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POMPEII AD 79: A NATURAL BONE DIAGENESIS EXPERIMENT

Antoine Zazzo* • Sébastien Lepetz

Archéozoologie, Archéobotanique: Sociétés, pratiques et environnements (UMR 7209), Sorbonne Universités, Muséum national d'histoire naturelle, CNRS, CP56, 55 rue Buffon, 75005 Paris, France.

ABSTRACT. This study aims at comparing the reliability of different types of apatite fractions for which collagen cannot be dated. We focused on the remains of individuals found at the necropolis of Porta Nocera near Pompeii, and for which the date of burial can be assessed independently. The dated human samples range between 1805 ± 49 and 5570 ± 120 ^{14}C yr BP and can display a large (up to 1200 ^{14}C yr) intra-individual age variability. We show that while a marine diet or an old-wood effect could explain the smallest age shifts, they are not able to explain the largest ones, and propose diagenesis as the main cause. The ^{14}C depletion is likely due to the influence of the ^{14}C-free CO_2 emissions of the nearby Vesuvius volcano and the Campi Flegrei volcanic system on the age of secondary carbonate incorporated into the bone and enamel crystallites during diagenesis. This study demonstrates that in volcanic contexts, a large deviation from expected age can be measured, even in calcined apatites. Our calculations indicate that while the absolute amount of contamination is lower in calcined bones than in burnt bone and enamel apatite, its impact on the ^{14}C age of the sample can be much higher due to the low carbon content of calcined bones.

KEYWORDS: burial practice, cremation, diagenesis, human bones, diet.

INTRODUCTION

Bone collagen is the most often targeted molecule for the direct radiocarbon dating of skeletal remains. This is mainly because the integrity and abundance of this protein can be assessed through a variety of tests including extraction yield, C/N ratio, and more recently, FT-IR analysis (Brock et al. 2013; Lebon et al. 2016). However, there are a number of contexts where collagen is not preserved. It can be rapidly degraded in arid and tropical environments under the combined influence of heat and water (Hedges 2002; Zazzo and Saliège 2011; Dal Sasso et al. 2014; Maurer et al. 2014). Anthropogenic modifications of bones, through burning, also lead to the destruction of bone collagen, leaving the archaeologist with the mineral phase of bones and teeth, bioapatite (Shipman et al. 1984; Stiner et al. 1995). ^{14}C dating of the carbonate in bioapatite has long been considered unreliable, but progress in the pretreatment protocols, together with a better understanding of bone crystallographic properties and *post mortem* diagenetic processes, helped to renew the debate. In the late 1990s, it was discovered that calcined bone apatite could be reliably dated due to the intense crystallographic reorganization occurring when bones are exposed to high (>600°C) temperatures (Lanting et al. 2001). This allowed archaeologists to date the remains of cremated humans (Nakamura et al. 2010; Olsen et al. 2011; De Mulder et al. 2012), but it was later found that ^{14}C dating of calcined bones is not without limitations. First, a series of laboratory (Hüls et al. 2010; Van Strydonck et al. 2010) and field (Zazzo et al. 2012; Snoeck et al. 2014) experiments demonstrated that a significant part (35–95%) of the carbon in calcined bones does not originate from the bone itself but from the combustion environment. Therefore, modification of the ^{14}C content of the bone during cremation is possible if the fuel and the bone initial ^{14}C content differ from each other (Olsen et al. 2013). Second, if postburial modifications appear limited for Holocene samples, the stability of calcined bones for more ancient (Paleolithic) periods remains questionable (Zazzo et al. 2013). Despite these caveats, calcined bone dating has become routine, at least for Holocene samples. The situation is less clear for unburnt bone and tooth enamel apatite. Pioneer work showed that bone apatite dating could provide reliable ages in arid environments (Saliège et al. 1995), allowing the reconstruction of the chronology of human occupations in the Sahara based on direct dates (Paris and Saliège 2007; Sereno et al. 2008; di Lernia et al. 2013; Berkani et al. 2015). However, large-scale

*Corresponding author. Email: antoine.zazzo@mnhn.fr.

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surveys across the globe suggest that isotopic exchange between bone apatite and soil carbonate starts rapidly following burial, leading to age shifts increasing as a function of time (Zazzo and Saliège 2011; Zazzo 2014; Cherkinsky et al. 2015). Age shifts (always towards younger ages) appear limited (<300 ^{14}C yr) in samples younger than 8000 BP, confirming that bone apatite can provide good estimates of the sample age for recent (mid-Holocene) samples. However, this was demonstrated by the comparison of ^{14}C ages obtained from coexisting apatite carbonate and collagen, and it is possible that samples that lack collagen would offer a different (higher or lower) surface area for exchange with the burial environment, leading to different conclusions. Unless the precise calendar age of the remains can be assessed independently, this approach is limited to skeletal remains for which collagen is available for dating, and therefore cannot be applied to calcined or burnt bones.

This study aims at comparing the reliability of different types of apatite fractions for which collagen cannot be dated. We focused on the cremated remains of individuals found at the Roman necropolis of Porta Nocera near the city of Pompeii, and for which the date of burial can be assessed independently.

MATERIAL AND METHODS

The necropolis of Porta Nocera is located in Pompeii, Italy. It was excavated between 2003 and 2007 and consists of several enclosures belonging to free slaves (Van Andringa et al. 2013) (Figure 1). The tombs are aligned to the southeastern exit of the city, alongside the road going to the gate of Stabies and to the harbor located to the mouth of the River Sarno. A funerary

Figure 1 Map showing the extension of the excavated area within the Porta Nocera necropolis (Pompeii, Italy) and the position of the sampled features (pyres and tombs).

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Figure 2 I. Location of Pompeii; II. Funerary monument from the enclosure of Publius Vesonius phileros (Enclosure 23 OS); III. Tomb of Gaia Vesonia (tomb 2); IV. Tomb of Bebryx, young 6-year-old slave (tomb 201); V. Examples of the sampled material. A: Calcined human bone from tomb 25. B: Unburnt human teeth from tomb 29. C: Calcined human teeth from tomb 25. D: Burnt *Donax* sp. from tomb 10 (SU 232124-6). E: Unburnt *Murex* sp. from occupation layer (SU 132501).

monument was built in the northern part of the enclosure, facing the road (Figure 2). It is composed of a high podium on top of which sits an edicule with a pediment presenting three statues. A vaulted niche was laid out on the podium, facing the interior of the enclosure. The stele epigraph indicates that this space was destined to receive the remains of the enclosure's holder, Publius Vesonius Phileros (tomb 1). The tomb's dedication specifies also that the deceased was an emancipated slave who previously belonged to Gaia Vesonia, whose cremated remains were deposited and discovered in the same enclosure (tomb 2). The concession

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(enclosure 23 OS), which was founded by Phileros around AD 60, is located within a funerary area well documented by epigraphy. This concession was installed on an area where several graves were already present since 40–30 BC. A detailed stratigraphic analysis, together with the analysis of the associated archaeological material (ceramics, coins, oil lamps, etc.), allowed to precisely date the burials (tombs 1 to 48) sometimes within a 10-yr uncertainty. This analysis revealed that the most ancient graves (T38 and T48) date from between 20 BC and AD 30, with the most recent date from AD 79, i.e. the day of the destruction of Pompeii following the eruption of the Vesuvius. The details of the phase determination and dating of the graves are given in Van Andringa et al. (2013: 125–7). Next to this enclosure, another enclosure (enclosure 21 OS) was excavated. This enclosure also received one of Gaia Vesonia's emancipated slave (Stallia Haphe) as well as other deceased persons (including tombs 201 and 203). Pyres located in the immediate vicinity were also excavated.

Eleven individuals were selected for ^{14}C dating (for a detailed description of the samples and contexts, see the Online Supplementary Material). Individual ages of the individuals were determined, when possible, following the methods of physical anthropology and are provided in Van Andringa et al. (2013: 862–5). Among them, three children were not incinerated, allowing dating of both the enamel and collagen fraction of the bone for two of them (T29 and T38). During the Roman period, very young children were usually not incinerated even if the cremation of adults was the usual practice. For the remaining eight individuals, degraded collagen from burnt bone, as well as bone apatite from burnt and calcined bone, was dated. Charcoal and shells found in association with the tombs or the pyre were also dated in order to estimate the local reservoir effect as well as the influence of the old-wood effect. Bone samples were powdered (<100 µm) prior to pretreatment using a mortar and pestle. For enamel, two different protocols were tested. Enamel samples were pretreated first in the form of millimeter chunks, then in the form of fine (<100 µm) powder. Charcoals were prepared following the classical acid-alkali-acid treatment. They were first immersed in 0.5N HCl for 3 hr, then in 0.05N NaOH for 0.5 hr, then in 0.5N HCl for 16 hr. Degraded collagen from burnt bone was isolated using a similar treatment: 10% HCl for 0.5 hr; 0.1N NaOH for 0.5 hr; 0.1N HCl for 0.5 hr. Bone and enamel apatite were pretreated using 1N acetic acid under weak vacuum at room temperature for 18 to 22 hr. The surface of the shells was acidified in 10% HCl for 10 s. The shells were rinsed, then finely powdered. Carbon dioxide (CO_2) derived from carbonate in shell aragonite and bone and enamel apatite was extracted using orthophosphoric acid (H_3PO_4) for 15–30 min at 70°C under vacuum. Charcoal and degraded collagen was combusted at 500°C in the presence of pure oxygen. Two charcoal samples were large enough to be dated using the classical liquid scintillation method. Preparation of benzene and counting were performed at the LOCEAN lab (UPMC, Paris). For the other samples, sealed tubes containing between 1–2 mg C in the form of CO_2 were sent to the ^{14}C laboratory of Tucson, Arizona, USA, for graphitization and ^{14}C measurement. Carbon isotope values were measured using isotope ratio mass spectrometry (IRMS). Pretreated shell (0.05 mg), unburned bone and enamel apatite (0.6 mg), and calcined bone apatite (1.8–2.7 mg) were reacted with 100% orthophosphoric acid at 70°C in individual vessels in an automated cryogenic distillation system (Kiel IV device), interfaced with a Delta V Advantage isotope ratio mass spectrometer. Over the period of analysis of the bioapatite samples, the analytical precision estimated from 16 samples of the laboratory internal carbonate standard (LM Marble, calibrated against NBS-19) was ±0.03‰ (1σ).

RESULTS

The results are presented in Table 1 and Figure 3. Charcoal ages ($n = 4$) range between 1960 ± 27 and 2328 ± 50 ^{14}C yr BP. Shells ($n = 6$) show a very large range in ^{14}C age, from 2400 ± 39 to 4035 ± 41 ^{14}C yr BP. The dated human bones show an even larger age range,

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Table 1 Carbon content, carbon isotope value, and radiocarbon age of the Porta Nocera samples.

Tomb	Material	Species	Thermal status	Fraction dated	%C	$\delta^{13}C$	F	Error	^{14}C age	Error	AMS lab #
15	wood	*Fagus* sp.	heated	charcoal	58.00	–26.4	0.775	0.003	2053	27	AA92547
15	wood	*Acer* sp.	heated	charcoal	47.00	–30.5	0.748	0.005	2328	50	AA92548
Pyre 5	wood	unknown	heated	charcoal	n.a.	n.a.	0.7835	0.003	1960	27	n.a.*
203	wood	unknown	heated	charcoal	n.a.	n.a.	0.778	0.003	2018	28	n.a.*
10	shell	*Donax trunculus*	unburnt	calcite	9.02	–1.3	0.642	0.003	3556	42	AA88428
10	shell	*Donax trunculus*	unburnt	calcite	11.57	–1.7	0.633	0.003	3670	41	AA88429
10	shell	*Donax trunculus*	unburnt	calcite	11.86	1.9	0.681	0.004	3087	40	AA88430
	shell	Muricidae	burnt	calcite	8.04	1.6	0.742	0.004	2400	39	AA88431
	shell	Muricidae	unburnt	calcite	11.72	1.7	0.605	0.003	4035	41	AA88432
25	shell	Muricidae	unburnt	calcite	11.62	2.2	0.720	0.003	2644	36	AA88435
1	bone	*Homo sapiens*	calcined	bioapatite	0.60	–23.9	0.755	0.004	2261	39	AA88433
2	bone	*Homo sapiens*	calcined	bioapatite	0.33	–22.7	0.758	0.003	2229	33	AA88434
5	bone	*Homo sapiens*	calcined	bioapatite	0.13	–13.2	0.552	0.003	4767	48	AA88436
6	bone	*Homo sapiens*	burnt	degraded collagen	4.17	–24.6	0.799	0.005	1805	49	AA88455
6	bone	*Homo sapiens*	burnt	bioapatite	0.82	–17.6	0.749	0.004	2322	38	AA88438
6	bone	*Homo sapiens*	calcined	bioapatite	0.27	–20.3	0.765	0.004	2148	40	AA88437
15A	bone	*Homo sapiens*	calcined	bioapatite	0.48	–23.4	0.774	0.003	2055	36	AA88439
15A	root	*Homo sapiens*	calcined	bioapatite	0.11	–17.4	0.669	0.004	3229	49	AA88440
19	bone	*Homo sapiens*	burnt	bioapatite	0.82	–12.9	0.723	0.005	2607	50	AA88453
19	bone	*Homo sapiens*	burnt	degraded collagen	10.72	–20.5	0.760	0.005	2210	50	AA88454
19	bone	*Homo sapiens*	calcined	bioapatite	0.29	–22.3	0.778	0.005	2012	49	AA88441
25	bone	*Homo sapiens*	calcined	bioapatite	0.43	–21.4	0.760	0.003	2207	32	AA88442
25	root	*Homo sapiens*	calcined	bioapatite	0.06	–22	0.767	0.005	2136	49	AA88443
29	enamel	*Homo sapiens*	unburnt	bioapatite	0.73	–9.2	0.672	0.004	3192	50	AA88446
29	enamel	*Homo sapiens*	unburnt	bioapatite	0.68	—	0.692	0.002	2961	28	AA102821
29	bone	*Homo sapiens*	unburnt	collagen	—	—	0.767	0.003	2127	27	AA102819
38	enamel	*Homo sapiens*	unburnt	bioapatite	0.89	–8.2	0.673	0.004	3182	50	AA88447
38	enamel	*Homo sapiens*	unburnt	bioapatite	0.74	—	0.691	0.002	2964	28	AA102822
38	bone	*Homo sapiens*	unburnt	collagen	—	—	0.782	0.004	1977	37	AA102820
48	enamel	*Homo sapiens*	unburnt	bioapatite	0.84	–8.1	0.668	0.004	3237	50	AA88448
201	root	*Homo sapiens*	calcined	bioapatite	0.06	–13.4	0.500	0.008	5570	120	AA88444

*Dates measured by liquid scintillation at the LOCEAN Lab (UPMC, Paris).

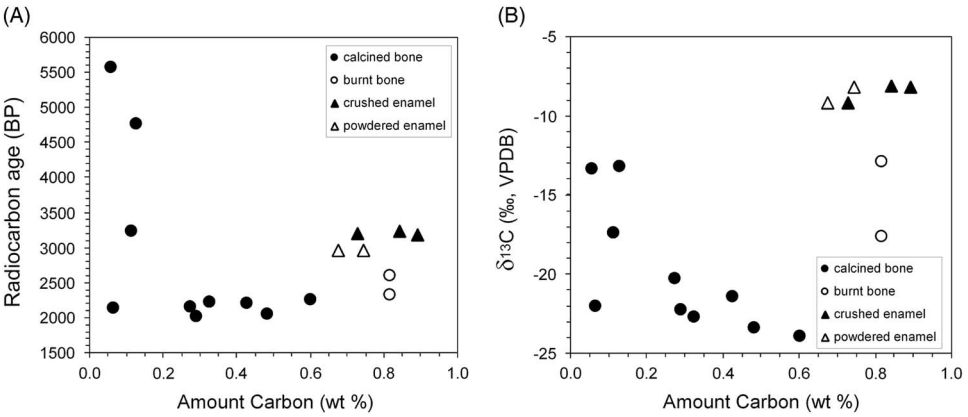

Figure 3 Relationship between the amount of carbon, the ^{14}C age (A) and the carbon isotope value (B) of the apatite samples from the Porta Nocera necropolis.

between 1805 ± 49 and 5570 ± 120 ^{14}C yr BP. Multiple sampling on some of the individuals shows large (up to 1200 ^{14}C yr) age variability. Carbon content in calcined bones is very variable and ranges between 0.06 and 0.60 wt% (0.28 ± 0.19% on average). Although based on a lower number of specimens, the carbon content of burnt bone (0.82%) and enamel (0.71 and 0.82%, respectively, for powdered and crushed enamel) appears higher and less variable. The carbon isotope value of calcined bone also is variable and ranges between –13.2 and –23.9‰. Calcined bone carbon content is negatively correlated with $\delta^{13}C$ values ($R^2 = 0.51$) and positively correlated with ^{14}C age ($R^2 = 0.36$). Correlations increase to 0.80 and 0.67, respectively, if only samples with ^{14}C age higher than 2200 ^{14}C yr BP are considered.

DISCUSSION

The ages of the burials range between 20 BC and AD 79. If we apply the IntCal13 ^{14}C calibration curve (Reimer et al. 2013) together with the OxCal v 4.2 software (Bronk Ramsey and Lee 2013), we can convert these calendar ages into ^{14}C ages. By doing so, we calculate that the ^{14}C ages of individuals buried in the Porta Nocera necropolis should range between about 1900 and 2035 ^{14}C yr BP. The most ancient graves (Grave 38 and 48) are from children, so no further correction due to the individual age of the deceased is necessary. While one date on degraded collagen from Grave 6 is more recent possibly due to contamination with young organic carbon (1805 ± 49 ^{14}C yr BP), most (18/21) of the ^{14}C ages measured on the skeletal remains from Porta Nocera are therefore too old. Deviation from expected age is small for collagen (0–150 ^{14}C yr) but can reach 3500 ^{14}C yr for calcined bone. In the following, we discuss the respective impact of diet, old-wood effect, and diagenesis to explain this unexpected ^{14}C age offset.

Marine diets are responsible for the incorporation of a marine reservoir age in skeletal remains (Yoneda et al. 2002; Zazzo et al. 2014). In the Roman Empire, marine food was common in the diet but probably more restricted to people with a high social status. At Herculaneum, the coupling of ^{14}C and stable isotopes performed in bone collagen of individuals who died during the AD 79 eruption showed that variable amounts of marine resources were included in their diet, affecting bone collagen ^{14}C ages by up to 84 ^{14}C yr (Craig et al. 2013). In our study, the collagen of two individuals could be dated. These two individuals were 1–2-yr-old children; therefore, most of their dietary input would have come from their mother's diet through breastfeeding. The first one (Grave 38, 1977 ± 37 ^{14}C yr BP) shows no evidence of

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Table 2 Estimation of the impact of wood inbuilt age on Porta Nocera calcined bone age.

		Calculated ^{14}C age			Measured ^{14}C age		Reservoir age		Transfer in calcined bone (^{14}C yr)	
Context	Period	range	average	error	^{14}C age	error	^{14}C yr	error	35% exchange	95% exchange
Tomb 15	AD 70–79	1896–1948	1922	37	2053	27	131	46	46	124
Tomb 15	AD 60–79	1896–1964	1930	48	2328	50	398	69	139	378
Pyre 5	AD 62–74	1912–1960	1936	34	1960	27	24	43	8	23
Tomb 203	AD 60–79	1896–1964	1930	48	2018	28	88	56	31	84
Average							**160**		**56**	**152**
Standard error							**164**		**58**	**156**

marine food in its diet as its calibrated age (36 BC–AD 65, 1σ) in is perfect agreement with the estimated burial date (20 BC–AD 30). The other one (Grave 29, 2127 ± 27 ^{14}C yr BP) is in strong disagreement with the estimated burial date (AD 70–79), suggesting that marine food could be responsible for a ~150 ^{14}C yr offset. This represents approximately 29–36% of the marine reservoir age of the Mediterranean near Naples (415–515 ^{14}C yr according to Siani et al. 2000), suggesting that the mother's diet during and after her pregnancy was composed for a large part of marine food.

In the case of cremated bones, diet is not likely to play a major role because most of the biogenic carbon is replaced by fuel-derived carbon during calcination (Hüls et al. 2010; Zazzo et al. 2012; Snoeck et al. 2014). This raises the possibility of the transfer of an inbuilt age from the wood to the bone if large trees (or trees cut several decades earlier) are used for the cremation (Olsen et al. 2013). An anthracological study was performed at Porta Nocera and revealed the presence of wood of various sizes, including small branches, bundles of wood, and larger trunks. The presence of nails and marks of squared in the pyres may also indicate the use of waste wood coming from elements of furniture (Coubray 2013). Thus, an inbuilt age is to be expected and its magnitude must be evaluated. The age of the contexts in which the charcoals were found is known with a precision of 10–20 calendar years, allowing to estimate the expected age offset due to inbuilt age. These upper and lower age limits were first converted into a ^{14}C age range via the IntCal13 calibration curve (Reimer et al. 2013) (Table 2), following the methodology described in Olsen et al. (2013). Testing the converted dates against the charcoal ^{14}C dates results in age differences ranging between 24 ± 43 and 398 ± 69 ^{14}C yr (160 ± 164 ^{14}C yr on average, $n = 4$). Open-air experiments have shown that carbon isotope exchange between the bone and the fuel ranges between 35 and 95% (Hüls et al. 2010; Zazzo et al. 2012; Snoeck et al. 2014). This leads to calculate that, on average, calcined bone dates can be shifted by 56–152 ^{14}C yr due to exchange with old-wood carbon. The eight cremated individuals died between AD 40 and 79. This translates to ^{14}C ages ranging between 1896 and 1978 BP. If we take in account the average age shift calculated above, we can estimate that the maximum age in calcined bone due to the old-wood effect should be about 2130 BP. Only 3 out of the 10 cremated samples are below this threshold. Burnt bone apatites are beyond, together with the two enamel samples (non-cremated) for which exchange with wood carbon cannot be invoked.

Instead, we propose that the ^{14}C depletion measured in archaeological apatites is due to the influence of the ^{14}C-free CO_2 emissions of the nearby Vesuvius volcano and the Campi Flegrei volcanic system at the Bay of Naples (Pasquier-Cardin et al. 1999; Chiodini et al. 2010). Although never measured before in humans, this pattern has already been observed in soils and plants living at the vicinity of a volcano (Pasquier-Cardin et al. 1999). This "volcano effect"

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could have been recorded *in vivo* (through diet) or during fossilization (through isotope exchange with CO_2 dissolved in percolating waters). Degassing of dead CO_2 at the Bay of Naples could also explain the anomalously high ^{14}C ages measured on some seashells (Table 1). Several lines of evidence suggest that diagenesis, rather than diet, can explain the pattern observed in archaeological apatites. First, while expected ^{14}C activities were measured in bone collagen, anomalously high ^{14}C ages were measured in enamel from the same individuals (T29 and T38). Since the two sampled individuals were newborns, differences in enamel apatite and bone collagen turnover cannot explain the difference in ^{14}C activity between the two tissues. Second, the fact that we measured a different ^{14}C activity in the same enamel samples treated according to two different protocols (powdered vs. millimeter chunks) also points to a contamination issue. Enamel ^{14}C activity increased by 2 pMC when treated in the form of powder, and became closer to ^{14}C activities measured in bone collagen. Powdered samples also contained less inorganic carbon following treatment (0.68 vs. 0.73 and 0.74 vs. 0.89 weight% for Grave 29 and 38 enamel, respectively). This confirms previous findings showing that the acid acetic treatment is more effective at removing secondary carbonates on finely powdered enamel than on small fragments (Zazzo 2014). Thus, it appears clearly that diagenesis, i.e. *post mortem* exchange of carbon between apatite and dissolved inorganic carbon, is responsible for the measured age shift. In this context, diagenetic carbon is depleted in ^{14}C compared to the buried skeletal remains. This conclusion appears to contradict the findings from a previous study showing that during diagenesis, the carbon source available for isotopic exchange is always enriched in ^{14}C (i.e. younger) compared to the fossil remains (Zazzo 2014). This conclusion was based on the ^{14}C dating of more than a hundred fossils buried in different contexts including ^{14}C-free sediments such as caves (Hedges et al. 1995; Zazzo et al. 2013) and limestone rocks (Zazzo et al. 2014). In surface or near-surface finds like archaeological burials or habitats, carbonates dissolved in percolating waters are close to the isotopic equilibrium with the atmosphere and have therefore a younger ^{14}C age than the fossils, leading to their apparently younger age as times goes by. Volcanic contexts, by providing a constant input of ^{14}C-free CO_2 to the soil, appear to be the exception that proves the rule.

The largest age shifts are measured in calcined bones. This could lead to the conclusion that calcined bones are more prone to diagenetic alteration than burnt bone, or enamel apatite, contradicting previously published evidence (Zazzo and Saliège 2011; Zazzo 2014), but a closer look at the data indicates that this may actually not be the case. A mass balance calculation allows estimating the contribution (in %) of dead carbon to the measured age. We considered two different end-members for initial (i.e. pre-diagenetic) ^{14}C age, depending on whether or not apatite ages are influenced by an old-wood effect (for calcined and burnt bones) or a marine diet (for enamel). As discussed above, both factors will lead to a maximum age of 2130 BP, which corresponds to a fraction modern carbon (F) value of about 0.7674. The results (Table 3) show that on average, contamination represents 8–10% of the total carbon in calcined bones depending on the initial F value chosen for the calculations. This is intermediate between burnt bones (4–6%) and powdered enamel (10–12%). However, large (0–35%) interindividual variations are calculated, and we note that calcined bone samples that deviate the most from the expected age are usually the ones that present the lowest carbon contents (Figure 3). These percentages were then multiplied by the carbon concentration of the apatite samples and converted in amount of dead carbon. By doing so, we calculate that calcined bones contain on average 0.8–1.4 µg dead C, i.e. 3.6–4.1 times less than burnt bones (3.3–5.0 µg dead C) and 6.1–8.6 times less than powdered enamel (7.0–8.3 µg C). This conclusion is more in line with previous work showing that postburial carbon isotope exchange is much lower in calcined bone than in enamel, unburnt and charred bone altogether, due to recrystallization during heating (Zazzo and Saliège 2011; Zazzo 2014). Our results show that a very small amount of

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Table 3 Estimation of the amount of dead carbon in Porta Nocera apatites.

				Fi = 0.7674		Fi = 0.784	
Tomb	Sample type	F	[C]meas (weight %)	dead C (%)	[C]dead	dead C (%)	[C]dead
T1	calcined bone	0.7547	0.60	1.7	0.010	3.7	0.022
T2	calcined bone	0.7577	0.33	1.3	0.004	3.3	0.011
T5	calcined bone	0.5524	0.13	28.0	0.036	29.5	0.038
T6	calcined bone	0.7654	0.27	0.3	0.001	2.3	0.006
T15A	calcined bone	0.7743	0.48	–0.9	–0.004	1.2	0.006
T19	calcined bone	0.7784	0.29	–1.4	–0.004	0.7	0.002
T25	calcined bone	0.7598	0.43	1.0	0.004	3.0	0.013
T201	calcined bone	0.5000	0.06	34.8	0.020	36.2	0.021
T15A	calcined bone	0.6690	0.11	12.8	0.014	14.6	0.017
T25	calcined bone	0.7665	0.06	0.1	0.000	2.2	0.001
Average			0.28	**7.8**	**0.008**	**9.7**	**0.014**
Standard deviation			0.19	**13.2**	**0.013**	**12.9**	**0.011**
T6	burnt bone	0.7490	0.82	2.4	0.020	4.4	0.036
T19	burnt bone	0.7229	0.82	5.8	0.047	7.7	0.063
Average			0.82	**4.1**	**0.033**	**6.1**	**0.050**
Standard deviation			0.00	**11.2**	**0.015**	**10.9**	**0.017**
T29	enamel, powdered	0.6917	0.68	9.9	0.067	11.7	0.079
T38	enamel, powdered	0.6914	0.74	9.9	0.074	11.8	0.087
Average			0.71	**9.9**	**0.070**	**11.7**	**0.083**
Standard deviation			0.05	**0.0**	**0.005**	**0.0**	**0.006**
T29	enamel, crushed	0.6721	0.73	12.4	0.091	14.2	0.104
T38	enamel, crushed	0.6729	0.89	12.3	0.110	14.1	0.126
T48	enamel, crushed	0.6683	0.84	12.9	0.109	14.7	0.124
Average			0.82	**12.5**	**0.103**	**14.3**	**0.118**
Standard deviation			0.08	**0.3**	**0.011**	**0.3**	**0.012**

contamination can impact the ^{14}C age of a sample that contains very little carbon (typically less than 0.3%). One of the side effects of bone exposure to high temperatures is the lowering of the carbonate content of bone (Person et al. 1996; Zazzo et al. 2009). Thus, there is a tradeoff between the advantage (recrystallization) and the disadvantage (lower carbon content) of calcination. Because volcanic CO_2 and calcined bone carbonate $\delta^{13}C$ values differ by about 20–25‰ (Pasquier-Cardin et al. 1999; Hüls et al. 2010), contamination can also be monitored using calcined bone apatite $\delta^{13}C$ values. As a general guiding rule, we propose that a prescreening using both carbon content and $\delta^{13}C$ values with thresholds set at 0.3% and –20‰, respectively, could be used to select the best samples for ^{14}C dating in volcanic contexts.

CONCLUSION

This study demonstrates that in volcanic contexts, large ^{14}C age shifts can be measured in relatively recent archaeological apatites, even calcined ones. We show that while a marine diet or an old-wood effect could explain the smallest age shifts, they are not able to explain the largest ones, and we thus propose diagenesis as the main factor. This unexpected result was likely caused by the large amounts of dead C diffusing in the soil following the AD 79 eruption, which created a strong gradient in ^{14}C concentration between the biogenic and diagenetic end-members and caused an increase in the apparent age of fossil apatites. It emphasizes the need to be cautious when working in volcanic environments. This study also has implications for apatites found in nonvolcanic contexts. Even if large age offsets were sometimes observed in calcined bones from Pompeii, most of them showed ^{14}C ages that could easily have been interpreted as "normal" without the strong stratigraphic and chronological constraints available for this historical site excavated with great care. Our quantitative estimate of the amount of dead carbon in the different apatite fractions provides a way to quantitatively assess the intensity of C isotope exchange in different types of apatite materials. It confirms the overall strong resistance of calcined bones relative to burnt bone and enamel apatite and suggests that ^{14}C dating of calcined bones should be restricted to samples with high (>0.3%) carbon content and low (< –20‰) $\delta^{13}C$ values.

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SUPPLEMENTARY MATERIAL

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