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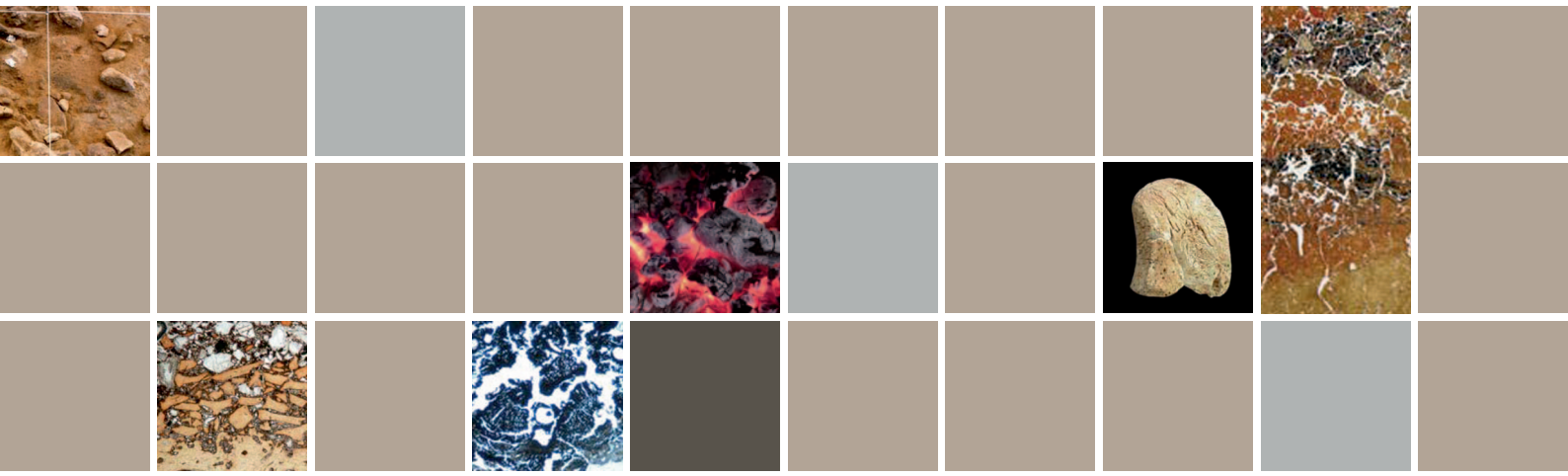
Isabelle THÉRY-PARISOT
Lucie CHABAL
Sandrine COSTAMAGNO

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



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Translation
Magen O'FARRELL

Layout
Yann BELIEZ

Cover
Fabien TESSIER

The contributions should be addressed to:

REVUE P@LETHNOLOGIE
Vanessa LEA, Research associates

TRACES - UMR 5608 of the CNRS
Maison de la recherche
5 allées Antonio Machado
31058 Toulouse cedex 9, FRANCE

Phone: +33 (0)5 61 50 36 98
Fax: +33 (0)5 61 50 49 59
Email: vanessa.lea@univ-tlse2.fr

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ISOTOPE GEOCHEMISTRY OF BURNED BONES: IMPLICATIONS FOR PALEODIETARY RECONSTRUCTION AND RADIOCARBON DATING

Antoine Zazzo

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Abstract

Though they are frequently found at archaeological sites, burned bones have long been neglected by geochemists. After a brief review of the mineralogy and diagenesis of vertebrate skeletal tissues, all the physico-chemical changes induced by the high temperature combustion of bones are summarized. The implications of these changes for the reconstruction of diets through stable isotope ratios analysis and for the radiocarbon dating of bone remains are then discussed. It is thus shown that the high-temperature (>600°C) re-crystallisation of the mineral fraction of bones: (1) provokes a fractionation of the isotopes that modifies the $\delta^{13}C$ of the bone and therefore makes it unsuitable for paleo-dietary reconstructions; (2) protects the bone from chemical interactions with the surrounding environment during fossilisation, thus making calcined bone a reliable material for radiocarbon dating.

The calcined bones can in turn be used to estimate the state of preservation of the unburned bones found at the same site when the collagen has not been preserved.

Key-words : bioapatite, stable isotopes, radiocarbon, diagenesis, diet

Introduction

Biogeochemistry is a powerful tool for reconstructing the diets of humans and animals in archaeological contexts. The analysis of the composition of stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) in the organic fraction (collagen) of bones, and of the ratios of trace elements (strontium/calcium and barium/calcium) of the mineral fraction (hydroxylapatite, or bioapatite) in bones has provided information on the nutrition of Neanderthals and anatomically modern humans (Balter 2007; Bocherens *et al.*, 2005; Fizet *et al.*, 1995; Richards *et al.*, 2000). Because bone tissues are continuously renewed, they provide information averaged over the last years of an individual's life. Teeth, which develop during the first few years of an individual's life, offer the opportunity to document the nutritional history of animals and humans with a high temporal resolution, on a scale of months or seasons (Balasse *et al.*, 2003, 2006; Balter *et al.*, 2008; Sponheimer *et al.,* 2006.). One of the advantages of this method is that it makes it possible to calculate the proportions of the main nutritional resources independently of their preservation at the archaeological site and thus to diminish the taphonomic bias (Balter 2007.). Moreover, the organic and mineral fractions of bones and teeth can be dated by the radiocarbon method. The advantage of direct dates of human and animal remains is that they are not dependent on the dates obtained for associated materials, whose strict contemporaneity with the bone remains is not always verifiable (Sealy et Yates 1994; Zilhao 2001).

Though they are frequently found at archaeological sites, burned bones have long been neglected by geochemists. Bone collagen, which has long been the preferred support for paleo-dietary reconstructions and dating, decomposes at low temperatures and thus become *a priori* useless. The mineral fraction of bone, on the other hand, has long be considered to offer limited reliability for paleo-dietary reconstructions or radiocarbon dating due to its limited resistance to diagenetic alterations (Tamers et Pearson, 1965; Schoeninger et DeNiro, 1982.). Meanwhile, paradoxically, the ensemble of physico-chemical changes associated with the combustion of bones at high temperatures make the mineral fraction of bones a support as reliable as collagen, and a very useful one when the latter has disappeared. Following a brief review of the mineralogy of bioapatites, I will describe the combination of physico-chemical changes induced by combustion. Finally, I will discuss the implications of these changes for the reconstruction of diets and for the radiocarbon dating of bone remains.

Composition and physico-chemical properties of bioapatites

The mineral fraction of the biominerals of vertebrates is composed of a calcium phosphate with the general formula $Ca_{10}(PO_4)_6OH_2$, or in terms of crystallographic sites, $Z_{10}B_6A_2$, and crystallising in the hexagonal system. We can also speak of carbonate hydroxylapatite (or bioapatite) due to the presence of carbonate ions that are essentially substituents in the B sites of phosphates. Although the mineralised tissues of vertebrates are all composed of carbonate hydroxylapatite, each one has its own characteristics in terms of the calendar and geometry of its development during ontogenesis, as well as at the level of its crystalline structure or even its physico-chemical characteristics.

The mineralisation of the hard tissue of vertebrates is initiated by an essentially collagenous organic matrix. This interconnection between the organic and the mineral and the mechanisms operating during the mineralisation process are specific to each tissue. Bone is a mesodermic tissue composed of 65% apatite and 35 % organic matter (Posner, 1987.). Dentine, which constitutes the bulk of the thickness of the tooth is also a mesodermic tissue whose mineral fraction (70-75%) is connected to an organic matrix of collagenous proteins. Unlike bone and dentine, enamel is a highly mineralised (about 97%) ectodermic tissue whose organic phase is gradually eliminated during the maturation phase (Weinmann *et al.*, 1942.). Due to this structural difference, the porosity decreases by a factor of 40 from bone to enamel (Brudefold et Soremark, 1967; Rowles, 1967; Trautz, 1967.) While, with few exceptions, the

teeth of mammals are developed during the first years of life and are not subsequently altered (Hillson, 2005), bone is a living tissue that undergoes continuous changes. Numerous ions, other than carbonate ions, can be incorporated into the bioapatites and this high chemical complexity reflects the role played by bone tissues in the regulation of an organism's needs.

Almost all the ions incorporated have an impact on the physico-chemical properties of the bioapatites (LeGeros et LeGeros, 1984.). Specifically, it seems that the differences in crystallinity between bone, enamel, and dentine can be partially explained by their different carbonate content. Bone is the tissue that has the highest carbonate content (about 6% by weight) while enamel has the lowest (3.5% by weight on average) (Elliot, 1985.) .When the divalent and planar carbonate ion replaces the trivalent and tetrahedral phosphate ion at the B sites, it modifies both the electrical neutrality and the symmetry of the crystal. The incorporation of carbonate ions into the crystalline network also induces an internal stress that has been shown by spectroscopy on synthetic apatites (Blumenthal, 1975.). This destabilization of the network causes an increase in the solubility of apatite (Gron, 1963; Okazaki, 1998.). Finally, the carbonate ion, which is smaller than the phosphate ion, is also responsible, when it is in the B position, for a large decrease of the *a* parameter of the crystal lattice and a slight decrease of the *c* parameter (Posner, 1987); it thus causes an overall decrease in the size of the crystallites. These differences then have repercussions for the solubility, size, and shape of the crystallites. The crystallites in the enamel are large (400 Å wide, 1600-10,000 Å long) and well crystallised (needle-shaped), while in the bone they are smaller (25-50 Å wide, 200-1,000 Å long) and less well crystallised (equiaxial) (Bottero, 1992.). These physico-chemical differences (in tissue porosity, size, and solubility of the crystals) are directly responsible for the quality of conservation during the diagenesis of the isotope signature acquired by the animal during its life.

Diagenesis of bioapatites

At the death of an individual, the thermodynamic equilibrium within its bone structure is disrupted. The result of the interaction between the tissue and the fluids percolating through the soil is called diagenesis. Extrinsic factors linked to the properties of the fossilisation environment, such as pH, temperature, pressure and the degree of saturation of the solution, determine the direction of the exchanges and the reaction kinetics. Intrinsic factors linked to the physico-chemical properties of the bioapatite, such as its solubility and porosity, control the intensity of the exchanges with the fluids. Since bone is the tissue with the greatest solubility and porosity, it is the most susceptible to exchanges with diagenetic fluids. The physical and chemical criteria for recognising diagenesis have generally been based on this tissue (Hedges, 2002.).

The sources of pollution are varied and concern both the organic and the mineral phase. They can be related to the addition of organic materials (humic and fulvic acids) or mineral materials (precipitation of secondary calcite) into the pores of the bones. They can also consist of isotope exchanges between the bone's carbonate and the dissolved inorganic carbon (DIC) in surface or groundwater, or of the dissolution/neo-formation of apatite when allowed by the pH conditions. Generally, these different modification mechanisms have the effect of rejuvenating bones, especially in temperate environments. The techniques developed to purify bones mainly concern the elimination of the secondary phases. To isolate the organic phase of bone, a treatment with sodium hydroxyde is typically employed, in between two immersions in hydrochloric acid to eliminate the secondary carbonates (acid-base-acid or ABA treatment.). Starting recently, this protocol is completed by an ultrafiltration stage, which allows separation of the collagen from low molecular weight organic molecules not removed during the ABA treatment (Higham *et al.*, 2006.).

To isolate the mineral phase of bone (bioapatite), a pre-treatment under vacuum with acetic acid allows the elimination of secondary calcites without altering the less soluble carbonate in bone (Balter *et al.*, 2002.). This approach is sufficient when there have not been further chemical exchanges between the bioapatite of the bone and the external environment, which is the case

when the bones have been protected from an aqueous environment. The most favourable environments for dating the mineral phase of bone are thus arid and semi-arid ones, in which, moreover, collagen is very poorly conserved (Saliège *et al.*, 1995; Braemer *et al.,* 2001; Sereno *et al.*, 2008.). Temperate environments are, on the contrary, much less favourable to the preservation of the geochemical composition of bones since the isotopic exchanges between the bone and the soil's DIC are frequent and no solution exists at present to eliminate this source of pollution. In these environments, the use of unburned bones is not an option. Tooth enamel, which is more resistant to isotopic exchanges because of the larger size of its crystals and its low porosity, is widely employed in archaeological studies (Balasse *et al.*, 2003; 2006.) It must be noted, however, that its utilisation is generally limited to measuring the ratios of stable isotopes ($\delta^{13}C$, $\delta^{18}O$.) Though still rare, the radiocarbon dating of tooth enamel is becoming increasingly common due to the decreased test sample sizes made possible by the AMS technique (Surovell 2000; Munoz *et al.*, 2008; Sereno *et al.*, 2008).

Morphological, physical and chemical modifications during combustion

The heating of bioapatites causes a series of macro- and microscopic, morphological, physical, and chemical changes. The evolution of these parameters can be studied in the laboratory during combustion experiments in order to establish at what temperatures these transformations take place (fig. 1.).

The heating of bones modifies their resistance and solidity (Newesely, 1989; Stiner *et al.*, 1995; van Strydonck *et al.*, 2005.) Burned bones develop fractures and display a considerable reduction in size (Holden *et al.*, 1995; Shipman *et al.*, 1984.) In addition to these morphological changes, colour changes are also observed. (Munro *et al.*, 2007.) The bones first become brown (200°C) and then black (300-400°C) due to the combustion and then carbonisation of the organic matter (fig. 2.) These are referred to as burned or charred bones. The progressive disappearance of the organic matter is indicated by a colour approaching beige-ochre at around 500–600 °C. Above this temperature, the bone becomes white. This is referred to as cremated or calcined bone. This evolution of colour can be utilised to make a semi-quantitative estimate of the bone's exposure temperature during heating (Bonucci et Graziani, 1975; Shipman *et al*., 1984; Taylor *et al.*, 1995).

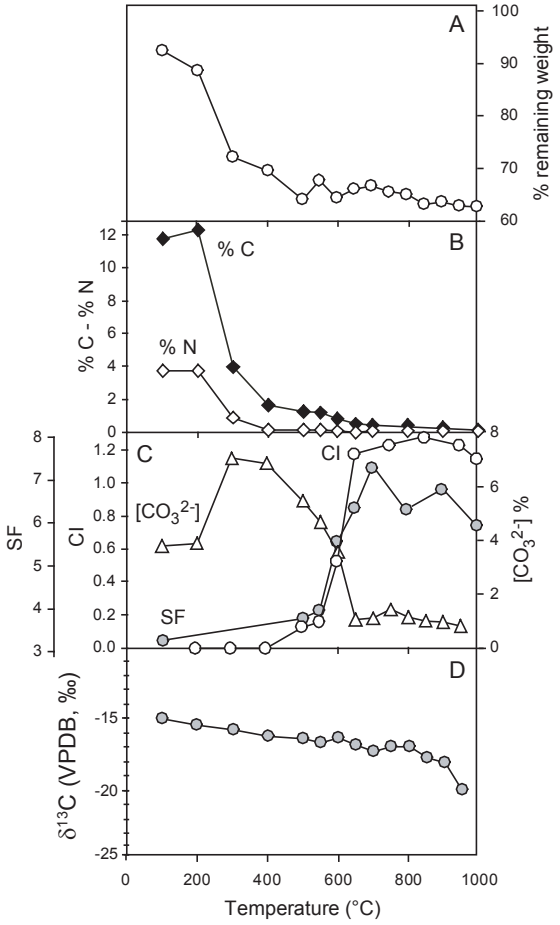

Fig. 1 - Effect of temperature on the behaviour of several physico-chemical properties of a modern bone heated to 100-1000°C. Between 100 and 400°C, heating causes a decrease in mass of about 35% (A) and in the carbon and nitrogen content (B); this is linked to the combustion of the bone's organic matter. Around 600°C, the recrystallisation of the mineral fraction of the bone causes an increase in the crystallinity index (CI) measured by X-ray diffraction, as well as in the splitting factor (SF) measured by Fourier transform infrared spectroscopy (C.) This recrystallisation is accompanied by a decrease in the bone's carbonate content (C) as well as a decrease in the $\delta^{13}C$ value (D). The detailed experimental conditions are described in Zazzo *et al*., (2009).

The heating of bone also results in a loss of mass (fig. 1A). This loss of mass is estimated at 35-40% during experiments conducted in the laboratory (Person

et al., 1996; Zazzo *et al.*, 2009). At low temperatures (< 225°C), this loss is linked to a dehydration of the bone (10-15% of the weight.) Between 225 and 550°C, it is associated with the combustion of the bone's organic matter (20-25% of the weight) and is accompanied by a decrease in the carbon and nitrogen content of the bone (fig. 1B.) At higher temperatures, the loss of mass is related to the decomposition of the bone's structural carbonate in the form of CO_2 (<5% of the weight) (Haas et Banewicz, 1980; Newesely, 1989; Shipman *et al.*, 1984; Stiner *et al.*, 1995; Zazzo *et al.*, 2009).

Fig. 2 - Burned archaeological bone (In Tékébrine, Niger) viewed in cross-section. The gradient of temperature to which the bone was subjected during cremation is visible from the core of the bone (black, carbonised) to the surface (white, calcined.) Scale= 5mm.

With regard to the mineral phase of bone, the most significant physico-chemical changes occur at around 600°C (Shipman *et al.*, 1984; Stiner *et al.*, 1995.) Above this temperature, the small apatite crystals recrystalise and increase in size (Holden *et al.*, 1995; Shipman *et al.*, 1984.). This recrystallisation is accompanied by a loss in carbonate content of about 50% (fig. 1C.) This loss decreases the stress within the crystal structure and results in an increase in the crystallinity index as measured by X-ray diffraction or infrared spectroscopy (Person *et al.*, 1995; Shipman *et al.*, 1984; Munro *et al.*, 2007; Zazzo *et al.*, 2009). Calcined bone is thus very similar to tooth enamel from a crystallographic point of view.

Finally, heating causes significant changes in the isotope composition of the mineral fraction of bioapatites (van Strydonck *et al.*, 2005; Olsen *et al.*, 2008; Zazzo *et al.*, 2009). These modifications result in a decrease in the $\delta^{13}C$ values that can be as high as 15% and whose magnitude is independent of the bone's initial value (fig. 3.). The comparison of the $\delta^{13}C$ of the charred (black) and calcined (white) portions of the same bone shows that only the calcined portions undergo these modifications. This observation is confirmed by cremation experiments and shows that the decrease in the $\delta^{13}C$ values is linked to the recrystallisation of the bioapatites at around 600°C (van Strydonck *et al.*, 2005; Zazzo *et al.*, 2009). It should be noted, however, that Munro *et al.* (2008) have observed an opposite trend (increase in the $\delta^{13}C$ associated with a decrease of the $\delta^{18}O$ values), though this discrepancy is not discussed.

Implications for the reconstruction of diets and for ^{14}C dating

The modification of carbon isotope ratios renders calcined bones unsuitable for the reconstruction of diets. In fact, the decrease in the $\delta^{13}C$ is highly variable within the same archaeological site (fig. 3), making it impossible to apply a uniform correction factor to all bones in order to return to their original value. The $\delta^{13}C$ of calcined bones is easily identified as "anomalous" in temperate environments where plants utilise exclusively C_3 photosynthesis. This is not the case in tropical environments where the two types of photosynthesis (C_3 and C_4) coexist. In these environments the $\delta^{13}C$ of calcined C_4 bones becomes similar to that of the non-calcined bones of animals that have consumed C_3 plants, making all paleo-dietary inferences impossible.

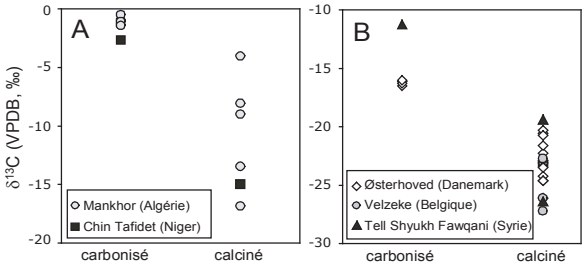

Fig. 3 - Carbon isotope composition ($\delta^{13}C$) of archaeological bones carbonised and calcined in C_4 (A) and C_3 (B) contexts. Data compiled based on Olsen *et al.*, (2008); van Strydonck *et al.*, (2005); Zazzo *et al.*, (2009).

We observed as well that the crystallographic transformations make calcined bone as resistant as tooth enamel to digenetic change. The small amount of residual carbon in calcined bones (around 0.5% by weight) is nevertheless sufficient for dating by AMS. Lanting *et al.* (2001) were the first to understand that this property of calcined bones was useful for radiocarbon dating. The dating of a large series of calcined bones (n=54) and associated charcoals, originating essentially from the Netherlands, demonstrates a perfect preservation of the bones during the last eleven millennia. In order to validate the method, it was important to demonstrate that the residual carbon indeed comes from the stock of mineral carbon originally present in the bone. In effect, during re-crystallisation, the crystal lattice must open up in order to reorganize itself and possible interactions with the external environment cannot be excluded. To test this hypothesis, Zazzo *et al.* (2009) designed several combustion experiments during which they varied various parameters: composition of the atmosphere, role of the organic matter of bone, speed and duration of heating, and temperature. They showed that the decrease of the $\delta^{13}C$ values is observed even when the bone does not contain organic matter and that it is not correlated with the concentration or with the $\delta^{13}C$ of the CO_2 present in the atmosphere during cremation. On the other hand, this decrease is only observed in the case of a rapid rise in temperature (fig. 1D.) These results support the hypothesis of a kinetic origin of the isotope fractionation, and thus validate the use of calcined bones as supports for ^{14}C dating.

Calcined bones offer another advantage: they can be used to evaluate the preservation of unburned bones present at the same site. In the absence of objective criteria of the preservation of the isotope composition in the mineral fraction of a bone, it is very difficult to establish with certainty the validity of a ^{14}C date obtained on bioapatite. This limitation has long hampered the dating of the mineral fraction of bones (Tamers et Pearson, 1965; Haynes, 1968; Hassan *et al.*, 1977; Hedges *et al.*, 1995.) Burned bones finally make it possible to surmount this difficulty. Indeed, the ^{14}C date of a burned bone can be measured independently in three different ways: on the mineral fraction of a carbonised bone (black), on the mineral fraction of a calcined bone (white), and on the organic fraction (the bone's residual collagen.) The structure of the mineral fraction of carbonised bone is very similar to that of unburned bone because it has not undergone recrystallisation. If the taphonomic conditions favour the preservation of the geochemical composition of the bioapatite, the ages derived from the carbonised and calcined bones must match. The two dates can be compared to that obtained on the carbonised bone's organic fraction.

N° target	sample reference	Site	Country	Fraction	colour	$\delta^{13}C$ (‰, VPDB)	radiocarbon age BP			Reference
SacA 11363	Bahla 2003	Bahla	Sultanate of Oman	calcined bioapatite	white	-18,2	3655	±	30	Munoz *et al.* (2008)
SacA 11362	Bahla 2003	Bahla	Sultanate of Oman	charred bioapatite	black	-18,5	3615	±	30	Munoz *et al.* (2008)
SacA 11364	Bahla 2003	Bahla	Sultanate of Oman	degraded collagen	black	-24,2	3690	±	30	Munoz *et al.* (2008)
SacA 11369	RJ1-F1	Ra's al-Jinz	Sultanate of Oman	calcined bioapatite	white	-16,6	4190	±	30	Munoz *et al* . (2008)
SacA 11370	RJ1-F1	Ra's al-Jinz	Sultanate of Oman	charred bioapatite	black	-2,5	4105	±	30	Munoz *et al.* (2008)
SacA 11371	RJ1-F1	Ra's al-Jinz	Sultanate of Oman	degraded collagen	black	-11,3	4100	±	30	Munoz *et al.* (2008)
SacA 11374	HD7-T5	Ra's al-Hadd	Sultanate of Oman	calcined bioapatite	white	-11,1	4100	±	30	Munoz *et al.* (2008)
SacA 11373	HD7-T5	Ra's al-Hadd	Sultanate of Oman	degraded collagen	black	-11,5	4045	±	30	Munoz *et al.* (2008)
Pa 1889	T1	Mankhor	Algeria	degraded collagen	black		5450	±	55	Saliège (pers. comm.)
Pa 2430	T1	Mankhor	Algeria	bioapatite	white		5255	±	100	Saliège (pers. comm.)
Pa 1891	96 B sup	Mankhor	Algeria	degraded collagen	black		5400	±	70	Saliège (pers. comm.)
Pa 1707	96 B sup	Mankhor	Algeria	bioapatite	white		5360	±	80	Saliège (pers. comm.)
Pa 1890	R2	Mankhor	Algeria	degraded collagen	black		5470	±	70	Saliège (pers. comm.)
Pa 1709	R2	Mankhor	Algeria	bioapatite	white		5365	±	80	Saliège (pers. comm.)
KIA-36268	Mdt-2107	Can Missert	Spain	calcined bioapatite	white		2745	±	25	van Strydonck *et al.* (2009)
KIA-36266	Mdt-2107	Can Missert	Spain	charred bioapatite	black		2330	±	25	van Strydonck *et al.* (2009)
KIA-36269	Mdt-2120	Can Missert	Spain	calcined bioapatite	white		2760	±	25	van Strydonck *et al* . (2009)
KIA-36267	Mdt-2120	Can Missert	Spain	charred bioapatite	black		2675	±	30	van Strydonck *et al.* (2009)
KIA-35567	MEV-3581	Can Missert	Spain	calcined bioapatite	white	-17,2	2815	±	30	van Strydonck *et al* . (2009)
KIA-36270	MEV-3579	Can Missert	Spain	charred bioapatite	black		2535	±	25	van Strydonck *et al.* (2009)
AAR-9396	na	Østerhoved	Danemark	calcined bioapatite	white	-23,2	3756	±	28	Olsen *et al.* (2008)
AAR-9390	na	Østerhoved	Danemark	charred bioapatite	black	-16,1	3614	±	27	Olsen *et al* . (2008)
AAR-8784	na	Østerhoved	Danemark	calcined bioapatite	white	-20,3	3682	±	43	Olsen *et al.* (2008)
AAR-8785	na	Østerhoved	Danemark	charred bioapatite	black	-16,0	3576	±	29	Olsen *et al* . (2008)

Tab. 1 - List of sites for which several ^{14}C ages were obtained on the different fractions of a single burned bone.

This last test allows us to evaluate the preservation of the mineral phase relative to the collagen, which is generally considered as more reliable for ^{14}C dating. If, on the other hand, the ages of the calcined and carbonised bones diverge, it is likely that the carbonised bone's mineral fraction has been altered. This means that the unburned bone was also altered and that it must not be considered reliable for ^{14}C dating. Table 1 shows a list of sites where two or even three fractions of the same bone have been dated. In the arid environment sites (Sahara, Arabian Peninsula), the age difference between the different fractions is very small, close to the experimental error. This result demonstrates the absence of significant isotope exchanges between the bioapatite and the diagenetic fluids and indicates that bioapatites, even not heated, can be dated. The situation is more complex in the temperate European sites and the carbonised bone can be rejuvenated by 100 to 400 years relative to the collagenous fraction or the calcined bone. In this case, only the calcined bioapatite (or the collagen, if preserved) will give a reliable ^{14}C age. The number of sites where this methodological work has been carried remains limited at present. It would be profitable, meanwhile, to extend this approach, supplemented by the systematic dating of tooth enamel, so as to better understand the conditions of the preservation of bioapatite geochemistry for the purpose of their radiocarbon dating.

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Author

Antoine Zazzo

CNRS - Muséum national d'Histoire naturelle,
UMR 7209 "Archéozoologie, Archéobotanique : Sociétés, Pratiques et Environnements",
USM 303 - Département Ecologie et Gestion de la Biodiversité,
CP 56, 55 rue Buffon, F-75231 Paris cedex 05 France.
zazzo@mnhn.fr

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