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Surface modification of monetite in water at 37 °C: characterisation by XPS

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Hydrolysis of dicalcium phosphate $CaHPO_4$ (DCPA) was studied as a function of time, in deionised water at 37 °C, with a high liquid/solid ratio (2500 ml g^{-1}) in order to avoid solubility limits being reached. Analyses of the liquid showed that DCPA dissolution is not congruent. Although the solutions were not saturated as regards the solubility of monetite, dissolution stopped after 4 days and a very thin film, a few tens of Å thick, was formed. Usual bulk analysis methods did not allow the composition of the film to be determined but X-ray photoelectron spectroscopy (XPS) showed that the film was composed of a calcium phosphate, probably apatitic, with an atomic Ca/P ratio close to 1.50. The change of Ca/P with time in solution indicates that two processes occur. The first is DCPA dissolution while the second corresponds to incorporation of part of the Ca ions released by dissolution, at the monetite surface, leading to an apatitic film through a topotactic reaction. Formation of this film, probably in heteroepitaxy with DCPA, explains the low dissolution observed in deionised water.

1 Introduction

Anhydrous dicalcium phosphate (DCPA or monetite, $CaHPO_4$) may be formed in fracture callus[1] and possibly in bone.[2] It is considered, like hydrated dicalcium phosphate (DCPD) and octacalcium phosphate (OCP), as a precursor of apatite formation. After implantation of DCPA, apatite is formed at the surface and promotes osteoblast development.[3] In addition, DCPA is a component of orthopaedic cements based on calcium phosphate.[4–6] Its evolution in aqueous solutions has therefore been the subject of numerous studies showing that the changes require the presence of ions in solution. With NaOH, NaF or NaCl in solution, monetite is quickly transformed into the corresponding apatite (HAP, FAP or ClAP),[7–10] while with CO_3^{2-} ions, carbonated apatite is obtained.[11–13] In a study of DCPA hydrolysis at 37 °C carried out with addition of calcium ions, Ishikawa and Eanes[14] determined the factors affecting nucleation, crystal growth and morphology on the apatite phase formed. Without additional ions, in pure water, DCPA undergoes hydrolysis which is very limited according to some authors, and practically absent according to others.[8]

To clarify the situation, we performed a study of the dissolution of monetite in pure water, at 37 °C, with a high liquid/solid ratio in order to avoid phenomena due to solubility limits. We focused our attention on the composition of the solution as a function of time and studied the solid obtained after hydrolysis, primarily by XPS. This technique was used because it allows the surface composition of samples to be determined to a depth of some tens of Å. The technique detects all elements except hydrogen and helium, which do not have core electrons. It can be applied to various materials: organic, mineral or metallic, conductors or insulators, powders or blocks, and is very convenient to analyse the uppermost surface of calcium phosphate.[15] Here we present results obtained on both solutions and on solids.

2 Materials and methods

Dissolution experiments using DCPA were performed on an analysis grade sample Ref. N° 22411293 (Prolabo).

The initial sample, and those obtained after dissolution experiments, were examined by chemical analysis (determination of calcium content by a compleximetric method using $Na_2(H_2edta)$ in the presence of zinc chloride and determination of orthophosphate content by the vanadomolybdate spectrophotometry method). Samples were also studied by X-ray diffraction (Seiffert diffractometer, Cu-Kα_1) and by IR spectroscopy (FTIR: Perkin-Elmer 1600). Specific surface areas were determined by the single-point Brunauer–Elmmet–Teller technique (BET: Quantasorb) and the morphology of the samples was examined by scanning electron microscopy (SEM: JEOL JSM-6400). The surface composition of the samples before and after dissolution was determined by X-ray photoelectron spectroscopy. Analysis was performed using an Escalab MKII (V.G.) spectrometer, fitted with an Al Kα source (1486.6 eV), and a 3-channeltrons detector, under a vacuum of the order of 10^{-9} Torr. To avoid any degradation under exposure, the X-ray power was limited to 100 W, and the pass-energy fixed at 50 eV. Samples were held in place with double sided adhesive tape. Calibration was made by referencing to aliphatic carbon C 1s ($E_b = 285.0$ eV), which is always present as an impurity in all samples.[16] For each sample, a general spectrum was recorded to identify the elements, and regional spectra recorded around chosen elements to allow their quantitative analysis and the study of their chemical environment. From the integrated intensity of the photoelectron peaks of the chemical elements, and using the Scofield sensitivity coefficients,[17] it was possible to analyse the composition of the samples quantitatively. The accuracy was of the order of 5% in the presence of standards (stoichiometric hydroxyapatite).

The initial sample had an atomic Ca/P ratio of 1.01 ± 0.01 while carbon and nitogen contents were very small, of the order of 0.1%. Its IR spectrum and XRD pattern correspond to those already reported by several authors.[18]

Dissolution experiments were performed by introducing 200 mg of powder into 500 ml of deionised water in a bath at 37 ± 0.1 °C, with stirring at 60 rpm under nitrogen. Samples were withdrawn at different times and filtered through a Millipore membrane (pore size: 0.45 µm). The small sampling volume, (*ca.* 1 ml) allows variations of the global volume during the experiment to be ignored. Calcium and phosphate levels were determined by colorimeteric assays (Technicon) to

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an accuracy of *ca.* 5%. The pH of the solution was monitored throughout.

In another experiment, dissolution was stopped at various times and powdered samples were recovered by filtration on a Millipore membrane (pore size: 0.45 μm), dried under vacuum, and then examined by the various techniques mentioned above, in particular by XPS.

3 Results

As already indicated, after dissolution, both the solution and recovered solid were studied.

3.1 Composition change of solution during dissolution

The amounts of calcium and phosphate ions released into solution were determined and the pH measured as a function of time obtained values are gathered in Table 1(/), from which the Ca/P atomic ratio in solution was calculated. The amount of calcium and phosphate ions released increased rapidly initially before levelling off. The Ca/P ratio in solution decreased with time and reached 0.62 after 7 days; the Ca/P ratio was always <1.00 (value for DCPA).

The variation of pH was also followed with time. A fast initial increase occurred (<15 min) probably due to partial dissolution of monetite leading to an equilibrium between various species in solution. After 15 min, the pH decreased monotonously corresponding to the transformation of HPO_4^{2-} ions to PO_4^{3-}.

3.2 Solid analysis during dissolution

3.2.1 Usual bulk analysis techniques. Powders recovered at various times were examined by chemical analysis (Ca/P atomic ratio), determination of specific surface area, SEM, FTIR and XRD.

Atomic Ca/P ratios are given in Table 2 and were found to increase slightly with time. Nevertheless, this variation is significant, since it is in accord with the solution data. The specific surface area did not change with time and it remained close to 6 $m^2 g^{-1}$. SEM did not reveal any changes in morphology indicating the absence of new phases (Fig. 1).

IR spectroscopy (Fig. 2) also showed no changes after 7 days. There was no evidence for bands corresponding to apatite [PO_4^{3-} groups at 1090, 1047 (ν3) and 962 (ν1) (vibrations), 602 and 572 cm^{-1} (ν4) (deformations); OH^- ions at 3560 cm^{-1}] or of octacalcium phosphate (917 and 862 cm^{-1}).

The XRD pattern of a sample after 7 days of dissolution is shown in Fig. 3 and also indicates the absence of new phases.

In summary, study of the solid by the usual bulk analysis techniques did not reveal any notable changes for DCPA, although changes were observed in solution. Changes in the solid, however, were apparent using XPS.

3.2.2 XPS analysis. The XPS spectrum of the initial sample is shown in Fig. 4. Photoelectron peaks of calcium, phosphorus and oxygen are evident. From the integrated intensities of the Ca 2p, P 2p and O 1s peaks and using Scofield's sensitivity coefficients, quantitative XPS was performed. The Ca/P ratio was refined using an additional factor determined for pure apatite. The correct ratio was obtained by multiplying the raw ratio computed from Scofield's coefficients, by 1.12.[16] Results are given in Table 3 from which it can be seen that the Ca/P atomic ratio at the surface of the solid increased with time from 1.00 to 1.54 after 7 days.

Table 2 Ca/P atomic ratio determined in the DCPA sample and calculated values from solution analysis, as a function of time

t/h	Ca/P (chemical analysis)	Ca/P (calculated)[a]
0	1.01	—
2	1.01	1.01
24	1.02	1.03
72	1.02	1.04
120	1.03	1.05
168	1.04	1.05

[a] Calculation according to solution data.

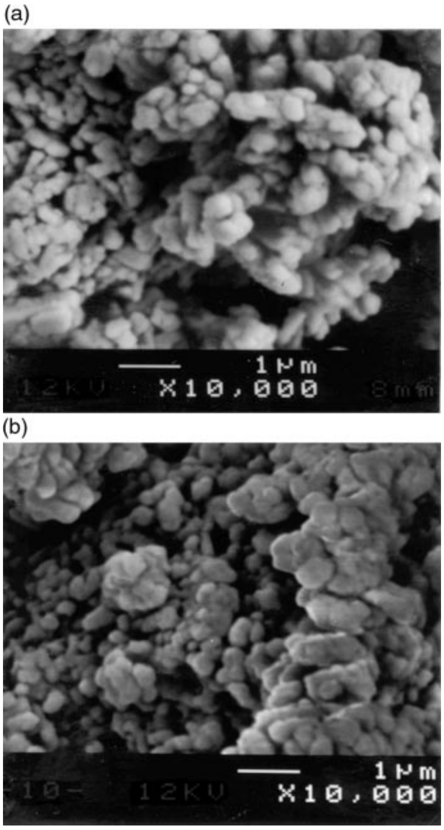

Fig. 1 Observation by SEM of monetite samples; (a) initial sample and (b) after 7 days of hydrolysis.

Table 1 pH and calcium or phosphate levels as a function of time, at 37 °C, during hydrolysis of DCPA in water

t/h	pH	[Ca^{2+}]/mg l^{-1}	[PO_4^{3-}]/mg l^{-1}	Ca/P (in solution)
0	6.97	—	—	—
0.25	7.70	2.56	8.12	0.75
2	7.65	3.67	12.28	0.71
24	7.50	6.68	27.61	0.67
48	7.40	7.80	31.25	0.63
72	7.37	7.99	31.56	0.62
96	7.32	8.35	32.39	0.62
120	7.30	8.52	32.51	0.62
144	7.28	8.53	32.69	0.62
168	7.26	8.56	32.60	0.62

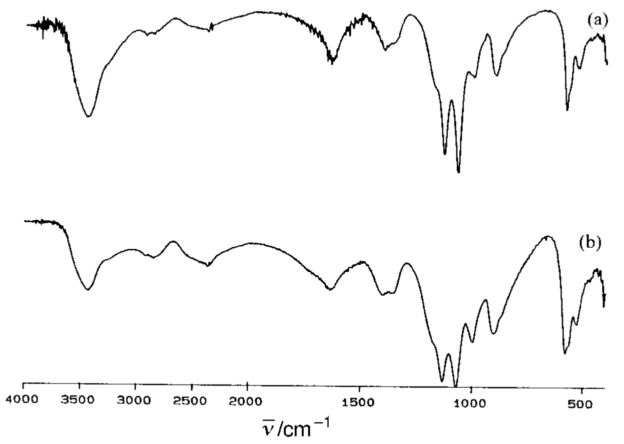

Fig. 2 IR spectra of monetite samples; (a) initial sample and (b) after 7 days of hydrolysis.

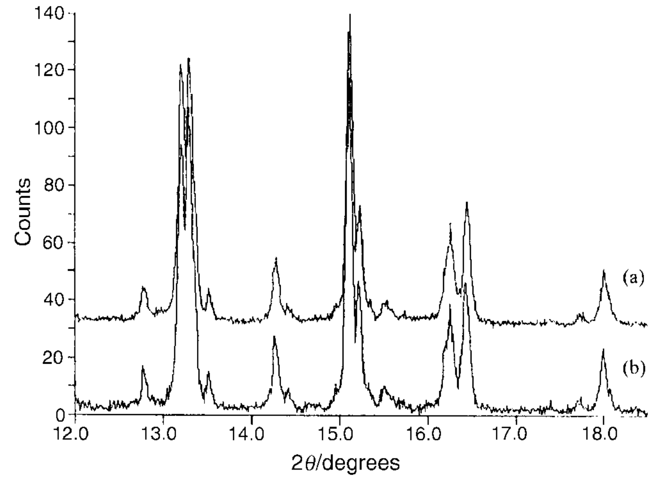

Fig. 3 XRD patterns of monetite samples; (a) initial sample and (b) after 7 days of hydrolysis.

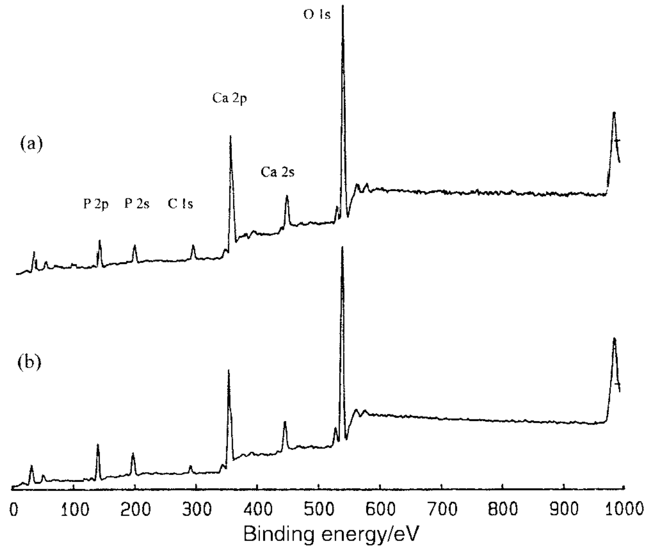

Fig. 4 XPS general spectra of monetite samples; (a) initial sample and (b) after 7 days of hydrolysis.

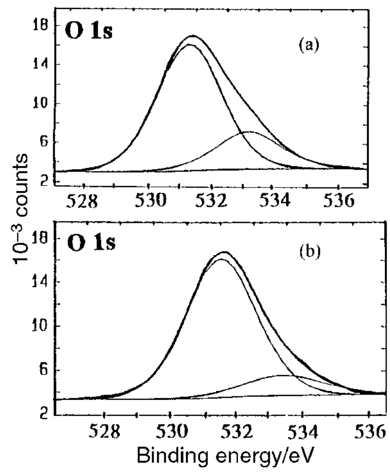

Fig. 5 Decomposition of O 1s peaks in monetite samples; (a) initial sample and (b) after 7 days of hydrolysis.

Furthermore, the O 1s peak is asymmetric both for the initial sample, and after 7 days (Fig. 5). It was decomposed into two components, O_I and O_{II}, the relative weights of which are indicated in Table 3. These components correspond to the two types of oxygen atom which can be distinguished in HPO_4^{2-}: three equivalent oxygen atoms are linked only to phosphorus, whereas one is linked to both P and H. The P–O–H oxygen atom is less charged than the P–O oxygen atoms, and appears at higher binding energy. In DCPA these components are in the ratio 75 : 25, in accord with the formula HPO_4 and have the same FWHM (2.5 eV). After 7 days of dissolution, the O_I/O_{II} ratio changed dramatically reaching 86 : 14. While the first peak (O_I) retained an FWHM of 2.5 eV, the second (O_{II}) became broader. This broadening is probably due to the presence of other tightly bound components such as OH^- and H_2O.

4 Discussion

This study shows that changes occur at the surface of DCPA when in contact with water at 37 °C. While calcium and phosphate ions are released this release decreases with time and stopped after 4 days. The Ca/P atomic ratio also decreases with time and was 0.75 after 15 min of dissolution; it finally reached a value of 0.62. Thus the dissolution of DCPA is not congruent and the results are in accord with previous data.[19,20]

From the amounts of calcium and phosphate released and the pH measured in solution, the level of super-saturation can be computed for DCPA, OCP, TCP and HAP (Table 4).[21,22] The solution is always undersaturated for DCPA which should continue to dissolve, and calcium and phosphate amounts increase, as observed for brushite (DCPD).[23] However dissolution was found to cease from which it can be deduced that a protective film formed at the surface of the DCPA. Super-saturation is low as regards OCP, but is much greater for TCP and especially HAP. As a consequence, the film is probably composed of tricalcium phosphate or hydroxyapatite. XPS analysis of the surface indicated which of the two materials was more likely to have been formed. The Ca/P atomic ratio determined by XPS was 1.54. This ratio is due entirely to the film only if its thickness is greater than the XPS analysis depth, otherwise, it corresponds to an average between the Ca/P ratios of the film and the analysed monetite. The thickness can be estimated by considering the following reactions which give either TCP or HAP [eqns. (1) and (2)].

$$9CaHPO_4+2/3H_2O \rightarrow 2/3Ca_9(PO_4)_5(HPO_4)(OH)+ 3Ca^{2+}+4H_2PO_4^-+HPO_4^{2-} \quad (1)$$

$$10CaHPO_4+6/5H_2O \rightarrow 3/5Ca_{10}(PO_4)_6(OH)_2+4Ca^{2+}+ 24/5H_2PO_4^-+8/5HPO_4^{2-} \quad (2)$$

The quantities of TCP or HAP formed at the surface of the sample were computed from the amounts of calcium and

Table 3 Binding energies (eV) and decomposition of Ca 2p, P 2p and O 1s signals in the initial DCPA sample, and after hydrolysis for 7 days

	Ca 2p/eV	P 2p/eV	O_I/eV P–O (%) [FWHM]	O_{II}/eV P–O–H (%) [FWHM]	Ca/P (Solid)
Initial	347.4	133.6	531.6 (77) [2.5]	533.2 (23) [2.5]	1.00
After 7days under stirring	347.5	133.6	531.4 (86) [2.6]	533.3 (14) [3.0]	1.54

Table 4 Computed species in solution, and relative super-saturation levels for various calcium phosphates during hydrolysis of DCPA in water at 37 °C

t/h	$[Ca^{2+}]$/mM	$[HPO_4^{2-}]$/mM	$[H_2PO_4^-]$/mM	$[CaHPO_4]$/mM	σ_{DCPD}	σ_{DCPA}	σ_{OCP}	σ_{TCP}	σ_{HAP}
0.25	0.062	0.064	0.018	0.0023	−0.86	−0.81	−0.35	−0.24	+2.95
2	0.086	0.094	0.029	0.0045	−0.81	−0.73	−0.15	+0.01	+4.06
24	0.175	0.189	0.081	0.0169	−0.63	−0.48	+0.38	+0.71	+6.83
48	0.186	0.199	0.108	0.0187	−0.61	−0.45	+0.36	+0.64	+6.39
72	0.187	0.197	0.114	0.0185	−0.62	−0.45	+0.33	+0.59	+6.15
96	0.190	0.194	0.126	0.0185	−0.62	−0.45	+0.30	+0.52	+5.82
120	0.192	0.191	0.130	0.0184	−0.62	−0.45	+0.28	+0.49	+5.69
144	0.193	0.189	0.134	0.0182	−0.62	−0.46	+0.26	+0.46	+5.53
168	0.194	0.185	0.138	0.0179	−0.62	−0.46	+0.22	+0.42	+5.38

phosphate released. Since calcium phosphates have a density of close to 3 g cm^{-3}, and the specific surface area of the DCPA used was 6 m^2 g^{-1}, the film thickness can be determined. This would be *ca.* 57 Å for TCP formation, and 44 Å for HAP. These values can be compared to the analysis depth of XPS. This depth depends on the mean free path of the generated electrons. The intensity of the photoelectron peak is related to the mean free path, λ, and z, the depth analysed by eqn. (3).

$$I = K\lambda[1 - \exp(-z/\lambda \sin\theta) \qquad (3)$$

It can be seen that 75% of the signal arises from a depth of up to λ, and 94.1% from a depth of up to 2λ. As a consequence, it is necessary to know the mean free path in order to estimate the analysis depth. The mean free path depends on the kinetic energy of the photoelectron which equals 1140 eV for electrons from the Ca 2p level and 1350 eV for electrons from the P 2p level. For these kinetic energies, the mean free path is roughly 20 Å and the analysis depth will therefore be *ca.* 40 Å. This is less than the film thickness computed for either film composition (TCP or HAP). Consequently, the underlying monetite was not detected by XPS and the Ca/P ratio determined by XPS corresponds to that of the film. Given this, we can assume that the film is composed of TCP. Also, the O 1s spectrum of the sample after 7 days of dissolution showed a broadening of the second component of the O 1s peak. This indicates that HPO_4 is always present and the broadening suggests the existence of other oxygen species such as OH^-. It can be deduced that the TCP formed shows an apatitic structure which is stable under the present experimental conditions.

We can postulate the mechanism of transformation of DCPA into apatite. The surface of the solid appears to play a decisive role in this mechanism since a protective film is formed. Such formation of a hydroxyapatite layer surrounding DCPA particles, decreasing their reactivity, has already been proposed by Martin and Brown[19,20] relating to calcium phosphate cements in which DCPA reacts with tetracalcium phosphate (TTCP) where strong super-saturation can exist around the particles, and induce HAP formation near DCPA. This assumption, however, does not apply here since the experiments were carried out under stirring. Also, Brown suggested heteroepitaxy between monetite and HAP which explains the formation of a continuous adherent film of an apatitic TCP. Slight crystallographic mismatch between a substrate and a film can be tolerated when the film is very thin (some tens of Å) as in our case. On the other hand, for thicker films (as in fast hydrolysis of monetite carried out at high temperature with additional ions) film strengths will be too high to allow epitaxial growth of a continuous film and detatchment will result. The film is then no longer protective, so hydrolysis can reach completion.

Since the value of the Ca/P ratio in solution changes with time, from 0.75 after 15 min to 0.62 after 4 days, it can be deduced that calcium is incorporated at the surface. Such incorporation of calcium into a calcium phosphate was observed by Brown *et al.* in the transformation of OCP into apatite.[24–26] This may result from two reactions: dissolution of OCP and partial incorporation of the calcium released into solution into OCP leading to the formation of apatite *via* a topotactic mechanism.

In the present case DCPA dissolution as well as incorporation of released calcium into DCPA can occur according to eqns. (4) and (5).

$$\alpha CaHPO_4 \rightarrow \alpha Ca^{2+} + \alpha HPO_4{}^{2-} \qquad (4)$$

$$\beta CaHPO_4 + \beta/2Ca^{2+} \rightarrow \beta/6Ca_9(PO_4)_5(HPO_4)(OH) + \beta H^+ \qquad (5)$$

$$(\alpha+\beta)CaHPO_4 + \beta/2Ca^{2+} \rightarrow \beta/6Ca_9(PO_4)_5(HPO_4)(OH) + (\alpha - \beta/2)Ca^{2+} + \alpha HPO_4{}^{2-} + \beta H^+ \qquad (6)$$

The sum of reactions (4) and (5) [eqn. (6)] is related to reaction (1). Moreover, from the Ca/P ratio of the solution, it is possible to determine the extent of each reaction at any moment, and thus, the quantity of monetite dissolved, the quantity of apatite formed, and the thickness of the film. Since the DCPA dissolution rate decreases quickly and the fact that the protective film is very thin (tens of Å), suggests that dissolution is controlled by diffusion of ions through the film.

The assumption of transformation of monetite into apatite by a topotactic mechanism, involving incorporation of calcium ions into the solid phase, explains the decisive role of calcium observed by various authors (*e.g.* Legeros[27] and Ishikawa and Eanes[14]). Addition of this ion allows fast and complete transformation of DCPA into apatite.

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