

THE CARBON ORIGIN OF STRUCTURAL CARBONATE IN BONE APATITE OF CREMATED BONES

Mark Van Strydonck^{1,2} • Mathieu Boudin¹ • Guy De Mulder³

ABSTRACT. In order to reveal a possible carbon exchange between carbon dioxide of the fuel and the bone apatite during the cremation process an experiment was set up using fossil fuel. Two setups were constructed, one using natural gas and one using coal. In both experiments, a carbon substitution in the apatite was revealed.

INTRODUCTION

The validity of radiocarbon dating of cremated bones has been proven in laboratory intercomparison tests (Naysmith et al. 2007) as well as in the dating of duplicate samples of charcoal/cremated bone (Lanting and Brindley 1998; De Mulder et al. 2007; Olsen et al. 2008). Post-depositional contamination of well-cremated bones seems to be limited to the deposition of secondary carbonate and no CO₃ radicals are trapped by substitution (Van Strydonck et al. 2009). Nevertheless, the fact that in several cases charred bones showed aberrant results even after proper pretreatment (Olsen et al. 2008; Van Strydonck et al. 2009) indicates that a possible CO₃ substitution must be considered. Moreover, in none of the comparison tests was the ¹⁴C date compared with historically well-dated cremations.

It has been demonstrated that the compactness of well-cremated bones forms a barrier (Van Strydonck et al. 2005) for the carbonate substitution—a barrier that does not exist in the case of burnt bones. However, most of the chemical changes in the bone do not occur during the post-depositional phase, but during the cremation: dehydration, burning of the collagen, changes in crystallinity, and loss of structural carbonate. Consequently, during the cremation the bone is very susceptible to chemical substitution. The aim of this paper is to test the hypothesis of a possible carbon exchange between the apatite and the atmosphere (CO_{2 AIR} + CO_{2 FUEL}) during the cremation process. Zazzo et al. (2009) did a similar experiment, but their conclusions were mainly drawn from stable isotope measurements and not from ¹⁴C measurements. They stated that low δ¹³C values of calcined bones must be explained by kinetic effects. Furthermore, they concluded that, although carbon exchange during cremation cannot be totally excluded, it is essentially the remaining fraction of the initially present carbonate in the bone that is highly fractionated during cremation.

MATERIAL AND METHODS

In the case of a normal ritual cremation, the difference in ¹⁴C content of the cremated body and the fuel will be in most cases minimal (see below) and a possible carbon exchange will be difficult to recognize. In order to circumvent this problem, no archaeological material was studied. Instead, fresh animal bones (bone and flesh) were calcined under conditions that emulate a normal cremation, but with the use of fossil fuel. The authors recognize that by doing so, a lot of experimental parameters could not be measured or controlled. But well designed and carefully controlled laboratory experiments often do not reflect real situations. Furthermore, a similar experiment, under well-controlled conditions, was performed by the Kiel laboratory (Hüls et al. 2010), enabling the respective results to be compared.

¹Royal Institute for Cultural Heritage, Jubelpark 1, 1000 Brussels, Belgium.

²Corresponding author. Email: mark.vanstrydonck@kikirpa.be.

³Department of Archaeology, Ghent University, Blandijnberg 2, 9000 Ghent, Belgium.

In a first attempt to imitate as close as possible a prehistoric cremation, a pyre was set up with coal instead of wood. The burning coal would create an atmosphere around the incinerating bone with a higher CO₂ concentration than in the free air ($p\text{CO}_2\text{PYRE} > p\text{CO}_2\text{AIR}$), but depleted in ¹⁴C. Unfortunately, it was impossible to keep the combustion going, so the experiment was split into 2 different tests. In test 1, part of the sample was calcined in the flame of a bunsen burner using natural gas (Figure 1). A brick housing was built (external dimensions: H = 36 cm, L = 40 cm; internal volume = ~13,000 cm³) to create an atmosphere around the cremating bone with $p\text{CO}_2\text{OVEN} > p\text{CO}_2\text{AIR}$, but depleted in ¹⁴C. The experiment was carried out twice: A) with the bone above the flame of the bunsen; B) with the bone in the flame of the bunsen (see Table 1). The temperature inside the oven stabilized at 800 °C. After 2 hr, an air sample from inside the brick oven was taken. This air sample gives information about the conditions inside the oven, although it must be taken into account that the $p\text{CO}_2$ is not uniform inside the oven. Around the burner, the $p\text{CO}_2$ will be much higher than in the rest of the oven. Furthermore, there is much more gas movement inside the oven than in a pyre heated with wood, due the constant burning of natural gas and continuous input of fresh air (oxygen).



Figure 1 Brick oven used in test 1 (left: general view, right: the bunsen and the calcined bones).

Table 1 Characteristics of the atmosphere inside the oven (test 1, bunsen).

Bunsen	Lab code	pMC	$\delta^{13}\text{C}$ (‰)	% by vol. CO ₂ in the oven
Test A	KIA-38450	2.99 ± 0.08	-27.33	2.9
Test B	KIA-38451	2.69 ± 0.08	-27.60	2.5

In test 2 (Figure 2, Table 2), the bone was cremated in a muffle furnace at 800 °C (internal volume ~6500 cm³) filled with ~500 g of coal (6% ash content). It must be taken into account, however, that inside the oven, the temperature can be higher due to the combustion of the flesh, collagen, and coal.

In this setup, there is less gas movement and a less virulent burning. After 1 hr of combustion, an air sample was taken on this occasion as well. The amount of CO₂ in both ovens was calculated by extraction of the CO₂ from a calibrated air sample. The second test was also split in two: C) calcination of 1 hr and a cooling down period overnight; D) a calcination of 5 hr and a cooling down period overnight. Finally, sample E was cremated for 5 hr in an electric furnace without the presence of any fossil CO₂ source. The $\delta^{13}\text{C}$ value of the cremated bones was compared to that of a fresh bone (F).



Figure 2 Electric furnace filled with coal and a quartz crucible containing the animal bone.

Table 2 Characteristics of the atmosphere inside the oven (test 2, muffle).

Muffle	Lab code	pMC	$\delta^{13}\text{C}$ (‰)	% by vol. CO_2 in the oven
Test C	KIA-38454	13.61 ± 0.13	-22.73	2.3
Test D	KIA-38455	17.74 ± 0.13	-20.60	7.9

After cremation, CO_2 was extracted with phosphoric acid from a ground sample. Before graphitization, the CO_2 gas was cleaned by heating for 30 min at 1000 °C in the presence of Ag and CuO (Van Strydonck and van der Borg 1990–91). An extra cleaning with KMnO_4 was necessary for sample C (see below). The graphite was then AMS dated (Nadeau et al. 1998). A CO_2 sample was taken for $\delta^{13}\text{C}$ measurement. The amount of carbon in the cremated bone was obtained by comparing the weight of the dry bone with the volume of the released CO_2 , measured in a calibrated volume under standard conditions, and recalculated to ‰ by weight. Crystallinity was measured by X-ray diffraction (XRD) analysis using a Bruker-D8 Advance and the crystallinity index (CI) was calculated according to Person et al. (1995). Also, FT-IR (Fourier transform infrared spectroscopy) was used to calculate the splitting factor (SF) using a Nicolet 380 with a Diamond ATR device (Wright and Schwarcz 1996; Olsen et al. 2008). All samples were measured in ATR mode.

RESULTS AND DISCUSSION

Although the brick oven in test 1 is a relatively open system with a constant gas flow, test results from A and B are comparable. The continuous gas flow in test 1, in contrast to the more gentle combustion of the coal in test 2, should explain the very low ^{14}C concentration in the atmosphere in the brick oven compared to the muffle oven. When making the mass balance, it becomes clear that the ^{14}C concentration in both ovens is too high if one accepts a simple mixing of fossil (fuel) CO_2 and atmospheric CO_2 [global averaged concentration of 0.0384% volume (Keeling et al. 2009) and ^{14}C activity of ~ 103 pMC]. Extra CO_2 from the combustion of the meat and the collagen of the bone should account for the extra ^{14}C in both ovens. The lower $\delta^{13}\text{C}$ values in test 1 compared to test 2 can result from the fact that in general, the $\delta^{13}\text{C}$ value of natural gas is lower than that of coal (Mook 2006).

Visual inspection shows that the bones are not fully cremated except for bone sample E (Table 3). According to different investigations summarized in Olsen et al. (2008), a splitting factor (SF) of 2 to 2.9 represents an unburnt bone. Values between 3 and 4 signify a bone burned at low temperature, values above 4 a partial recrystallization, and values above 7 complete recrystallization of the bone (Table 4). Although in general this is in agreement with our observations, some discrepancies can be noted if one looks at the results in detail. It is obvious from the visual inspection that bone 2D is better cremated than bone 1A, yet the SF of bone 1A points to a higher degree of cremation than 2D. The crystallization index (CI) factor of all bones points towards a good cremation of the bones (Person et al. 1995). A possible explanation for this discrepancy is the inhomogeneity of the samples described above. The FT-IR spectra of bone 2C (Figure 3b) calcined in contact with coal shows a weak adsorption around 700 cm^{-1} and a stronger adsorption around 2013 cm^{-1} , indicating the presence of a cyanamide. The same peaks, but less outspoken, were present in the spectrum of bone 2D, but absent in bones 1A, 1B, and E (Figure 3a). This points to the formation of cyanamide apatite (Dowker and Elliott 1979) due to the presence of ammonia in the atmosphere of the oven. Since the peak is not present in the spectra of bones 1A, 1B, and E, this ammonia comes from the combustion of the coal and not from the burning of the bone organic matter (amide). It should be noted here that graphitization of the CO_2 from sample 2C was only possible after a KMnO_4 cleaning, a step that was unnecessary in all other cases.

Table 3 The visual aspect of the cremated bones.

Bone	Aspect
1A	Part of the bone is white but a large part is still black
1B	Most of the bone is white but inside the bone there are still parts that are darker
2C	Mostly very white but inside of the bone is still light gray
2D	Mostly very white but inside of the bone is still light gray
E	White bone

Table 4 The crystallization index (CI) and splitting factor (SF) of the cremated bones.

Bone	CI (XRD)	SF (FT-IR)
Fresh bone	n/a	3.09
1A	1.54	6.08
1B	1.39	6.18
2C	1.44	5.43
2D	1.42	4.66
E	1.44	5.09

Carbon Content of the Calcinated Bones

A fresh bone contains between 2–4% of carbonate (McKinley 1997). This is much more than what was observed in cremated bones from archaeological sites (3.14–0.6‰) (Van Strydonck et al. 2009). The carbon content of the laboratory cremations in this experiment is in agreement with that of the archaeological bones. Table 5 also shows that in both tests, a shorter and/or less virulent cremation results in higher carbon content. Carbon exchange is shown by the much lower ^{14}C content of the bones calcined in a ^{14}C -depleted atmosphere. The reproducibility is reasonably well for test 1 as it is for test 2, but that there is a large discrepancy between both tests. The difference in activity between the bone calcinated under natural atmospheric conditions and the fresh bone is 1.53 ± 0.53 pMC. This difference is probably also caused by substitution during calcination under atmospheric conditions. In spite of the fact that the results in Table 1 and 2 give only an indication of the proper-

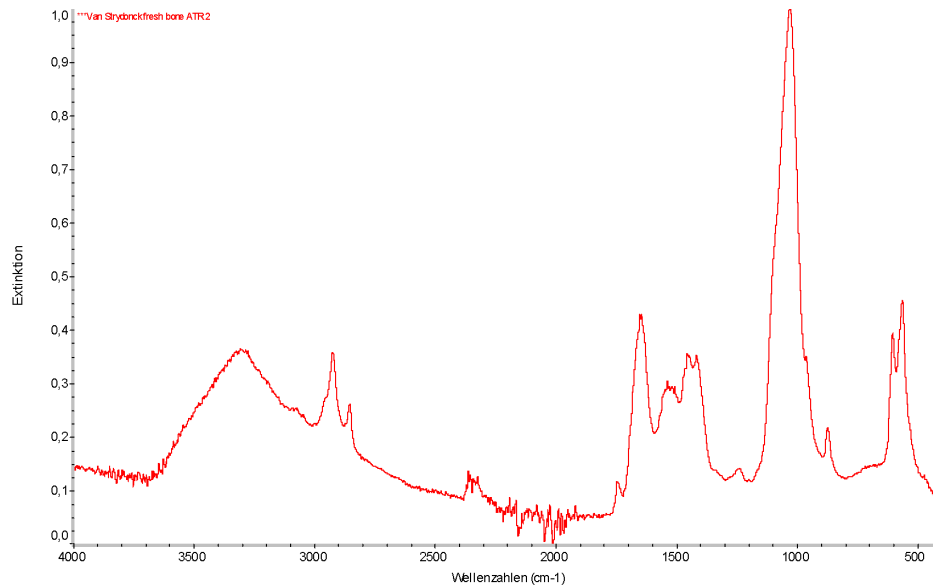
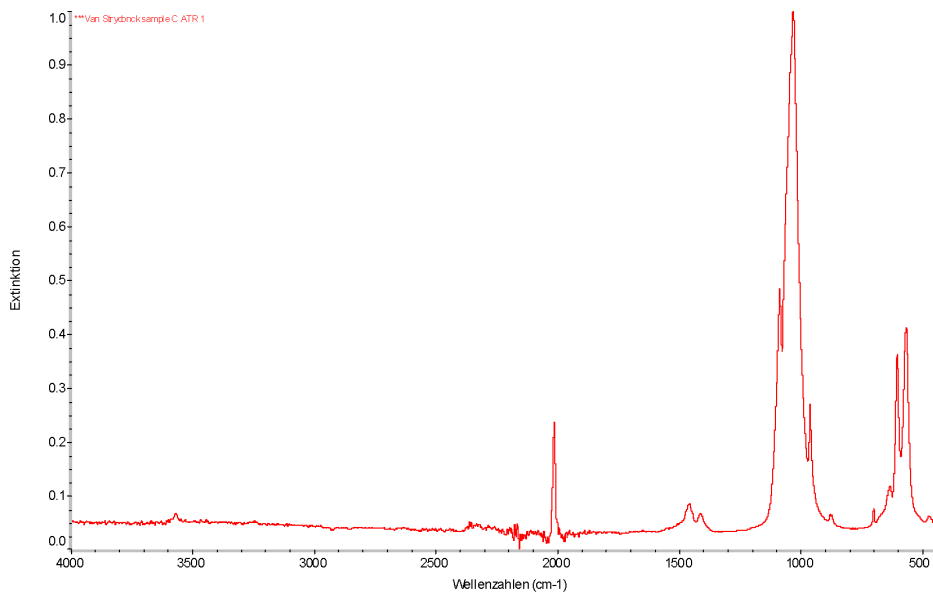


Figure 3a FT-IR spectrum of the fresh bone sample

Figure 3b FT-IR spectrum of sample 2C. Note the adsorption lines at 700 and 1013 cm^{-1} .

ties of the atmosphere inside the ovens at a certain moment in the experiment, it can be noted that the degree of substitution is much higher in test 1 (~78% fossil C) than in test 2 (~53% fossil C), indicating that the atmospheric conditions inside the oven and not only the temperature has an influence on the degree of substitution.

Table 5 Carbon content and isotope analyses of the cremated bones.

Lab code	^{14}C (pMC)	$\delta^{13}\text{C}$ ‰	C/total bone (‰ by weight)
Bunsen			
1A KIA-38431	26.32 ± 0.16	-19.36	2.0
1B KIA-38452	23.86 ± 0.16	-21.66	1.7
Muffle			
2C KIA-38453	55.98 ± 0.22	-19.74	1.0
2D KIA-38452	56.20 ± 0.23	-19.75	0.6
Air			
E KIA-38458	102.25 ± 0.36	-18.61	0.6
Fresh bone			
F KIA-38945	103.78 ± 0.39	-14.81	n/a

CONCLUSIONS AND ARCHAEOLOGICAL CONSEQUENCES

Although the tests described in this paper do not allow us to make precise calculations as should be possible under strict laboratory conditions (Hüls et al. 2010), it becomes clear that during the cremation process there is not only a decrease of the carbon content in the apatite but also a carbon substitution. Although previous studies (Van Strydonck et al. 2005; Zazzo et al. 2009) have shown that the decrease in carbon and the fractionation that goes along with it is a process that does not stop as long as the calcination is continuous, further investigation has to reveal when and how the substitution exactly takes place. The fact that carbonate degeneration and carbon substitution occurs simultaneously makes it very difficult, maybe even impossible, to interpret the $\delta^{13}\text{C}$ data.

The consequences for the accuracy of ^{14}C dates from cremated bones are not easy to define. Thus far, there are not many publications studying the fuel in prehistoric pyres. Most deal with the identification of the firewood and not with the age of the trees. The anthracological study of charcoal remains from cremation graves points to the use of some specific wood types in Belgium and the Netherlands. Oak (*Quercus* sp.) and alder (*Alnus* sp.) are the most recognized species of firewood during the Early Iron Age (Hissel et al. 2007) and also in Gallo-Roman cemeteries (De Groote et al. 1999/2000; In't Ven et al. 2005). Oak is well suited as firewood; it burns long and steady, but only becomes decent firewood after a process of some years. It must be kept in an open area for 2 yr and then needs drying for another 2 yr in a sheltered place unless branch wood was used. The appearance of fungus on some samples at the cemetery of Damme-Sijsele is probably an indication of the use of old (construction) wood for the pyre. Anthracological research on the Swiss Plateau and the Jura Mountains has proven that during the beginning of the Late Bronze Age, fresh-cut branches of oak were used as a combustible (Fischer 1998). Alder also has good burning qualities when it is dry. Because it is less durable than oak, it was probably deliberately collected as firewood (In't Ven et al. 2005).

Limited amounts of ash (*Fraxinus excelsior*) were found in the cremation graves of the Early Iron Age urnfield at Mierlo-Geldrop (Hissel et al. 2007) and the Gallo-Roman cemetery of Huise (De Groote et al. 1999/2000). Among the charcoal remains from the Gallo-Roman cemeteries, birch (*Betula* sp.) could also be identified (De Groote et al. 1999/2000; In't Ven et al. 2005). In a Gallo-Roman cremation grave at Gent, birch was dominant as firewood. There are clear indications for the use of green wood that had just been cut and was still not dry, and also the use of older, dead birch (Deforce 2008).

Other types of wood used on pyres—e.g. elm (*Ulmus* sp.), beech (*Fagus sylvatica*), and willow (*Salix* sp.)—are encountered in small numbers among the charcoal remains. Anthropological studies

of funerary rites in Thailand have revealed that different types of wood were used during the cremation process, but varieties, which are reduced to ash, are always selected (Pautreau et al. 1994). The wooden beams used to construct the pyre and the coffin are difficult to burn due to their quality (Pautreau and Mornais 2005). Anthropological information seems to indicate that very old trees were never used. One of the oldest representations of an ancient pyre comes from a Greek red amphora (500–490 BC; see Figure 4). It does not show the use of large trees. If further investigation can prove that relatively young trees were used as firewood for the pyre, the old-wood effect would be comparable to the reservoir age of the calcined bones (Geyh 2001); thus, a possible carbon exchange will not be recognizable in the ^{14}C date. Furthermore, the cremation conditions seem to significantly influence the carbon substitution. The atmosphere around a wooden open-air pyre will be refreshed continuously so that the concentration of fuel CO_2 should be much lower than in the experiments discussed here. A real open-air cremation test has to confirm this hypothesis. However, even if the old-wood effect does not play any role due to the use of relatively young trees, it becomes clear that $\delta^{13}\text{C}$ values of the apatite carbon almost certainly cannot be used for dietary studies because the origin of the carbon is unsure.

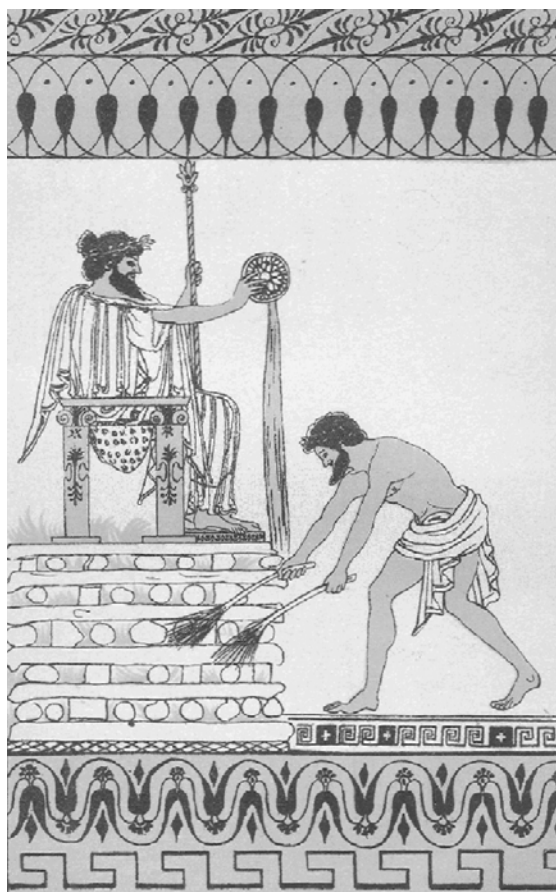


Figure 4 King Croesus of Lydia on the funeral pyre, lit by his servant Euthymos. Attic Red-Figure Amphora (500–490 BC) from Vulci, attributed to Myson (Louvre, Paris).

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