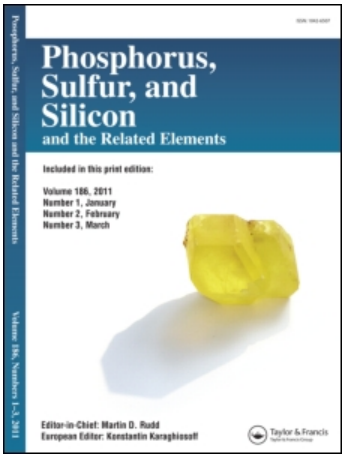

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ACTION OF SULFUR DIOXIDE ON PHOSPHOCALCIC HYDROXYAPATITE AT DIFFERENT TEMPERATURES

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ACTION OF SULFUR DIOXIDE ON PHOSPHOCALCIC HYDROXYAPATITE AT DIFFERENT TEMPERATURES

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Depending on temperature and heating time, the reaction between sulfur dioxide and phosphocalcic hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ gives, either a mixture of calcium sulfate and β-calcium pyrophoshate (β-$Ca_2P_2O_7$), or a mixture of calcium sulfate and a compound of β-tricalcium phosphate structure with the formula $Ca_{21-x}(PO_4)_{14-2x}(SO_4)_{2x}$ with $0 \leq \times \leq 1$, already mentioned in a previous paper. The limiting compound $Ca_{20}(PO_4)_{12}(SO_4)_2$ called calcium phosphosufate (CPS), corresponding to $x = 1$, is obtained with appropriate conditions of heating temperature, heating time, flow of sulfur dioxide, which are specified.

Selon la température et la durée du chauffage, la réaction entre le dioxyde de soufre et l'hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ donne, soit un mélange de sulfate de calcium et de pyrophosphate de calcium β (β-$Ca_2P_2O_7$), soit un mélange de sulfate de calcium et d'un composé isomorphe du phosphate tricalcique β déja signalé dans un précedent article et dont la formule est $Ca_{21-x}(PO_4)_{14-2x}(SO_4)_{2x}$ avec $0 \leq x \leq 1$. Le composé limite $Ca_{20}(PO_4)_{12}(SO_4)_2$, appelé phosphosulfate de calcium (CPS) correspond à $x = 1$, est obtenu dans des conditions précises de température, de durée de chauffage et de débit de dioxyde de soufre qui sont précisés.

Key words: Hydroxyapatite; β-tricalcium phosphate; β-pyrophosphate; sufate-ion-containing calcium phosphate; calcium phosphosulfate.

INTRODUCTION

A previous paper[1] dealt with the synthesis and the physico-chemical study of a series of compounds whose general formula is $Ca_{21-x}(PO_4)_{14-2x}(SO_4)_{2x}$ ($0 \leq x \leq 1$) these were prepared by solid state reaction between β-tricalcium phosphate (β-TCP) and calcium sulfate in the air, at temperatures up to 1100°C. Jarcho[2] reported that an hydroxyapatite (HAP) heated at 900°C in the same furnace as $CaSO_4$ (both of the boats are close to each other) gives a compound with a β-TCP-structure similar to a calcium phosphosulfate. $CaSO_4$ is decomposed at 900°C:

$$CaSO_4 \rightarrow SO_3 + CaO$$

SO_3 gives the well known equilibrium $SO_3 \leftrightarrow SO_2 + \frac{1}{2} O_2$. So, hydroxyapatite reacts with the gas mixture ($SO_3 + SO_2 + O_2$) at 900°C.

The purpose of the present investigation is to study the action of sulfur dioxide on hydroxyapatite at different heating temperatures and heating times, to specify the reactions that occur and to determine the conditions of formation of calcium phosphosulfate.

RESULTS AND DISCUSSION

X-ray diffraction results show that a mixture of phases was always observed even after 10 hours of heating at 700 and 800°C (Figures 2 and 3). The nature of the phases and their crystallographic parameters are given in the Tables I and II. After 15 minutes at 900°C, the $CaSO_4$ lines and those of a phase with a β-TCP-structure were present, but the lines of HAP were absent (Table III). After 1 hour at 900°C, only the lines of a single β-TCP-structure phase were present (Figure 4). Lattice parameters $\underline{a}_H$ and $\underline{c}_H$ (in the hexagonal system) of the β-TCP-structure phase increased with the heating time up to a limit value after 1 hour at 900°C. The limit value of $\underline{a}_H$ and $\underline{c}_H$ is the lattice parameters of calcium phosphosulfate[1] (CPS) $Ca_{20}(PO_4)_{12}(SO_4)_2$. Whatever the heating time may be (more than 15 minutes) at 1000–1100°C, X-ray diffraction patterns only show the CPS phase.

In all cases infrared spectra supported the X-ray diffraction results (Figures 5 and 6). After heating for 15 minutes at 900°C (Figure 7a) HAP bands are no longer observed. The intensity of the anhydrous $CaSO_4$ band[10] at 677 cm^{-1} decreased when the heating time was more than 15 minutes, the same observation was made with the 948 and 975 cm^{-1} bands of the PO_4^{3-} groups of β-TCP.[11] After 1 hour at 900°C, the IR spectra only shows bands of the CPS phase (Figure 7c).

Results of the chemical analysis of Ca^{2+}, PO_4^{3-}, $P_2O_7^{4-}$, and SO_4^{2-} of the samples heated at 700°C for 100 hours are shown in Table IV. The Ca/P atomic ratio of the solids remains unchanged and equal to that of the initial HAP. The $SO_4^{2-}/P_2O_7^{4-}$ ionic ratio is 4/3.

The results indicate that SO_2 reacts with HAP as soon as the temperature reaches 700°C to give:

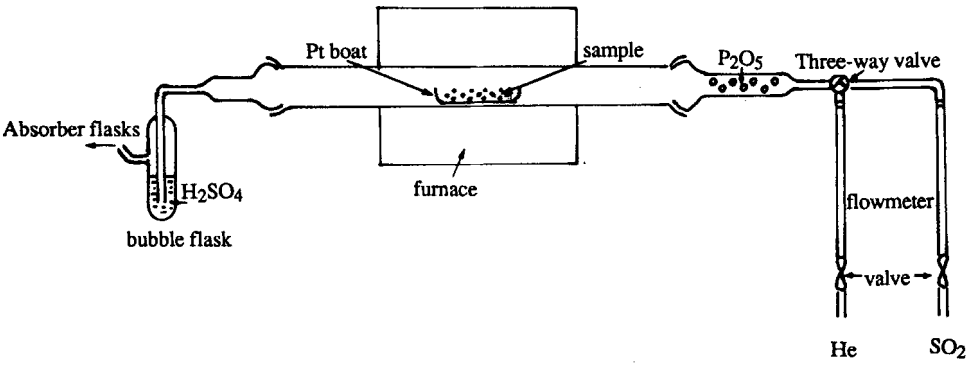

FIGURE 1 Setup used for the heating of HAP under SO_2 (see Experimental Section for discussion).

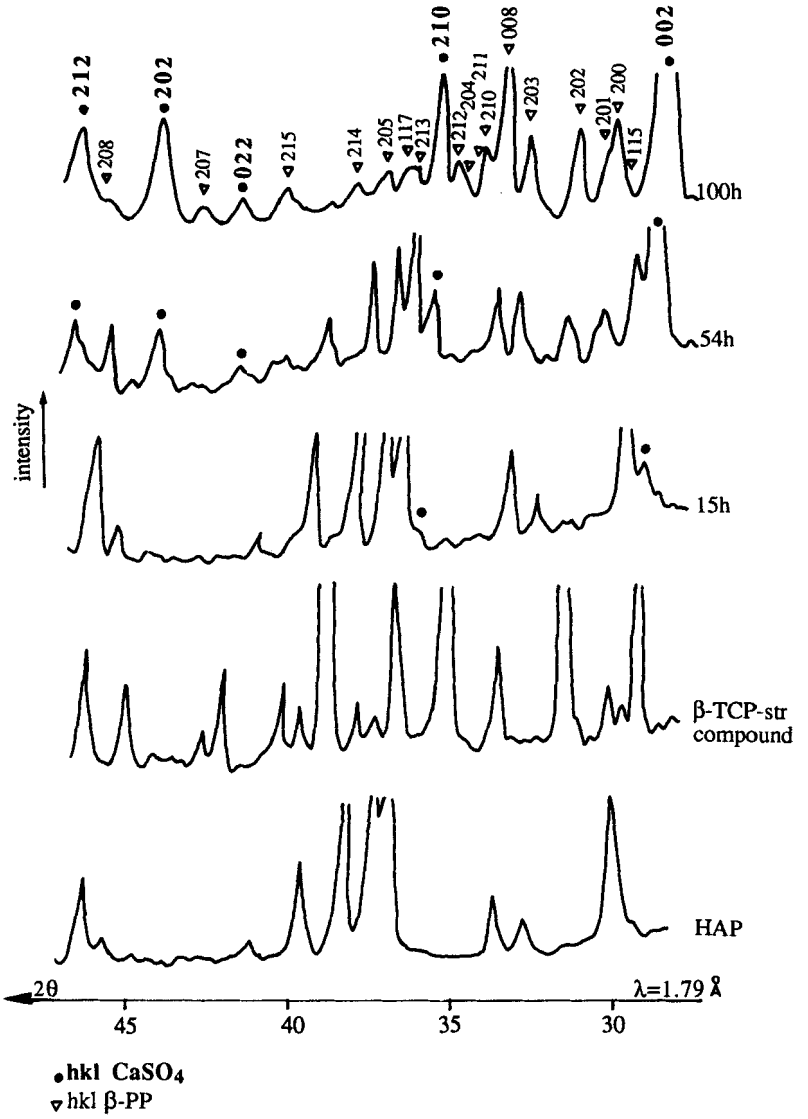

FIGURE 2 X-ray diffraction patterns of solids after heating of HAP under SO_2 to 700°C for different times.

1) A mixture of HAP, β-calcium pyrophosphate (β-PP) and $CaSO_4$ if the reaction lasts less than 100 hours but the action of SO_2 on HAP does not bring enough oxygen to the reaction and we have to consider the equilibrium:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Our experiments were carried out under dynamic conditions, so, the former equilibrium is shifted to the formation of SO_3. To check this point, we performed two

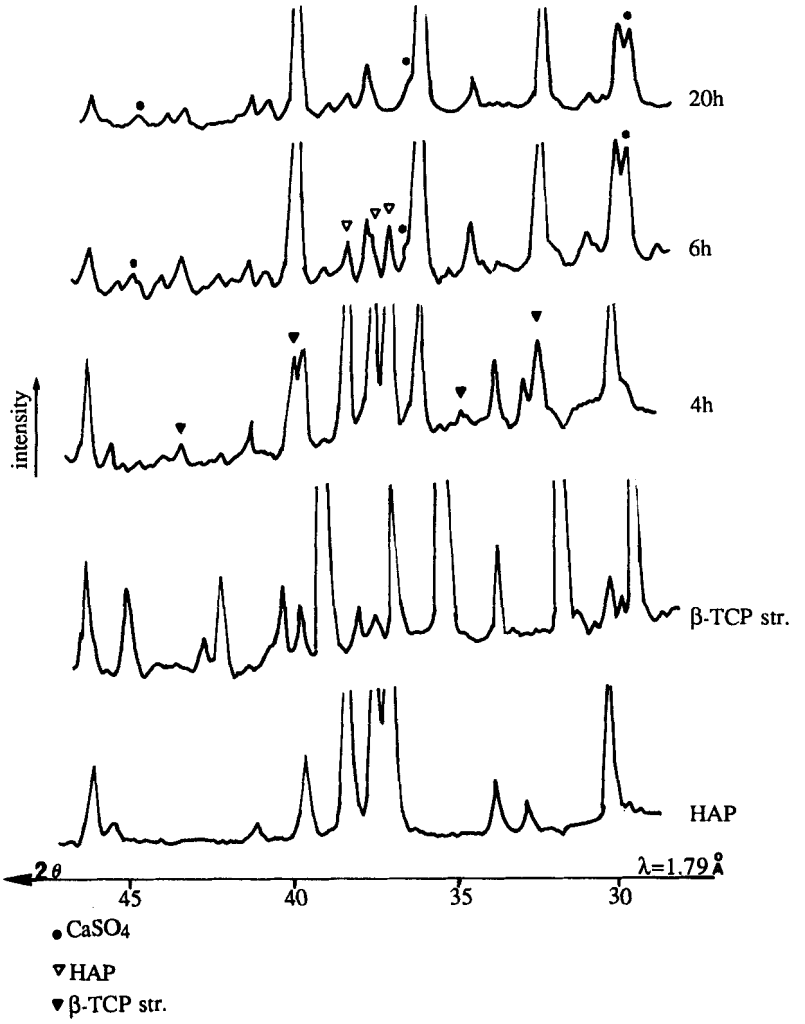

FIGURE 3 X-ray diffraction patterns of solids after heating of HAP under SO_2 to 800°C for different times.

TABLE I

Observed phases and lattice cell parameters of HAP when heated under SO_2 to 700°C

Time hours	Observed phases	HAP* lattice parameters a_H(Å)	c_H(Å)
0	HAP	9.420(1)	6.881(1)
4	HAP + $CaSO_4$	9.421(1)	6.880(1)
15	HAP + $CaSO_4$	9.419(1)	6.879(2)
36	HAP + $CaSO_4$ + β-$Ca_2P_2O_7$	9.419(3)	6.880(2)
54	HAP + $CaSO_4$ + β-$Ca_2P_2O_7$	-	-
84	HAP + $CaSO_4$ + β-$Ca_2P_2O_7$	-	-
100	$CaSO_4$ + β-$Ca_2P_2O_7$	-	-
124	$CaSO_4$ + β-$Ca_2P_2O_7$	-	-

* ( ) = standard deviation

TABLE II

Observed phases and lattice parameters of the β-TCP-structure phase obtained when HAP was heated under SO_2 to 800°C

Time (hours)	Observed phases	β-TCP-structure lattice parameters a_H (Å)**	c_H (Å)**
0	HAP - -		
2	HAP + β-TCP-str.*+ $CaSO_4$	-	-
4	HAP + β-TCP-str.+ $CaSO_4$	-	-
6	HAP + β-TCP-str.+ $CaSO_4$	10.445(3)	37.40(2)
10	β-TCP-str.+ $CaSO_4$	10.449(1)	37.41(2)
20	β-TCP-str.+ $CaSO_4$	10.453(2)	37.44(1)
48	β-TCP-str.+ $CaSO_4$	10.457(3)	37.43(1)

* β-TCP-str. = β-TCP-structure phase
** () = standard deviation

TABLE III

Observed phases and lattice parameters of the β-TCP-structure phase when HAP was heated under SO_2 to 900°C

Time	Observed phases	β-TCP-str.* phase lattice parameters a_H (Å)**	c_H (Å)**
0	HAP	-	-
15'	β-TCP-str. + $CaSO_4$	10.452(3)	37.41(2)
30'	β-TCP-str. + $CaSO_4$	10.459(2)	37.43(1)
1 h	β-TCP-str.	10.466(1)	37.45(1)
4 h	β-TCP-str.	10.467(1)	37.45(1)
12 h	β-TCP-str.	10.466(1)	37.45(1)
β-TCP pur		10.441(1)	37.405(7)
CPS***		10.466(2)	37.45(1)

* β-TCP-str.= β-TCP-structure
** ( ) = standard deviation
*** calcium phosphosulfate $Ca_{20}(PO_4)_{12}(SO_4)_2$

reactions *at 700°C*: one between HAP and a mixture of SO_2 (3 $l.h^{-1}$) + O_2 (0.5 $l.h^{-1}$), and the second between HAP and SO_2 alone (3 $l.h^{-1}$). In the first case, after only 2 hours a β-PP and $CaSO_4$ mixture was obtained; in the second case, more than 100 hours were needed to complete the reaction. It seems that traces of oxygen are present in the reaction media, so we can write the following reaction:

$$Ca_{10}(PO_4)_6(OH)_2 + 4xSO_3 \rightarrow (1 - x)Ca_{10}(PO_4)_6(OH)_2 + 3xCa_2P_2O_7 + 4xCaSO_4 + xH_2O$$

2) A mixture of β-PP and $CaSO_4$ in the molor ratio β-PP/$CaSO_4$ = $\frac{3}{4}$, when the

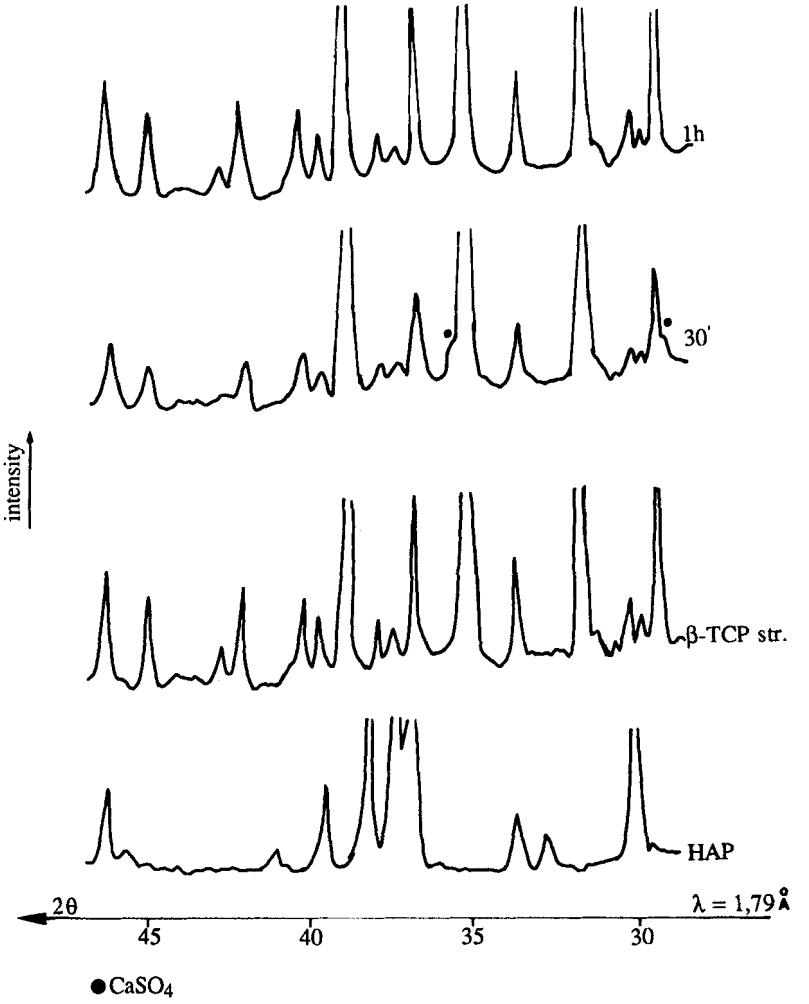

FIGURE 4 X-ray diffraction patterns of solids after heating of HAP under SO_2 to 900°C for different times.

reaction lasts for more than 100 hours, we can write:

$$Ca_{10}(PO_4)_6(OH)_2 + 4SO_3 \rightarrow 3Ca_2P_2O_7 + 4CaSO_4 + H_2O$$

Sulfur is oxidized and phosphorus keeps its initial oxidation state.

At 800°C, HAP, $CaSO_4$ and the β-TCP-structure phase were observed by X-ray diffraction and IR when the heating time was less than 10 hours. When it was more than 10 hours, HAP disappeared, the $CaSO_4$ IR bands diminish in intensity and the β-TCP-structure phase lattice parameter values tended forward those of the CPS.

At 900°C, X-ray diffraction and IR reveal $CaSO_4$ and the β-TCP-structure phase when the heating time was less than 1 hour. When it was more than 1 hour, only the β-TCP-structure phase was observed and its lattice parameters are those of the

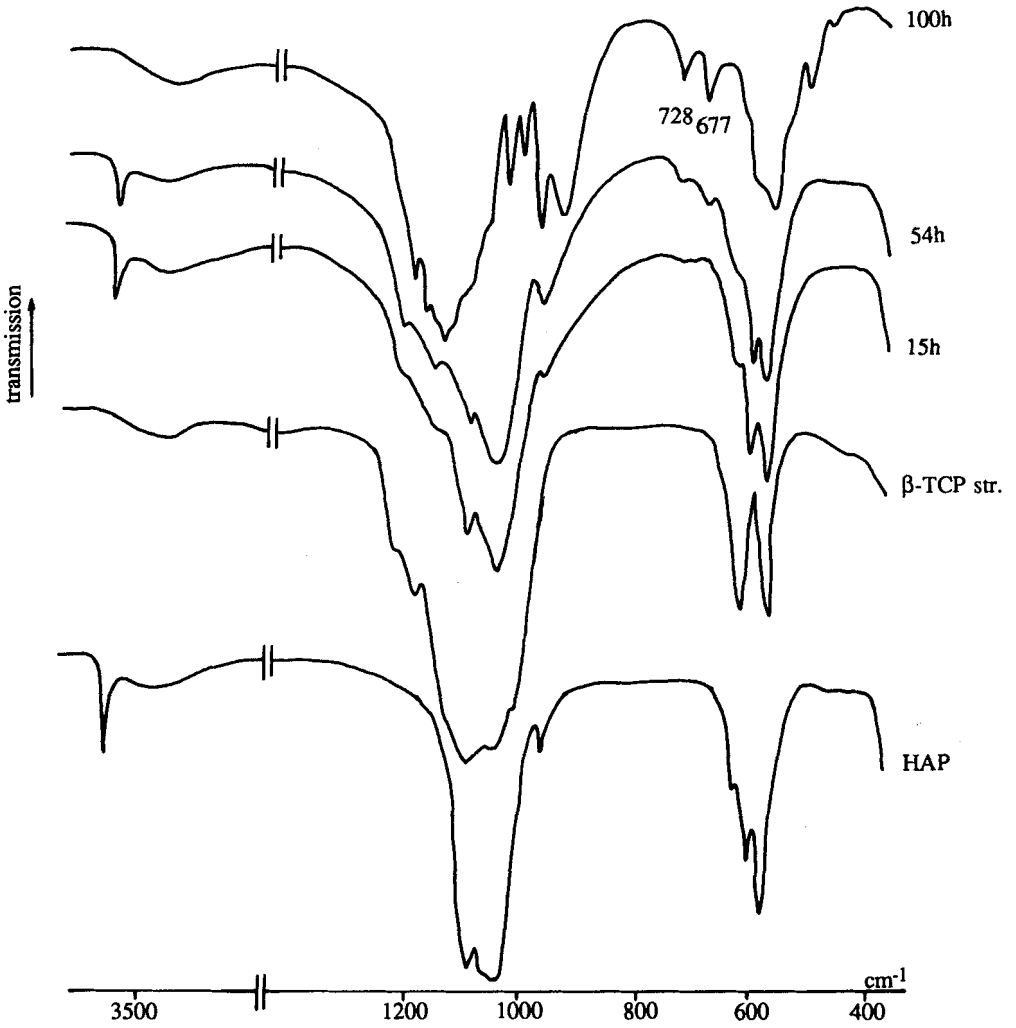

FIGURE 5 Infrared absorption spectra of solids after heating of HAP under SO_2 to 700°C for different times.

CPS. When the temperature was 1000 or 1100°C, CPS was obtained after less than 15 minutes of heating.

We can conclude that HAP reacts with SO_3 to give, at 800–900°C, $CaSO_4$ + β-TCP-structure phase; then $CaSO_4$ and the β-TCP-structure phase react together to give calcium phosphosulfate (CPS): $Ca_{20}(PO_4)_{12}(SO_4)_2$.

It may be asked if the formation of the β-TCP-structure phase at 800–900°C is not preceded by the formation of a poorly crystallized and very reactive calcium pyrophosphate although it does not appear on the X-ray diffraction patterns or IR spectra. We showed elsewhere[12] that calcium pyrophosphate reacts easily with $CaSO_4$. To confirm this point, we treated HAP with SO_2 at 750°C for 15 and 24 hours. IR spectrography and X-ray diffraction patterns actually showed the presence of β-PP after 15 hours (Figures 8 and 9). The presence of β-PP is a necessary step

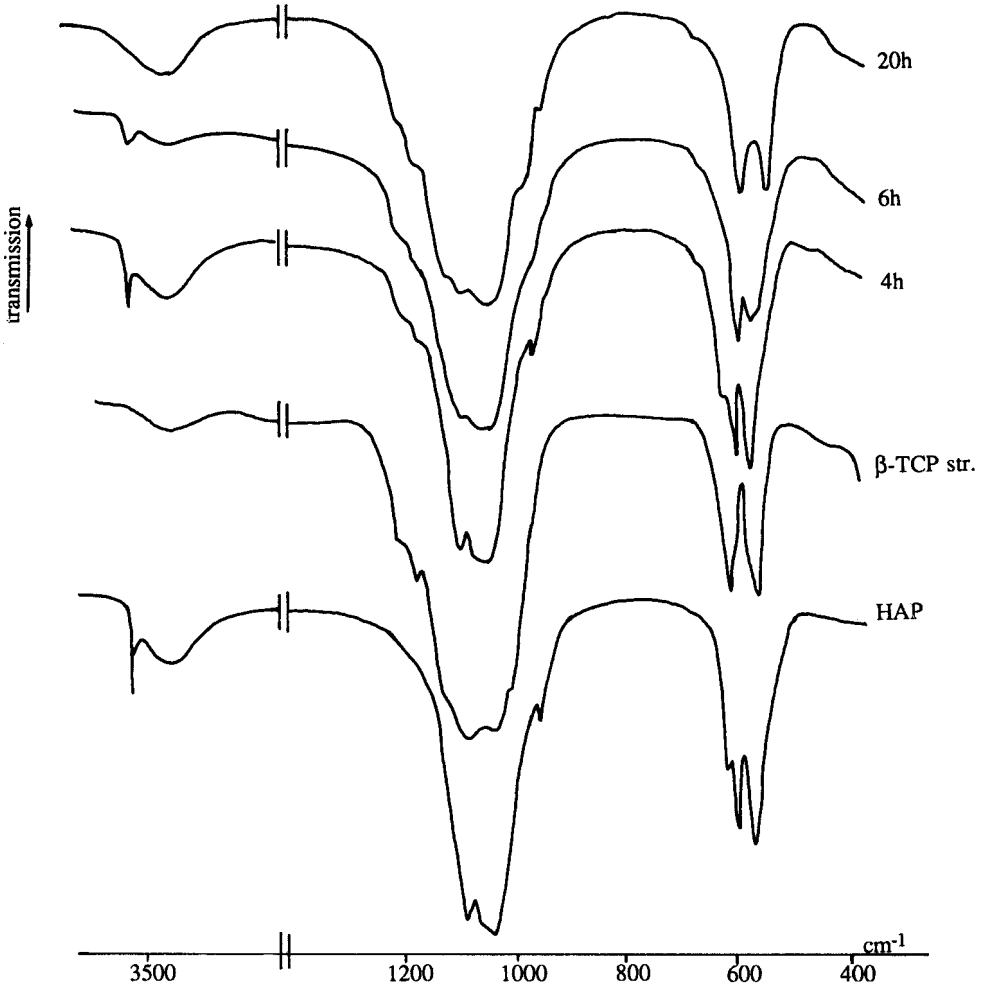

FIGURE 6 Infrared absorption spectra of solids after heating of HAP under SO_2 to 700°C for different times.

in the formation of the β-TCP-structure phase. We can write the following reaction mechanism:

$$Ca_{10}(PO_4)_6(OH)_2 + 4SO_3 \rightarrow 3Ca_2P_2O_7 + 4CaSO_4 + H_2O$$

$$\downarrow$$

$$\frac{3}{7-x}\underset{(\beta\text{-TCP-structure phase})}{Ca_{21-x}(PO_4)_{14-2x}(SO_4)_{2x}} + \frac{7(1-x)}{7-x}CaSO_4 + 3SO_3$$

$$\downarrow$$

$$\frac{1}{2}Ca_{20}(PO_4)_{12}(SO_4)_2$$

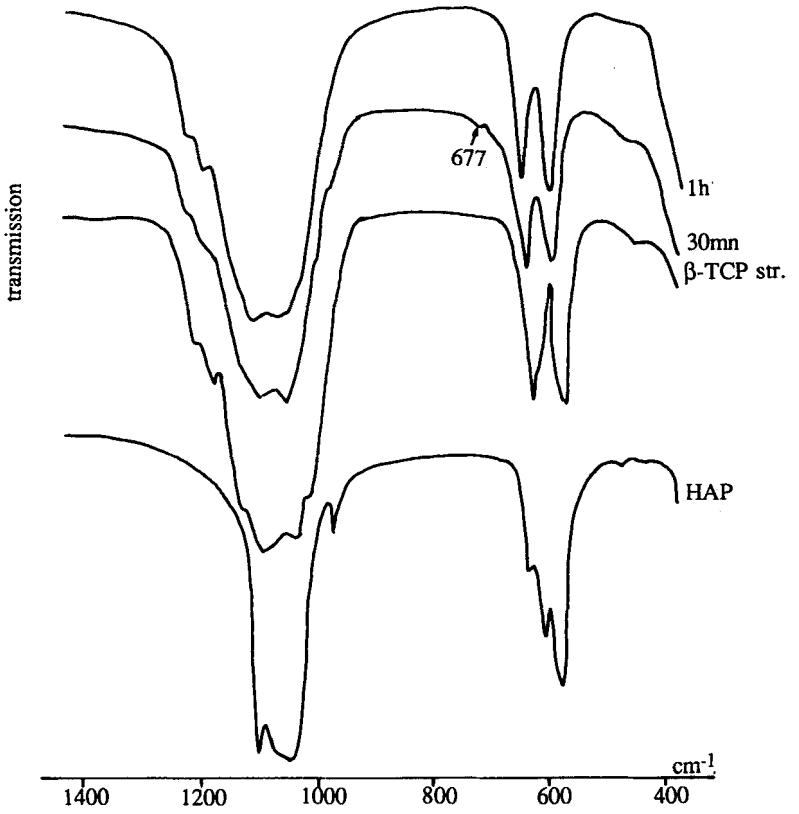

FIGURE 7 Infrared absorption spectra of solids after heating of HAP under SO_2 to 900°C for different times.

TABLE IV

Chemical analysis (% weight) of the sample obtained after 100 hours of heating to 700°C

Ca^{2+} 1	PO_4^{3-} 2	$P_2O_7^{4-}$ 3	SO_4^{2-} 4	1+2+3+4	$SO_4^{2-}/P_2O_7^{4-}$ ionic	Ca /P atom.
30,04	0	39,7	29,1	99,2	1,327 ~4 /3	1,662

that means altogether:

$$Ca_{10}(PO_4)_6(OH)_2 + SO_3 \rightarrow \frac{1}{2} Ca_{20}(PO_4)_{12}(SO_4)_2 + H_2O$$

The reaction between HAP and SO_3 at 900°C allowed us to prepare the series of compounds $Ca_{21-x}(PO_4)_{14-2x}(SO_4)_{2x}$ ($0 \leq x \leq 1$) with the β-TCP-structure phase. The limiting compound ($x = 1$) is the calcium phosphosulfate whose formula is $Ca_{20}(PO_4)_{12}(SO_4)_2$.

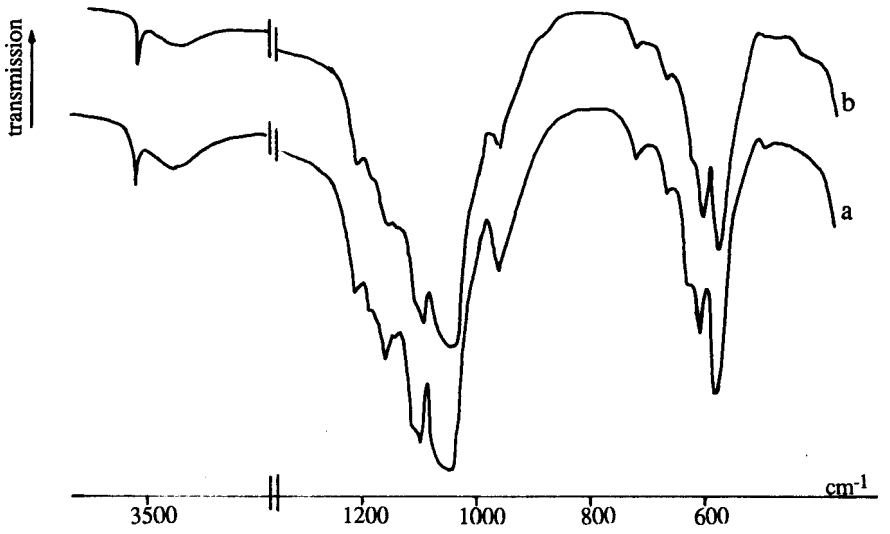

FIGURE 8 Infrared absorption spectra of solids after heating of HAP to 750°C under SO_2 for 15 and 24 hours.

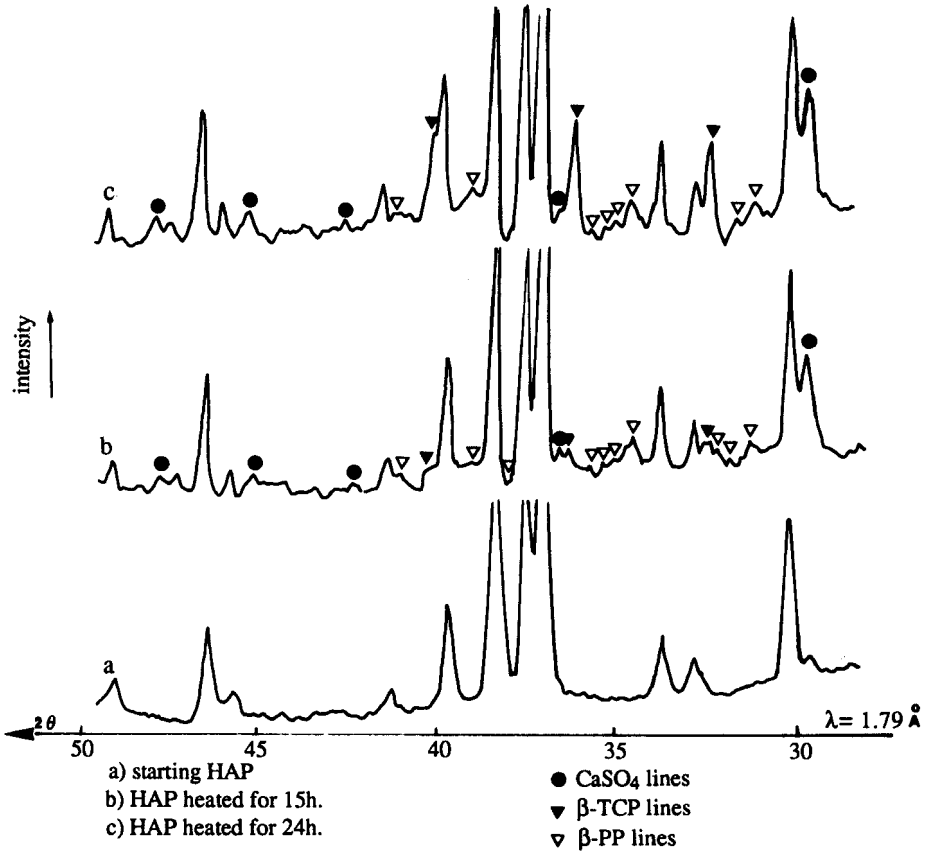

FIGURE 9 X-ray diffraction patterns of solids after heating of HAP to 750°C under SO_2 for 15 and 24 hours.

EXPERIMENTAL

The setup used for the investigation is presented in Figure 1. Sulfur dioxide (H_2O content < 40 ppm) was dried over P_2O_5 before entering the furnace. Hydroxyapatite (HAP) (Ca/P atomic ratio = 1.67) was prepared in the laboratory.[3,4] Its particle size determined by sieving was less than 120 μm. We determined that HAP heated to 900°C in the air did not show the most intense X-ray diffraction line of β-TCP (indexed 02.10 in the hexagonal system). If β-TCP (Ca/P atomic ratio = 1.50) is present as an impurity in HAP powder, it means that the Ca/P ratio of the initial HAP is less than 1.67.

Hydroxyapatite powder was put in a platinum boat and introduced into a furnace at the working temperature (Figure 1). First of all, the furnace was flushed with high-purity helium (flow 3 $l.h^{-1}$). Then sulfur dioxide was introduced (3 $l.h^{-1}$). At the end of the experiment, He flowed again for 15 minutes, finally the sample was air quenched.

This synthesis was studied at 700, 800 and 900°C, some heatings were performed at 1000–1100°C. The heatings lasted from 15 minutes to more than 100 hours, depending on the temperature, in order to study the influence of time and temperature on the nature of the final products.

X-ray diffraction patterns were recorded at room temperature with the cobalt $K_{\alpha 1}$ radiation (λ = 1.78892 Å) and a Seeman-Bohlin camera. Precise Bragg angles of the sample were measured with respect to lines of NaCl used as internal standard.[5] Lattice parameters of HAP were calculated with 10 of the lines (indexed 00.2, 11.2, 30.0, 20.2, 31.0, 22.2, 21.3, 32.1, 41.0 and 00.4) those of the β-TCP structure with 12 of the lines (indexed in the hexagonal system 10.10, 21.4, 30.0, 02.10, 12.8, 22.0, 21.10, 10.16, 40.4, 30.12, 04.8 and 32.7), using a least squares refinement method.

Transmission infrared spectra were recorded with two Perkin-Elmer spectrophotometers: 457 and FTIR 1710, using pellets consisting of 1 mg powder in 300 mg KBr.

The phosphorus content of the orthophosphates was analysed by the colorimetric method described by Gee and Deitz.[6] The relative error on phosphorus determination was about 0.2%. Calcium was determined by complexometry with EDTA in the presence of Zn and eriochrome black T indicator.[7] The relative error was about 0.5%.

Two methods were used to measure to SO_4^{2-} content:

1) a gravimetric one, derived from Morris and Bozalek's method,[8] used when the solids were present as a mixture of phases.

2) a second one, based upon the decomposition of sulfate by thermogravimetry,[9] when the samples were into single phase. The relative error was about 0.7%.

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