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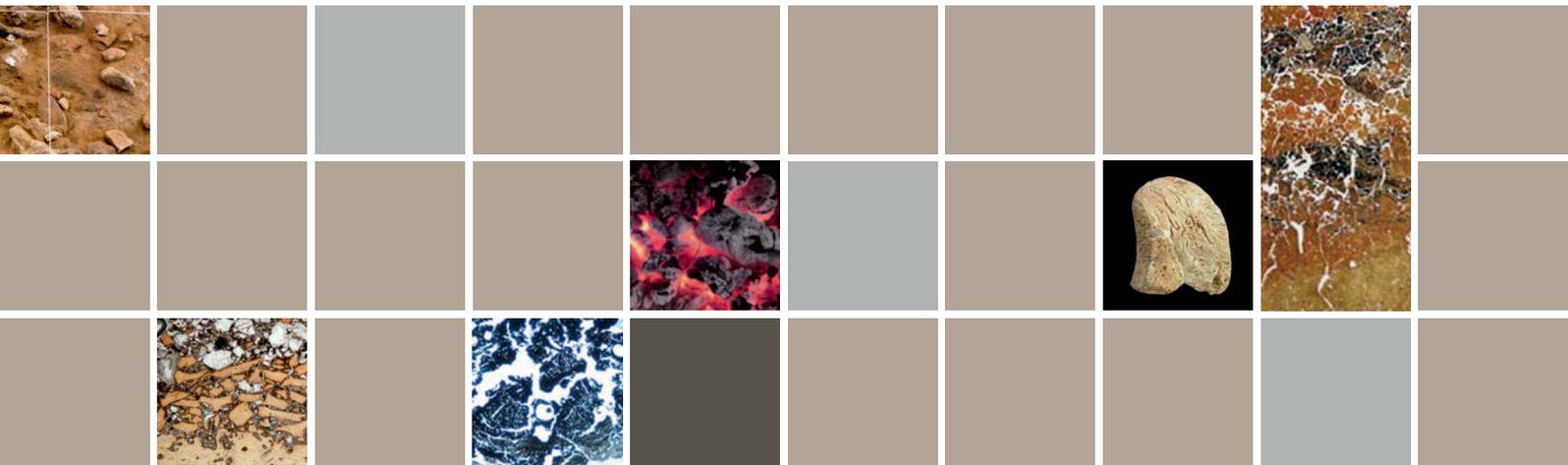
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**THE TAPHONOMY OF BURNED ORGANIC RESIDUES AND  
COMBUSTION FEATURES IN ARCHAEOLOGICAL CONTEXTS**



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# CHARACTERIZATION OF BURNT BONES IN ARCHAEOLOGICAL CONTEXT: A COMPARATIVE STUDY OF MODERN AND FOSSIL MATERIAL BY INFRARED SPECTROSCOPY

Matthieu LEBON

## abstract

The identification of burnt bones in an archaeological context can entail characterization techniques such as infrared spectroscopy. However, it is often difficult to clearly distinguish bones burnt at low temperatures (<500°C) because the alterations that occur during heating are similar to those that occur during burial. Moreover, these analyses are generally carried out on samples reduced to powder and they do not permit us to take into account the heterogeneity of the bone material.

In order to address these various problems, we became interested in the  $\nu_1\nu_3\text{PO}_4$  domain, whose study, on modern bones burnt under experimental conditions, allowed us to establish parameters that make it possible to evaluate the crystallinity of the samples (1030/1020 ratio) and to gather information on the crystal structure of the mineral phase (wavenumbers of the peaks centred near 961, 1022, 1061, and 1092  $\text{cm}^{-1}$ .) In particular, the wavenumbers of these various peaks have made it possible to identify bones burnt at temperatures as low as 250°C in the Magdalenian levels of the site of Bize-Tournal, while crystallinity by itself allowed only the clear identification of bones burnt above 500°C. This method can therefore contribute to an improved identification of bones burnt at low temperatures in an archaeological context. Moreover, this analytical protocol will make it possible to study the spatial variations in the composition of bone material by infrared micro-spectroscopy and thus to define and distinguish the alterations occurring during heating and during diagenesis.

**Keywords :** burned fossil bones, modern reference base, carbonated hydroxyapatite, FTIR, FTIR imagery,  $\nu_1\nu_3\text{PO}_4$  domain

## Introduction

Since humans first started using fire, burnt bones have represented a large part of the burned organic residues associated with archaeological levels. This material can result from various activities such as cooking meat, utilizing bones as fuel, or certain funerary practices (Buikstra & Swegle, 1989; Théry-Parisot *et al.*, 2002; Cain, 2005.) These different activities are manifest by different heating intensities and durations whose estimation can be crucial to the identification of the origin of burned bone materials.

The changes in colour or texture undergone by the bone during heating can make it possible to identify the burnt bones in most cases, and to estimate the maximum temperatures reached. Different degrees of alteration have thus been established on the basis of the changes in the colour of bones during heating (Shipman *et al.*, 1984; Nicholson, 1995; Stiner *et al.*, 1995.) The colour of the bones begins to evolve at 200°C, with the bone assuming an increasingly dark brown colour and achieving almost complete carbonisation at nearly 350°C. Above this temperature, the carbonised organic material is gradually eliminated and the bone's colour becomes progressively lighter, becoming grey (500-650°C) and then white once the calcination is complete (700°C) (fig.1.)

Various analytical techniques have been developed to remedy this situation and to reliably characterise burnt bones. This is notably the case of x-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and electron microscopy, which have made it possible to follow the significant modifications made to the structure and composition of the bone's mineral phase during heating. Notably, an increase in crystallinity (size and degree of perfection of the crystallites) at high temperatures has been demonstrated (Shipman *et al.*, 1984; Stiner *et al.*, 1995; Person *et al.*, 1996; Reiche *et al.*, 2002; Piga *et al.*, 2008.)

The composition of bones is indeed deeply modified during heating. *In vivo* bone is a complex material made up of a mineral phase associated with an organic matrix composed mainly of collagen. The composition and structure of the mineral phase of bone are close to those of hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) but they differ due to the presence of numerous impurities. The major constituents (calcium and the phosphate and hydroxyl groups) can be replaced by minor elements ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ...) or by trace elements ( $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ...) These impurities are at the origin of deformations of the crystal lattice of the mineral phase and they set a limit to the size of crystallites. For example, carbonates can represent over 5% of the total weight of the mineral phase and this phase can

146



**Fig. 1** - Examples of various categories of heat-induced alterations as defined by Stiner *et al.*, 1995.

However, it appears that various taphonomic processes during burial can influence the appearance of bones. This is the case, for example, of iron and manganese oxides, which are responsible for a brown or black colouring of bone surfaces, making difficult the identification of burnt bones in archaeological contexts (Shahack-Gross *et al.*, 1997).

also be described as a slightly crystallised carbonate-hydroxyapatite (LeGeros, 1981).

The organic material, composed mostly of collagen, is quickly destroyed during burning and its carbonisation is complete at about 300°C. Above 450°C, the products of carbonisation of the organic material are in turn gradually eliminated and only the mineral phase persists

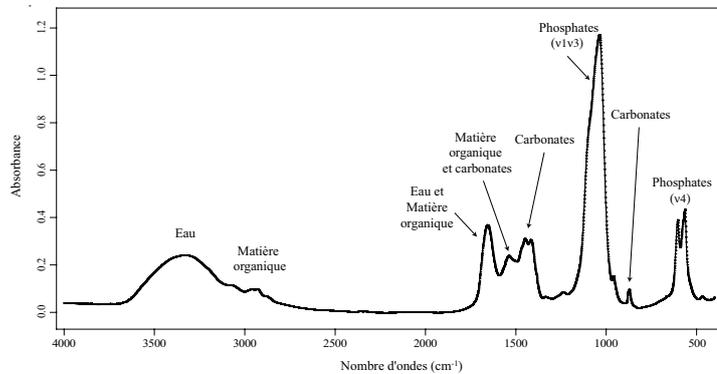
above 600°C. The mineral phase is also affected during heating: water is gradually eliminated starting at 100°C and the proportion of carbonates decreases rapidly above 300°C. The result is a gradual decrease of the number of defects in the mineral phase, defects that become negligible near 500°C. Their disappearance induces a characteristic increase in the size of crystallites at high temperatures (Person *et al.*, 1996; Hiller *et al.*, 2003.)

Infrared spectroscopy is a technique especially suited to the characterisation of these modifications in the composition of the mineral phase during heating because it allows the study of the structure and composition of this phase, as well as those of the organic phase when it is preserved (Fig.

2.) Furthermore, this technique is used particularly in archaeology to determine the state of preservation of the mineral phase of fossil bones through an assessment of their crystallinity. This parameter can be measured by calculating the splitting factor (SF), calculated from the degree of separation of the individual absorbance peaks  $\nu_4$  of the phosphate groups centred near 565 et 605  $\text{cm}^{-1}$  (Termine and Posner, 1966 ; Weiner and Bar-Yosef, 1990.) The SF value augments with an increasing degree of crystallinity. However, the utilisation of the splitting factor has shown its limitations both in the context of the identification of burnt bones and in the assessment of the state of preservation of bones recovered in an archaeological context. It seems that the increase in crystallinity that occurs during exposure of the bones to edaphic or climatic elements is of the same magnitude as that which occurs during moderate heating (below 500°C.) Therefore, the identification of the lower heating stages of fossil bones by infrared spectroscopy remains difficult (Stiner *et al.*, 1995.) Moreover, it seems that the crystallinity cannot reflect all modifications undergone by the mineral phase during diagenesis (Trueman *et al.*, 2008.)

Finally, this method of analysis requires sampling in a powder form and therefore does not allow us to take into account the heterogeneity of the bone material.

Over the past few years, it has become possible to combine infrared spectroscopy with microscopy to study the spatial distribution of the constituents of a material with a resolution of about 50 to 100  $\mu\text{m}$  in



**Fig. 2** - Infrared spectrum of a modern unburnt bone. The various absorption peaks make it possible to quantify the various components of the mineral and organic phases of the bone.

the laboratory. If applied to bones, this technique will allow a better understanding of the modifications that occur in the bone tissue during heating. The technical specifications of these instruments generally do not allow the study of the spectral region between 600 and 400  $\text{cm}^{-1}$  and therefore make it impossible to calculate the SF currently used to evaluate the crystallinity of the samples.

The goal of this work is to present the development of an infrared spectroscopic method that allows both a precise identification of bones burnt at low temperatures and the application of infrared micro-spectroscopy to the study of fossil bone material.

The  $\nu_4$  phosphate domain, on which the calculation of the SF is based, is not the only phosphate domain accessible in the infrared range. The  $\nu_1\nu_3\text{PO}_4$  domain, which is characterised by a large and intense band that ranges between 1200 and 900  $\text{cm}^{-1}$ , has been the object of numerous studies in infrared micro-spectroscopy, especially in the biomedical field. Various studies have shown that this domain can be decomposed into over a dozen component peaks, and that their number and wavenumber could provide information on the composition of the bone mineral phase (Rey *et al.*, 1991; Leung *et al.*, 1990; Gadaleta *et al.*, 1996.) In particular, it has been shown that the ratio of the areas

or amplitudes of the components centred near 1030 et 1020  $\text{cm}^{-1}$  makes it possible to estimate the crystallinity of bones *in vivo* (fig. 3a) (Paschalis *et al.*, 1996 ; Boskey and Pleshko-Camacho, 2007.) These different peaks, very near each other, are difficult to observe and their identification requires the use of mathematical treatments, such as Fourier self-deconvolutions, or mathematical derivatives of the spectrum (Fig. 3b) (Rey *et al.*, 1991 ; Gadaleta *et al.*, 1996.)

The analytical protocol proposed here is based on a qualitative and quantitative study of the  $\nu_1\nu_3\text{PO}_4$  domain carried out by jointly using the derivative infrared spectra and the spectral decompositions. This method was developed with an experimental reference base of modern bones heated to various temperatures and for various lengths of time in order to better understand the changes that occur in the mineral phase during heating. It was then possible to compare the results obtained to those obtained from the fossil bone materials from the Magdalenian levels of the site of Bize-Tournal (Aude).

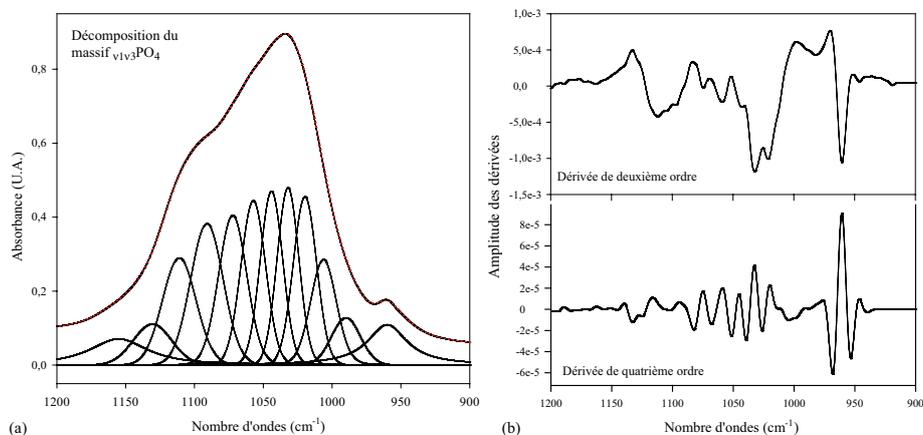
## Materials and Methods

The first stage of this work consisted of creating a reference base of modern bones composed of of ox humerus diaphyses. After removal of the bone marrow and flesh, the cortical part of the bone was ground up in order to obtain a particle size between 1.25 and 2 mm. Sub-samples of about 0.75 g were then heated for

15, 30, 45, 60, 90, and 120 minutes to temperatures between 120°C and 900°C in a muffle furnace under oxidising conditions. This reference standard after heating is shown in figure 4.

The fossil samples studied come from the Magdalenian levels of the site of Bize-Tournal (ensemble IV, level G, layer 1.) These samples, which are fairly recent (15,000 BP), display a good state of preservation, which motivated their selection for this study. The traces of carbonisation and calcination are numerous and easily identifiable by microscopy (Tavoso, 1987; Patou-Mathis *et al.*, 1999; Magniez, in press) This material can thus constitute a fossil reference base that allows testing of the method developed. In order to facilitate the comparison between the modern reference and the fossil material, the Bize-Tournal samples were classified on the basis of their colour into the seven categories of heating defined by Stiner *et al.* (1995) and shown in figure 1. For each of the 23 fossil samples selected, approximately 25 mg of material were collected for the infrared analyses. The size of these samples is small and the heating categories identified macroscopically refer only to the sampled zone.

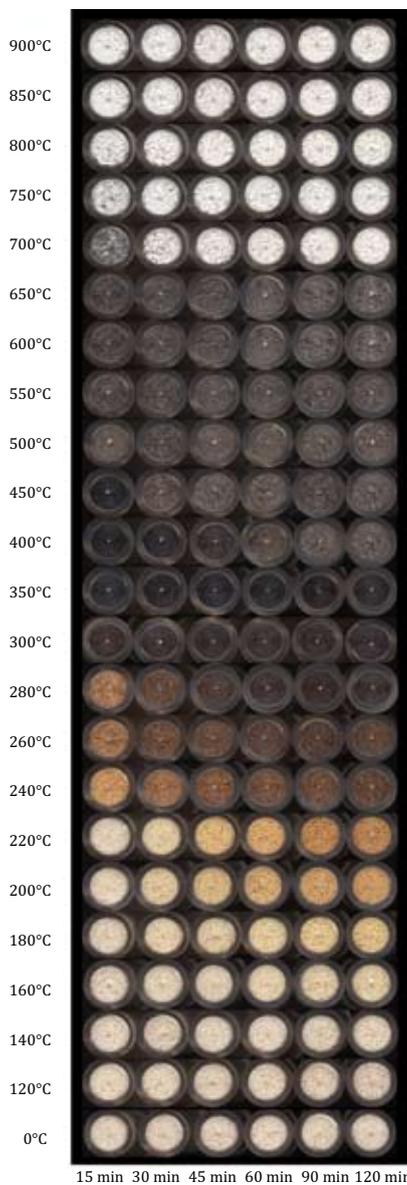
The infrared data were obtained utilizing the KBr pellet technique. A few milligrams of each sample were ground up in acetone in order to obtain a particle size of less than 5  $\mu\text{m}$ . The pellets were then prepared by mixing  $2.5 \pm 0.02$  mg of this powder brought up to 1 g with potassium bromide (KBr.) Finally, 300 mg of



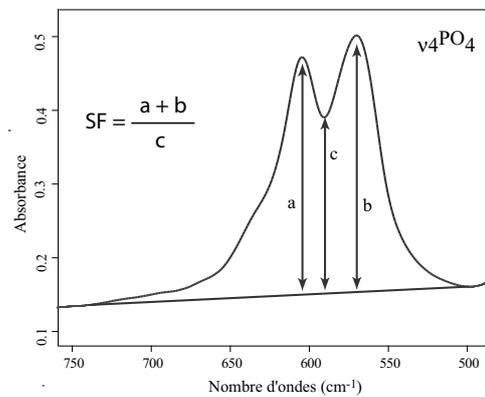
**Fig. 3 -** (a) Diagram of the various component peaks of the  $\nu_1\nu_3\text{PO}_4$  domain identifiable from the second and fourth derivative spectra between 900 and 1200  $\text{cm}^{-1}$  (b.)

this mixture were pressed at 11T/cm<sup>-1</sup> for 1.5 minutes (Fröhlich, 1989.) The infrared spectra were recorded on a Vector 22 Bruker spectrometer by accumulating 64 scans with a resolution of 2 cm<sup>-1</sup>. The spectral range of the ν<sub>1</sub>ν<sub>3</sub>PO<sub>4</sub> domain included between 800 and 1200 cm<sup>-1</sup> was selected for each specimen. The second and fourth order derivatives of this range of the infrared spectrum were calculated utilising an algorithm of the Savitsky and Golay type and a smoothing of respectively 7 and 15 points. The derivatives of the infrared spectra could thus be used to identify the wavenumbers of the components of the

ν<sub>1</sub>ν<sub>3</sub>PO<sub>4</sub> domain. It was then possible, knowing the wavenumber of these different components, to model this domain starting from simple components of the Gaussian type, placed at the wavenumbers identified in the derivatives, and to adjust the area of each of them by the least square method until the simulated spectrum best matched the experimental one. It was also possible to assess the crystallinity of the bones by the splitting factor according to the model developed by Weiner and Bar-Yosef (1990) by adding the absorbances of the peaks centred near 565 cm<sup>-1</sup> and 605 cm<sup>-1</sup> divided by the absorbance of the baseline between them. Each of these absorbances is measured in relation to the baseline drawn between 500 and 700 cm<sup>-1</sup> (fig. 5.)



**Fig. 4** - Reference base of modern bones heated to between 120 and 900°C for 15, 30, 45, 60, 90, or 120 minutes.



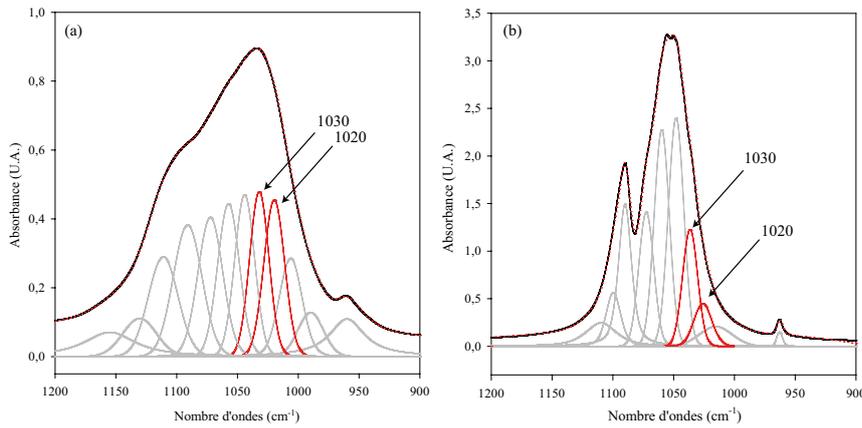
**Fig. 5** - Method for measuring the splitting factor according to the model established by Weiner and Bar-Yosef (1990). The splitting factor is calculated from the sum of the absorbances of the two ν<sub>4</sub>PO<sub>4</sub> peaks centred near 565 (a) and 605 cm<sup>-1</sup> (b) divided by the absorbance of the baseline between them (c.)

### Study of the modern reference base

#### Assessment of the crystallinity: 1030/1020 indexes and splitting factor

The work of Gadaleta *et al.*, (1996) and Paschalis *et al.* (1996) has shown that it is possible to assess the crystallinity of the mineral phase of the specimens by measuring the ratio between the area or amplitude of a peak assigned to the phosphates in a well crystallised pure apatite and that of a peak assigned to the phosphates in a poorly crystallised apatite. Figure 6 shows the ν<sub>1</sub>ν<sub>3</sub>PO<sub>4</sub> domain of a sample of





**Fig. 6** - Relative absorbance of the peaks centred on average near 1030 and 1020  $\text{cm}^{-1}$  for a modern bone: unburnt (a) and heated to 900°C (b.)

unburnt modern bone (a) and of a sample heated to 700°C during 30 minutes (b.). The peaks centred near 1030 and 1020  $\text{cm}^{-1}$  have very similar amplitudes in the case of the unburnt samples, indicating the coexistence of a well crystallised mineral phase and of another less well crystallised one, in relatively equal proportions. The  $\nu_1\nu_3\text{PO}_4$  domain of the bones burnt at high temperature, on the other hand, shows a peak at 1030  $\text{cm}^{-1}$  largely dominant relative to that centred near 1020  $\text{cm}^{-1}$ . The evolution of this 1030/1020  $\text{cm}^{-1}$  ratio as a function of temperature allows the observation of a trend entirely similar to that observed for the splitting factor; these two indexes are indeed correlated ( $r^2 = 0.95$ ;  $p < 0.001$ ; fig. 7.) It seems therefore that the 1030/1020 ratio can be used to assess the crystallinity of the burnt bones and that it provides information similar to that obtained through the splitting factor.

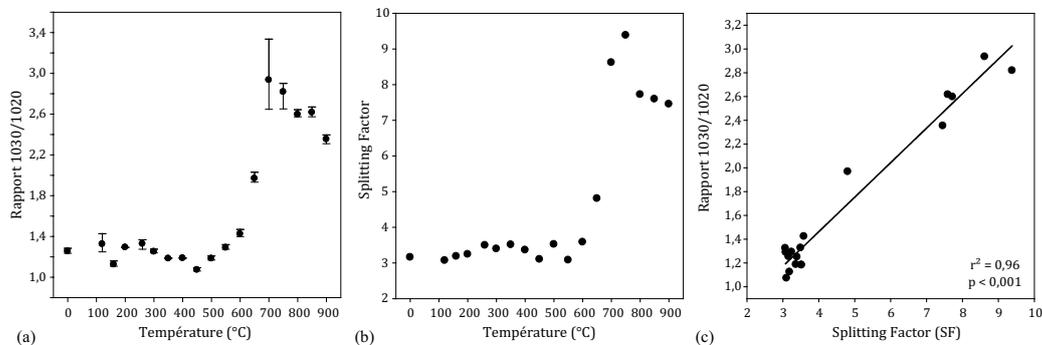
#### Changes in the general appearance of the derivatives

During heating, the  $\nu_1\nu_3\text{PO}_4$  domain undergoes significant changes that translate notably in the appearance of a

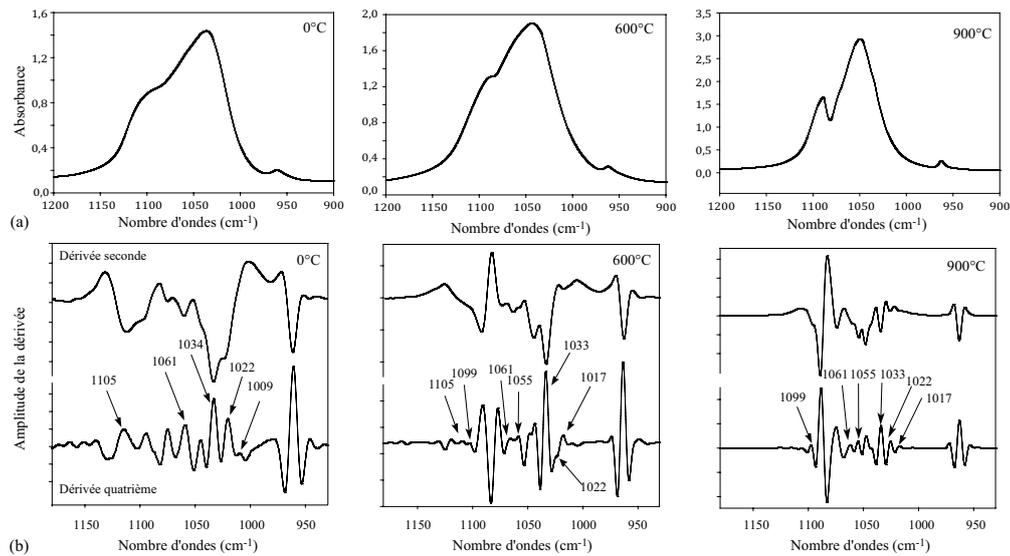
peak centred near 1090  $\text{cm}^{-1}$ , which becomes clearly distinct starting at 600°C. This peak, visible only in samples heated to high temperatures, makes it possible to distinguish the unburnt samples and those burnt at low temperatures from those heated to at least 600°C (fig. 8a.).

The second and fourth derivatives show much more complex appearances that make it possible to display more subtle changes in this domain. These changes in the appearance of the derivatives allow the identification of at least three temperature ranges: 0-450°, 500-600°C, and temperatures above 600°C (fig. 8b.).

The number of peaks is similar for the unburnt samples and for those burnt up to 450°C. These peaks, identified on the basis of literature data, can be assigned at the same time to phosphate groups located on the one hand in a very pure crystallised hydroxyapatite, and on the other hand in a poorly crystallised carbonated hydroxyapatite. The coexistence of these two phases within the mineral phase is typical of the *in vivo* bones, whose mineral phase contains significant proportions



**Fig. 7** - Evolution of the value of the 1030/1020 index (a) and of the splitting factor (b) as a function of the temperature for modern specimens heated to between 120 and 900°C for 30 minutes. Correlation between the 1030/1020 ratio and the splitting factor for the same specimens (c.)



**Fig. 8** - Appearance of the  $\nu_1\nu_3\text{PO}_4$  domain (a) and of the second and fourth order derivatives of this domain (b) for modern specimens: unburnt, and heated to 600°C and 900°C.

of carbonate ( $\text{CO}_3^{2-}$ ) and hydrophosphates ( $\text{HPO}_4^{2-}$ ) ions (Young and Holcomb, 1984; Pasteris *et al.*, 2004.).

Near 450°C, the appearance of the derivatives is heavily modified and new peaks appear near 1017, 1056, and 1098  $\text{cm}^{-1}$ . These peaks could correspond to a new type of calcium phosphate generated at high temperatures, such as whitlockite, or they could be the result of artefacts of the derivation.

Above 600°C, the derivative spectra display a very different appearance due to the disappearance of several component peaks on the boundaries of the domain: the components centred near 1140 and 1150 disappear at around 650°C and those centred near 1114 and 1128 disappear at around 850°C. These peaks are assigned to the hydrophosphate groups present in the mineral phase of impure apatites (Rey *et al.*, 1991; Gadaleta *et al.*, 1996) and therefore their disappearance at high temperatures indicates an improvement in the quality of the mineral phase.

#### *Wavenumber variations of the component peaks centred near 961, 1022, 1061, and 1092 $\text{cm}^{-1}$*

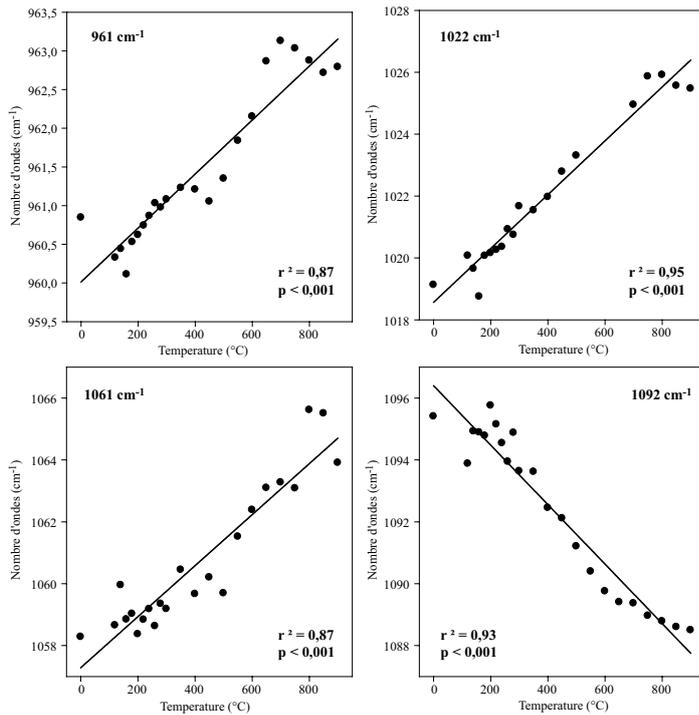
Among these different components of the  $\nu_1\nu_3\text{PO}_4$  domain, four peaks display clear wavenumber variations during heating. They are the peaks centred near 961,

1022, 1061, and 1092  $\text{cm}^{-1}$ , with a positive shift for the first three peaks and a negative one for the last (fig. 9.). Comparing these data with those from earlier studies on synthetic apatites or *in vivo* bones, it was possible to verify that the wavenumbers observed in our samples, unburnt or burnt at low temperatures, correspond to those generally observed in the literature for poorly crystallised apatites containing  $\text{CO}_3^{2-}$  and  $\text{HPO}_4^{2-}$  ions. The wavenumbers observed in our specimens heated to high temperature correspond, on the contrary, to those generally observed for pure, well crystallised apatites (Rey *et al.*, 1991; Paschalis *et al.*, 1996; Pasteris *et al.*, 2004). It seems therefore that the variation in the wavenumber of these peaks indicates an improvement of the quality of the mineral phase during heating (Lebon *et al.*, 2008.).

### Study of the fossil material

#### *Assessment of the crystallinity: 1030/1020 indexes and splitting factor*

The 1030/1020 index and the splitting factor were calculated for each of the fossil specimens. The values of the splitting factor measured on the unburnt specimens are close to 3.5 (category 0; fig. 10.) For the samples of the heating categories 1 to 4, the measured



**Fig. 9** - Wavenumber shift of the peaks centred near 961, 1022, 1061, and 1092 cm<sup>-1</sup> as a function of temperature for modern specimens heated for 30 minutes.

of the stage of heating are very similar and Figure 10c shows the correlation between the two indexes ( $r^2 = 0,98$  ;  $p < 0,001$ ).

*Appearance of the derivative spectra of the fossil specimens*

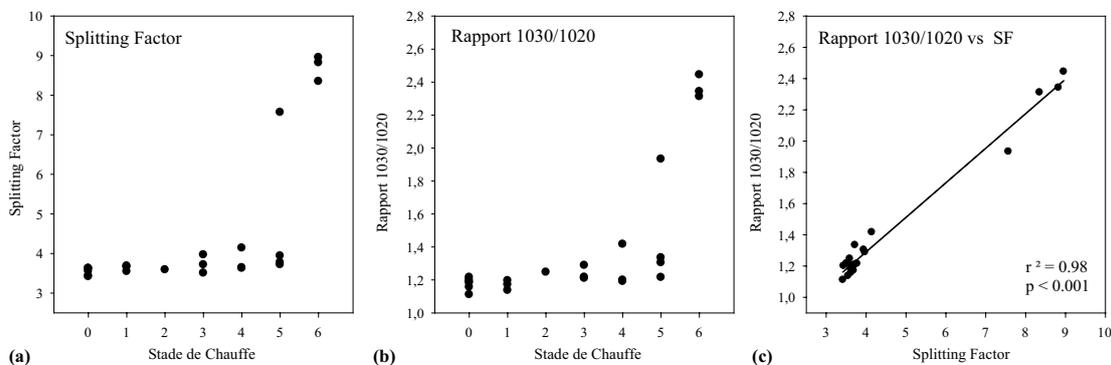
The general appearance of the infrared spectra, and more specifically of the  $\nu_1\nu_3\text{PO}_4$  domain, of these fossil specimens is quite similar to that of the modern reference specimens. Changes can however be observed in the appearance of the derivatives of the  $\nu_1\nu_3\text{PO}_4$  domain, as a function of the heating degree determined for these specimens on the basis of macroscopic criteria. In particular, it seems possible to clearly distinguish, by the appearance of the derivative spectra, the unburnt fossil bones or those heated to temperatures lower than 500°C, from those that have been burnt at temperatures between 500°C and 600°C, or at temperatures higher than 600°C (figure 11.).

values range between 3.55 and 4.14 and therefore are not clearly distinguishable from those of the unburnt specimens. Only the samples of categories 5 and 6 display SF values clearly distinct from those of the unburnt samples, with values approaching 9 for certain samples belonging to category 6.

The 1030/1020 ratio displays values close to 1.2 for the unburnt fossil samples and increases to values close to 2.4 for samples that show complete calcination (stage 6.) The trends observed for these two indexes as a function

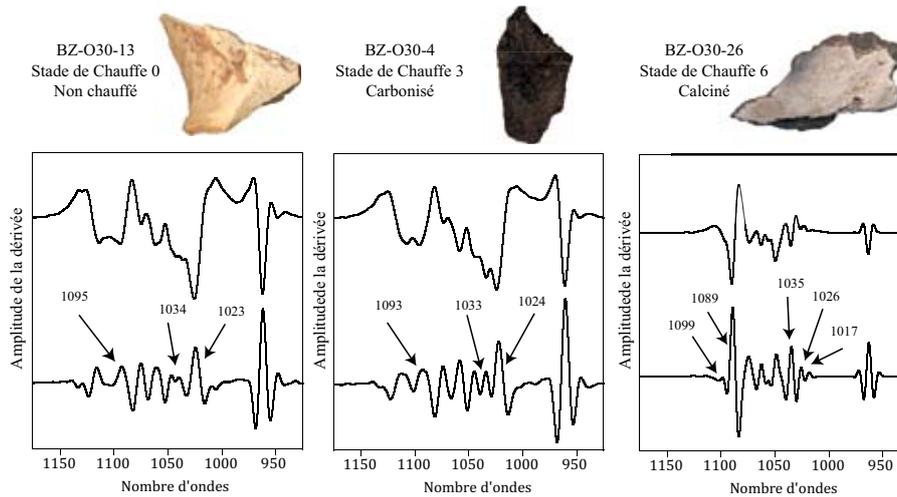
*Wavenumber variations of the component peaks centred near 961, 1022, 1061 and 1092 cm⁻¹*

It was also possible to measure the wavenumber of the four peaks centred near 961, 1022, 1061, and 1092 cm<sup>-1</sup> for each of the fossil samples. The wavenumbers of these peaks as a function of the heating stage of the



**Fig. 10** - Value of the splitting factor (a) and of the 1030/1020 index (b) as a function of the temperature for modern specimens heated to between 120 and 900°C for 30 minutes. Correlation between the 1030/1020 ratio and the splitting factor for the same specimens (c.).





**Fig. 11** - Appearance of the second and fourth order derivatives of the  $\nu_1\nu_3\text{PO}_4$  domain of the specimens BZ-O30-13, BZ-O30-4, and BZ-O30-26 from the Magdalenian levels of the Bize-Tournal site.

specimen are shown in figure 12. For these specimens, the wavenumbers of the first three peaks are correlated to the heating stages to a lesser degree than is the case for the previously studied modern specimens. The peak centred at  $1092\text{ cm}^{-1}$  does not show a significant correlation with the stage of heating of the specimen. These weak correlations between the wavenumbers of the peaks and the heating stages make it difficult to identify the burnt bones by this criterion.

## Discussion

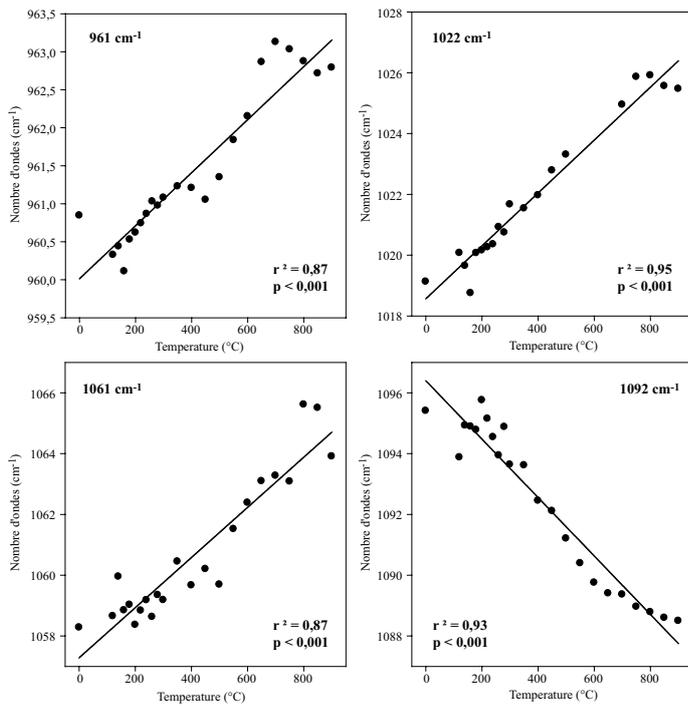
During burning, the composition of the mineral of bone phase undergoes significant changes that can be shown with characterisation techniques such as infrared spectroscopy.

The identification of burnt bones by infrared spectroscopy generally involves an assessment of the degree of crystallinity through measurement of the splitting factor. The study reported here on the  $\nu_1\nu_3\text{PO}_4$  domain of a reference base of burnt modern bones and of fossil specimens from Magdalenian levels of the site of Bize-Tournal has made it possible to demonstrate the informative potential of this spectral region for the identification of burnt samples.

It is confirmed that the evolution of the composition of the mineral phase of bone during burning is manifest in significant modifications of the appearance of the  $\nu_1\nu_3\text{PO}_4$

domain, identifiable especially in derivative spectra: these modifications make it possible to distinguish three ranges of heating temperatures ( $0\text{-}500^\circ\text{C}$ ,  $500\text{-}600^\circ\text{C}$ ,  $>600^\circ\text{C}$ .) It has also been found that the  $\nu_1\nu_3\text{PO}_4$  domain allows a good assessment of the degree of crystallinity because the values of the 1030/1020 index are strongly correlated to those of the splitting factor, both for modern and fossil material.

Moreover, several components of the  $\nu_1\nu_3\text{PO}_4$  domain display a wavenumber variation as a function of the heating temperature in the case of modern material. These wavenumber variations occur mainly between  $120^\circ\text{C}$  and  $650^\circ\text{C}$ , while, above this temperature, the wavenumber remains fairly stable for the four peaks. In contrast, the change of the splitting factor during heating occurs essentially between  $600$  and  $700^\circ\text{C}$ , thus indicating an increase in the size of the crystals also identifiable by electron microscopy and x-ray diffraction. In infrared spectroscopy, the wavenumber variations of the absorption peaks can be related to modifications of the molecular environment of the groups considered. Such modifications of the molecular structure at low temperatures could be revealed earlier through XRD by significant changes in the unit cell parameters (Rogers and Daniels, 2002; Etok *et al.*, 2007.) These changes, which occur mainly between  $120$  and  $500^\circ\text{C}$ , could result notably from the elimination of carbonates and water present in the mineral phase. The variations in the wavenumbers of the observed



**Fig. 12** - Wavenumbers of the peaks centred near 961, 1022, 1061, and 1092 cm<sup>-1</sup> as a function of the burning stage for the specimens from the Magdalenian levels of the Bize-Tournal site.

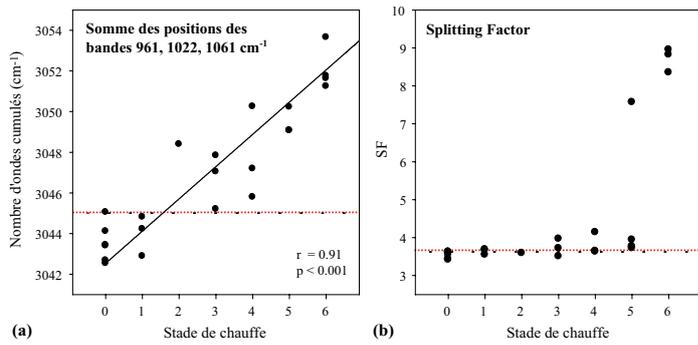
peaks would thus indicate an improvement in the quality of the mineral phase during heating, while the splitting factor would mainly characterise the increase in the size of the crystallites induced at high temperatures by an improved organisation of the crystal lattice.

In the case of fossil material, the wavenumbers of the observed peaks as a function of the stage of heating display less clear trends; this limits the use of this criterion to assess the heating temperature. Such variations, indicative of the changes in the composition of the mineral phase, can result from various diagenetic processes. The utilisation of the wavenumber of these peaks could therefore contribute also to the evaluation of the degree of alteration of unburnt bones. Three of these peaks show a significant upward shift in their wavenumber as a function of the degree of heating, although the coefficients of determination are weak. These are the peaks centred on average near 961, 1022, and 1061 cm<sup>-1</sup>. In order to minimise the effect of individual variations of these wavenumbers and to increase the spread between specimens belonging to different

categories, the wavenumbers of these peaks were added together. This makes it possible to more clearly detect the stage of heating of the specimens (fig. 13.) In fact, the cumulative wavenumbers of the unburnt specimens (category 0) are clearly distinct from those of specimens belonging to at least stage 2. In contrast, only the specimens belonging to stages 5 and 6 are clearly distinguished from unburnt specimens when the splitting factor is used; this limits its potential for characterising the more lightly burnt bones in an archaeological context. The utilisation of the wavenumber of these peaks seems then to allow the identification of the bones burnt from stage 2, or about 240°C, and up for the Bize-Tournal material.

Another advantage of the use of the  $\nu_1\nu_3\text{PO}_4$ , between 1200 and 900 cm<sup>-1</sup>, is that it can be studied by infrared micro-spectroscopy. In fact, the spectral range of infrared micro-spectroscopy is generally limited between 4000 and 600 cm<sup>-1</sup> and therefore it does not allow measures of the splitting factor. It was possible to carry out some preliminary tests by infrared micro-spectroscopy on polished thin sections of burnt modern bone (protocol established by Miller *et al.*, 2007), in order to study the spatial distribution of the crystallinity and the relative concentration of carbonates within the mineral phase. Figure 14 shows the spatial variability of these two parameters for a fragment of ox diphyis heated to 500°C for 45 minutes: its peripheral portion shows the onset of calcination while the interior portion is still carbonised. It can be seen that the crystallinity is higher in the external zone, submitted to higher temperatures, and that it is, in contrast, lower in the interior portion where the carbonate concentration remains high. It seems therefore that exposing the bone to heat results in a gradual diffusion of the temperature within the specimen and in the establishment of a composition gradient. The use of infrared micro-spectroscopy to study these composition gradients could thus make it





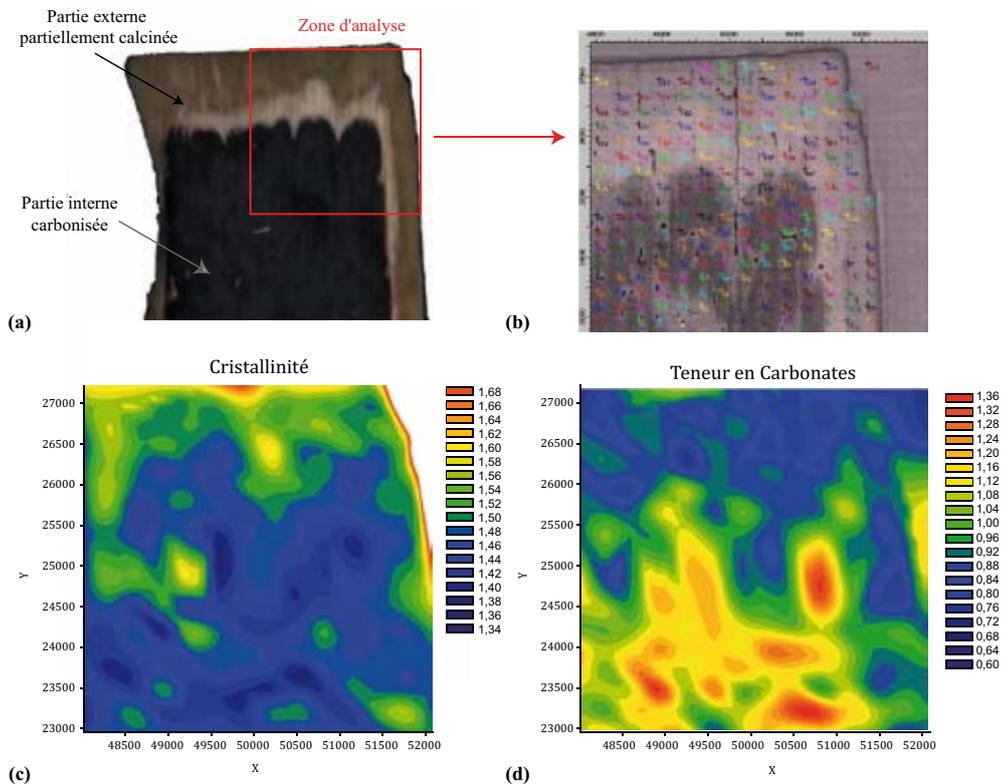
**Fig. 13** - Cumulative wavenumbers of the peaks centred near 961, 1022, and 1061  $\text{cm}^{-1}$  (a) and values of the splitting factor (b) as a function of the burning stage for the Bize-Tournal specimens. The dotted line represents the maximum value observed for the unburnt specimens (category 0.)

possible to assess, not only the heating temperature, but also the time during which the specimen was exposed to the heat. This technique can also make it possible to consider the spatial variability of the composition of unburnt bones and thus contribute to a better understanding of the heterogeneities of the alterations occurring in bones during diagenesis. It

could then be possible to identify zones diagenetically less modified, at whose level the heating signal would be preserved.

### Conclusion

The results obtained through this work have demonstrated the interest of the  $\nu_1\nu_3$  phosphate domain in the study of the changes in bone composition during heating. The 1030/1020 index was found to be effective in the assessment of the crystallinity in a way entirely equivalent to that of the splitting factor, both for modern and fossil bones, whether burnt or not. The utilisation of this index in the context of infrared micro-spectroscopic analyses can therefore make it possible to take into account the structure and the heterogeneity of the changes undergone during both heating and diagenesis. This type of study will thus make it possible to better define the effects of heating on a



**Fig. 14** - Infrared mappings carried out on polished thin sections of a fragment of compact bone heated to 500°C for 45 minutes (a.) After selecting an area of 4.5  $\text{mm}^2$ , about 200 points of analysis were carried out (b) in order to establish a distribution of the values of crystallinity (c) and of the relative carbonate content (d) within the mineral phase.



micro-scale and to attempt to define more reliable markers of thermal treatment.

This study has also made it possible to detect wavenumber variations for certain component peaks of the  $\nu_1\nu_3\text{PO}_4$  domain. These variations, which occur at a lower temperature than the crystallinity, seem to indicate an improvement in the organisation of the crystal lattice, which could be the result of the elimination of the carbonates and water present in the bone mineral phase. Such criteria represent sensitive markers of the modifications of the composition during heating. Although these markers appear to be modified during diagenesis, they nevertheless made it possible to identify bones burnt at temperatures as low as 240°C in the case of material from Magdalenian levels. The application of this analytical protocol thus makes it possible to characterise burnt bones, as well as the temperatures and durations of the heating phase; it could also contribute to a better identification of the activities at the origin of the bones in various archaeological contexts.

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