



From bone to ash: Compositional and structural changes in burned modern and archaeological bone



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ABSTRACT

The composition and structure of experimentally heated modern bone and cremated bone fragments from various archaeological sites were analysed by Fourier Transform Infrared Spectroscopy (FTIR) in Attenuated Total Reflectance (ATR) mode before and after pre-treatment with acetic acid. The results confirm that time and temperature have an impact on the degree of calcination but also highlight that, once fully calcined, the final composition and structure of bone are influenced by temperature alone. A combination of several infrared indices makes it possible to discriminate between bones cremated under different conditions. The study of archaeological samples revealed that their carbonate composition is quite different to modern calcined bone and that some samples, originating from high-carbonate geological contexts, have significantly higher carbonate concentration compared to modern specimens, even after pre-treatment. The results suggest that FTIR yields information on not just the structure of burned bone, but also potentially about the modes of burning, including cremation, and the depositional conditions.

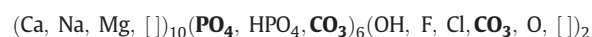
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1. Introduction

Burned bones are frequently observed in the archaeological record, resulting from cooking practices, accidental exposure to fire, use of bone as fuel, or from mortuary practices, i.e. cremation, a common rite in many cultures and civilisations throughout pre/history. Whether burning took place accidentally or purposefully, the material residue includes calcined bone fragments. In many situations where soil conditions are not conducive to the preservation of unburned bone, they are all that survive. Gathering more information about these remains will help scholars to better understand cremation and cooking practices in past cultures.

Bone is composed of mineral, an organic component and water. The organic fraction of bone is largely made of collagen closely linked to the mineral fraction (Vaughan, 1970). The latter is a carbonate-substituted apatite or bioapatite, similar in composition and structure to hydroxyapatite – $\text{Ca}_5(\text{PO}_4)_3(\text{OH})_2$ – with phosphates (PO_4^{3-}) partially replaced by carbonates (CO_3^{2-}) and carbonates occupying some of the hydroxyl (OH^-) positions (Skinner, 2005). The carbonates which replace hydroxyl groups and phosphates are known as A and B carbonates respectively (LeGeros et al., 1969). The presence of hydroxyl groups in bone apatite continues to be the topic of debate: some scholars believe that a number of hydroxyl groups are present (Taylor et al., 2001; Mkukuma et al., 2004; Leventouri, 2006) while others argue that bone

apatite does not contain detectable concentrations of hydroxyl groups (Rey et al., 1995; Loong et al., 2000; Pasteris et al., 2004; Wopenka and Pasteris, 2005). This debate notwithstanding, the composition of bone apatite can be summarized as the following formula, with the most frequent components set in bold and [] representing potential vacancies in the structure (LeGeros et al., 1986; Skinner, 2005):



Since carbonates have a different geometry and charge to phosphates and as they are much bigger than hydroxyl groups, their presence in the crystal structure creates distortions that reduce the crystallinity of bioapatite compared to hydroxyapatite (Skinner, 2005). Crystallinity is an indication of atomic order and relative crystal sizes of bioapatite. Because of its low crystallinity, bone apatite is highly reactive. After death, at ambient temperature, crystallinity tends to increase (Lee-Thorp, 2002; Trueman et al., 2004) making bioapatite less reactive. The same process occurs during heating (Kyle, 1986) and it is currently believed that due to the higher crystallinity observed in calcined bone, it is more resistant to diagenesis than unburned bone (Zazzo and Saliège, 2011) making it a material of choice for radiocarbon dating.

This is of particular importance when studying structural modifications as one of the main changes occurring in bone during cremation in addition to colour changes, is in its crystallinity (Stiner et al., 1995). The present study focusses on the chemical and structural changes caused by heating above 500 °C. The three main components of bone (water, organics and apatite) will be differently affected by heat. The organic and water components rapidly burn off (Van Strydonck et al.,

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2005); in parallel, the structure and composition of the mineral phase are modified. Stiner et al. (1995) developed the Burn Colour Code to assess the degree of calcination (Table 1), based on the series of colour changes from cream to black in charred bones (300–500 °C) and then to white for calcined bone (above 600–700 °C).

These colour changes are the result of changes in composition and structure. Laboratory experiments have shown that carbonate concentrations in bone apatite decrease from ca. 6% in raw bone to 0.5 to 1% in calcined bone (Van Strydonck et al., 2005; Zazzo et al., 2009). First, water evaporates below 225 °C. An initial fraction of CO₂ is lost between 225 and 500 °C as a consequence of the combustion of the organic phase. Above 500 °C, the decomposition of structural and secondary carbonates results in the loss of a second fraction of CO₂. Thus carbonates substituted within the bioapatite crystal structure are the last to be emitted (Van Strydonck et al., 2005).

Experiments have shown that the loss of CO₂ is not only dependent on temperature but also on time (Van Strydonck et al., 2005). The temperature at which bone is completely calcined is still the topic of some debate. Some scholars have suggested temperatures above 650 °C (Stiner et al., 1995), others that bone is already calcined at 600 °C (Lanting et al., 2001; Naysmith et al., 2007), at 625 °C (Person et al., 1996), or only at 725 °C (Van Strydonck et al., 2009). It is likely that these differences are the result of different exposure times and bone fragment sizes used in the experiments. Once full calcination is reached (white colour) only the inorganic fraction (bone apatite) survives though its composition and structure have been significantly modified (Fig. 1). Isotopically, it has been shown that the carbonates present in bone apatite after calcination are not all endogenous but that a significant fraction originates from the combustion atmosphere (Hüls et al., 2010; Zazzo et al., 2012).

The compositional and structural modifications of bone apatite during calcination have been assessed using infrared spectroscopy, mostly on experimentally heated bone (e.g. Thompson et al., 2009, 2013; Lebon et al., 2010). However, due to the different experimental conditions (time, temperature) used, the relative impacts of temperature and exposure time remain unclear. Furthermore, although the higher crystallinity observed in calcined bone likely makes it more resistant to diagenesis (Zazzo and Saliège, 2011; Quarta et al., 2013), the impact of burial environment on the composition and structure of cremated bone fragments has not been investigated yet.

Here, we focus on fully calcined bone and explore how infrared analysis can contribute to an assessment of its composition and structure, and how this information can be used to understand ancient cremation practices and to detect potential post-burial alterations. To do so, modern experimental samples and more than a hundred cremated bone samples from 13 archaeological sites in the UK and Ireland were analysed before and after pre-treatment with acetic acid. The latter was used to remove potential diagenetic apatites and exogenous carbonates.

2. Materials and methods

2.1. Samples

Modern samples comprised animal bone pieces that were heated in a laboratory muffle furnace or burned on outdoor pyres. The archaeological

Table 1
Burn Colour Code (Stiner et al., 1995).

Burn Colour Code	Description
0	Not burned – cream/tan
1	Slightly burned – localised and less than half carbonised
2	Lightly burned – more than half carbonised
3	Fully carbonised – completely black
4	Localised less than half calcined – more black than white
5	More than half calcined – more white than black
6	Fully calcined – completely white

samples are from sites in Ireland and the United Kingdom ranging in age from the Mesolithic to the Middle Bronze Age; they are all human with the exception of two medium–large mammal bone fragments from the Mesolithic site of Asfordby. The sites present a wide range of geological contexts from chalk and limestone (high-carbonate) to granite and basalt (non/low-carbonate). All samples are summarized in Table 2.

2.2. Laboratory experiments and outdoor cremations

For the laboratory experiments (labelled 'LAB'), a cow tibia was selected. Its diaphysis was cut into 80 fractions–20 slices of about one centimetre (Fig. 2) divided into quarters of approximately the same weight (ca. 10 g). The heating experiments were carried out in a muffle furnace, in durations from half an hour to 24 h (0.5, 1, 2, 4, 8, 12, 18 and 24 h), with temperatures ranging from 500 to 900 °C. Two bone fragments were randomly selected for each of the resulting 40 (8 durations * 5 temperatures) heating experiments. Several animal joints (cow, pig, lamb and chicken) were also burned on outdoor pyres (labelled 'OUT'). The temperature, as monitored using a thermocouple, ranged between 600 and 900 °C. It varied in time and space because of the non-controllable factors typical of outdoor experiments (e.g. wind). The set-up for these outdoor cremations is described in detail in Snoeck and Schulting (2013).

We recognise that the results obtained on the sliced cow tibia heated in a muffle furnace are not directly comparable to samples burned on outdoor pyres due to the absence of flames, lack of environmental impact (e.g. wind, humidity), lack of flesh and skin, etc. In addition, the fact that the cow tibia was cut before heating could also have an impact as some areas of the bone were directly in contact with the combustion atmosphere, which would not have been the case had a carcass or even a complete uncut joint been burned whole on an outdoor pyre. Additionally, the experimental work was carried out on a range of animal bone that are then compared to human bone. Nevertheless, we believe that the results presented here represent a contribution towards a better understanding of the effects of heating and burning on the composition and structure of bone apatites.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analyses were carried out using the Attenuated Total Reflectance (ATR) mode. This allows for rapid measurement as it only requires the samples to be powdered and does not require the powders to be pressed into pellets. The results obtained by this method are not directly comparable with those obtained using the transmission mode and KBr pellets (Thompson et al., 2009; Beasley et al., 2014), but, the ATR mode is now commonly used for the study of calcified tissues.

The samples were first crushed using a mortar and pestle and then analysed by FTIR–ATR (Agilent Technologies Cary 640 FTIR with GladiATR™ from Pike Technologies). Each sample was pressed onto the diamond crystal and measured in triplicate (on different aliquots if sufficient material was available). The background was measured and subtracted and a baseline correction was carried out using Agilent Resolution Pro software. The spectra were normalised and the three spectra were averaged before calculation of a suite of infrared indices that describe the composition and structure of the bone. To ensure better reproducibility of the measurements carried out by FTIR–ATR, only spectra with a minimum absorbance of 0.06 for the highest phosphate peak at c. 1035 cm⁻¹ were taken into account. Multiple measurements in our laboratory have shown that above 0.06, reproducibility of the measurements is significantly improved.

Several infrared indices have been proposed for the study of bioapatites and cremated bone. Most of them have been defined using the transmission mode but they can also be applied to spectra in reflectance mode (ATR) as long as all samples are measured in the same mode (Thompson et al., 2009; Beasley et al., 2014). Here we used a selection of published indices and introduced a further calculation: the hydroxyl to

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