Thermochimica Acta, 152 (1989) 125-134
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

STUDY OF THE THERMAL DECOMPOSITION OF CARBONATE GROUPS IN SEDIMENTARY APATITES BY THERMOGRAVIMETRIC ANALYSIS

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SUMMARY

Many groups can substitute phosphate sites in sedimentary rock apatites. The main properties of these apatites (solubility, thermal behaviour, ...) are affected by the degree of substitution by carbonates.

Thermogravimetric analysis of these compounds show secondary reactions occurring simultaneously with decomposition reactions of carbonate groups. Properties of carbonate groups decomposition are deduced from experimental factors study as processing gases, heating rate and grinding. Secondary reactions are due to high calcium content of sedimentary rocks and the presence of minerals associated.

Several kinds of carbonate groups with different thermal stabilities occur in mechanically activated apatites. The presence of these types in sedimentary rock apatites, more or less substituted, is discussed.

INTRODUCTION

The apatites of the principal sedimentary phosphate deposits appear to be diversely substituted according to the origin of the ore. The presence of carbonate groups in the phosphore sites is the most general and the most important of these substitutions.

Different environments of carbonate ions substituted for phosphate groups have been revealed in some synthetic apatites, bones or dental enamels (ref. 1 to 5). In the case of sedimentary apatites, the spectrometric techniques, widely used in this field, do not distinguish the possible different components of the vibration bands of these ions (ref. 6 and 7).

Thermogravimetry is a technique adapted to the study of this kind of substitution because of thermal instability of the carbonate groups. The thermograms of the sedimentary fluorapatites (fig. 1) generally show three distinct losses between room temperature and 200°C, 200°C and 450°C, 450°C and 1200°C.

Carbon dioxide and the water vapor are the main components of the released gaseous products. The loss of water correspond to the total loss observed below 200°C and to the main losses between 200°C and 450°C. The carbon dioxide begins to be evolved weakly from 200°C, the decarbonatation reactions taking place mainly between 600°C and 1000°C, in various stages (ref. 5, 7 and 8).

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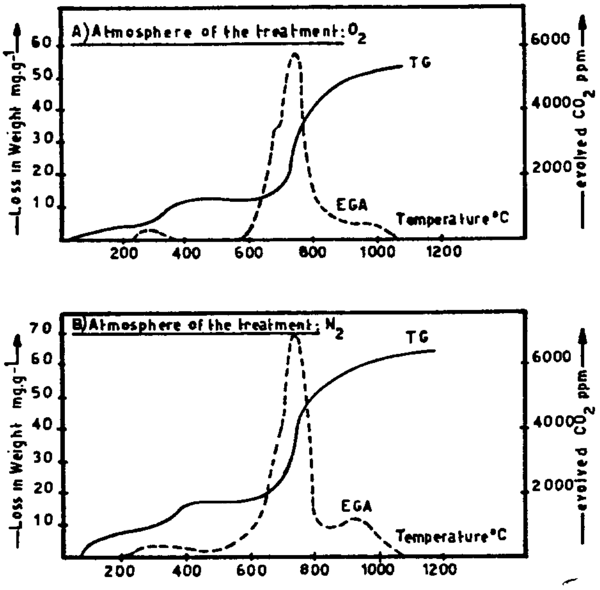

Fig. 1. Thermogravimetric analysis and CO_2 released under oxygen and nitrogen (sample : layer II Daoui, phosphated elements).

PREPARATION OF SAMPLES AND EXPERIMENTAL TECHNIQUES

The different samples studied are scrubbed into thick pulp in order to wear away the grains. The granulometric fraction 160 µm-250 µm obtained by humid cutting undergoes a densimetric separation at 2.96. The heavy part is recovered and manually reduced to a particle size < 125 µm. The separation of the mineral phases associated with the apatite inside the oolite by these physical methods is incomplete.

The use of chemical purification methods (treatment with triammoniumcitrate solution at pH8 or with buffer acid solution) used for the dissolution of free carbonates in the sedimentary phosphates, brings about changes in composition and properties of the apatitic phases.

The thermogravimetric analysis was carried out on a SETARAM B-70 balance fitted with a 1600°C furnace. The heating rate of the furnace is generally fixed at 3.5°C min^{-1} for tests carried out under nitrogen or oxygen and at 7.0°C min^{-1} for tests under carbon dioxide. In the case of tests under nitrogen or oxygen, the carbon dioxide, released from the sample and carried by the flowing gas, is determined continuously by a non-dispersive infrared BECKMAN 864 analyser. The CO_2 in the gas is expressed in volume ppm for one gram of product and for a gas flow of 0.1 l min^{-1}.

The study of the influence of a forced grinding of the samples is obtained with the aid of an oscillating crusher in tungsten carbide, operating in water or dry.

RESULTS AND DISCUSSION

1. Study of the release noted between 200°C and 450°C

This loss is of little importance : in the case of the present product, it equals about 0.20% CO_2 or 5% of the total carbonates (fig. 2 -curve 1).

The treatment of the sample, before thermogravimetric analysis, in an acid medium, shows that a pH below 5 is necessary to ensure the solubility of this CO_2 (fig. 2 - cur. 2 and 3). Thus, the possibility of a free carbonate decomposition can be dismissed due to the very low temperature of the phenomenon and the high chemical stability noticed.

The origin of the release below 400°C, noticed on bone tissues (ref. 2 to 4),

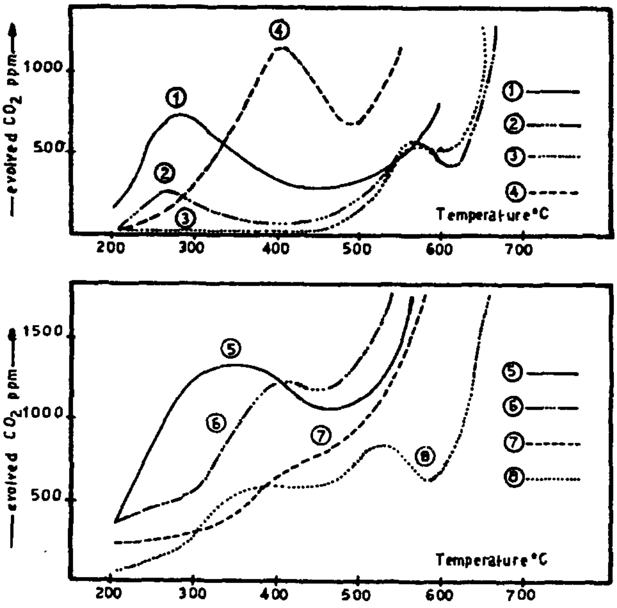

Fig. 2. CO_2 released under nitrogen between 200°C and 600°C (sample : layer II Daoui, 63 µm-1000 µm fraction). Curves : (1) sample untreated. (2) sample treated at pH5. (3) sample treated at pH4. (4) sample treated at pH4 and then dry ground for 60 min (5) sample dry ground for 5 min (6) sample dry ground for 60 min (7) sample dry ground for 240 min (8) sample dry ground for 5 min then treated at pH5.

has been subject of various hypotheses: groups adsorbed or substituted for phosphate ions at the surface of the crystal, or even substituted for phosphate ions inside the structure. In the latter case, the release is then the result of the reaction of the carbonates with water of crystallisation contained in the apatite crystal or with $P_2O_7^{4-}$ groups resulting themselves from the pyrolysis of HPO_4^{2-}.

The granulometric reduction of the sample in water does not alter the characteristics of the studied release. On the contrary, the dry grinding for a few minutes fixes atmospheric CO_2 on the solid at a level of about 0.40% CO_2. The CO_2 fixed shows properties close to those of the CO_2 initially present in the sample (fig.2 - cur. 5). If the grinding is pursued, the importance of the fixed CO_2 diminishes (fig.2 - cur. 6 and 7). The fixing of CO_2 by grinding is possible on the samples previously treated in an acid medium (fig.2 - cur. 4). The thermogravimetric analysis of these products shows very important weight losses between 25°C and 500°C (fig. 5). These losses, due to the water, are dependent on the intensity of the grinding.

The fixation of CO_2 during the dry grinding of the sample is due to a surface phenomenon. As a matter of fact, the importance of this CO_2 is directly linked to the B.E.T. surface of the product : the presence of active surface and sites created during the grinding induces the fixation of CO_2 and atmospheric water vapors. The similarity of the behaviour of this CO_2 with that noticed on the unground product leads one to suggest for the latter also a surface localisation onto the crystallites.

2. Study of the releases noted above 450°C

2.1. Influence of the atmosphere of the treatment

The different weight losses noticed above 450°C between analysis carried out under nitrogen, carbon dioxide and oxygen are due to the presence of organic matter in the samples (ref.9). So, under N_2 atmosphere (fig.1), the reducing ambience generated by the pyrolysis of the organic matter favours reducing reactions of the sulfate groups belonging to the apatite network. The losses of weight noted are higher than those obtained under oxygen, especially in the temperature range 600°C - 700°C.

In the case of the products under discussion, with weak contents of organic matter , the combustion reactions of these materials do not alter the aspect of the CO_2 emanation. However, on the release linked to the decarbonatation of the apatite, a shoulder between 650°C and 700°C, attributable to this combustion (fig. 1), appears sometimes.

The reaction of decarbonatation noticed between 600°C and 800°C - 850°C under N_2 or O_2 is split under CO_2 (fig.3). The first loss (or α loss) takes place at a temperature below that of the loss noted in the case of the other treatment atmospheres (-30°C with regard to the maxima of these peaks). The second loss (or β loss) takes place between 850°C and 1200°C. The loss noted above 850°C under N_2 or O_2, observed with greater difficulty under CO_2, exists in the same temperature field. During cooling, thermogravimetric analysis indicates an increase in weight at a temperature a little bit below than the one corresponding to the β loss.

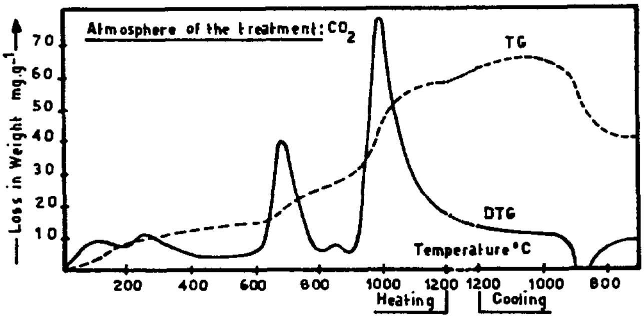

Fig. 3. Thermogravimetric analysis under carbon dioxide (sample : layer II Daoui, phosphated elements).

Calcite has been detected by infrared spectroscopy in products treated under CO_2 at a temperature between the end of α loss and the beginning of β loss. This calcite however could originate from a recarbonatation of the samples subsequently at its calcination. After elimination of this calcite through acid dissolution, the refined sample shows a weak release mainly noted between 820°C and 970°C, a temperature field corresponding to the highest losses noted during treatment under nitrogen or oxygen. This shows that β loss is linked to the presence of calcite in the sample.

Is this calcite initially present in the untreated sample or is it generated during the thermogravimetric analysis ? Tests carried out with the aid of a high temperature chamber set on an X-ray diffractometer, provide an answer. The relative intensity of 104 reflection of the calcite, indirectly determined through superposition of this plan with 210 reflection of the apatite, increase in the temperature field relative to α loss. After a short level, the decrease of this intensity, noted between 800°C and 950°C, shows the decomposition of the calcite previously produced. The presence of calcite, originally associated with the sample is probable, in view of the intensities noted on the sample at the room temperature and at 950°C. During the cooling, the quantity of calcite produced is variable. More generally, the respective importance of these different phenomena depends on the condition of the preparation of the samples.

The lowering of the maximum temperature of decarbonatation observed under CO_2 atmosphere in relation to the realized analysis under the other treatment ambiences results most likely from the presence, under oxygen or nitrogen, of calcite whose dissociation displaces towards the higher temperatures the apparent maximum of the loss associated with the decarbonatation of the apatite. This calcite would arise from the calcite initially associated with the apatite as well as from calcite generated from products of decarbonatation of the apatite (CaO and CO_2) present from 650°C, according to the reaction :

$\text{Ap-}CO_3 \longrightarrow \text{Ap.} + CaO + CO_2 \longrightarrow \text{Ap.} + CaCO_3.$

This type of reaction has been noted, under our working conditions, on mixtures of magnesite and calcium hydroxide, for instance.

The displacement of the maxima of the releases according to heating rate of the samples allows the determination of an apparent activation energy. The use of derivative thermogravimetry data according to Sewell's approach (ref. 10), leads to an energy of 210 $kJ.mol^{-1}$ under oxygen atmosphere. This apparent energy, for reasons mentioned above, does certainly not characterize the decarbonatation process of apatite. Under CO_2 atmosphere, no sensible change of the temperatures corresponding to the reaction maxima in relation to the heating rate is revealed. This demonstrates the existence of apparently very high activation energies. As for the calcite (β loss), the published values (ref.11) are effectively clearly higher than those found in air.

2.2. Influence of the grinding of the sample

The dry or wet grinding favours the α loss at the expense of the β loss and the increase in weight. These observations do not correspond with the effects expected from a granulometric reduction of the product :

the possibility of fixing gaseous CO_2 should be better after grinding.

These smaller calcite contents can be explained through the existence of reactions of the following type :

$CaO + SiO_2 \longrightarrow CaSiO_3$ or $CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$

which diminish the quantity of calcium oxide available to react with CO_2 (fig. 4).

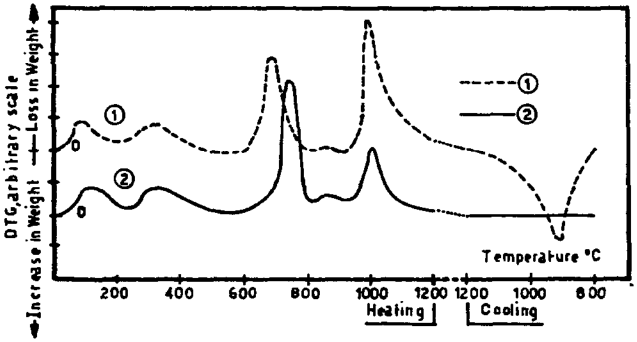

Fig. 4. Influence of an addition of quartz (sample : layer II Daoui, phosphated elements). Curves : (1) sample untreated. (2) sample with an addition of 10% of quartz.

The study of the treatment atmosphere and of the grinding has shown the influence of the products of apatite decarbonatation and the mineral phases associated with observed losses. Furthermore, by dry grinding, a progressive disorganization of the apatite network (ref.12) is noted with a fragmentation of the crystallites, an apparition of micro-strains inside the crystal and a decrease of the diffracted ray intensities (amorphization). Thermally , a splitting of the decarbonatation reaction observed between 600°C and 800°C (fig.5) results from this disorganization. The temperatures of maxima of these different losses do not change according to the importance of the mechanical activation, only the intensities associated to these phenomena are modified. These losses therefore correspond to defined energetic states.

2.3. Influence of the substitution of the apatite

Under oxygen or nitrogen, the importance of the losses observed between 600°C and 850°C and above 850°C are directly linked to the degree of substitution of phosphate groups by carbonate groups (fig.6), but there appears to be no modification concerning the temperature fields where these losses occur.

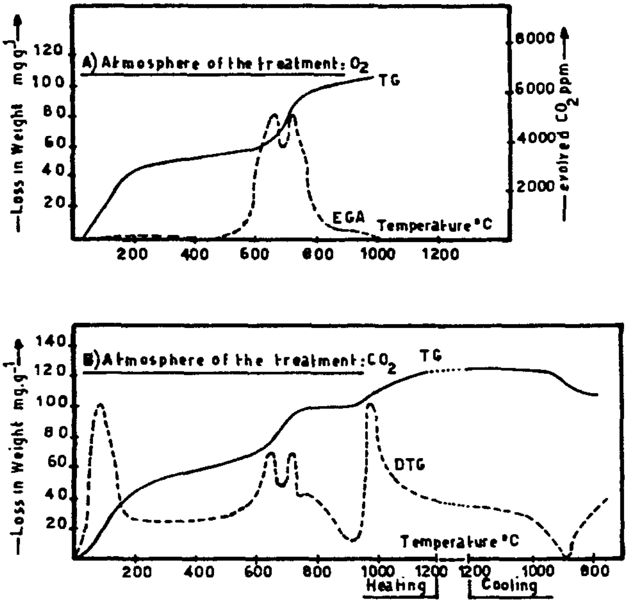

Fig. 5. Influence of dry grinding (sample : layer II Daoui, phosphated elements, ground for 60 mn).

The importance of the reaction at high temperature is equally determined, for the substituted apatites, by the heating rate of the sample and its granulometry. However, under CO_2, the characteristics of this reaction (importance and temperature field of the release) do not seem to be very much modified with regard to the other treatment atmospheres. A weak CO_2 pressure is therefore necessary and sufficient to observe this release in the case of substituted apatites.

These losses have been variously interpreted. Taking into consideration the behaviour observed on synthetic apatites, Jemal and Khattech (ref. 5) associate the low temperature loss with the substitution of PO_4^{3-} ions by (CO_3^{2-} , □) groups and the high temperature loss with the decomposition of (CO_3^{2-} , F^-) groups. On the contrary, Baumer et al. (ref. 7) reach the opposite conclusion.

The work of Lehr et al. (ref.13) has shown a strong correlation between the presence of carbonate groups and excess of fluoride in the sedimentary apatites : the substitution (CO_3^{2-} , F^-) seems therefore fundamental in the case of these apatites. Slightly substituted apatites and thermally treated

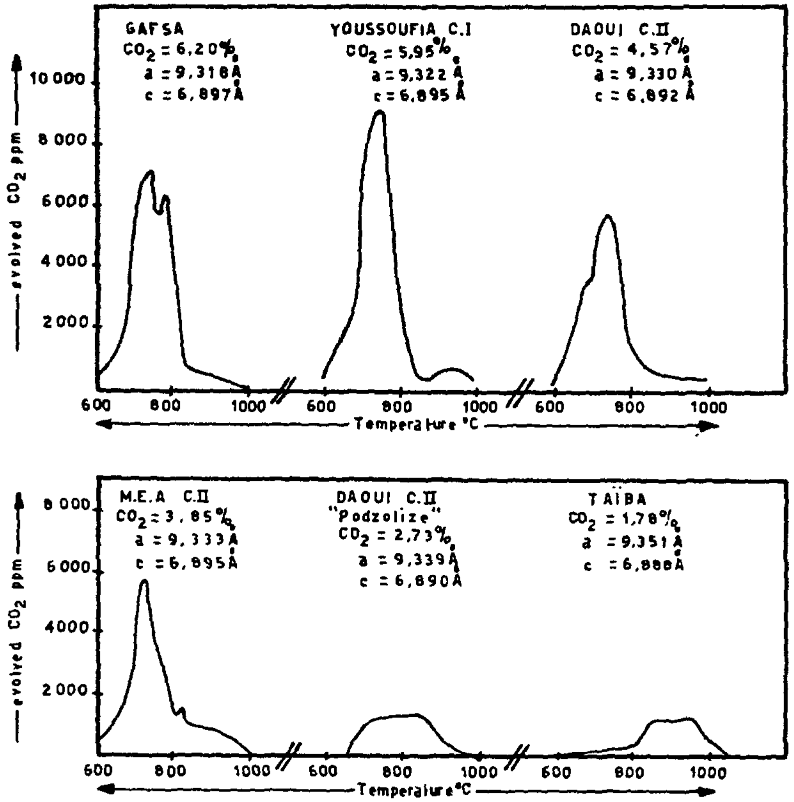

Fig. 6. CO_2 released under oxygen during thermogravimetric analysis between 600°C and 1000°C of phosphated elements of various origins.

apatites show different crystallographic parameters from more substituted apatites (a parameter clearly higher, c parameter slightly lower) : the geometry of sites occupied by carbonate groups depends on the substitution of the apatite. McConnell suggests the existence of two possible different orientations for the carbonate groups substituted for phosphate groups (ref. 14 and 15).

We think that the effective existence of carbonates according to these orientations is linked to the parameters of the apatite. The so-called parallel orientation at the c axis would correspond to the decomposable carbonates at high temperature and would exist in the case of slightly substituted natural apatites. For more heavily substituted apatites, this form would only appear transiently after a reorientation of the carbonate groups, with at least one diffusional stage in gaseous state.

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