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SIMULTANEOUS THERMOGRAVIMETRY AND GAS CHROMATOGRAPHY DURING DECOMPOSITION OF CARBONATE APATITES

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SUMMARY

Thermal decomposition of various samples of synthetic B type carbonate apatite is followed by simultaneous TG/GC technique. GC recordings were performed repeatedly during heating. The results have confirmed the presence of two kinds of carbonate in the lattice. Direct CO_3-apatites release N_2 on heating while apatites prepared in acetate medium show CO and H_2 beside H_2O and CO_2. Heating biological apatites (B.A.) in He atmosphere induces also departure of N_2, CO and CH_4. These findings suggest that organic molecules may be incorporated inside the apatitic structure of B.A.

INTRODUCTION

Carbonate apatites derive from fluorapatite $Ca_{10}(PO_4)_6F_2$ or hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ by substituing CO_3 for PO_4 or X (X = F or OH). The product is called "type A" when CO_3 anions are located along the helicoïdal axis in the X positions. On the other hand, the apatite is called a "type B" one when CO_3 substitutes for PO_4. Biological apatites which are the inorganic phases of calcified tissues (enamel, dentine and bone) are thought to belong to "type B" CO_3-apatites. Hence considerable effort has been devoted to study the later type of apatites. Nevertheless, in spite of their multiplicity, there is no agreement on the mode of replacement for the PO_4 anions. Thus three substitution mechanisms have been proposed :

i../ CO_3 for PO_4 with the occurrence of vacancies in anion and cation sites (1,2).

ii./ CO_3F for PO_4 (3).

iii/ a double substitution (CO_3 for PO_4 and CO_3F for PO_4) with the occurrence of one vacancy in Ca sites and another one in the X sites (4,5). This later substitution mode leads to assignment of the following formula to the CO_3-containing apatites :

$$Ca_{10-x+u}\,(PO_4)_{6-x}\,(CO_3)_{x-u}\,(CO_3F)_u\,F_{2-x+u}$$

where x is total PO_4 substituted and u is PO_4 substituted as CO_3F.

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Experimental methods used up to now in studying carbonate apatites are often based on spectroscopy and chemical analyses. Thermogravimetry has been used occasionally while chromatography has never been applied to these materials. The purpose of this paper is to show that simultaneous TG/GC technique can also give much information that couldn't be obtained by using other analytical techniques, and consequently contribute to better understanding of the substitution modes of CO_3 for PO_4 in B-type apatites.

SAMPLE PREPARATION

Apatite samples were prepared by the Legeros method (6) using Labarthe's modification (2). This method consists of dropping at the rate of about 15 ml per minute one of two solutions into the other one. The first of the solutions (A solution) is a Ca solution (Calcium is introduced as nitrate or acetate), and the second (B solution) is a diammonium phosphate/ammonium carbonate solution. Mixing these solutions leads to hydroxycarbonate-apatite sample. Fluor carbonate-apatite is precipitated when ammonium fluoride is previously added to B solution. The precipitates were dried and their purity was checked by X-ray diffraction and IR spectroscopy. Nevertheless it has been shown (2,4) that the amount of incorporated CO_3 depends not only on Ca/P ratio in B solution but also on the mixing procedure. When precipitation occurs in phosphate/Carbonate medium (dropping A into B solution) some properties of the apatite are slightly different from those of the product obtained by dropping B into A solution. Hence these two preparation methods have been discerned by calling them "direct" and "reverse" method respectively. As seen later, simultaneous TG/GC technique shows many more differences between the samples prepared by using either one or the other of these two precipitation methods.

EXPERIMENTAL PROCEDURE

TG/GC device

Weight losses were recorded using a B60 SETARAM thermodbalance mounted over a furnace, the temperature of which may be raised at 150 degrees/h or 300 degrees/h. The sample (about 100 mg) is placed in an alumina crucible which is suspended from the balance beam inside a narrow alumina tube (12 mm inside diameter). Temperature of the sample is recorded with a Pt/Pt-Rh thermocouple which is located a few millimeters under the bottom of the crucible. Helium (or argon) gas is introduced into the apparatus at the bottom and the top, and the resulting flow goes through a drying tube into an INTERSMAT double column GC analyser. The ascending flow which carries the evolved gases is introduced at a lower rate to ensure that they do not remain inside the balance chamber.

During heating, TG and DTG curves are recorded. We record at the same time GC peaks that correspond to injections of the gas mixture into the analyzer. In order to follow the concentration of each gas, GC injections are repeatedly performed at one(or five) minute(s) intervals.

Preliminary Experiments

It is necessary to check whether or not the GC profiles represent accureately the weight losses to which they correspond. For that we recorded TG, DTG and GC profiles during heating samples of pure calcium carbonate which release amounts of CO_2 similar to that we expected from apatite samples. Figure I shows an example of recordings. One can notice that the shape of DTG curve is similar to the CO_2 peaks envelope, but the latter appears about five minutes after the first. So in our experimental conditions (when the volume between the sample and the detector is sufficiently reduced) GC profiles give a picture of what's happening in the sample. Nevertheless, that's true only when decomposition releases only one gas ; when two or more gases are evolved on heating, DTG and GC envelope are different in shape and examination of both of them is necessary in understanding the phenomena which took place.

DECOMPOSITION OF SYNTHETIC CO_3-APATITES

Fluor CO_3-apatites precitated using Ca nitrate

"Reverse" apatites. Figure 2 shows an example of recordings obtained on a 10.4 % carbonated sample. Three decomposition steps are observed. The first two correspond to dehydration processes (see TG and DTG curves) and the last stage corresponds to decarbonation reaction. No gas other than carbon dioxide has been detected. CO_2-GC profile, which has been previously moved backwards in order to insure coincidence with DTG curve on figure 2, is similar to the later curve. At higher tamperature two maxima appear on these curves one at 680°C and the other at 820°C. Decomposition of similar less carbonated apatites (down to 3 %) shows that the first maximum on the GC envelope and DTG curve is always present while the second one vanishes as CO_3 amount diminishes (7). These findings agree with the assumption that two kinds of carbonate may exist in B type apatites.

"Direct" apatites. As previously observed, "direct" CO_3-apatites were precipitated in phosphate/carbonate medium. These apatites show on decomposition a dehydration stage followed by decarbonation process. Figure 3 gives an example of recordings obtained on heating a 13.2 % carbonated apatite at 150 degrees/h. One can notice that decarbonation takes place in 3 steps. Several other experimental results published elesewhere have shown that all of the three maxima are present whatever is the amount of carbonate inside the apatite (down to 7 % CO_3) (8). In other respects decomposition of some other apatites prepared with or without ammonium carbonate had led to the conclusion that the first maximum appearing on DTG and GC envelope curves results from decomposition of carbamate anion which is introduced in precipitation medium through commercial ammonium carbonate (8). It is not surprising that carbamate

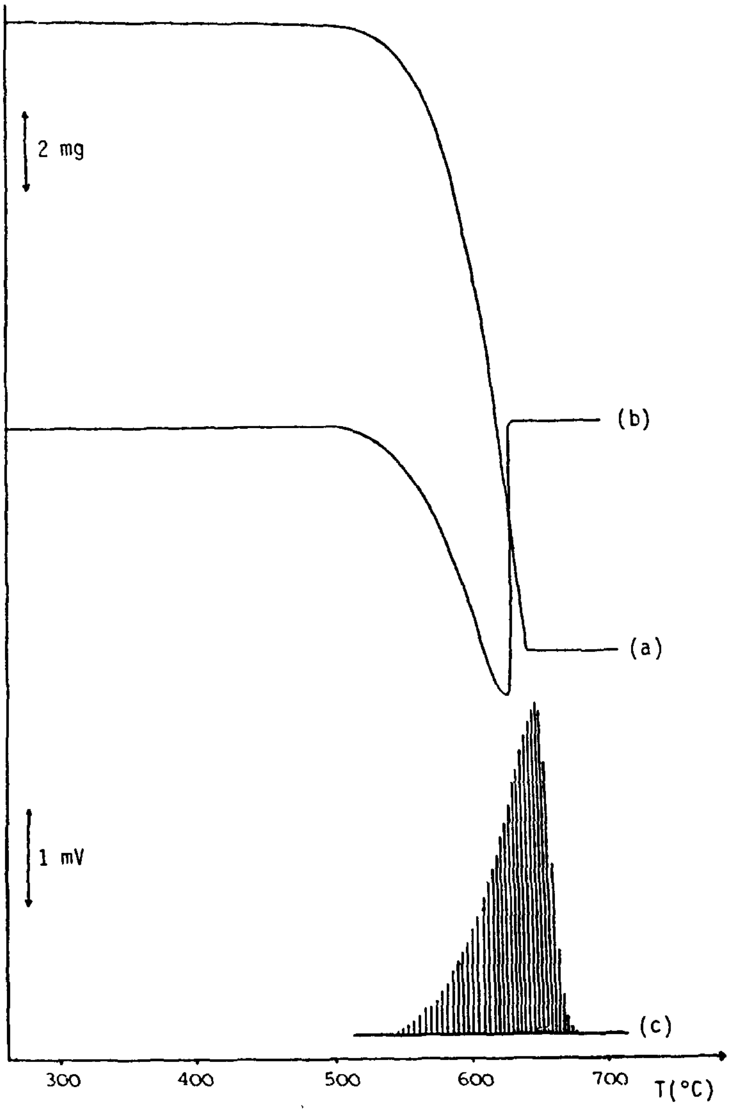


Fig. 1. Decomposition of calcium carbonate at 300 degrees/h.
a : TG curve. b : DTG curve and c : CO_2 chromatographic peaks.

ion (NH_2COO^-) can be incorporated inside the lattice as acetate ion can. Evidence for the introduction of the later ion has been established by other authors (5,9) and confirmed by ourselves (10), Moreover, apart from that maximum, decomposition of properly so-called apatitic carbonate occurs in 2 steps ; which confirms again the presence of two kinds of CO_3 in these products.

We further tried to check whether these conclusions remain valid when decomposition is performed in other heating conditions. Two samples having 13.4 % and 7 % carbonate were heated at 300 degrees/h. Figure 4 shows that decomposition of these samples occurs also in three steps but at about 550 °C nitrogen gas has been observed. Nitrogen, the amount of which is too small to be detected at lower heating rate, occurs from decomposition of ammonium species ; this have been detected by IR and labelling techniques in other studies (8, 11, 12) performed on "direct" hydroxy and fluor CO_3-apatites.

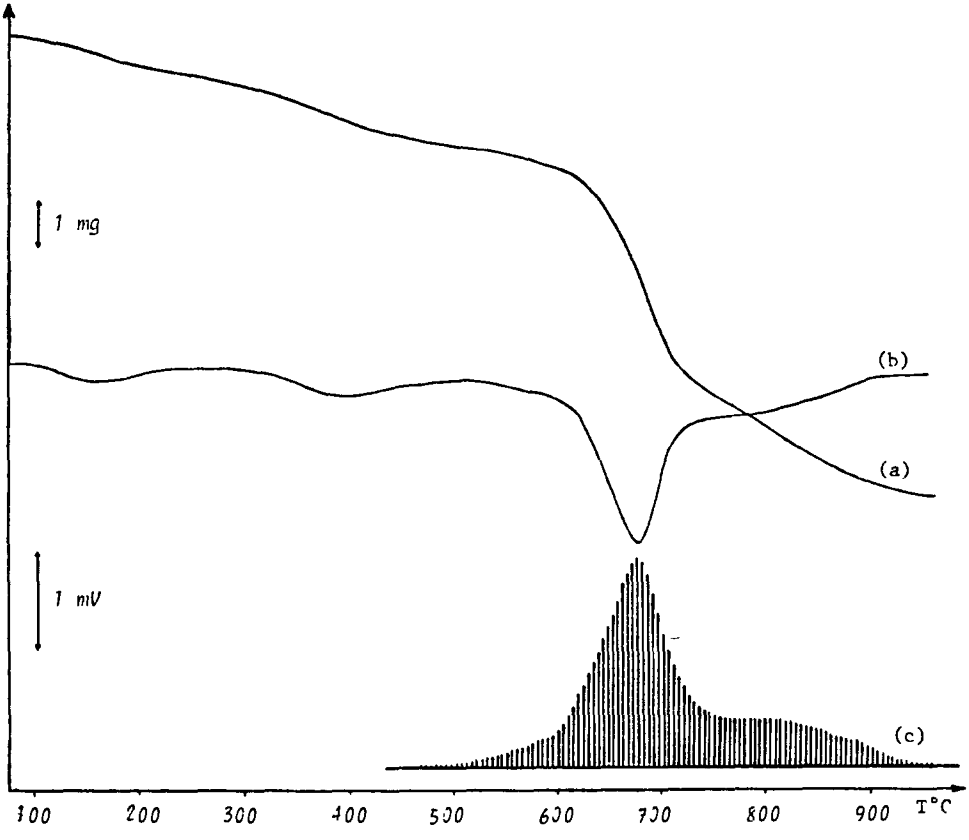
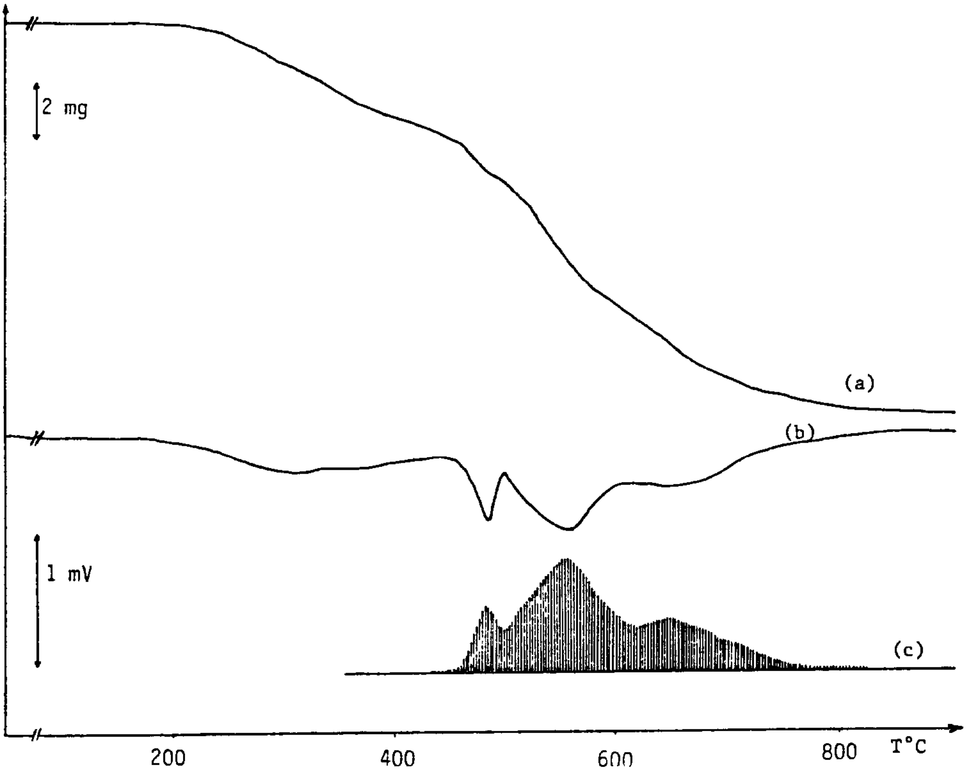


Fig. 2. Decomposition of a "reverse" F-CO_3-apatite sample (10,4 % CO_3) at 300 degrees/h.a : TG curve. b : DTG curve and c : CO2-GC peaks.



-Fig. 3. Decomposition of a "direct" F-CO_3 Apatite sample (10,4 % CO_3) at 150 degrees/h. a : TG curve b : DTG curve and c : CO_2 GC peaks.

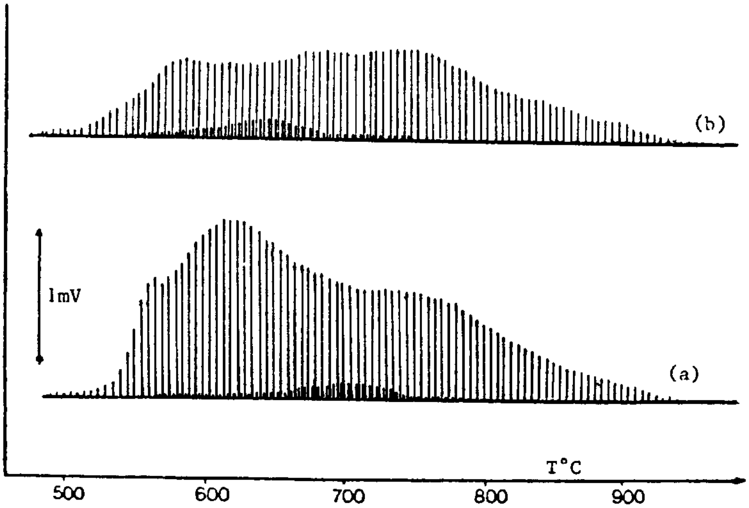


Fig. 4. GC recordings of two "direct" FCO_3 Apatite samples heated at 300 degrees/h. a : 13,2 % CO_3 and b : 7,0 % CO_3.

But N_2 has never been detected on heating "reverse" CO_3-apatites at 300 degrees/h.

Apatites precipitated using Ca acetate

The apatite structure may incoporate ions as big as acetate anion. This anion is introduced in the lattice when the product is precipitated by using Ca acetate instead of Ca nitrate. We performed thermal decomposition of such products prepared with or without fluoride using "reverse" or "direct" precipitation method (13). Figures 5 and 6 show examples of GC recordings obtained with "reverse" fluor and hydroxy CO_3-apatites respectively. One can notice the presence of CO gas at high temperature. In other experiments performed on the same samples by using a molecular sieve column and argon as carrier gas, we have detected in both cases H_2 gas appearing within the same temperature range other than CO gas (10). H_2 and CO come from acetate anion ; this latter ion is more stable in hydroxy CO_3-apatites than in fluor CO_3-apatite, since it decomposes at higher remperatures, a conclusion previously

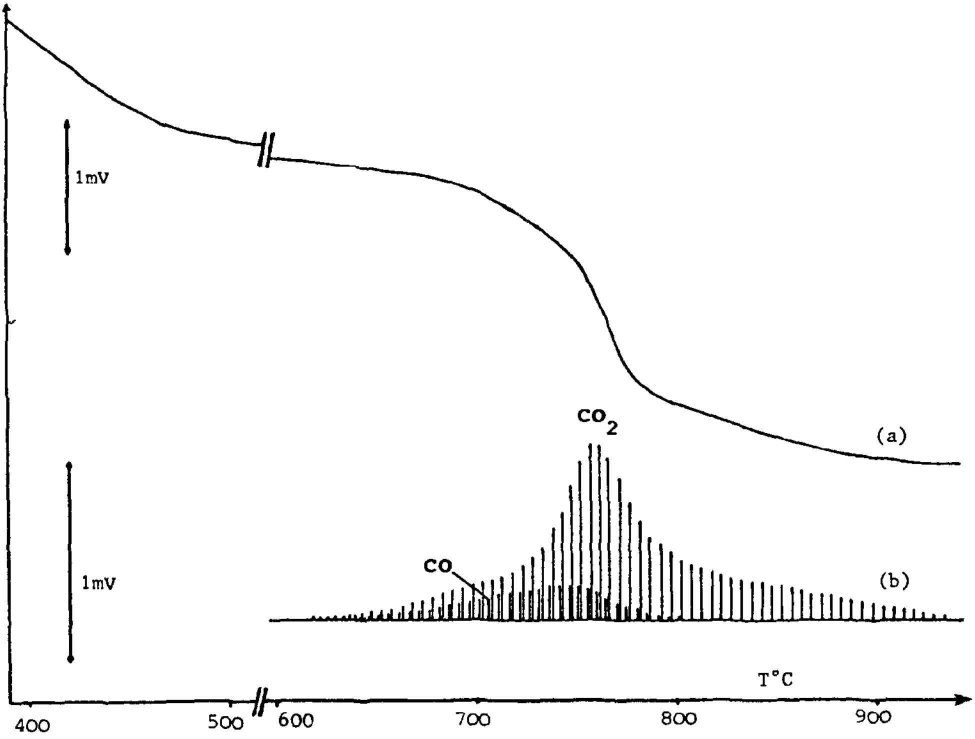


Fig. 5. TG curve (a) and GC recordings (b) of a fluor carbonate apatite sample precipitated in acetate medium.
column : Porapak S. Gas carrier : Helium.

established by Vignoles (5). In the case of similar "direct" apatites we observed also nitrogen among the decomposition gases.

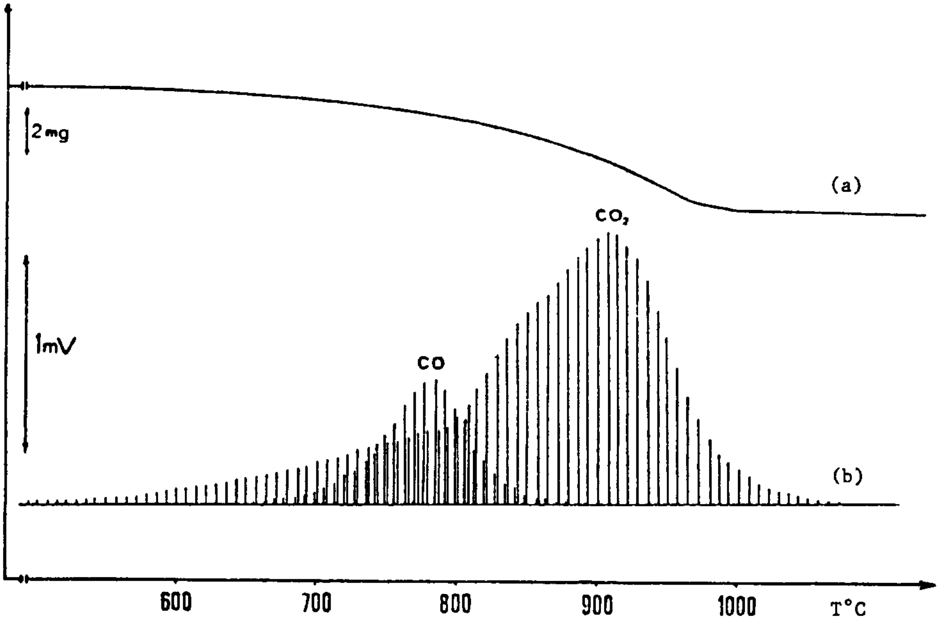


Fig. 6. TG curve (a) and GC recordings (b) of an hydroxy carbonate apatite sample precipitated in acetate medium.
Column : Porapak S. Gas carrier : Helium.

BIOLOGICAL APATITES

Biological apatites (or B.A.) are found as the principal so-called "mineral" phase of normal tissue calcifications (enamel, dentine, cementum and bone) and found associated with other phosphate or non-phosphate minerals in pathological calcifications. They are idealized as CO_3-hydroxyapatites. According to Legeros results (14) CO_3 substites for PO_4 in B.A., whereas Montel and coworkers (15) found that B.A. can be ascribed as "type A,B" CO_3-apatites. Both of these results have been reached through IR recordings and structural (X-ray) considerations. These techniques have also allowed Legeros (16) to state that 2 kinds of water are present in B.A. : (i) adsorbed H_2O which is "loosely bound" and may be released reversibly below 200 °C, and (ii) lattice H_2O which is "tightly bound" and assumed to be due to "H_2O for OH and/or HPO_4 for PO_4 substitutions". It can also be released above 200 °C.

Simultaneous TG/GC experiments are performed on samples of enamel, dentine or bone previously ignited in air at 300 or 500 °C. Figure 7 shows TG, DTG and GC profiles recorded on an enamel sample. One can notice the presence of lower

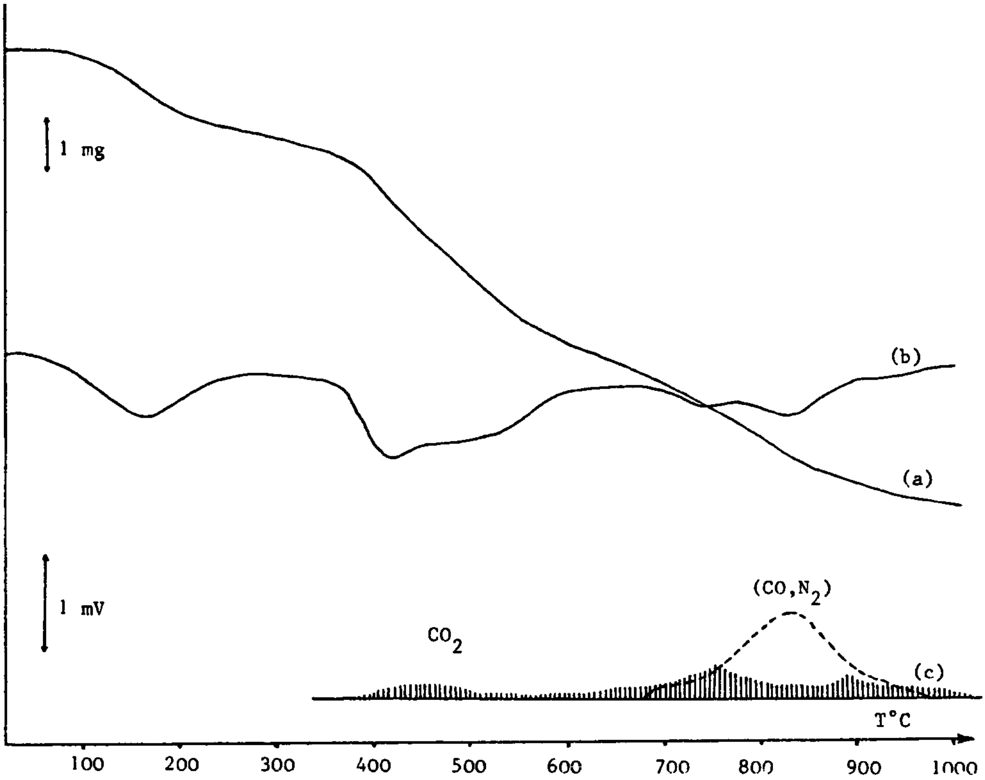


Fig. 7. Decomposition of enamel previously ignited in air at 300 degrees. a : TG curve ; b : DTG curve and c : GC recordings obtained on a Porapak S column.

temperature removable water, the maximum release of which appears at about 150 °C ; it corresponds to adsorbed water. Near 400 °C, H_2O and CO appear togather indicating that tightly bound water doesn't come from H_2O for PO_4 substitution but rather from HPO_4 for PO_4 substitution, probably according to the reaction : $2\ HPO_4^{=} + CO_3^{=} \longrightarrow 2\ PO_4^{\equiv} + CO_2 + H_2O$. Evidence for the occurrence of this reaction near that temperature has been established previously by other investigators (17). At higher temperature CO_2 is released at different stages suggesting that two kinds of apatitic CO_3 exist in enamel. Furthermore two other gases (CO and N_2) were detected between 700 and about 1000 °C. Release of such gases at so high temperature is believed to be due to the presence of organic molecules in ignited enamel. Incorporation of glycinate anion (NH_2-CH_2-COO^-) in apatitic structure has been previously established (15).

The presence of different kinds of carbonates in dentine is not as striking as in enamel (figure 8), where adsorbed water and gases coming from high temperature decomposition of organic material (CH_4, N_2 and CO) are also present.

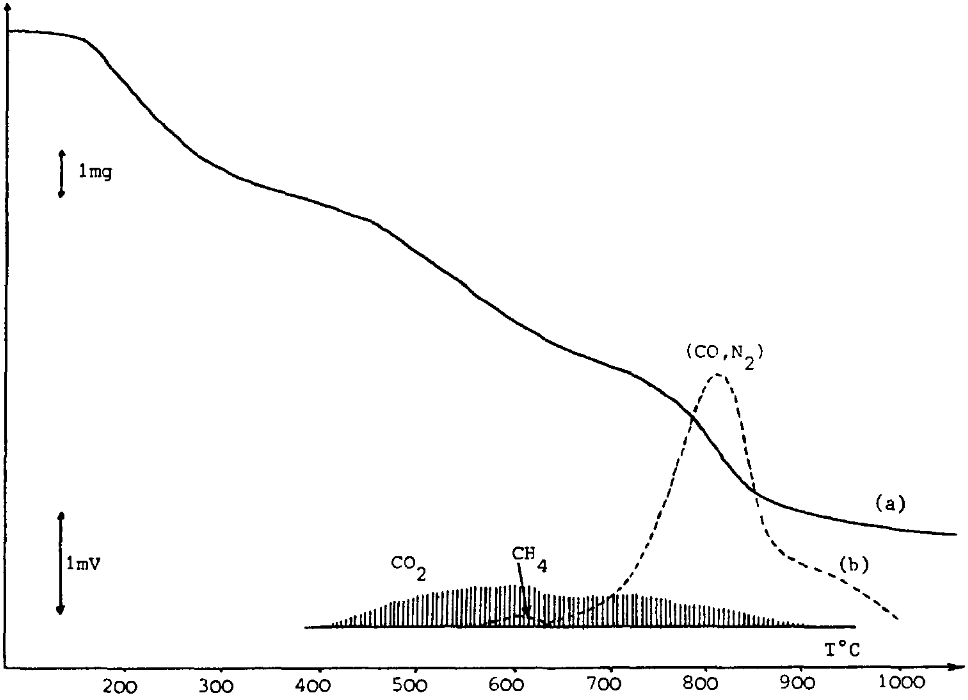


Fig. 8. Decomposition of dentine previously ignited at 300 °C in air
a : TG curve ; b : GC recordings obtained on a Porapak S column.

Figure 9 and 10 show the results obtained on bone samples previously ignited in air at 300 and 500 °C respectively. We can see adsorbed and lattice water besides CO_2, CO, N_2 and CH_4. This later gas disappears after ignition at higher temperature (500 °C) while CO and N_2 remain present. These results suggest also the presence of different kinds of carbonates inside that material.

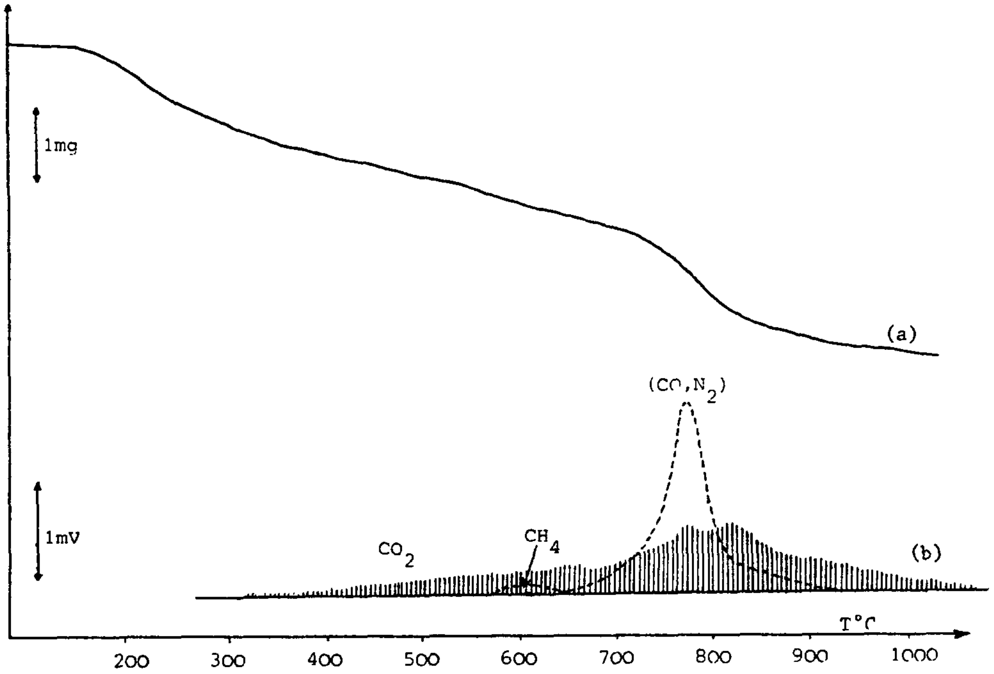


Fig. 9. Decomposition of bone previously ignited at 300 °C in air
a : TG curve b : GC recordings obtained on a Porapak S column,

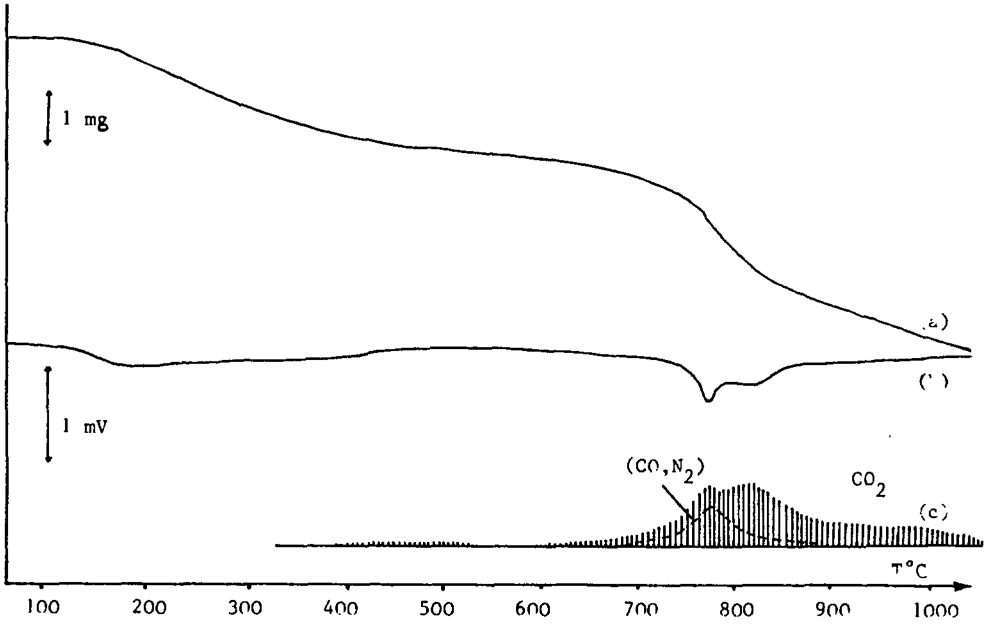


Fig. 10, Decomposition of bone previously ignited at 500 °C in air.
a : TG curve ; b : DTG curve and C : GC recordings obtained on a Porapak S column.

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REFERENCES

1 G. Bonel, Contibution à l'étude de la carbonatation des apatites, Ann. Chim., 7 (1972) 127-144.
2 J. C. Labarthe, G. Bonel et G. Montel, Sur la structure et les propriétés des apatites carbonatées de type B phospho-calciques, Ann. Chim., 8 (1973) 1-24.
3 J. R. Lehr, G. H. Mc Lellan, J. P. Smith and A. W. Frazier, Caracterization of apatites in commercial phosphate rocks, in : Coll. Inter. sur les phosphates minéraux solides, Toulouse (Fr), May 16-20, CNRS, (1972) Vol.2, pp. 29-44.
4 M. Vignoles, G. Bonel et G. Bacquet, Etude physico-chimique des apatites carbonatées phospho-calciques semblables à la francolite, Bull. Mineral. 105 (1982) 307-311.
5 M. Vignoles, Contribution à l'Etude des Apatites Carbonatées de type B, Thèse Doctorat d'Etat (1984), INP. de Toulouse.
6 R. Z. Legeros, Effect of carbonate on the lattice parameters of apatite, Nature, 206 (1965) 403-4.
7 I. Khattech et M. Jemal, Decomposition thermique de fluorapatites carbonatées de type "B" inverses, Thermochim. Acta, in press.
8 I. Khattech et M. Jemal, Etude de la décomposition thermique de fluorapatites carbonatées, Thermochim. Acta, 95 (1985) 119-128.
9 G. Bacquet, Vo Quang Truong, M. Vignoles; EPR Detection of acetate ions trapping in B type carbonated fluorapatites, J. Sol. State Chem., 39 (1981) 148-153.
10 I. Khattech et M. Jemal, Sur la décomposition thermique d'apatites précipitées en présence d'ions acétate, Ann. Chim. Fr., 10 (1985) 653-6.
11 Y. Doi, Y. Moriwaki, T. Aoba, M. Okazaki, J. Takahashi and K. Joshin, carbonate apatites from aqueous and non-aqueous media studied by ESR, IR and X-Ray diffraction : Effect of NH_4^+ ions on crystallographic parameters, J. Dent. Res., 61(2) (1982) 429-434.
12 M. Vignoles, G. Bonel and R. A. Young, Occurence of nitrogen species in precipitated B-type carbonated hydroxyapatites, Calcif. Tissue Int., 40 (1987) 64-70.
13.I. Khattech, Sur la décomposition thermique d'apatites carbonatées de de type B synthétiques, Application aux apatites naturelles, Thèse de Spécialité (1986), Université de Tunis, Tunisia.
14 R. Z. Legeros and J. P. Legeros, Phosphate Minerals in Human Tissues, in : J. Nriagu and P. Moore (Eds), Phosphate Minerals, Spriger-Verlag, Berlin 1984, pp. 351-385.
15 G. Montel, G. Bonel, J. C. Heughebaert, J. C. Trombe and C. Rey, New concepts in the composition, crystallization and growth of the mineral component of calcified tissues, J. Cryst. Growth, 53 (1981) 74-99.
16 R. Z. Legeros, G. Bonel and R. Legeros, Types of "H_2O" in Human Enamel and in precipitated apatites, Calcif. Tiss. Res., 26 (1978) 111-118.
17 D. J. Greenfield J. D. Termine and E. D. Eanes, Calcif. Tiss. Res., 14 (1974) 131-8, cited by J. C. Heughebaert, Contribution à l'Etude de l'Evolution des Orthophosphates de Calcium Précipités Amorphes en Orthophosphates Apatitiques, Thèse de Doctorat (1977), INP. Toulouse.