Radiocarbon, Vol 56, Nr 2, 2014, p 591–602 DOI: 10.2458/56.17454

CARBON EXCHANGES BETWEEN BONE APATITE AND FUELS DURING CREMATION: IMPACT ON RADIOCARBON DATES

C Snoeck[1] • F Brock • R J Schulting

Research Laboratory for Archaeology and the History of Art, University of Oxford, Dyson Perrins Building, South Parks Road, Oxford OX1 3QY, United Kingdom.

ABSTRACT. An important advance in the radiocarbon dating of archaeological material occurred in the late 1990s, with direct dating of cremated human remains. A crucial part of the argument was the demonstration that comparable results could be obtained from paired dates of charcoal and calcined bone from the same contexts. Recent studies, however, have noted the influence of carbon from the fuel sources, raising a question over the interpretation of the paired charcoal/bone dates. Here, fleshed modern animal joints were burned with "old" fuel of known age, providing experimental evidence under natural conditions, demonstrating a clear effect of the fuel source on the carbon isotopic composition of calcined bone. In most situations in which branchwood was used as fuel, dates on calcined bone should not show any significant offset, as the wood will be of a similar age to the cadaver. For cases in which old wood, coal, or peat are used as fuel, we expect an offset of some decades/centuries, potentially up to millennia. We observed, however, that the amount of ^{14}C intake from the fuel is extremely variable (from 39 to 95%). A strong correlation between age offset and δ^{13}C values suggests that the latter might be useful in identifying large inputs from ^{14}C-depleted fuels. A level of caution is recommended when ^{14}C dating calcined bone in cases where fuels with an inbuilt age may have been used in the cremation process.

INTRODUCTION

Radiocarbon dating of cremated bone has been undertaken for over a decade since it was first shown that the results obtained were comparable to those on materials from associated contexts, most commonly on charcoal (Lanting and Brindley 1998; Lanting et al. 2001; Naysmith et al. 2007). Minor differences have been observed between cremated bone and charcoal dates. When the bone appears younger than the associated charcoal, this difference is usually attributed to the "old-wood effect" (Lanting et al. 2001). Comparison with dendrochonologically dated wood suggested that part of the "old wood" age was actually transferred to the bone during cremation (Olsen et al. 2012). This was investigated through laboratory experiments and the results indicate that the carbon isotopic composition of cremated bone apatite could be explained by four different mechanisms: (1) carbon exchanges between bone apatite carbonate and the fuel combustion gases; (2) time- and temperature-dependent fractionation of the bone apatite carbonate; (3) admixture of organic carbon (bone collagen, flesh, skin, and fats); and (4) contamination with atmospheric CO_2. Since the atmosphere is composed of only 0.04% CO_2, it can be assumed that its contribution is, in most cases, negligible. Therefore, there are three main possibilities, or combinations thereof, to explain the observed modification of the isotopic composition of bone after cremation (Zazzo et al. 2009; Van Strydonck et al. 2010, 2013; Hüls et al. 2010).

Experimental burning of dry archaeological bone with modern wood has also been carried out outdoors, confirming the influence of the combustion atmosphere on the carbon composition of cremated bone and suggesting that fuel carbon is indeed transferred from wood to bone (Zazzo et al. 2012). This implies that ^{14}C dates obtained from calcined bone and associated charcoal will be close to one another even if of different ages before cremation. Consequently, the dates obtained from calcined bone will reflect in part the age of the wood used for cremation instead of the bone's true age. It is likely, though, that the exchange of carbon between bone and wood would not be reflected in the ^{14}C dates if young wood was used for cremation (Van Strydonck et al. 2010), or, in other words, if the

---

[1] Corresponding author: christophe.snoeck@rlaha.ox.ac.uk.

Proceedings of the Radiocarbon and Archaeology 7th International Symposium
Ghent, Belgium, April 2013 | Edited by Mark Van Strydonck, Philippe Crombé, and Guy De Mulder

age difference between wood and bone is insignificant (Zazzo et al. 2012). While making an important contribution, a problem with this experiment is that defleshed, ancient bone differs substantially from fleshed modern bone, in both its composition and structure. By using archaeological bone with only a small amount of bone collagen left (and no flesh, skin, or fats) in their experiments, Zazzo et al. (2012) removed one of the potential sources of carbon.

MATERIALS AND METHODS

Modern Bone Samples

Several fresh animal joints were obtained from local butchers, including a lamb leg, two pig ribs, a trotter and a scapula, and a cow tibia cut in two. The lamb leg, pig ribs, and cow tibia were partially defleshed while the pig trotter and scapula still retained all flesh and skin. The latter samples in particular were selected to imitate the characteristics of a recently deceased human individual as closely as possible. A small fragment of each bone was sampled before cremation for infrared and isotopic analyses.

Fuel Samples

Three different fuels were selected for the cremations: manufactured coal briquettes (Homefire Smokeless Fuel, CPL Products, UK) and two dendrochronologically dated timbers. A sample of the manufactured coal was ^{14}C dated. However, because it is manufactured coal (potentially heterogeneous), the age range could be much larger than shown by a single date. The two timbers were provided by Dr Daniel Miles of the Oxford Dendrochronology Laboratory: Wood 1 (AD 1730–1805) and Wood 2 (AD 1453–1607). These dates were compared to the calibration curve to obtain fraction modern carbon values (F^{14}C, Table 1). Stable carbon isotopic (δ^{13}C) measurements were also carried out on the fuel samples before cremation.

Table 1 F^{14}C and δ^{13}C values for the dendrochronologically dated woods and manufactured coal.

Fuel	Dendro date	F^{14}C	δ^{13}C (‰)
Wood 1 (208–283 yr)	AD 1730–1805	0.9787 ± 0.0029	−24.8
Wood 2 (406–560 yr)	AD 1453–1607	0.9554 ± 0.0029	−27.0
Manufactured coal (OxA-24943)		0.0543 ± 0.0007	−24.3

Experimental Outdoor Cremations

The experimental outdoor cremations took place on two different days to avoid cross-contamination; the cremation with manufactured coal briquettes on one day and the two pyres fueled with dendrochronologically dated wood on the other. The bones and the pyres on which they were burned, as well as the cremation durations, are listed in Table 2.

Table 2 Cremated bone fragments and cremation time.

Bone	Pyre fuel	Cremation time*
Lamb leg	Manufactured coal	90 min
Pig rib 1	Wood 1 (AD 1730–1805)	75 min
Pig rib 2	Wood 2 (AD 1453–1607)	60 min
Cow tibia (part 1)	Wood 1 (AD 1730–1805)	75 min
Cow tibia (part 2)	Wood 2 (AD 1453–1607)	60 min
Pig trotter	Wood 2 (AD 1453–1607)	90 min
Pig scapula	Wood 2 (AD 1453–1607)	90 min

*It was intended to burn all bones for 90 min but some experiments were cut short due to rain.

A small brick wall was built around and between the pyres in order to partially protect them from wind and, more importantly, to limit cross-contamination between the pyres. Once lit and burning well, the animal joints were placed directly onto the fire. After 90 min (or less in some cases due to rain), the bones were removed and the different parts were separated into two fractions: charred (black and dark gray) and calcined (light gray and white) bone. The results obtained by Zazzo et al. (2012) showed that, when conducting outdoor cremation experiments, once the bone has been calcined, there is no correlation between carbon exchange and cremation time on outdoor fires, so that the burns of less than 90 min should be unaffected. The temperature of the coal fire was estimated using calcite; upon recovery these were shown to have undergone thermal transformation, confirming that the fire had reached at least 700°C, the minimum temperature at which calcite is thermally degraded (Rodriguez-Navarro et al. 2009). This is sufficient to fully calcine bone (Lanting et al. 2001; Van Strydonck et al. 2009). The temperature of the wood fires was measured with a thermocouple, and was found to vary with time and position between 650 and 950°C.

Carrying out outdoor cremation experiments has many advantages compared to laboratory experiments, but this is done at the expense of a lack of control over the cremation temperature and ambient atmosphere. Nevertheless, it is more representative of authentic cremations; it allows the use of larger samples, and the ability to observe gradual macroscopic changes visually. Our experiments are intended to complement those that have been undertaken in controlled laboratory conditions (e.g. Hüls et al. 2010; Van Strydonck et al. 2010).

Analytical Methods

Black (charred) and white (calcined) bone fragments from the experimental fires were selected for infrared spectroscopy analyses, as well as for ^{14}C dating and stable isotopic measurements. For ^{14}C dating, the burned bone fragments were treated with sodium chlorite (1.5% at pH 3) for 48 hr to remove any remaining organics. This was followed by a treatment with acetic acid (1M) to eliminate calcite and adsorbed carbonate. The bones were then further treated with phosphoric acid (85%), and the CO_2 released was trapped cryogenically and converted into graphite before being ^{14}C dated (Lanting et al. 2001; Brock et al. 2010). A fragment of the manufactured coal used for the cremation was also dated, after having been treated with HCl (1M) in order to demineralize it, NaOH (0.2M) to remove any humic acid, and with HCl (1M) for a second time to remove dissolved atmospheric CO_2 from the preceding base wash (Brock et al. 2010). The dates were obtained by accelerator mass spectrometry (AMS) at the Oxford Radiocarbon Accelerator Unit.

Untreated fragments of charred and calcined bones were also analyzed by FTIR-ATR (Agilent Technologies Cary 640 FTIR with GladiATR™ from Pike Technologies, US). Three aliquots were analyzed for each sample. The carbonate to phosphate ratio (C/P) was measured using the carbonate absorption band at ~1415 cm^{-1} and the phosphate band at ~1035 cm^{-1} (Wright and Schwarcz 1996; Olsen at al. 2008; Thompson et al. 2009). The infrared splitting factor (IRSF) was measured as detailed in Weiner and Bar-Yosef (1990): the intensity of the peaks at ~605 and ~565 cm^{-1} are summed and then divided by the absorbance of the valley between these two peaks. The C/P provides an indication of the amount of carbonate left in the bone after cremation, while the infrared splitting factor (IRSF) gives information about the order of the atoms within the crystal lattice (higher IRSF for higher atomic order) and is calculated in order to assess modifications in the structure and crystallinity of bone apatite during cremation. Unburned fragments of each sample were also analyzed by FTIR-ATR. The results obtained via reflectance mode (ATR) are not directly comparable with those obtained by the transmission method (Thompson et al. 2009). Nevertheless, as long as the same mode is used to characterize all samples, it is possible to assess variations in carbonate content and crystallinity (no ATR correction was carried out here).

For unburned bone collagen δ^{13}C measurements, skin and flesh were removed mechanically. Lipids were removed by soaking the bone in a chloroform:methanol (1:2) mixture and ultrasonication. The bone was then demineralized with HCl (0.5M at 4°C). The collagen was subsequently extracted by adding pH 3 water at 75°C. The supernatant solution containing the dissolved collagen was then freeze-dried (O'Connell et al. 2001). Three aliquots of approximately 1 mg of dried collagen were analyzed by mass spectrometry (Sercon Geo 2022 IRMS coupled to a Sercon Europa EA–GSL running with continuous flow of helium carrier gas 80 mL/min). The δ^{13}C values of unburned bone apatite carbonate were measured by mass spectrometry at the Bradford University Stable Light Isotope Facility (Thermo Delta V Advantage equipped with Gasbench II) after pretreatment with sodium hypochlorite (1.5%) to remove organics and 100% phosphoric acid at 70°C to liberate CO_2.

RESULTS

Structural Changes

The infrared measurements of the bone fragments before and after cremation (charred and calcined) are presented in Table 3. The values reported are an average of the measurements taken on three aliquots of each sample. Some bone fragments were completely calcined (white) and no charred fragment could be recovered for infrared analysis.

Table 3 Infrared results.

		C/P			IRSF		
Sample	Fuel used	Unburned	Charred	Calcined	Unburned	Charred	Calcined
Lamb bone	Coal	0.561	0.170	0.054	2.6	3.5	4.8
Pig rib 1	Wood 1	0.345		0.064	2.8		4.9
Pig rib 2	Wood 2			0.060			4.9
Cow tibia 1	Wood 1	0.299	0.173	0.052	3.0	3.8	5.4
Cow tibia 2	Wood 2		0.246	0.035		3.3	5.7
Pig trotter	Wood 2	0.351		0.065	2.8		5.6
Pig scapula	Wood 2	0.336		0.068	2.8		4.6

The IRSF increases from unburned to charred and calcined bone. This is a consequence of the structural and compositional changes that occur during cremation. Organics are completely removed, a large amount of carbonates are lost, and hydroxides are incorporated into the structure, most likely replacing lost carbonates. As hydroxides are smaller than carbonates, there is an increasing atomic order resulting in a more compact structure and higher IRSF values (between 4.5 and 6 for calcined bone). Much carbonate is lost during cremation; the C/P ratios are below 0.07 in calcined bone, compared to 0.3 or higher in unburned bone. The charred bone fragments have a higher C/P ratio and a lower IRSF, showing, as expected, that the cremation was incomplete. The loss of carbonates and organics (amides), as well as the intake of hydroxides, can be seen on spectra of the unburned and calcined pig scapula (Figure 1). Most modern unburned and calcined mammalian bone fragments will have very similar infrared spectra. The better resolution of the two phosphate peaks is yet another indication of the more ordered structure of calcined bone apatite compared to unburned bone. There is also a small peak around 2010 cm^{-1} that could represent cyanamide (cf. Hüls et al. 2010; Van Strydonck et al. 2010). The broad peak present in unburned bone between 3500 and 2800 cm^{-1} is due to hydroxide ions present in organic materials and/or adsorbed water.

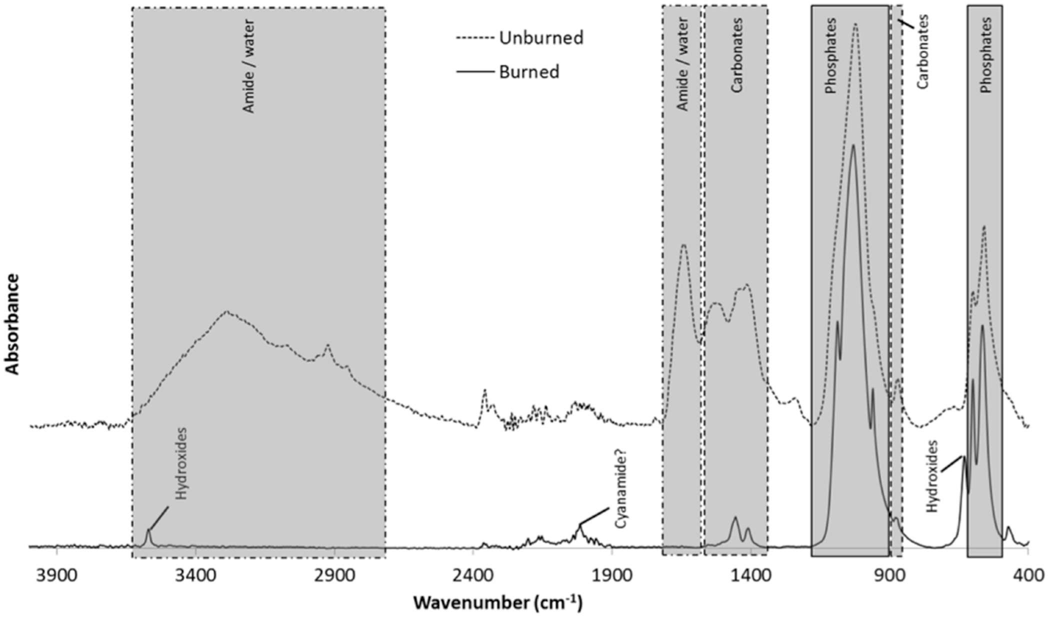

Figure 1 FTIR-ATR spectra of unburned (dotted) and calcined (solid) pig scapula

Changes in Stable Carbon Isotopic Composition

The stable carbon isotopic measurements are reported in Table 4. There is a drastic, but highly variable, decrease in the $\delta^{13}C$ values of bone apatite from unburned to calcined bone. For the organic fraction, both collagen ($\delta^{13}C_{col}$) and a mix of flesh, fat, and skin ($\delta^{13}C_{org}$) were measured. As expected, the values for the latter are below collagen values (Tieszen 1994). In the following calculations, however, only collagen values were considered since it is likely that most fats, flesh, and skin would burn away faster than collagen, and so would contribute only minimally to the final carbon composition of cremated bone bioapatite.

Table 4 Stable carbon isotopic and radiocarbon dating results.

Sample (OxA-)	Fuel used	$\delta^{13}C_{col}$ (‰)	$\delta^{13}C_{org}$ (‰)	$\delta^{13}C_{ap}$ (‰) unburned	$\delta^{13}C_{ap}$ (‰) burned	F^{14}C	Date (BP)
Lamb bone (24942)	Coal pellets	−22.4	−27.3	−15.3	−18.1	1.0314 ± 0.0030	Post-1950
Lamb bone (24941)	Coal pellets				−24.9	0.6298 ± 0.0022	3714 ± 29
Pig rib 1 (27257)	Wood 1	−20.3	−22.4	−12.4	−25.4	0.9896 ± 0.0028	84 ± 23
Pig rib 2 (27258)	Wood 2				−22.5	1.0030 ± 0.0029	Post-1950
Cow tibia 1 (27259)	Wood 1	−23.2	−29.1	−14.8	−24.4	1.0218 ± 0.0028	Post-1950
Cow tibia 2 (27260)	Wood 2				−24.8	1.0158 ± 0.0031	Post-1950
Pig trotter (27261)	Wood 2	−23.1	−26.5	−16.5	−28.9	0.9602 ± 0.0027	326 ± 22
Pig scapula (27262)	Wood 2	−23.5	−25.3	−16.1	−26.8	0.9961 ± 0.0030	31 ± 24

All $\delta^{13}C$ values of calcined bone are below their respective collagen values, suggesting that there is indeed an exchange of carbon with endogenous organics and/or fuels during cremation. The amount of carbon exchange is measured using the equations below. Equation 1 supposes that the apatite exchanges carbon only with the CO_2 present in the burning atmosphere (e.g. emitted by the burning fuel; Hüls et al. 2010; Zazzo et al. 2012), while Equation 2 supposes that the original carbon of bone apatite is entirely replaced by collagen or fuel carbon during cremation and evaluates the intake coming from each source (0% representing an intake of only endogenous collagen carbon; 100% reflecting only fuel carbon).

$$\%Carbon\ exchange\ with\ fuel\ 1 = \frac{\delta^{13}C_{ap-burned} - \delta^{13}C_{ap-unburned}}{\delta^{13}C_{fuel} - \delta^{13}C_{ap-unburned}} \tag{1}$$

$$\%Carbon\ exchange\ with\ fuel\ 2 = \frac{\delta^{13}C_{ap-burned} - \delta^{13}C_{collagen}}{\delta^{13}C_{fuel} - \delta^{13}C_{collagen}} \tag{2}$$

With both equations, some bone fragments appear to have exchanged more than 100% of carbon with the fuels (Table 5), suggesting that another phenomenon has to be taken into account. This does not suggest, however, that there is any exchange with atmospheric CO_2, since its isotopic value is around −7.8‰. Another possibility could be that the $\delta^{13}C$ of the CO_2 released during fuel combustion is depleted compared to that of the unburned fuel. The latter hypothesis potentially contradicts results presented in other studies where charcoal is depleted in ^{13}C compared to unburned wood, implying that the CO_2 released is enriched in ^{13}C compared to unburned wood (e.g. Turney et al. 2006; Cousin et al. 2008; Hall et al. 2008). Nevertheless, in the study carried out by Turney et al. (2006), the $\delta^{13}C$ values of the wood samples burned at 600°C are very close to those measured at 800°C, suggesting that above 600°C (at which stage full calcination of bone apatite is not yet reached), the CO_2 released by the wood will have a constant $\delta^{13}C$ values that is equal to that of the charcoal recovered after cremation with an approximate depletion in ^{13}C of 1 to 2‰ compared to the wood before burning. In addition, no exchange greater than 100% has been observed in previous research (Hüls et al. 2010; Zazzo et al. 2012) where the $\delta^{13}C$ values of the combustion atmosphere CO_2 or remaining charcoal were measured. This further suggests that the $\delta^{13}C$ values of the fuel CO_2 exchanging with bone apatite (i.e. above 600°C) must be depleted compared to the unburned fuel. Another possibility, as suggested by Hüls et al. (2010), is that there could be a carbon fractionation between the carbon present in the surrounding combustion atmosphere and bone apatite carbonate. Indeed, a fractionation has been shown to occur between calcite and CO_2 at high temperatures (Scheele and Heofs 1992). Plans are underway to test this hypothesis.

Table 5 Carbon (^{13}C and ^{14}C) exchange calculations.

Sample	Fuel used	% ^{13}C Exchange 1	% ^{13}C Exchange 1*	% ^{13}C Exchange 2	% ^{13}C Exchange 2*	% ^{14}C Exchange
Lamb bone (charred)	Coal pellets	31	25	<0	<0	2
Lamb bone	Coal pellets	107	87	132	64	42
Pig rib 1	Wood 1	105	90	113	78	86
Pig rib 2	Wood 2	69	61	33	25	52
Cow tibia 1	Wood 1	96	80	75	33	44
Cow tibia 2	Wood 2	82	70	42	28	39
Pig trotter	Wood 2	118	99	149	98	95
Pig scapula	Wood 2	98	83	94	60	59

If one assumes for heuristic purposes a depletion of 2‰ compared to unburned fuel (Equations 1* and 2*), then no bone exchanges more than 100% of carbon with the fuel (Table 5). Equations 2 and 2* present an exchange below 0% for the charred lamb bone, indicating that a significant amount of endogenous bone apatite carbon is still present.

$$\%Carbon\ exchange\ with\ fuel\ 1^{*}=\frac{\delta^{13}C_{ap-burned}-\delta^{13}C_{ap-unburned}}{\left(\delta^{13}C_{fuel}-2‰\right)-\delta^{13}C_{ap-unburned}} \tag{1*}$$

$$\%Carbon\ exchange\ with\ fuel\ 2^{*}=\frac{\delta^{13}C_{ap-burned}-\delta^{13}C_{collagen}}{\left(\delta^{13}C_{fuel}-2‰\right)-\delta^{13}C_{collagen}} \tag{2*}$$

Radiocarbon Dates

The ^{14}C results for charred and calcined bone fragments are presented in Table 4. As with the δ^{13}C values, the high variability in these dates is most likely due to variable carbon exchanges with collagen and fuel. If the bone exchanges more carbon with collagen, it will appear to be only slightly older than its true age, while if the bone exchanges primarily with the fuel, it can potentially appear much older than it actually is. The amount of carbon exchange with the fuel was measured with the equation below with an F^{14}C value of 1.055 taken as an average for present-day carbon (Zazzo et al. 2012). This is very similar to the values obtained by Hüls et al. (2010) for modern bovine bone collagen (1.050) and apatite (1.062).

$$\%Carbon\ exchange\ with\ fuel=\frac{\mathrm{F}^{13}C_{ap-burned}-1.055}{\mathrm{F}^{13}C_{fuel}-1.055}$$

The amount of carbon exchanged with old fuel is significant in all calcined bone fragments, ranging from 39 to 95%. Zazzo et al. (2012) measured carbon exchange between 48 and 91% and Hüls et al. (2010) between 36 and 86% for calcined bone. Thus, we found a similar range even though more endogenous organics were present in and around some of the animal joints (pig trotter and scapula) during cremation. In terms of uncalibrated dates obtained, the modern pig trotter returned a date of 326 ± 22 BP when burned with wood ~480 yr old. This result is actually the most dramatic, as it indicates the replacement of nearly all of the bone's carbon with fuel carbon. It is interesting to see that this sample was fully fleshed, and thus had the largest amount of organic carbon. This supports the hypothesis according to which flesh, fat, and skin burn away before being able to exchange with apatite carbonates.

DISCUSSION

High IRSF (above 4.5) and low C/P ratios (below 0.07) confirm that the white burned bone samples were fully calcined and suitable for ^{14}C dating. The large variation of ^{13}C and ^{14}C exchanges (Table 5) could be explained by variation in the amount of collagen and fuel carbon around the bone during cremation. The lower exchanges with fuel observed for the cow tibia compared to the pig trotter and scapula seem to further confirm this model. Indeed, the cow tibia was much bigger and, even though it was defleshed, contained much more collagen than the pig trotter and scapula.

Figure 2 plots the different F^{14}C exchange percentages calculated against the δ^{13}C exchange percentages (excluding the lamb bone burned with manufactured coal, since this fuel could potentially release CO$_2$ with a much wider F^{14}C range compared to dedrochronologically dated wood, and burning bodies with coal is not representative of most archaeological cremations, though see below). In Equations 2 and 2*, the upper δ^{13}C values are determined by collagen δ^{13}C values and not by the value obtained for overall fat, flesh, and skin. Indeed, during the cremation process fat, flesh,

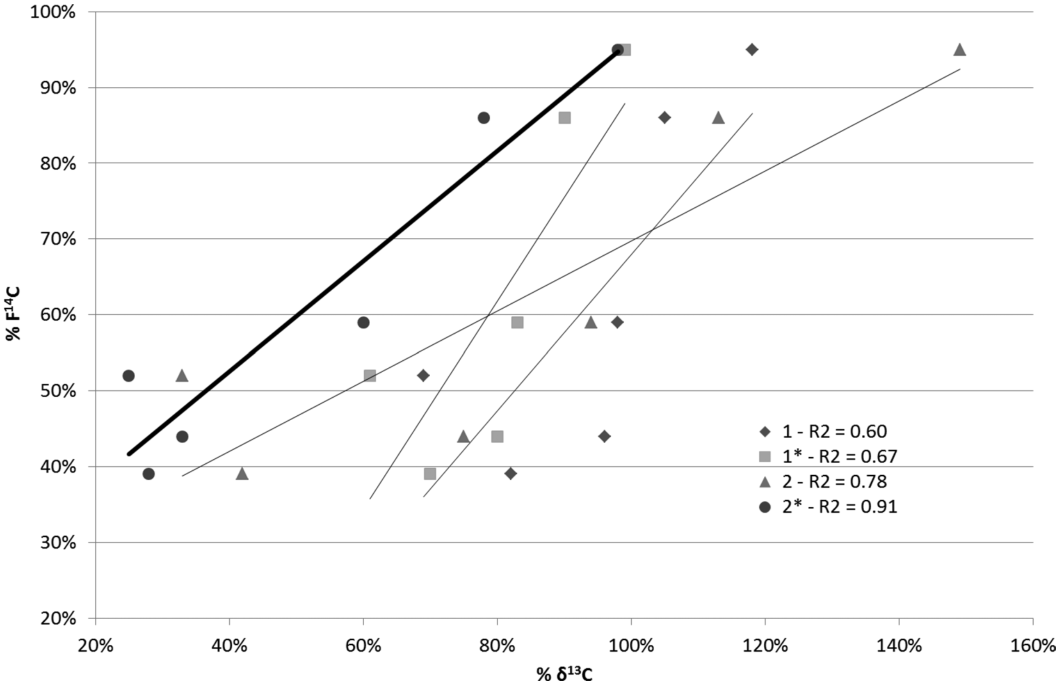

Figure 2 % exchange $F^{14}C$ versus % exchange $\delta^{13}C$ excluding coal fire

and skin are likely to burn away before collagen does. Furthermore, collagen is closely linked to bone apatite, potentially facilitating carbon exchanges between apatite and collagen compared to exchanges between flesh, fat, and skin and apatite. Nevertheless, the authors admit that this is still work in progress and that this assumption has to be verified by further experiments.

Table 6 summarizes the R^2 values and the average difference between the % $\delta^{13}C$ and % $F^{14}C$ for each comparison. The strongest correlation ($R^2 = 0.91$) can be found when one considers that (1) the original carbon in bone apatite is entirely replaced by collagen or fuel carbon during cremation, and (2) the $\delta^{13}C$ of the CO_2 released during fuel combustion is depleted (by ~2‰) compared to the $\delta^{13}C$ of the fuel (Equation 2*).

Table 6 Comparison of the four equations (excluding coal fire).

Equation	R^2	Δ %	% $F^{14}C$ equation	p value
1	0.60	−32 ± 14	1.03 * % $\delta^{13}C$ – 0.36	0.069
1*	0.67	−18 ± 14	1.37 * % $\delta^{13}C$ – 0.48	0.047
2	0.78	−22 ± 26	0.46 * % $\delta^{13}C$ + 0.23	0.020
2*	0.91	9 ± 11	0.73 * % $\delta^{13}C$ + 0.23	0.003

If it can be confirmed that the assumptions behind Equation 2* are correct, it appears that, instead of reflecting the degree of cremation, $\delta^{13}C$ values reflect the origin of the carbon with which the bone apatite has exchanged. Lower $\delta^{13}C$ values suggest a greater intake of CO_2 originating from the fuel, while less negative values highlight an intake of collagen carbon. Our results confirm a correlation between the $F^{14}C$ and $\delta^{13}C$ values of cremated bone, as had been noted in previous studies (Hüls et al. 2010; Zazzo et al. 2012). In addition, the incorporation of collagen carbon into the carbonate fraction of bioapatite has been further highlighted. In the study by Zazzo et al. (2012), all calcined bone apatite $\delta^{13}C$ values are below their respective collagen $\delta^{13}C$ values. The same can be said for the experiments carried out by Hüls et al. (2010), except for the two samples burned without CO_2, in which case collagen is the only additional source of carbon present; the final carbon isotopic composition will therefore lie between apatite and collagen $\delta^{13}C$ values.

Furthermore, the gradients of Equations 1* and 2* (1.37 and 0.73, respectively) show that to have a perfect correlation between the ^{13}C and ^{14}C exchange (gradient of 1), a mixture of the original apatite carbonate and collagen carbon have to be present in the final composition of cremated bone apatite. This is in line with the results obtained by Hüls et al. (2010) and Zazzo et al. (2012), where slopes of 1.15 and 1.04, respectively, were obtained (only considering exchanges between fuel and endogenous bioapatite carbonates). The slope of 1.04 (close to 1) obtained by Zazzo et al. (2012) could potentially be explained by the lower proportion of collagen present in archaeological bone.

The cremation of a human body is, however, a complex process, more so than has been represented by our experiments on small joints of meat. Experiments of complete animal bodies, such as the one carried out by Sheridan (2003; Figure 3), should be conducted from an isotopic point of view in order to increase even more the current knowledge on isotopic exchanges occurring during cremation. The placement of the body on the pyre could potentially affect the differential uptake of endogenous versus fuel carbon. Those parts of the body closer to the pyre, for example, could be exposed to more fuel carbon, while those further away could be more affected by collagen carbon. At the same time, those parts that are further away from the flames are less likely to be fully calcined.

Figure 3 Cremating "Miss Piggy" (courtesy of Alison Sheridan)

ARCHAEOLOGICAL IMPLICATIONS

The degree to which ^{14}C determinations on archaeological calcined bone are affected by fuel carbon will depend entirely on the age of the fuel used. In the great majority of cases in prehistoric Europe and elsewhere, we would expect that the offset will be minimal, since branchwood and small trunks would be the most likely sources of wood for cremation pyres (cf. Van Strydonck et al. 2010). These might have inbuilt ages in the decadal range, but the adult human skeletal can have a similar inbuilt age due to slow carbon turnover (Geyh 2001). That most dates on calcined bone fit with expectations based on other lines of evidence (e.g. associations with material culture with independently derived chronologies) supports this assumption (e.g. Sheridan 2003). Infant cremations might be expected to be subject to greater bias, but this would only be a factor with very high-resolution dating. On the other hand, it is entirely possible that, on occasion, significantly older wood would be used in cremations. The wood of choice for Early Neolithic houses and mortuary structures across northwest Europe, for example, was oak (Coudart 1998; Smyth 2010). The use of structural house timbers for a cremation pyre—whether for practical or, more likely, symbolic reasons—could very well introduce an offset on the centennial scale, particularly as the house itself may have stood for some generations before falling into ruin or being dismantled to provide fuel. Such considerations may provide an explanation for a small number of unexpectedly early ^{14}C determinations on calcined bone (e.g. Tully court tomb, Co. Fermanagh, Northern Ireland; Schulting et al. 2012). Furthermore, variable but sometimes substantial offsets have been noted when dating charcoal and short-lived material (charred cereals, hazelnut shells) from the same archaeological contexts, implying that the use of substantial timbers (or dead wood) for even domestic hearths was not unusual (Whitehouse et al., forthcoming).

In other contexts, the effect might be much more dramatic. Coal has been suggested as one of the fuels used for a Bronze Age cremation in South Wales, and its use in the Romano-British period has been indicated in a public cremation pyre at Trenthome Drive, York (Dearne and Branigan 1995). We would anticipate an offset of centuries to millennia were the calcined bone to be dated. There is also some evidence for the use of peat as a pyre fuel in Bronze Age northwest Europe (Photos-Jones et al. 2007; Sharman 2007; Sørensen and Bille 2008). Finally, in a forensic context, the use of coal or petroleum-based fuels could potentially supply very misleading ^{14}C results to investigators in terms of whether unidentified cremated human remains were recent or ancient.

CONCLUSION

Additional experimental cremations still need to be carried out before the issue of carbon exchanges between bone apatite, endogenous collagen, and fuel can be fully understood. The results presented here suggest that only a small fraction of original bone apatite carbon remains in the bone after cremation, and that there is a significant carbon uptake from the different possible sources (mainly endogenous collagen and fuels, and a very limited amount, if any, of atmospheric CO_2). The amount of carbon intake from each different source is highly variable and appears to depend on the fuel used, the environmental conditions (e.g. wind), the position of the corpse/bone on the fire, etc. It is very likely that different cremated bone fragments of the same body will have different carbon isotopic composition (δ^{13}C and F^{14}C) after cremation, depending on the extent to which the bone is exposed to CO_2 generated by the body's own collagen and to that arising from the fuel. This in turn will be highly variable, depending on the position of the body, its size, the shape of the cairn, wind conditions, and so forth.

Only if the age difference between corpse and fuel is minimal will a ^{14}C date of calcined bone reflect the former's true age. In the great majority of cases, this is indeed likely to be the case, since the fuel for the pyre would be dead branch wood, brush, and small felled trees. In other words, ^{14}C dates on calcined bone in most circumstances should be a true reflection, even if indirectly, of the sample's age. If, however, there is a significant age difference between the corpse and fuel, then there can be a variable but potentially very large offset, though this itself is highly variable. The preliminary results presented here suggest that the ^{14}C dates of calcined bone (based on their color, C/P ratio, and IRSF) with higher δ^{13}C values are likely to be closer to the bone's true age since these still contain endogenous apatite carbon and/or have taken in carbon mainly from the body itself (collagen). This relationship is indicated by the correlation observed between the variation in $\delta^{13}C$ and $F^{14}C$ values on calcined bone.

The growing body of experimental results indicating the significant contribution of fuel carbon to cremated bone suggests that caution may be warranted in accepting the primacy of ^{14}C results on calcined bone when they conflict with other lines of evidence: particularly so in the case of outlying individual determinations that are significantly older than expected (though arguably these should be flagged in any case, as one would for any outlying or unexpected date on any other material, such as charcoal or bone collagen). Smaller systematic offsets, however, will be very difficult to detect, but may potentially skew chronologies on the order of decades. While in past circumstances, such small offsets would be well within the error limits of the ^{14}C method, recent and ongoing improvements in sample preparation and instrument precision, combined with increasingly sophisticated statistical analyses, mean that differences of this order may very well be significant.

ACKNOWLEDGMENTS

This research is enabled by the generous financial support of the Wiener-Anspach Foundation (http://fwa.ulb.ac.be). The authors are very grateful to Dr Daniel Miles from the Oxford Dendrochronology Laboratory who provided the dendrochronologically dated wood. The butchers (Hedges, John Lindsey and Son) from the Oxford Covered Market are also thanked for supplying the various animal samples. The authors would like to thank everyone who helped with laboratory work: A Bowles, J Davies, P Ditchfield, B Emery, R A Staff (Research Laboratory for Archaeology and the History of Art, University of Oxford); A Gledhill (Stable Light Isotope Facility, Bradford University); and N Charnley (Department of Earth Science, University of Oxford). Finally, T Higham, J Lee-Thorp, C Bronk Ramsey (Research Laboratory for Archaeology and the History of Art, University of Oxford), J McKinley (Wessex Archaeology) and A Sheridan (National Museums of Scotland) are acknowledged for their advice and comments. The comments of three reviewers are also much appreciated, and helped clarify a number of points in the paper.

REFERENCES

Brock F, Higham T, Ditchfield P, Bronk Ramsey C. 2010. Current pretreatment methods for AMS radiocarbon dating at the Oxford Radiocarbon Accelerator Unit (ORAU). *Radiocarbon* 52(1):103–12.

Coudart A. 1998. *Architecture et Société Néolithique. L'unité et la Variance de la Maison Danubienne*. Paris: Editions de la Maison des Sciences de l'Homme.

Cousin J, Chen W, Fourmentin M, Fertein E, Boucher D, Cazier F, Nouali H, Deweale D, Douay M, Rothman LS. 2008. Laser spectroscopic monitoring of gas emission and measurements of $^{13}C/^{12}C$ isotopic ratios in CO_2 from a wood-based combustion. *Journal of Quantitative Spectroscopy and Radioactive Transfer* 109(1):151–67.

Dearne MJ, Branigan K. 1995. The use of coal in Roman Britain. *The Antiquaries Journal* 75:71–105.

Geyh M. 2001. Bomb radiocarbon dating of animal tissues and hair. *Radiocarbon* 43(2B):723–30.

Hall G, Woodborne S, Scholes M. 2008. Stable carbon isotope ratios from archaeological charcoal as palaeoenvironmental indicator. *Chemical Geology* 247(3–4):384–400.

Hüls CM, Erlenkeuser H, Nadeau M-J, Grootes PM, Andersen N. 2010. Experimental study on the origin of cremated bone apatite carbon. *Radiocarbon* 52(2):587–99.

Lanting JN, Brindley AL. 1998. Dating cremated bone: the dawn of a new era. *Journal of Irish Archaeology* 9:1–7.

Lanting JN, Aerts-Bijma AT, van der Plicht J. 2001. Dating of cremated bones. *Radiocarbon* 43(2A):249–54.

Naysmith P, Scott EM, Cook GT, Heinemeier J, van der Plicht J, Van Strydonck M, Bronk Ramsey C, Grootes PM, Freeman SPHT. 2007. A cremated bone intercomparison study. *Radiocarbon* 49(2):403–8.

O'Connell TC, Hedges REM, Healey MA, Simpson AHRW. 2001. Isotopic comparison of hair, nail and bone: modern analyses. *Journal of Archaeological Science* 28(11):1247–55.

Olsen J, Heinemeier J, Bennike P, Krause C, Hornstrup KM, Thrane H. 2008. Characterisation and blind testing of radiocarbon dating of cremated bone. *Journal of Archaeological Science* 35(3):791–800.

Olsen J, Heinemeier J, Hornstrup KM, Bennike P, Thrane H. 2012. "Old wood" effect in radiocarbon dating of prehistoric cremated bones? *Journal of Archaeological Science* 40(1):30–4.

Photos-Jones E, Ballin Smith B, Hall AJ, Jones RE. 2007. On the intent to make cramp: an interpretation of vitreous seaweed cremation 'waste' from prehistoric burial sites in Orkney, Scotland. *Oxford Journal of Archaeology* 26(1):1–23.

Rodriguez-Navarro C, Ruiz-Agudo E, Luque A, Rodriguez-Navarro AB, Ortega-Huertas M. 2009. Thermal deposition of calcite: mechanisms of formation and textural evolution of CaO nanocrystals. *American Mineralogists* 94:578–93.

Scheele N, Hoefs J. 1992. Carbon isotope fractionation between calcite, graphite and CO_2: an experimental study. *Contribution to Mineral Petrology* 112(1):35–45.

Schulting RJ, Murphy E, Jones C, Warren G. 2012. New dates from the north, and a proposed chronology for Irish court tombs. *Proceedings of the Royal Irish Academy* 112C:1–60.

Sharman PM. 2007. Excavation of a Bronze Age funerary site at Loth Road, Sanday, Orkney. *Scottish Archaeological Internet Report* 25. http://archaeologydataservice.ac.uk/archives/view/sair/contents.cfm?vol=25.

Sheridan A. 2003. New dates for Scottish Bronze Age cinerary urns: results from the National Museums of Scotland Dating Cremated Bones Project. In: A Gibson, editor. *Prehistoric Pottery: People, Pattern and Purpose*: British Archaeological Reports, International Series 1156. Oxford: Archaeopress. p 201–26.

Smyth J. 2010. The house and group identity in the Irish Neolithic. *Proceedings of the Royal Irish Academy* 111C:1–31.

Sørensen TF, Bille M. 2008. Flames of transformation: the role of fire in cremation practices. *World Archaeology* 40(2):253–67.

Thompson TJU, Gauthier M, Islam M. 2009. The application of a new method of Fourier Transform infrared spectroscopy to the analysis of burned bone. *Journal of Archaeological Science* 36(3):910–4.

Tieszen LL. 1994. Subsistence strategies and dietary assessments. In: DW Owsley, Jantz RL, editors. *Skeletal Biology in the Great Plains: Migration, Warfare, Health, and Subsistence*: Washington, DC: Smithsonian Institution Press. p 261–82.

Turney CSM, Wheeler D, Chivas AR. 2006. Carbon isotope fractionation in wood during carbonization. *Geochimica et Cosmichimica Acta* 70(4):960–4.

Van Strydonck M, Boudin M, De Mulder G. 2009. ^{14}C dating of cremated bone: the issue of sample contamination. *Radiocarbon* 51(2):553–68.

Van Strydonck M, Boudin M, De Mulder G. 2010. The carbon origin of structural carbonate in bone apatite of cremated bones. *Radiocarbon* 52(2):578–86.

Van Strydonck M, Decq L, Van den Brande T, Boudin M, Ramis D, Borms H, De Mulder G. 2013. The protohistoric 'quicklime burials' from the Balearic Islands: cremation or inhumation. *International Journal of Osteoarchaeology*. doi: 10.1002/oa.2307.

Weiner S, Bar-Yosef O. 1990. States of preservation of bones from prehistoric sites in the Near East: a survey. *Journal of Archaeological Science* 17(2):187–96.

Whitehouse NJ, Schulting RJ, McClatchie M, Barratt P, McLaughlin R, Bogaard A, Colledge S, Marchant R, Gaffrey J, Bunting MJ. Forthcoming. Neolithic agriculture on the European western frontier: the boom and bust of early farming in Ireland. *Journal of Archaeological Science*. http://dx.doi.org/10.1016/j.jas.2013.08.009.

Wright LE, Schwarcz HP. 1996. Infrared and isotopic evidence for diagenesis of bone apatite at Dos Pilas, Guatemala: palaeodietary implications. *Journal of Archaeological Science* 23(6):933–44.

Zazzo A, Saliège J-F, Person A, Boucher H. 2009. Radiocarbon dating of calcined bones: Where does the carbon come from? *Radiocarbon* 51(2):601–11.

Zazzo A, Saliège J-F, Lebon M, Lepetz S, Moreau C. 2012. Radiocarbon dating of calcined bones: insights from combustion experiments under natural conditions. *Radiocarbon* 54(3–4):855–66.