# Biomolecular Analysis of Ceramic Containers, Skeletal Remains, Anthropogenic Sediments and Organic Artefacts from the Royal Tomb at Qatna

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يؤمن القبر الملكي في تل المشر فة/قطنا القديمة / فرصة لا مثيل لها للبحث باستخدام تحليل الأنسجة، لقد أغلق القبر وبشكل كامل منذ دمار القصر الملكي، وقد اكتشف ولحسن الحظ في حالة ممتازة من الحفظ وخاصة موجو داته "بقايا هياكل عظمية إنسانية وحيوانية" موز عة على غرف الدفن الأربعة.

عرد. عدد كبير من الأواني لفخارية والحجرية نشاهد بقاياها في المكان، وأرض القبر مشبعة بالبقايا العضوية تم در استها من خلال نشاطات الدر اسات الوراثية.

لدينا ر غبة بإعادة فهم بعض النشاطات التي كانت تمار س في المدفن الذي يستخدم كغر فة دفن للطبقة العليا في المدينة.

وخلال الدراسة المركزة على عينات الأنسجة والمواد المأخوّذة من قعر القبر ومحتويت الأواني الفخارية، "بقايا الهياكل العظمية والبقايا العضوية". وهنا تصنف استراتيجية العمل على العينات المأخوذة وبرنامج التحليل والفرز بأنه الطريق الموعود إلى عمل ناجح وباهر.

Abstract

The Royal tomb at the site of Tell Mishrifeh (ancient Qatna) provides an unparalleled opportunity for investigation using an integrated biomolecular approach. The tomb has been sealed since the destruction of the palace thus, the finds were discovered *in situ* and appear to be in an excellent state of preservation. Skeletal remains of humans and animals are distributed throughout the four chambers of the tomb, many of the pottery and stone vessels have visible residues in place and even the tomb floor holds substantial organic deposits deriving from anthropogenic activity. We aim to reconstruct some of the activities which took place throughout the tomb's use as a high status burial chamber, through the application of a range of biomolecular and elemental analyses focusing on the floor sediments, vessel contents, skeletal remains and organic artefacts. Here we describe the sampling strategies, analytical programme and preliminary findings for what promises to be an exciting and rewarding project.

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## 1. Introduction

The biomolecular investigations of archaeological finds from Tell Mishrifeh, being undertaken at Bristol University, focus primarily on the Royal Tomb discovered beneath the northern edge of the Palace. At the time of writing we are in the early stages of a three year project. The tomb (Fig. 1), dug into the natural rock cliff, consists of an antechamber, main chamber and three side chambers. A major feature of the tomb is that it has been sealed since the destruction of the Palace by fire in the Bronze Age. The finds have not been buried and there has been very little inundation of groundwater, therefore are in a remarkable state of preservation. The contents of the tomb were found in situ and include ca. 2000 artefacts including jewellery and carved decorative objects, human and animal bones, sarcophagi and many stone and pottery vessels, many with visible organic residues still in place. Even the floor of the tomb remained undisturbed showing evidence of substantial organic deposits; these are essentially anthropogenic sediments arising from the use of the tomb which have not been subjected to weathering or bioturbation activity and thus offer considerable potential for reconstructing different areas of activity. The remarkable preservation of the tomb and nature of the artefacts contained therein, offers an unparalleled opportunity to investigate key aspects of Bronze Age burial practice through analysis of the organic residues associated with the various classes of find.

## 2. Sampling strategies

Sampling campaigns were performed during the original excavation in December 2002 (anthropogenic sediments), September/October 2003 (vessels and contents, further anthropogenic sediments) and August/September 2004 (further vessels and contents, human remains, potsherds from the Palace and organic artefacts). These have resulted in over 500 individual samples. Further sampling will also take place during the summer of 2005 to collect human, animal and plant remains. Visible residues, contents and fabric samples were collected from the vessels which include simple food, drink and storage containers, in addition to more specialised forms which were imported or traded over considerable distances. Potsherds from a storage area of the Palace were also selected as a comparison to those within the tomb. The anthropogenic sediments were systematically sampled from the tomb floor, including areas which were visually assessed as being the foci of human activity and from other less intensively used areas. Human tissue, plant remains and textiles were sampled with guidance from an anthropologist, micromorphologist, textile expert and archaeologists. Small samples of artefacts of organic origin, such as a carved lion's head container and various items of jewellery which appear to be composed of, or incorporate, a resinous substance(s), were sampled from Damascus Museum.

#### 3. Analytical programme

This project offers scope for testing hypotheses relating to: (i) the nature of the organic based commodities contained in the various vessel types, including identification of commodities that were traded or imported from other regions; (ii) the role of specific commodities in the burial ritual, including a number of exceptional examples of possible 'wine' or 'beer' vessels containing copious residues; (iii) the processes of formation of the organic sediments within the tomb in relation to burial practices and ritual activities; and (iv) the nature and composition of the organic artefacts found within the tomb. The majority of the biomolecular analyses will be performed according to established protocols as described below, although opportunities also exist for the development of new procedures, all interpretations will be made in conjunction with the findings of the many other specialists, e.g. ceramicists, faunal and human bone specialists, micromorphologists, etc.

#### 3.1 Organic residue analyses of pottery vessels

The tomb contained ca. 200 ceramic and stone vessels of widely varying forms (Fig. 2); while these forms can proffer valuable clues to the nature of the contents and will assist in directing the chemical analyses only lipid residue analysis can provide direct chemical evidence for determining their actual mode of use. The types of organic commodities encountered in archaeological vessels fall into three major categories, namely, foodstuffs, beverages and exotics (i.e. ointments, perfumes, incense etc.).

#### 3.1.1 Food vessels

Such vessels would have been used for the presentation, preparation, storage and transport of con-



Fig. 1. Plan of the Royal Tomb at Tell Mishrifeh.

sumable commodities. The major foci in the analysis of this vessel type will be the preserved lipids since these offer considerable opportunities for determining the nature of their contents. Lipid residue analysis via gas chromatography (GC), GC-mass spectrometry (GC/MS) and GC-combustion-isotope ratio-MS (GC-C-IRMS) has enabled the detection and characterisation of a wide range of commodities including ruminant adipose fats, non-ruminant adipose fats, dairy fats<sup>3</sup>, epicuticular plant waxes<sup>4</sup>, plant oils/lipids<sup>5</sup>, beeswax<sup>6</sup> and coniferous and triterpenoid plant resins7. Many of the food vessels contained within the tomb displayed visible remains of their contents, including ceramic platters holding large quantities of morphological remains, e.g. animal bones, which appear to be the remains of meals or offerings. Analyses will be performed of both visible residues and those absorbed within the ceramic matrix<sup>8</sup>. Given the majority of the vessels are intact, a modified sampling strategy was adopted. Visible residues were removed from the interior surfaces of vessels using a scalpel, while ceramic fabric samples, containing absorbed residues, were removed using a modelling drill equipped with an abrasive bit. After addition of internal standard, sub-samples are extracted with a mixture of chloroform and methanol (2:1 v/v) to obtain the total lipid extract (TLE). After derivatisation, TLEs or fractions thereof are analysed using GC, GC/MS and GC-C-IRMS. Compositional information from these residue analyses will be combined with the results of macro-analysis of morphological remains, e.g. animal bones present within vessels. We will also work with epigraphers to relate vessel contents to inscriptions and ceramicists to relate



Fig. 2. Photograph showing the range of vessels types found within the tomb.

vessel forms to residue type and geographical origin. This combination of analyses will allow comprehensive relationships between vessel types and contents to be assessed.

#### 3.1.2 Vessels used for beverages

Vessels used for the transport and storage of alcoholic beverages (wine/beer) are certain to have existed in antiquity, however, residues of such products have never been adequately characterised from archaeological contexts<sup>9</sup>. The tomb contains multiple examples of possible wine or beer vessels holding copious homogeneous residues. Since there has been no water-logging of the tomb we have a unique opportunity to study remains of potentially water soluble residues. Few vessels of this type have been recovered from such

- <sup>7</sup> BECK SMART OSSENKOP 1989: 369-80; CHARTERS EVERSHED - GOAD - HERON - BLINKHORN 1993: 91-101
- <sup>8</sup> Copley Berstan Dudd Docherty Mukherjee Straker - Payne - Evershed 2003: 1524-1529; Evershed - Heron -Goad 1990: 1339-1342; Evershed - Dudd - Copley - Berstan - Stott - Mottram - Buckley - Crossman 2002: 660-668; Mottram - Dudd - Lawrence - Stott - Evershed 1999: 209-221.
- <sup>9</sup> McGovern Glusker Moreau Nuñez Beck Simpson -Butrym - Exner - Stout 1999: 863-864.

<sup>&</sup>lt;sup>3</sup> Evershed - Heron - Charters - Goad 1992: 187-208; Dudd - Evershed 1998: 1478-81; Copley - Berstan - Dudd -Docherty - Mukherjee - Straker - Payne - Evershed 2003: 1524-9.

<sup>&</sup>lt;sup>4</sup> Evershed - Heron - Charters - Goad 1992: 187-208; Evershed - Heron - Goad 1991: 540-544; Charters - Evershed - Blinkhorn - Quye 1997: 1-7.

<sup>&</sup>lt;sup>5</sup> COPLEY - ROSE - CLAPHAM - EDWARDS - HORTON - EVERSHED 2001: 593-597; COPLEY - ROSE - CLAPHAM - EDWARDS - HOR-TON - EVERSHED 2001: 538-542.

<sup>&</sup>lt;sup>6</sup> Charters - Evershed - Blinkhorn - Denham 1995: 113-27.

a favourable environment. While lipid residues may aid in the identification of these residues, the analysis of inorganic and insoluble components will also be investigated. Our recent studies of fermented beverages, produced in laboratory experiments involving replica vessels<sup>10</sup>, have already provided insights into the types of chemical indicator that may be diagnostic. Based on this the following lines of enquiry are being pursued: (i) characterisation of diagnostic marker compounds characteristic of fermentable substrates, such as lipids released from cuticular waxes or more polar compounds such as the phenolic acids (e.g. hydroxybenzoic acids, hydroxycinnamic acids and their derivatives and flavanoids) which are found in grapes and survive the fermentation process<sup>11</sup>; (ii) higher plant resins believed to have been added to wine (the original 'resinated' wine), as flavour enhancers and preservatives will be targeted<sup>12</sup>; (iii) yeast derived lipids in both visible and absorbed resides will be targeted as these will aid in the detection of fermented beverages; (iv) the identification of inorganic compounds such as tartaric acid salts and oxalates may provide complementary evidence for alcoholic beverages, although these markers have to be used with great caution. Spectroscopic and spectrometric techniques are being developed to identify specific biomarkers for the most likely beverage types. While several of the possible biomarkers for wines and beers are non-specific, the use of a combination of these criteria, in addition to the assessment of vessel forms, will help to identify fermented products and any organic compounds which may have been added to them during their production.

#### 3.1.3 Specialised vessels

This class of vessel, including those constructed of ceramic and stone fabrics, is likely to have contained 'exotic' products such as ointments, perfumes or incense. Although any volatile compounds present in perfumed goods will have evaporated, lipid residue analysis will prove useful for the identification of oil and fat based products<sup>13</sup>, as well as resinous materials, e.g. pistacia<sup>14</sup> and frankincense<sup>15</sup>, which are known to persist at archaeological sites for many millennia. Visible residues and ceramic fabric samples have been collected from several vessels of this type and are being submitted to analysis by GC and GC/MS as described above.

## 3.2 Biomolecular analysis of anthropogenic sediments and sarcophagi contents

The sediments contained within the tomb are quite exceptional since the chamber is rock-cut and no soils would have been present prior its use as a tomb. Since these sediments are entirely anthropogenic in origin they offer truly unique potential as a sink of chemical indicators of human activity. The range of sediment samples are essential for distinguishing, through chemical (and morphological) analyses, between the different functional areas of the tomb, as they will reflect burial or ritual activities. The major contributors to the sediments are likely to be decomposed human and animal tissues, plant remains, embalming agents or treatments, and food offerings. Small fragments of wood observed in some areas suggest wooden artefacts were present, e.g. biers used to carry the dead or superstructures associated with decoration of the tomb. Due to the unusual nature of formation of these sediments, their analysis provides a novel analytical challenge. Approximately 40 sediment samples have been collected to date, these are being analysed for a variety of biomarkers including: (i) adipocere derived fatty acids and sterols, such as cholesterol and coprostanol, indicative of the presence of human tissue<sup>16</sup>; (ii) phenolic markers indicative of the presence of wood or other plant tissues, such as reed or rush<sup>17</sup> (iii) biomarkers for beeswax or other plant and insect waxes and 'exotic' commodities, such as resins, perfumes and ointments, which may have been used to treat the bodies of the dead18; and (iv) evidence for food remains which may have been presented as ceremonial offerings. An hierarchical approach has been adopted, progressing from bulk analyses, such as organic (C, H, N) and

- <sup>10</sup> Chivall 2003.
- <sup>11</sup> Gil-Muñoz Gómez-Plaza Martínez López-Roca 1999: 259-272.
- <sup>12</sup> Murray Boulton Heron 2000: 577-608.
- <sup>13</sup> Dudd Evershed 1998: 1478-1481; Condamin Formenti -Metais - Michel - Blond 1976: 195-201.
- <sup>14</sup> Stern Heron Corr Serpico Bourriau 2003: 457-469.
- <sup>15</sup> Evershed Van Bergen Peakman Leigh Firbank Horton - Edwards - Biddle - Kjolbye Biddle - Rowley Conwy 1997: 667-668; Van Bergen - Peakman - Leigh Firbank - Evershed 1997: 8409-8412.
- <sup>16</sup> Evershed Connolly 1994: 577-583; van Bergen Bland -Horton - Evershed 1997: 1919-1930.
- <sup>17</sup> VAN BERGEN BLAND HORTON EVERSHED 1997: 1919-1930; VAN BERGEN - POOLE - OGILVIE - CAPLE - EVERSHED 2000: 71-79.
- <sup>18</sup> Buckley Evershed 2001: 837-841.

inorganic (inductively coupled plasma-atomic emission spectroscopy and phosphate analysis) elemental analyses. Sediment samples will be analysed for their lipid content largely as described for the pottery samples above<sup>19</sup>. Off-line and online pyrolysis-GC/MS will be used to screen for lignin biomarkers<sup>20</sup>. Quantitative assessments of the various indicator compounds will allow a 'chemical map' to be produced which will help to define the uses of the different areas of the tomb.

## 3.3 Biomolecular analysis of human bones and tissue and animal bones

The bones of several individuals were contained within the sarcophagi and on the tomb floor and the remains of a further individual were discovered on a stone bench in Chamber 4. Animal bones were also found in various areas on the floor of the tomb. Due to the largely mixed nature of the bone assemblage the principal biomolecular information that will be obtained concerns the diets of individuals. Extraction of collagen from these bones will allow  $\delta^{13}$ C and  $\delta^{15}$ N values to be determined<sup>21</sup>. The remains of the individual in Chamber 4 are being analysed using lipid residue analysis, as well as Pv-GC/MS where samples are of a very small size, enabling us to decipher what was placed on the different areas of the stone bench. Degradation experiments will also be performed to further our understanding of the degradative processes occurring to a human body in such a context.

#### 4. Integration of biomolecular information

By integrating the information obtained from analysis of the many pottery and stone vessels and their contents, anthropogenic sediments, human and animal bones, we will be able to build up a picture of how this tomb was used, gaining substantial insights into the activities involved in the burial ritual. Due to the paucity of information currently available, the information we gain from this specific tomb will significantly add to our wider understanding of Eastern Mediterranean Bronze Age commodities, trade, diet, burial practices and ritual beliefs.

#### 5. Results to date

Initially a number of preliminary studies on a relatively small number of samples have been undertaken in order to assess the preservation of organic materials from the context.

#### 5.1 Resin artefacts

Among the many finds in the tomb was a series of artefacts made from a homogeneous amorphous organic material, possibly a type of plant resin. Resins are sticky, water-insoluble metabolic byproducts exuded by plants. They are composed of complex mixtures of mono-, sesqui-, di- and triterpenoids and possess structures based on isoprene (C<sub>5</sub>H<sub>o</sub>) units<sup>22</sup>. Under natural forest conditions, the volatile fractions of most resins evaporate, while the non-volatile dienic functions can polymerise over geological time and become fossilised<sup>23</sup>. Resins have been attractive as materials for use in adhesives, coatings, pigments and incense since antiquity; and have also been used to make jewellery and small sculptures, particularly in the case of fossil resins, such as amber and the various hard copals<sup>24</sup>. The diverse origins, chemical complexity and diagenetic alteration of aged resins require the application of a wide range of organic geochemical techniques for their characterisation. Due to the polymeric nature of these materials and the small (submilligram) samples available, the most suitable technique is Py-GC/MS, the use of which is enhanced by simultaneous thermally assisted hydrolysis and methylation (THM) with tetramethylammonium hydroxide (TMAH)<sup>25</sup>. Initial analyses have focused on four artefacts, two beads (MSH02G-i1448 and MSH02G-i2329), a carved lion's head container (MSH02G-i0759), and a lid for the lion's head (MSH02G-i0766), in order to determine the origin of the material used in their production.

Analyses have revealed that the four samples are composed of the same material, containing a range of mono- and diterpenoid biomarkers and succinic acid (Fig. 3 and structures 1-8), the presence of

- <sup>23</sup> LANGENHEIM 1969: 1157-1169; LAMBERT POINAR 2002: 628-636.
- <sup>24</sup> Mills White 1994: 95-128.
- <sup>25</sup> Anderson Winans 1991: 2901-2908.

<sup>&</sup>lt;sup>19</sup> Bull - Elhmmali - Roberts - Evershed 2003: 149-161.

<sup>&</sup>lt;sup>20</sup> VAN BERGEN - BLAND - HORTON - EVERSHED 1997: 1919-1930; VAN BERGEN - POOLE - OGILVIE - CAPLE - EVERSHED 2000: 71-79.

 <sup>&</sup>lt;sup>21</sup> Richards - Hedges - Molleson - Vogel 1998: 1247-1252;
PRIVAT - O'CONNELL - Richards 2002: 779-790; Ambrose - Buikstra - Krueger 2003: 217-226.

<sup>&</sup>lt;sup>22</sup> Mills - White 1994: 95-128.



Fig. 3. Partial pyrogram and photograph of resin bead MSH02G-i1448 pyrolysed at  $610^{\circ}$ C in the presence of TMAH.

methyl dehydroabietate and related compounds point to a coniferous resin source. The best known materials with the observed chemical and physical properties are ambers and copals. Radiocarbon dating of the artefacts and analysis of a series of reference resins are currently being undertaken. This will establish whether the artefacts were made from fossilised or recent resin, and help to determine their origin.

## 5.2 Py-GC/MS analysis of anthropogenic sediments from the tomb

An important question relating to the nature of the tomb in antiquity is whether large quantities of wood were present, e.g. the presence of wooden superstructures such as funerary beds/platforms and shrines. The presence of small fragments of wooden material, along with darkened areas of sediment on the tomb floor provides a clue to the likely location of wooden artefacts placed in the tomb whilst in use. Although morphologically identifiable wooden remains are scarce in the present state, biomarker compounds should be detectable for the purpose of determining the locations of decayed organic materials. A preliminary investigation has been carried out on two sediment samples from the tomb, one obtained from under a stone bench where there was little evidence of organic input (MSH02G-i0185) and the other from a suspected organic rich region of the

tomb floor where wooden structures may have been present (MSH02G-q1361). When pyrolysed in the presence of TMAH, no organic compounds were detected from the material obtained from under the stone bench, this is believed to be rubble from the cutting of the tomb from the limestone bedrock and therefore indicates that no organic material was present prior to its use as a tomb. Conversely, pyrolysis of sample MSH02Gg1361, revealed several classes of compound (Fig. 4a and structures 9-16) including: fatty acid methyl homologous esters (FAMEs): series of alkenes/alkanes and methoxy benzene derivatives. The FAMEs may derive from either free fatty acids or bound, esterified fatty acids that have been liberated by hydrolysis and subsequently methylated during thermochemolysis with TMAH. The presence of longer chain FAMEs (C20 - C26) are indicative of the presence of higher plant matter, in the sediment, whilst the high abundance of the C<sub>180</sub> FAME could potentially indicate an animal derived input; however, further analysis would be necessary to confirm this. The presence of homologous alkanes/alkenes, are reported to derive from resistant, non-hydrolysable aliphatic macromolecules such as cutan and suberan, which are found in plant tissues such as cuticles and bark<sup>26</sup>.

After cellulose, lignin is the most abundant biopolymer in vascular plants and accounts for approximately 25% of the mass of woody tissues<sup>27</sup> and consists of a polyhydroxyphenolic macromolecular structure, which has not yet been fully determined. As a vascular plant decomposes, lignin becomes a geopolymer that is degraded at a much slower rate than other biopolymers and as a result, is well preserved and often enriched in geochemical systems. It was therefore anticipated that pyrolytically formed lignin marker compounds would be present in the sediment where wood was present in antiquity. Fig. 4 contains several compounds which are known to derive from the guacyl and syringyl lignin subunits (see structures below). Of note is the presence of benzoic acid derivatives, which have been suggested to derive from oxidation of the benzaldehyde equivalent as wood ages, supporting the theory that decayed wood has contributed to the tomb sediment<sup>28</sup>. The

<sup>&</sup>lt;sup>26</sup> Nierop 1998: 1009-1016.

<sup>&</sup>lt;sup>27</sup> Hatcher - Minard 1996: 593-600.

<sup>&</sup>lt;sup>28</sup> Challinor 1995: 93-107; McKinney - Hatcher 1996: 217-228.



Fig. 4. Pyrograms of a) sediment from tomb floor (MSH02G-q1361) and b) wood recovered from inside vessel MSH02G-q1139, pyrolysed at 610  $^{\circ}$ C in the presence of TMAH.

absence of pyrolysis products incorporating aliphatic side chains, which are observed in abundance in modern wood, suggests that the lignin has undergone extensive chemical alteration through time<sup>38</sup>.

In order to support the theory that these lignin marker compounds are derived from wood, a sample of a fragment of material which has been identified as wood (MSH02G-q1139) was pyrolysed in the presence of TMAH (Fig. 4b). The presence of



Fig. 5. Partial chromatogram of the lipid residue from potsherd MSH04G-q0318 from the Palace at Qatna.

longer chain FAMEs (C20-C28) is similar to the distribution observed in Fig. 4a, apart from the much higher abundance of the  $C_{26:0}$  FAME. The relative abundance of the C<sub>18:0</sub> FAME in Fig. 4b compared to that in Fig. 4a suggests that this fatty acid is derived from a non-wood source, possibly human or animal tissue. The identities and distribution of lignin pyrolysis products correlate closely with those observed in the sediment sample, again supporting the presence of degraded wood in the sediment. Of additional interest in Fig. 4b is the presence of several compounds whose mass spectra suggest a terpenoid structure, with the identity of stigmasta-3,5-diene, the dehydration product of the major plant sterol sitosterol, being confirmed. The exact identities of the other terpenoid compounds are as yet undetermined, but may provide a means to identifying the species of tree from which the wood derived.

#### 5.3 Lipid residue analysis of potsherds

A total of 21 potsherds and one surface residue obtained from an area within the Royal Palace at Qatna believed to have been a storeroom were lipid extracted and analysed by HTGC and GC/MS. The majority of lipid extracts comprise mainly free fatty acids, particularly C<sub>16:0</sub> and C<sub>18:0</sub>, which together with the mono, di and triacylglycerols (MAGs, DAGs and TAGs), are characteristic of a degraded animal fat (Fig. 5). The total lipid content of the sherds was variable with concentrations varying from  $<5 \ \mu g \ g^{-1}$  to  $>3000 \ \mu g \ g^{-1}$ . This difference could be due to several factors, such as the specific depositional environment of each sherd, the nature of the commodity and means of processing in the pottery vessel (e.g. storage or cooking), the number of times the vessel was used and the nature of the sherd (i.e. whether a rim or body sherd). Overall, 8 of the 21 vessels (38%) exhibit lipid concentrations considered to be significant. Further analysis using GC-C-IRMS, will provide information on the origin of the animal fat present within the vessels (i.e. porcine, ruminant or dairy fat). The high percentage of vessels suitable for isotope analysis provides evidence that the preservation found at the site may prove to be better than expected for the region.

#### 6. Summary

The analyses so far completed on samples of resin artefacts, sediments, and potsherds from the Royal

Tomb and Palace at Qatna indicate that there is indeed good preservation of organic materials from this context. The major findings to date are: (i) the four suspected resin artefacts were confirmed to be composed of a resin with a coniferous tree source, all were fashioned from the same material; (ii) decayed wood, plant matter and potentially animal derived lipids were identified in a sample of sediment from the tomb floor and therefore contributed to the formation of the anthropogenic sediments; and (iii) lipid residue analysis of a selection of potsherds from the site have shown the level of preservation to be higher than expected for this region. The majority of vessels analysed were found to contain degraded animal fat.

There is great potential for further biomolecular analysis of archaeological finds from the Palace and Royal Tomb at Qatna. Initial analyses have shown a high level of preservation from a diverse

Bibliography

- AMBROSE S.H. BUIKSTRA J. KRUEGER H.W. 2003: Status and gender differences in diet at Mound 72, Cahokia, revealed by isotopic analysis of bone, *Journal of Anthropological Archaeology* 22, 217-226.
- ANDERSON K.B. WINANS, R.A. 1991: Nature and Fate of Natural Resins in the Geosphere.1. Evaluation of Pyrolysis-Gas Chromatography Mass-Spectrometry for the Analysis of Natural Resins and Resinites, *Analytical Chemistry* 63, 2901-2908.
- BECK, C.W. SMART, C.J. OSSENKOP, D.J. 1989: Residues and linings in ancient Mediterranean transport amphoras, ACS Symposium Series 220, 369-380.
- BUCKLEY, S.A. EVERSHED, R.P. 2001: Organic Chemistry of embalming agents in Pharaonic and Graeco-Roman mummies, *Nature* 413, 837-841.
- CHARTERS, S. EVERSHED, R.P. BLINKHORN, P. QUYE, A. 1997: Simulation experiments for determining the use of ancient pottery vessels: the behaviour of epicuticular leaf wax during boiling of a leafy vegetable, JAS 24, 1-7.
- BULL, I.D. ELHMMALI, M.M. ROBERTS, D.J. EVERSHED, R.P. 2003: The application of steroidal biomarkers to track the abandonment of a Roman wastewater course at the Agora (Athens, Greece), *Archaeometry* 45, 149-161.
- CHALLINOR, J.M. 1995: Characterization of Wood by Pyrolysis Derivatisation Gas-Chromatography Mass-Spectrometry, *Journal of Analytical and Applied Pyrolysis* 35, 93-107.
- CHARTERS, S. EVERSHED, R.P. GOAD, L.J. HERON, C. -BLINKHORN, P.W., 1993: Identification of an adhesive used to repair a Roman jar, *Archaeometry* 35, 91-101.

range of organic materials. Ultimately, the findings of biomolecular investigations being undertaken at Bristol will be integrated with the data from the many other specialists involved in the project in order to build up a comprehensive picture of how the tomb was used.

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- CHARTERS, S. EVERSHED, R.P. BLINKHORN, P.W. DENHAM, V. 1995: Evidence for the mixing of fats and waxes in archaeological ceramics, *Archaeometry* 37, 113-127.
- CHIVALL, D. 2003: Brewing in Antiquity: An Investigation into the Application of Organic Residue Analysis for the detection of Fermented Beverages in Archaeological Pottery. unpublished MSci Thesis, University of Bristol.
- COPLEY, M.S. ROSE, P.J. CLAPHAM, A. EDWARDS, D.N. -HORTON, M.C. - EVERSHED, P. 2001a: Detection of palm, fruit lipids in archaeological pottery from Qasr Ibrim, Egyptian Nubia, *Proceedings of the Royal Society London Biology* 268, 593-597.
- COPLEY, M.S. ROSE, P.J. CLAPHAM, A. EDWARDS, D.N. -HORTON, M.C. - EVERSHED, R.P. 2001b: Processing palm fruit in the Nile Valley-biomolecular evidence from Qasr Ibrim, *Antiquity* 75, 538-542.
- COPLEY, M.S. BERSTAN, R. DUDD, S.N. DOCHERTY, G. -MUKHERJEE, A.J. - STRAKER, V. - PAYNE, S. - EVERSHED, R.P. 2003: Direct Chemical evidence for widespread dairying in prehistoric Britain, *Proceedings of the National Academy of Sciences of the United States of America* 100, 1524-1529.
- CONDAMIN, J. FORMENTI, F. METAIS, M.O. MICHEL, M. -BLOND, P. 1976: The application of gas chromatography to the tracing of oil in ancient amphorae, *Archaeometry* 18, 195-201.
- DUDD, S.N. EVERSHED, R.P. 1998: Direct demonstration of milk as an element of archaeological economies, *Science* 282, 1478-1481.
- EVERSHED, R.P. HERON, C. GOAD, L.J. 1990: Analysis of organic residues of archaeological origin by high tem-

perature gas chromatography and gas chromatography-mass spectrometry, *Analyst* 115, 1339-1342.

- EVERSHED, R.P. HERON, C. CHARTERS, S. GOAD, L.J. 1992: The survival of food residues: New methods of analysis, interpretation and application, *Proceedings of the British Academy* 77, 187-208.
- EVERSHED, R.P. VAN BERGEN, P.F. PEAKMAN, T.M. LEIGH-FIRBANK, E.C. - HORTON, M.C. - EDWARDS, D. - BIDDLE, M. - KJOLBYEBIDDLE, B. - ROWLEY CONWY, P.A. 1997: Archaeological frankincense, *Nature* 390, 667-668.
- EVERSHED, R.P. DUDD, S.N. COPLEY, M.S. BERSTAN, R. -STOTT, A.W. - MOTTRAM, H. - BUCKLEY, S. - CROSSMAN, Z.M. 2002: Chemistry of archaeological animal fats, Accounts of Chemical Research 35, 660-668.
- EVERSHED, R.P. 1992: Chemical-composition of a bog body adipocere, *Archaeometry* 34, 253-265.
- EVERSHED, R.P. CONNOLLY, R.C. 1994: Post mortem Transformations of sterols in bog body-tissues, JAS 21, 577-583.
- GIL-MUÑOZ, R. GÓMEZ-PLAZA, E. MARTÍNEZ, A. LÓPEZ-ROCA, J.M. 1999: Evolution of phenolic compounds during wine fermentation and post-fermentation: Influence of grape temperature, *Journal of Food Composition and Analysis* 12, 259-272.
- HATCHER, P.G. MINARD, R.D. 1996: Comparison of dehydrogenase polymer (DHP) lignin with native lignin from gymnosperm wood by thermochemolysis using tetramethylammonium hydroxide (TMAH), Organic Geochemistry 24, 593-600.
- LAMBERT, J.B. POINAR JR., G.O. 2002: Amber: the organic gemstone, Accounts of Chemical Research 35, 628-636.
- LANGENHEIM, J.H. 1969: Amber a Botanical Inquiry, Science, 163, 1157-1169.
- McGovern, P.E. Glusker, D.L. Moreau, R.A. Nuñez, A. - Beck, C.W. - Simpson, E. - Butrym, E.D. - Exner, L.J. -Stout, E.C. 1999: A funerary feast fit for King Midas, *Nature* 402, 863-864.
- MCKINNEY, D.E. HATCHER, P.G. 1996: Characterization of peatified and coalified wood by tetramethylammonium hydroxide (TMAH) thermochemolysis, *International Journal of Coal Geology* 32, 217-228.

MILLS, J.S. - WHITE, R. 1994: Natural resins and lacquers In

The Organic Chemistry of Museum Objects Butterworth-Heinemann, Oxford, 95-128.

- MOTTRAM, H.R. DUDD, S.N. LAWRENCE, G.J. STOTT, A.W. - EVERSHED R.P. 1999: New chromatographic, mass spectrometric and stable isotope approaches to the classification of degraded animal fats preserved in archaeological pottery, *Journal of Chromatography*, 833, 209-221.
- MURRAY, M.A. BOULTON, N. HERON, C. 2000: Viticulture and wine production, in: P.T. Nicholson, I. Shaw (eds), *Ancient Egyptian Materials and Technology*, Cambridge University Press, Cambridge, 577-608.
- NIEROP, K.G.J. 1998: Origin of aliphatic compounds in a forest soil, Organic Geochemistry 29, 1009-1016.
- PRIVAT K.L. O'CONNELL T.C. RICHARDS M.P. 2002: Stable isotope analysis of human and faunal remains from the Anglo-Saxon cemetery at Berinsfield, Oxfordshire: Dietary and social implications, *JAS* 29: 779-790.
- RICHARDS, M.P. HEDGES, R.E.M. MOLLESON, T.I. VOGEL, J.C. 1998: Stable Isotope Analysis Reveals Variations in Human Diet at the Poundbury Camp Cemetery Site, JAS 25, 1247-1252.
- STERN, B. HERON, C. CORR, L. SERPICO, L. BOURRIAU, J. 2003: Compositional variations in aged and heated pistacia resin found in late Bronze Age Canaanite amphorae and bowls from Amarna, Egypt, Archaeometry 45, 457-469.
- VAN BERGEN, P.F. BLAND, H.A. HORTON, M.C. EVERSHED, R.P. 1997: Chemical and morphological changes in ancient seeds and fruits during preservation by desiccation, *Geochimica et Cosmochimica Acta* 61, 1919-1930.
- VAN BERGEN, P.F. PEAKMAN, T.M. LEIGHFIRBANK, E.C. EVER-SHED, R.P. 1997: Chemical evidence for archaeological frankincense: Boswellic acids and their derivatives in solvent soluble and insoluble fractions of resin-like materials, *Tetrahendron Letters* 38, 8409-8412.
- VAN BERGEN, P.F. POOLE, I. OGILVIE, T.M.A. CAPLE, C. -EVERSHED, R.P. 2000: Evidence for demthylation of syringyl moieties in archaeological wood using pyrolysis/gas chromatography/mass spectrometry, *Rapid Communications in Mass Spectrometry* 14, 71-79.