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TGMS analysis of archaeological bone from burials of the late Roman period

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Abstract The use of thermogravimetric analysis–mass spectrometry (TGMS) to study the state of preservation of archaeological bones has been investigated. As part of a collaborative multi-analytical study, bones exhumed from graves of the late Roman period in France and Italy were examined. A decrease in organic matter for the archaeological bones compared to that for new bone was confirmed, demonstrating that diagenesis of aged bones can be detected using TGMS. Different amounts of collagen were determined for bones from different graves and could, for the majority of specimens, be correlated with the visually observed preservation states.

Keywords Archaeology · Bone · Collagen · TGMS

Introduction

Bone recovered from archaeological sites can provide archaeologists with valuable information about funeral rituals. Bones undergo complex diagenetic processes during burial and their state of preservation depends on a number of environmental factors. More emphasis has been placed on studying the inorganic components of bone that make up about 70% of bone, but an examination of the organic component may add to an understanding of the diagenesis process. Collagen makes up 20–30% of new bone.

This study forms a part of collaborative investigations into burials of the late Roman period exhumed in France and Italy [1]. Bone samples were obtained from two French archaeological sites in Anché and Naintré [2]. In 2000, sarcophagi of stone containing lead sarcophagi were found on a farm in Anché. Examination of the skeletons revealed the body of an adult dating to 240–392 AD and the other of a child dating from 128–316 AD Fig. 1 illustrates the Anché graves during exhumation. The graves of another late Roman period adult and child had been uncovered in Naintré in 1997, dating to the second half of the third century AD These too were contained in lead sarcophagi within stone sarcophagi. Bones for the study were also obtained from a collective burial contained in the Catacomb of Saint Peter and Marcellinus in Rome, where bodies had been "mummified" [3]. This burial, exhumed in 2002, is estimated to be from 28–132 AD, and the bodies were individually wrapped in white cloth.

Thermogravimetric analysis–mass spectrometry (TGMS) was employed in the current study to examine the organic material remaining in the archaeological bone samples. TGMS has been demonstrated as a suitable technique for characterising the bones and has been successfully employed for the study of forensic bones [4–6]. TGA data shows mass losses at particular temperatures that may be correlated with the organic and inorganic phases present in bone. It is also possible to determine the relative proportion of collagen remaining using this approach.

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Fig. 1 The grave sites of the child (*left*) and the adult (*right*) at Anché (photograph by Dr. Bernard Farago-Szekeres)

Materials and methods

Bone samples were collected from the five grave sites: the two burials at Anché, the two burials at Naintré, and one grave from the catacomb in Rome. Specimens were collected from different parts of each skeleton.

The bone specimens were examined using a Setaram Setsys 16/18 thermobalance coupled with a Balzers ThermoStar mass spectrometer. The experiments were carried out by placing approximately 15–20 mg of ground bone sample into a platinum crucible and heating at a rate of 10 °C min^{-1} from ambient temperature to 1,100 °C under flowing high purity argon gas (20 mL min^{-1}). Temperature calibration was carried out using indium, tin, aluminium, gold, and silver. Baseline curves measured under the same experimental conditions were acquired to account for buoyancy effects on the balance. Based on earlier TGMS work on bone, the MS mass-to-charge ratios selected for analysis were 12, 18, 28, 29, 30, 32, 44, 48, 54, 64, 66, 67, 70, 72, 78, 81 and 91 amu [4]. A 1-s acquisition time for each mass unit was set, thus requiring 0.13 min (or 1.3 °C) for each cycle.

Results and discussion

Each bone specimen collected was initially examined using optical microscopy and the state of preservation of each bone was recorded. Table 1 summarises the overall state of preservation of the bones from each grave based on visual examination. There was variation in the appearance of bones from different graves. The child in Anché and the adult in Naintré showed bones in a relatively good state of preservation, with the integrity retained. By comparison, the other skeletons from Rome, the Anché adult, and the Naintré child were degraded and friable.

TGMS analyses were carried out on multiple bones taken from each grave. All the samples analysed showed the common features illustrated in Fig. 2. This shows the typical TG data obtained for the bones, illustrating data for a bone from the grave of the Anché child. The profiles may be divided into three steps following the mass loss. The MS data for each fragment were examined as a function of temperature and particular m/z values could be associated with the mass loss steps in the TG data. The first mass loss step occurs from approximately 50 up to 200 °C and corresponds to water desorption ($m/z = 18$). In the second step, the mass loss observed up to about 600 °C may be attributed to the pyrolysis of organic substances, principally collagen, contained in the bones. The degradation of the organic material was characterised by $m/z = 18$, 30, 32, 44, 54, 64, 70, 72, 78, 81, and 91 [4]. In the third step, between 600 and 1100 °C, the mass loss corresponds to the decomposition of the mineral phase. Carbon dioxide is released from carbonated apatite ($m/z = 44$). Other authors have demonstrated that the main solids produced are β-tricalcium phosphate and hydroxyapatite [4, 7–9].

Table 1 Bone preservation states and compositions

Bone source	Number of samples analysed	Preservation state from microscopy	Water/w%	Organic phase/w%	Inorganic phase/w%
Rome	5	Poor	7.0	7.8	85.2
Anché adult	5	Poor	5.5	5.2	89.3
Anché child	2	Good	9.1	17.1	73.8
Naintré adult	6	Good	5.4	4.3	90.3
Naintré child	5	Poor	7.5	15.3	77.2

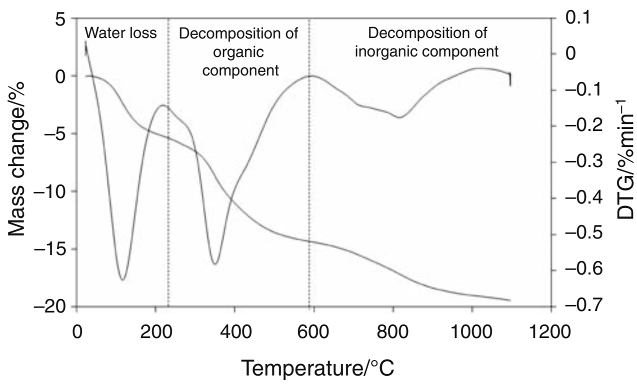

Fig. 2 TGMS data for bone from the grave of the Anché child

The proportions of water, organic, and inorganic material were measured for each sample using the mass loss information. The average values for all the bones examined from each site are reported in Table 1. The proportion of water is relatively constant for all the samples. All samples show a lower content of organic material than that of fresh bone (approximately 30 w%), which is in keeping with the expected diagenesis occurring in the burials over such a period of time. The composition values were found to be similar for samples obtained from within individual graves, but some variation was observed for bones obtained from different graves.

For the bones observed to show a poor state of preservation from Anché, the analysis shows less collagen remaining in the bones compared to the bones showing better preservation. For the bones from Rome, which were particularly friable, analysis reveals a low level of collagen. However, this trend is not observed for the bones from Naintré. For bones from this site, the badly preserved bones contain a higher percentage of collagen compared to the perceived better preserved bones. This anomaly may be explained by the influence of additional environmental factors. Elemental analysis of the bones (data not shown here) reveals the presence of substantial quantities of lead in the bones of both graves at Naintré and substitution of lead for calcium in the mineral component appears to have occurred [1]. The modification of the mineral phase may influence the bone stability and, as a consequence, the state of preservation may not necessarily be correlated with the amount of remaining collagen.

Conclusions

TGMS analysis was carried out on archaeological bone specimens exhumed from several sites in France and Italy. The technique was used to determine the proportion of organic material contained in each bone. The analysis was able to demonstrate a decrease in organic content compared to new bone for all samples due to the diagenesis of such aged bones. It was noted that there are different amounts of collagen detected in bones from different grave sites. For most of the specimens investigated, there is a correlation between the amount of collagen preserved and the visual state of preservation of the bones, as determined by optical microscopy. Different observations were made for bones from graves at one site, where the mineral phase was modified by the presence of lead. The modification indicates that the amount of collagen may not always be directly correlated with the perceived state of preservation. Further studies of these bones have been carried out using infrared spectroscopy, X-ray diffraction and scanning electron microscopy and the results will be reported in an upcoming publication.

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