)_{1-x}$), or dicalcium phosphate dihydrate (DCPD, $CaHPO_42H_2O$), depending on the initial phosphate concentration. With 0.1 $mol\,l^{-1}$ H_3PO_4, TTCP hydrolysed to form DCPD within several minutes. In 0.025 $mol\,l^{-1}$ H_3PO_4 and 0.1 $mol\,l^{-1}$ KH_2PO_4, TTCP hydrolysed to form Ca-def OHAp through DCPD. In the latter solution, a small amount of octacalcium phosphate (OCP, $Ca_8(H_2PO_4)_2(PO_4)_45H_2O$), was detected as an intermediate product. In 0.025 $mol\,l^{-1}$ KH_2PO_4, TTCP hydrolysed directly to form Ca-def OHAp. In 0.01 $mol\,l^{-1}$ H_3PO_4, hydrolysis of TTCP was not completed, although Ca-def OHAp was only a product. Thus the final product and the degree of hydrolysis depended on the pH and the overall Ca/P ratio in the reaction system. The rate of Ca-def OHAp formation seemed to be controlled by the dissolution rate of TTCP rather than the crystallization rate of the OHAp.

1. Introduction

Calcium phosphate cement, invented by Brown and Chow [1] is a promising material for a hard tissue alternative. The cement powder is usually an equimolar mixture of tetracalcium phosphate (TTCP, $Ca_4(PO_4)_2O$), and dicalcium phosphate (DCPA, $CaHPO_4$). When the powder is mixed with water or a diluted phosphoric acid solution, it hardens to form hydroxyapatite (OHAp, $Ca_5(PO_4)_3OH$), without any by-product. The hardening reaction will occur around pH 8, close to the singular point where the solubilities of TTCP and DCPA are exactly the same. It was reported that the singular point was at approximately pH 7.8 and 25 °C [1]. We found that the reaction proceeded fastest at approximately pH 8, between a pH of 6 and 10, in a 0.15 $mol\,l^{-1}$ KCl solution at 37 °C [2]. There are several studies on apatite formation from a mixture of TTCP and DCPA [3–6]. In those studies, the reaction seemed to depend largely on the dissolution and/or hydrolysis behaviour of both TTCP and DCPA. There are only a few reports on solubility [7, 8] or the solubility product of TTCP [9, 10] and hydrolysis of TTCP itself [11–13]. Monma *et al.* [11] reported that 20% TTCP was hydrolysed in 0.5 $mol\,l^{-1}$ NH_4Cl at pH 6 and 40 °C within 3 h, to form octacalcium phosphate (OCP, $Ca_8(H_2PO_4)_2(PO_4)_45H_2O$). On the other hand, Radin and Ducheyne [12] reported that TTCP was hydrolysed to form poorly crystallized carbonated apatite in a simulated physiological solution buffered to pH 7.4 at 37 °C within 2 days. Xie and Monroe [13] investigated the hydrolysis of TTCP at various constant pH values and in H_3PO_4 at various concentrations. TTCP was completely hydrolysed to non-stoichiometric hydroxyapatite in the pH range 4.5 and 6.0. At pH 3.5, TTCP was converted to DCPA. At higher pH, above 7, as the pH increased, hydrolysis of TTCP was delayed, though the hydrolysis product was OHAp. However, the reaction process was not fully understood. In the present study, we determined the solubility product of TTCP and also investigated the hydrolysis of TTCP in phosphoric acid and potassium hydrogen phosphate solutions.

2. Experimental procedure

2.1. Materials and methods

TTCP was synthesized from a solid-state reaction between $CaHPO_4$ and $CaCO_3$ at 1500 °C for 6 h. Its purity was confirmed by X-ray diffraction; its average

TABLE I Equilibrium constants used for the thermodynamic calculation

Reaction	Equilibrium constant	Log K
$H_3PO_4 \rightarrow H_2PO_4^- + H^+$	$K_1 = (H_2PO_4^-)(H^+)/(H_3PO_4)$	− 2.219
$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	$K_2 = (HPO_4^{2-})(H^+)/(H_2PO_4^-)$	− 7.203
$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$	$K_3 = (PO_4^{3-})(H^+)/(HPO_4^{2-})$	− 11.984
$Ca^{2+} + H_2PO_4^- \rightarrow CaH_2PO_4^+$	$KCH_2P = (CaH_2PO_4^+)/(Ca^{2+})(H_2PO_4^-)$	1.504
$Ca^{2+} + HPO_4^{2-} \rightarrow CaHPO_4$	$KCHP = (CaHPO_4)/(Ca^{2+})(HPO_4^{2-})$	2.646
$Ca^{2+} + PO_4^{3-} \rightarrow CaPO_4^-$	$KCP = (CaPO_4^-)/(Ca^{2+})(PO_4^{3-})$	6.337
$Ca^{2+} + OH^- \rightarrow CaOH^+$	$KCOH = (CaOH^+)/(Ca^{2+})(OH^-)$	1.288
$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$	$KCOH_2 = (Ca(OH)_2)/(Ca^{2+})(OH^-)^2$	2.671
$H_2O \rightarrow H^+ + OH^-$	$KW = (H^+)(OH^-)$	− 13.661

particle size was around 10 μm. For determination of the solubility product of TTCP, 1 g TTCP powder was suspended in 100 ml distilled water at 37 °C and magnetically stirred at around 300 r.p.m. Nitrogen gas was flowed through the solution to eliminate CO_2 in the atmosphere. The solution pH was continuously measured with a glass electrode. At appropriate time intervals, 2 ml solution were extracted and analysed for calcium and phosphate after filtration.

Atomic absorption analysis was used for determination of the calcium concentration in the filtrate, and spectrophotometric analysis was used for phosphate with the molybdenum blue method at 830 nm. For the hydrolysis experiment, the TTCP powder was suspended in H_3PO_4 or KH_2PO_4 solution with concentrations of 0.01–0.1 mol l^{-1} at a powder-to-solution ratio of 2 g/100 ml. The solution was kept at 37 °C with stirring under a nitrogen gas flow. A certain amount of the suspension solution was extracted at appropriate time intervals. The solution was filterd with a membrane filter, and the filtrate was analysed for calcium and phosphate using the same method described above. The solid phase was washed with distilled water several times and with ethanol, then dried in an oven at 37 °C. X-ray diffraction and infrared absorption analyses were performed on the dried solid.

2.2 Calculation of K_{sp} of TTCP

In the case of dissolution of TTCP in the $CaO–H_3PO_4–H_2O$ system, the equilibrium reaction should be considered as shown in Table I. Thermodynamic equilibrium constants for the reaction at 37 °C are also shown in Table I. These values were obtained from those reported by Vereecke and Lemaitre [14]. In Table I, the first three equations show the dissociation of phosphoric acid, and the next five equations represent the formation of soluble complex species; the final equation shows dissociation of water. For the material balance, the following two equations should be satisfied.

$$T_{Ca} = [Ca^{2+}] + [CaH_2PO_4^+] + [CaHPO_4] + [CaPO_4^-] + [CaOH^+] + [Ca(OH)_2] \quad (1)$$

$$T_p = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [CaH_2PO_4^+] + [CaHPO_4] + [CaPO_4^-] \quad (2)$$

where T_{Ca} and T_p are the total concentrations of calcium and phosphorus, respectively, in the solution and square brackets indicate the concentration of the species. Equation 3 is also obtained from the electrical neutrality requirement.

$$2[Ca^{2+}] + [CaH_2PO_4^+] + [CaOH^+] + [H^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [CaPO_4^-] + [OH^-] \quad (3)$$

The solubility product of TTCP is defined as follows [9] :

$$K_{sp} = (Ca^{2+})^4 (PO_4^{3-})^2 (OH^-)^2 \quad (4)$$

where parentheses represent the molar activity of each species, which corresponds to the equilibrium constant of the following reaction;

$$Ca_4(PO_4)_2O + H_2O = 4Ca^{2+} + 2PO_4^{3-} + 2OH^- \quad (5)$$

The activity or concentration of each species in the solution saturated with TTCP was calculated with the BASIC program based on a FORTRAN program reported by Bard and King [15]. When the ionic strength of the solution was high, it was necessary to use the activity coefficient for determination of the concentration. The ionic strength, μ, of a solution and the activity coefficient of an ionic species, γ_i, are determined by the following equations [14]

$$\mu = (1/2)\Sigma C_i Z_i^2 \quad (6)$$

$$-\log \gamma_i = A(T)\, Z_i^2 \mu^{1/2} / [1 + B(T) a_i \mu^{1/2}] \quad (7)$$

where C_i is the concentration of ionic species i, Z_i the valence $A(T)$ and $B(T)$ are constants depending on temperature, T, and a_i is the effective diameter of the hydrated ion, i.

3. Results

Table II shows the concentration of calcium and phosphorus in distilled water equilibrated with TTCP at 37 °C for up to 8 h. The pH of the solution calculated from the concentration was in good agreement with the values observed, within 0.2 pH unit. Prolonged immersion (e.g. 3 days) of TTCP in water resulted in the formation of a trace amount of OHAp, and the pH calculated was lower by 1 pH unit than that observed. Therefore, the solubility product of TTCP defined by Equation 4 was calculated from the analytical calcium

TABLE II Solubility of TTCP in distilled water and its solubility product at 37 °C

Time (h)	Ca (mM)	P (mM)	pH obs.	pH calc.	pK_{sp}
0.08	0.1544	2.795×10^{-2}	9.818	10.017	37.22
0.25	0.1493	2.193×10^{-2}	10.007	10.028	37.41
0.5	0.1936	1.855×10^{-2}	10.094	10.172	36.91
1	0.221	1.159×10^{-2}	10.311	10.258	36.97
1.5	0.2225	8.918×10^{-3}	10.391	10.269	37.16
2	0.2484	6.676×10^{-3}	10.467	10.324	37.18
3	0.2728	4.026×10^{-3}	10.541	10.372	37.42
4	0.2965	2.584×10^{-3}	10.635	10.411	37.65
5	0.3231	2.395×10^{-3}	10.655	10.448	37.56
6	0.3339	3.914×10^{-3}	10.61	10.459	37.09
7	0.3283	1.123×10^{-3}	10.612	10.458	38.18
8	0.3519	2.089×10^{-3}	10.637	10.485	37.53
				av.	37.36 ± 0.35

and phosphate concentration up to 8 h, as shown in Table II, and was found to be 37.36 ± 0.35 as pK_{sp} (= − logK_{sp}). This value seemed to be much higher than the reported value of 42.4 [10]; that is, the solubility of TTCP was higher.

Fig. 1 shows the changes in pH, calcium and phosphorus concentrations with time in 0.1, 0.025, and 0.01 mol l^{-1} H_3PO_4 solutions. With 0.1 mol l^{-1} H_3PO_4, the initial pH of the solution was 1.9, and the pH rapidly increased to 3.5 just after the addition of TTCP. Then the pH gradually increased to 5.5 after 1 day. The concentration of calcium was as high as 23 mol l^{-1} 10 min after the start of the reaction. Then it decreased linearly within 6 h and was kept constant up to 1 day. Rapid decrease in the concentration of phosphorus was also observed within 10 min, and the amount of the decrease reached 53 mol l^{-1}, almost half of the initial phosphorus concentration. The concentration of phosphorus was still continuing to decrease up to 6 h; this corresponded to the change in calcium concentration. With the 0.025 mol l^{-1} H_3PO_4 solution, the initial pH was 2.3 and it rapidly increased up to 5.5, immediately after the addition of TTCP. Then the pH gradually increased and was kept around 6.5 within the first 60 min. The final pH after 1 day was about 10. The concentration of phosphorus rapidly decreased within 5 min to 6 mmol l^{-1}, that is, about one-quarter of the initial phosphorus concentration. The phosphorus concentration was kept around 2 mol l^{-1} from 20–50 min, then it decreased again. The change in calcium concentration with time showed the same tendency as that in the phosphorus concentration. Those changes seemed to correspond to the change in pH. With the 0.01 mol l^{-1} H_3PO_4 solution, the pH of the solution rapidly increased just after the start of the reaction (2.4 to 5.9) and then gradually increased to about 11 within several hours. The concentration of phosphorus also decreased in the fist several minutes and then continued to decrease gradually.

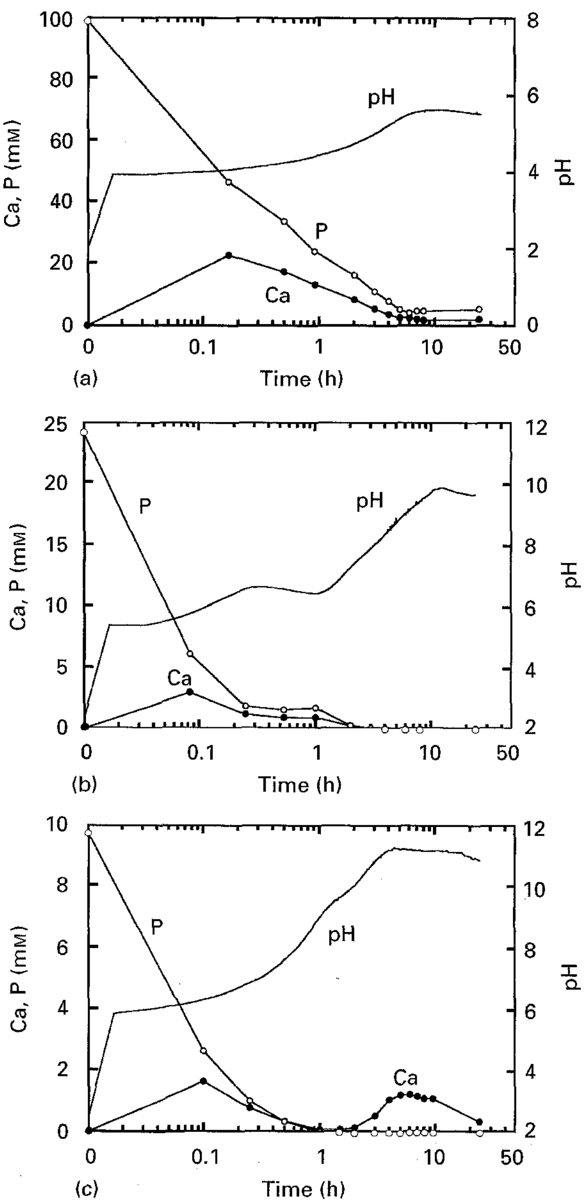

Figure 1 Change in pH, calcium and phosphorus concentrations with time in (a) 0.1 M, (b) 0.025 M and (c) 0.01 M H_3PO_4 solutions.

Fig. 2 shows changes in pH, calcium and phosphorus concentrations with time in 0.1 and 0.025 mol l^{-1} KH_2PO_4 solutions. With the 0.1 mol l^{-1} KH_2PO_4, the initial pH of the solution was 4.55, and it rapidly increased to about 6. Although the pH of the solution gradually increased with time, it was almost around 7. This was due to the buffering action of the phosphate solution. The phosphorus concentration decreased within the first several minutes, as in the phosphoric acid solutions. However, the phosphorus concentration was kept around 60 mol l^{-1}, even after 1 day. On the other hand, the calcium concentration was as low as 0.2 mol l^{-1} throughout the reaction. In the 0.025 mol l^{-1} KH_2PO_4 solution, the initial pH was 4.67, and it increased to 6 immediately after the start of the reaction. The pH gradually increased and reached 12 after 1 day. After a rapid decrease in phosphorus concentration within the first several minutes, the concentration continued to decrease during the reaction. However, the decreasing rate of the phosphorus concentration was not so high as in the 0.025 mol l^{-1} H_3PO_4. This difference occurred because a certain amount of hydrogen phosphate ion must exist to compensate the charge of K^+ ions in the 0.025 mol l^{-1} KH_2PO_4. The calcium concentration was kept low, as in the 0.1 mol l^{-1} KH_2PO_4 solution.

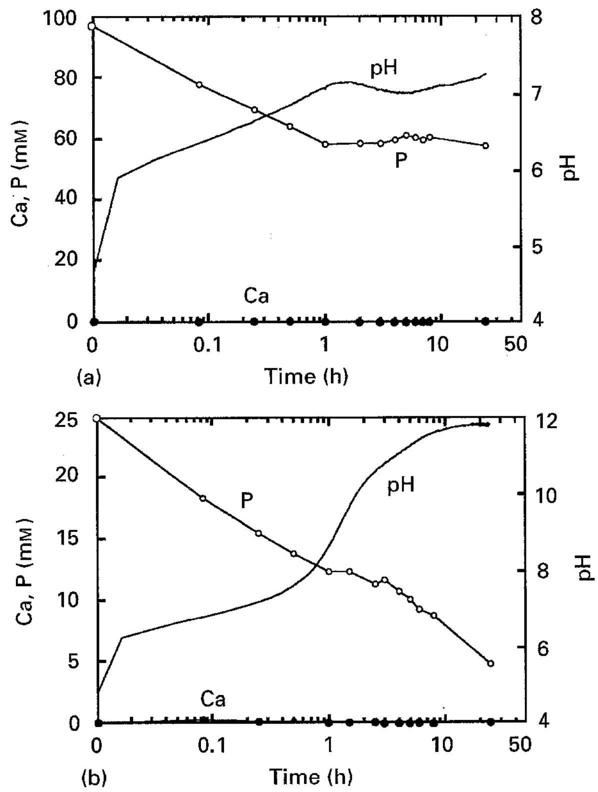

Figure 2 Change in pH, calcium and phosphorus concentrations with time in (a) 0.1 M and (b) 0.025 M KH_2PO_4 solutions.

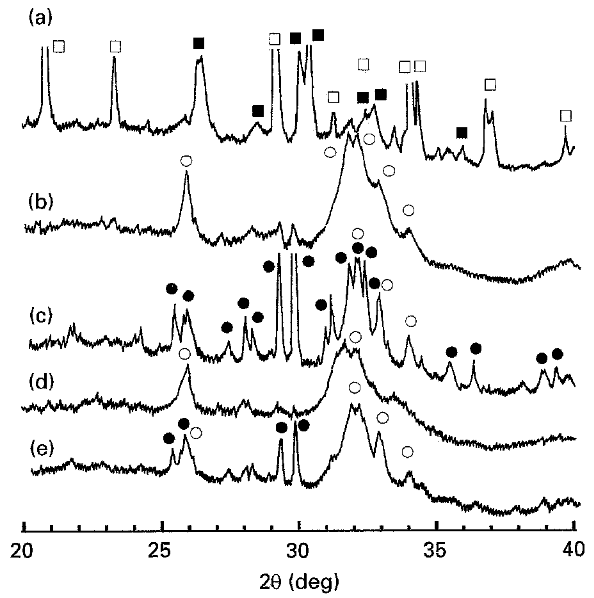

Figure 3 X-ray diffraction patterns for the solid after hydrolysis for 1 day in the H_3PO_4 and KH_2PO_4 solutions. (a) 0.1 M H_3PO_4, (b) 0.025 M H_3PO_4, (c) 0.001 M H_3PO_4, (d) 0.1 M KH_2PO_4, (e) 0.025 M KH_2PO_4. (□) DCPD, (■) DCPA, (○) OHAp, (●) TTCP.

Fig. 3 shows X-ray diffraction patterns for the solid after hydrolysis for 1 day in the H_3PO_4 and KH_2PO_4 solutions. With 0.1 mol l^{-1} H_3PO_4 (Fig. 3a), the main hydrolysis product was DCPD and a small amount of DCPA was also formed. DCPA is formed by dehydration of DCPD in water at 60–90 °C [16] or precipitated at a temperature as high as 100 °C in the solution containing calcium and phosphate ions [17]. It is not clear at present how DCPA was formed in 0.1 mol l^{-1} H_3PO_4. The diffraction peaks were very broad (Fig. 3b–e) showing that the hydrolysis product, OHAp, had poor crystallinity. Fig. 4 shows the change in fractions of solid phases during the hydrolysis obtained from the result of X-ray diffraction analysis. In 0.1 mol l^{-1} H_3PO_4, most of TTCP had already disappeared and DCPD was formed within 5 min. The final product was DCPD, although a small amount of DCPA was also formed, as already described. In 0.025 mol l^{-1} H_3PO_4 (Fig. 4a), DCPD was formed during the initial stage of the hydrolysis. However, it disappeared within 1 h, and TTCP was completely hydrolysed to OHAp in 24 h. In 0.01 mol l^{-1} H_3PO_4 (Fig. 4b), hydrolysis of TTCP was not completed after 24 h. Although it is not shown in the figure, the extent of TTCP hydrolysis was unchanged even after 7 days. In 0.1 mol l^{-1} KH_2PO_4 (Fig. 4c), DCPD was also formed at the beginning of the reaction; as in 0.1 or 0.025 mol l^{-1} H_3PO_4, it quickly disappeared, within a few hours. X-ray diffraction analysis also revealed that a small amount of OCP was formed during hydrolysis in 0.1 mol l^{-1} KH_2PO_4 at an early period of the reaction. However, OCP disappeared as the hydrolysis proceeded and the solution pH increased. DCPD was not formed in 0.025 mol l^{-1} KH_2PO_4 (Fig. 4d), and TTCP was directly transformed into apatite, although the conversion rate was smaller. It took almost 3 days to complete the hydrolysis.

4. Discussion

The reaction process of TTCP depended on the concentration of the phosphate solution. As the powder-to-solution ratio used was 2 g/100 ml, the overall molar ratio of calcium to phosphorus in the reaction system was 1.83, 1.63 and 1.04 in 0.01, 0.025 and 0.1 mol l^{-1} phosphate solutions, respectively. With the exception of 0.1 mol l^{-1} H_3PO_4, the final product of hydrolysis was OHAp, which has a stoichiometric Ca/P ratio of 1.67. As described later, the OHAp is calcium-deficient apatite, which has a non-stoichiometric Ca/P ratio between 1.51 and 1.66. In 0.01 mol l^{-1} H_3PO_4, which has an overall Ca/P ratio of 1.83, phosphorus was not sufficient to form OHAp, and this explains only that conversion of TTCP into OHAp was not completed even after 7 days. On the other hand, in 0.01 mol l^{-1} H_3PO_4, DCPD was the only hydrolysis product, forming instantaneously within several minutes after the start of the reaction. In that reaction system, the Ca/P ratio was 1.04, and this ratio was close to that for DCPD. Moreover, pH was around 4 at an early stage of the hydrolysis when DCPD was formed. In this pH range, DCPD is thermodynamically as stable as OHAp, and this explains the formation of DCPD as the final product. In 0.025 mol l^{-1} H_3PO_4, which has a ratio close to that of OHAp, TTCP was hydrolysed to form OHAp within 1 day, although DCPD was also formed 5 min after the start of reaction. With the KH_2PO_4 solution, OHAp was also formed in the 0.025 mol l^{-1} solution without formation of DCPD. However, in the 0.1 mol l^{-1} KH_2PO_4, solution which has a low Ca/P ratio corresponding to DCPD, TTCP was converted

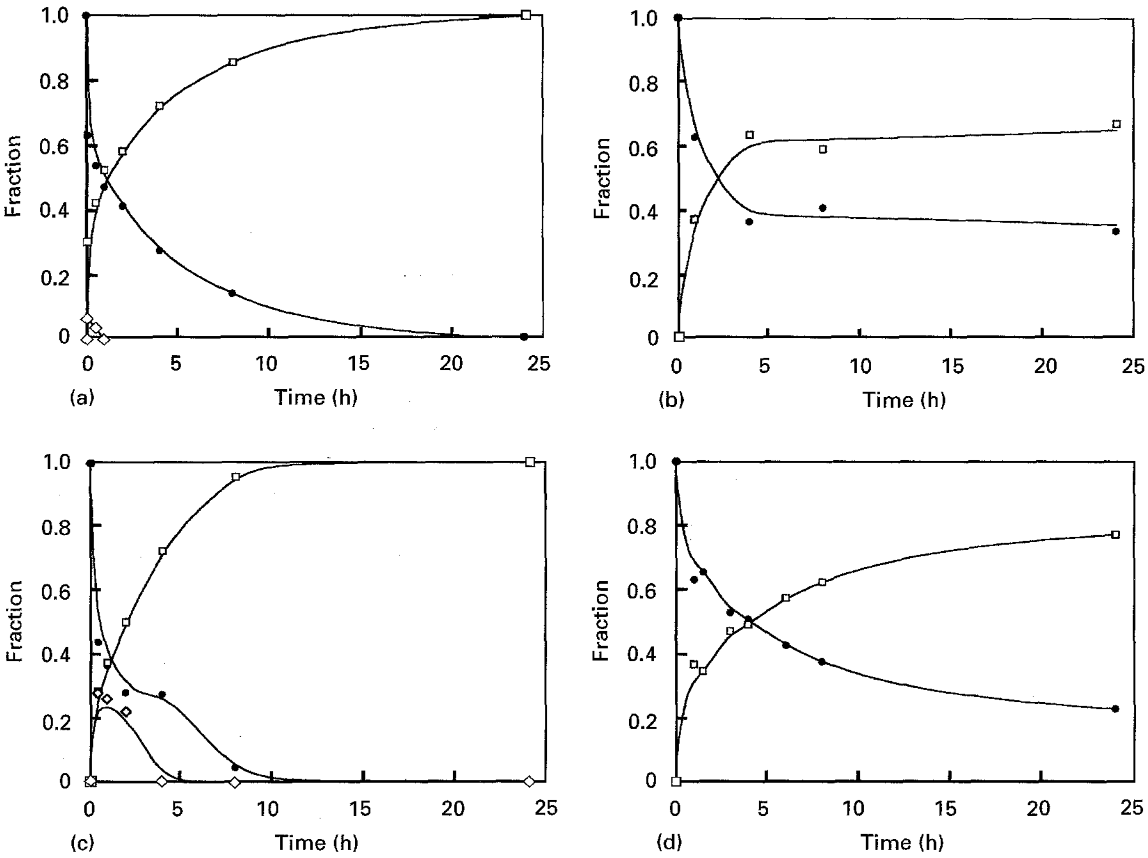

Figure 4 Change in fraction of each phase during hydrolysis in (a) 0.025 M H_3PO_4, (b) 0.01 M H_3PO_4, (c) 0.1 M KH_2PO_4 and (d) 0.025 M KH_2PO_4 solutiuons. (●) TTCP, (□) OHAp, (◇) DCPD.

to OHAp via DCPD. Fulmer *et al.* [18] reported that calcium-deficient OHAp was formed via DCPD in the reaction between monocalcium phosphate monohydrate (MCPM), TTCP and $Ca(OH)_2$ with various mixing ratios. In their study, DCPD was formed in the first 15 min, even though the solution pH was already approximately 7, where DCPD was not a stable phase. They concluded that the formation of DCPD was favoured kinetically. This conclusion was also reflected in the present study. Thus, the initial rapid decrease in phosphorus concentration was mainly caused by formation of DCPD, as shown in Figs. 1a, b and 2a. Fulmer and Brown [6] investigated the reaction between TTCP and DCPA in 0.01 and 0.1 $mol\,l^{-1}$ NaH_2PO_4 and Na_2HPO_4 solution. DCPD was formed in the NaH_2PO_4 solution and OHAp was formed via DCPD in Na_2HPO_4. As DCPA is an acidic phosphate, the pH of the solution did not become high enough for OHAp to form and DCPD formation was favoured. However, in the Na_2HPO_4 solution, OHAp was formed through DCPD. As already described, a small amount of OCP was also formed in 0.1 $mol\,l^{-1}$ KH_2PO_4 at the early stage of the reaction. Tung *et al.* [19] reported that OCP was formed between pH 6.2 and 7.4 by the hydrolysis of DCPD. The hydrolysis in 0.1 $mol\,l^{-1}$ KH_2PO_4 proceeded at a pH of approximately 7. Moreover, as shown in Fig. 3c, the DCPD which formed at the beginning of the reaction, disappeared, while the fraction of TTCP reacted was not changed even after 2–4 h reaction time. This fact suggested that OCP would form by the hydrolysis of DCPD.

Fig. 5 shows the degrees of supersaturation (SS) and undersaturation (US) for the solution with respect to OHAp and TTCP, respectively, during the hydrolysis in 0.025 $mol\,l^{-1}$ H_3PO_4, 0.025 and 0.1 $mol\,l^{-1}$ KH_2PO_4. SS and US were defined as follows: $SS = [(Ca^{2+})^5(PO_4^{3-})^3(OH^-)]/K_{sp}(OHAp)$, $US = [(Ca^{2+})^4(PO_4^{3-})^2(OH^-)^2]/K_{sp}(TTCP)$. The activity of each species was calculated as described in the Section 2. The SS determining the rate of crystal growth of OHAp was lower in 0.1 $mol\,l^{-1}$ KH_2PO_4 than in 0.025 $mol\,l^{-1}$ H_3PO_4 or KH_2PO_4, although the hydrolysis rate was greatest in 0.1 $mol\,l^{-1}$ KH_2PO_4. However, US controlling the dissolution rate of TTCP was lowest during the hydrolysis in the 0.1 $mol\,l^{-1}$ KH_2PO_4 solution. This fact suggests that the dissolution of TTCP controlled its conversion into OHAp. In fact, the hydrolysis in 0.1 $mol\,l^{-1}$ KH_2PO_4 proceeded at pH levels between 6 and 7.5, at which TTCP still had a relatively high solubility. With the hydrolysis in the 0.025 $mol\,l^{-1}$ H_3PO_4 and KH_2PO_4 solutions, the pH was kept as low as 7 for 1 h, but it tended to increase up to 10 and 11.5. Such a high pH level was unfavourable for the dissolution of TTCP and delayed apatite formation. Another possible explanation for the most rapid conversion of TTCP in 0.1 $mol\,l^{-1}$ KH_2PO_4 was the difference in the hydrolysis path; that is, apatite formation proceeded via DCPD and OCP as intermediates. In fact, TTCP from another source hydrolysed eventually to form a certain amount of OCP. That TTCP was synthesized at a different temperature and had a different particle size. That caused the differences in the dissolution rate of

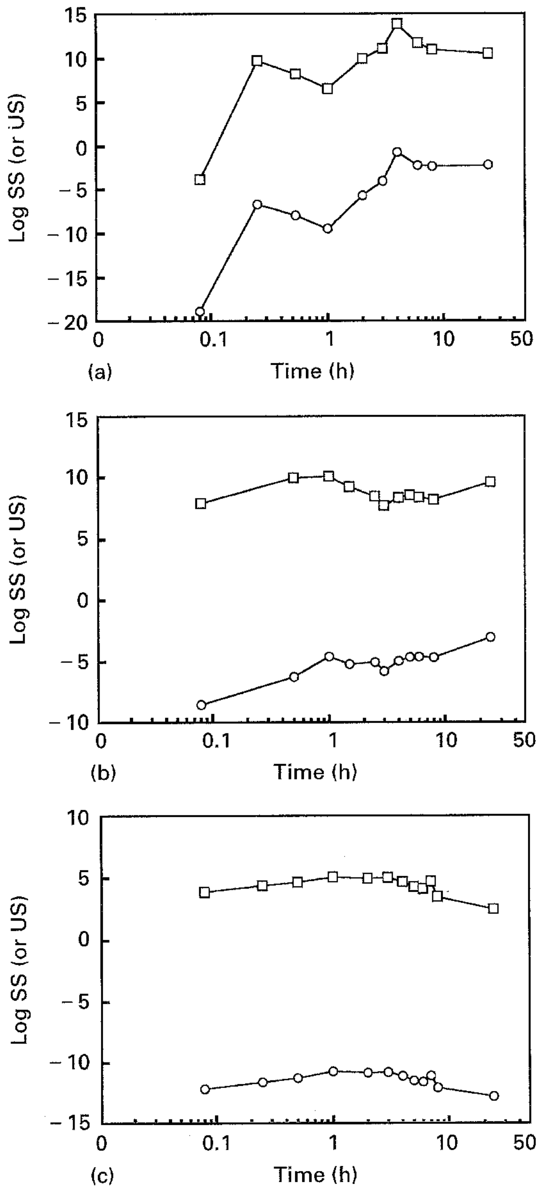

Figure 5 (□) Supersaturation degree (SS) and (○) undersaturation degree (US) during hydrolysis in (a) 0.025 M H_3PO_4, (b) 0.025 M KH_2PO_4 and (c) 0.1 M KH_2PO_4 solutions with respect to (□) OHAp and (○) TTCP.

TTCP and in the hydrolysis process. This is now under investigation.

It is said that calcium-deficient hydroxyapatite (Ca-def OHAp) easily forms in a solution containing calcium and phosphorus ions or is synthesized by the hydrolysis of DCPD or DCPA. Various chemical formulae were proposed for the Ca-def OHAp in which the lattice site of the PO_4^{3-} ion was partly occupied by the HPO_4^{2-} ion and the deficient charge was compensated by the defect in the Ca^{2+} ion or both Ca^{2+} and OH^- ions. An example of the formula is described as $Ca_{5-x}(HPO_4)_x(PO_4)_{3-x}(OH)_{1-x}(0 < x < 1)$ [20]. In any formula of Ca-def OHAp, the Ca/P ratio is usually between 1.5 and 1.67 and it is lower than 1.67 for the stoichiometric ratio in OHAp. The infrared spectrum of the hydrolysis product showed a small peak around 870 cm^{-1}, indicating the existence of HPO_4^{2-} in the apatite structure [21]. Table III shows the Ca/P ratio of the final hydrolysis product of TTCP in 0.025 and 0.1 $mol\,l^{-1}$ KH_2PO_4 and 0.025 $mol\,l^{-1}$ H_3PO_4.

TABLE III Ca/P ratio of the hydrolysis product

Hydrolysis product	Ca/P
0.025 M H_3PO_4 1 day	1.61
0.025 M KH_2PO_4 3 day	1.63
0.025 M KH_2PO_4 7 day	1.66
0.1 M KH_2PO_4 1 day	1.36
0.1 M KH_2PO_4 4 day	1.41
0.1 M KH_2PO_4 7 day	1.51

With the 0.025 $mol\,l^{-1}$ KH_2PO_4 or H_3PO_4 solution, the ratio was between 1.61 and 1.66, close to the stoichiometric ratio. With the 0.1 $mol\,l^{-1}$ KH_2PO_4 solution, the ratio was much lower than the stoichiometric ratio within 4 days; however, it increased to 1.51 with time. Eanes and Meyer [22] investigated the maturation of the calcium phosphate crystals formed by conversion of spontaneously precipitated amorphous calcium phosphate (ACP) at pH 7.4. ACP was converted to OHAp through an OCP-like structure, and the Ca/P ratio of OHAp increased with time. The increase in the Ca/P ratio of the hydrolysis product of TTCP with time also showed the improvement in crystallinity of the Ca-def OHAp. In the 0.1 $mol\,l^{-1}$ KH_2PO_4 solution, a small amount of OCP formed during the hydrolysis. This fact suggested that the hydrolysis in the solution might proceed through the formation of OCP as in the hydrolysis of ACP.

Acknowledgements

This study was supported, in part, by USPHS Grant DE05030 to the American Dental Association Health Foundation from the National Institutes of Health–National Institute of Dental Research and is part of the dental research programme conducted by the National Institute of Standards and Technology in cooperation with the American Dental Association Health Foundation. Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institutes of Health or the American Dental Association Health Foundation or the National Institute of Standards and Technology or that the material or equipment identified is necessarily the best available for the purpose.

References

1. W. E. BROWN and L. C. CHOW, in "Cements Research Progress 1986", edited by P. W. Brown (American Ceramic Society, Westerville, OH, 1987) pp. 351–79.
2. S. MATSUYA, S. TAKAGI and L. C. CHOW, *J. Dent. Res.* **70** (Special Issue) (1991) 308.
3. P. W. BROWN and M. FULMER, *J. Am. Ceram. Soc.* **74** (1991) 934.
4. P. W. BROWN, N. HOCKER and S. HAYLE, *ibid.* **74** (1991) 1848.
5. P. W. BROWN, *ibid.* **75** (1992) 17.
6. M. FULMER and P. W. BROWN, *J. Biomed. Mater. Res.* **27** (1993) 1095.

7. C. P. A. T. KLEIN, J. M. A. DE BLIECK-HOGERVORST, J. G. C. WOLKE and K. DE GROOT, *Biomater.* **11** (1990) 509.
8. P. DUCHEYNE, S. R. RADIN and L. KING, *J. Biomed. Mater. Res.* **27** (1993) 25.
9. L. C. CHOW and W. E. BROWN, *J. Dent. Res.* **54** (Special Issue A) (1975) 74.
10. L. C. CHOW, *J. Ceram. Soc. Jpn* **99** (1991) 954.
11. H. MONMA, M. GOTO, H. NAKAJIMA and H. HASHIMOTO, *Gypsum Lime* **202** (1986) 151.
12. S. R. RADIN and P. DUCHEYNE, *J. Biomed. Mater. Res.* **27** (1993) 35.
13. L. XIE and E. A. MONROE, in "Materials Research Symposium Proceedings", Vol. 17, "Specialty Cements with Advanced Properties", edited by B.E. Sheetz *et al.* (Materials Research Society, Pittsburgh, PA, 1990) pp. 25–39.
14. G. VEREECKEA and J. LEMAITRE, *J. Crystal Growth* **104** (1990) 820.
15. A. J. BARD and D. M. KING, *J. Chem. Ed.* **42** (1965) 127.
16. T. OZAWA, T. UJIIE and K. TAMURA, *J. Chem. Soc. Jpn* (1980) 1352.
17. J. C. ELLIOT, "Structure and Chemistry of the Apatites and Other Calcium Orthophosphates", (Elsevier Science, Amsterdam, 1994) pp. 32.
18. M. FULMER, R. I. MARTIN and P. W. BROWN, *J. Mater. Sci. Mater. Med.* **3** (1992) 299.
19. M. S. TUNG, L. C. CHOW and W. E. BROWN, *J. Dent. Res.* **64** (1985) 2.
20. J. C. ELLIOT, "Structure and Chemistry of the Apatites and Other Calcium Orthophosphates", (Elsevier Science, Amsterdam, 1994) pp. 125–7, 149–51.
21. R. Z. LEGEROS, "Calcium Phosphates in Oral Biology and Medicine" (Karger, Basel, 1991) pp. 19–21.
22. E. D. EANES and J. L. MEYER, *Calcif. Tiss. Res.* **23** (1977) 259.

Received 22 December 1994
and accepted 15 December 1995