Identification of archaeological ivories using FT-Raman spectroscopy

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Abstract

FT-Raman spectroscopy has been used successfully for the non-destructive identification of modern ivories and is evaluated here for the identification of osseous materials from archaeological sites. Results on archaeological ivories are reported and the problems faced in matching FT-Raman spectra to standards for the validation of these materials are highlighted. Archaeological specimens of different dates, provenance and taphonomic history, including both conserved and unconserved items, have been analysed.
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1. Introduction

The analytical characterisation of biomaterials and their degradation products is important for a wide range of specimens from both archaeological excavations and forensic crime scene environments. The deposition of materials in burial environments starts a complex chain of events which results in loss or change of material through degradation and the acquisition of components from the surroundings; the recognition of the factors which affect specimen integrity and which may provide clues as to changes in molecular composition arising from the burial environment is an essential part of the subsequent analytical portfolio.

Physical and biological attack on biomaterials often results in problems of specimen deterioration and fragility, with consequent changes in colour and the deposition of debris being observed. These effects, which are often particularly useful in the characterisation of geological soil specimens in the neighbourhood of an excavation, can hinder the application of optical spectrometric techniques for the evaluation of biomaterials associated with the scenario. This can be especially relevant, for example, in the infrared examination of fabrics and artefacts from waterlogged burial sites, because the absorption by water of infrared radiation is significant; often the desiccation of these specimens is not particularly achievable since specimen rupture or disintegration may result. Also, the loss of infrared radiation transmission at wavenumbers lower than $1000 \, cm^{-1}$ in such cases, especially for cellulose materials with hydroxyl groups, means that access to an important region of the electromagnetic spectrum for the characterisation of mineral debris is denied. Many of these problems can be avoided using Raman spectroscopy [1].

The identification of the raw materials of osseous finds, such as bone, antler and ivory, from archaeological sites is a specialist field requiring a knowledge of the chemistry, morphology, growth, macro- and microstructures, and decay pathways of these materials. Where traces of the gross morphology survive, it may be possible to identify the part of the skeleton which has been used and possibly even the species from which the material was derived. However, where fabrication processes, wear or decay have removed or obscured the morphology it may be possible to say little more than that an object has been "cut from the shaft of the long bone of a large mammal" or perhaps only that an object is "antler rather than post-cranial bone". In these cases the size and shape will play a role in the identification process, but more importantly, the macro- and microstructure of the fragment and the way in which it has decayed may give some vital clues to its origins [2].

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Fig. 1. Longitudinal section of walrus tusk.

The identification of objects made from dentine, such as elephant ivory, can be equally difficult where the outer cementum and enamel layers have been lost [3]. The standard text on the identification of ivories [4] largely deals with the description of complete modern teeth and thin sections cut from them, so its use with archaeological artefacts is strictly limited. Fortunately, the fine structure of elephant ivory and the juxtaposition of primary and secondary dentine in walrus ivory, for instance, produce very distinctive features which can be used by experts to differentiate them. Under certain conditions of burial these features can be well preserved or even enhanced by staining or etching. Although Espinoza and Mann [5] have devised a method for separating modern elephant from mammoth ivory by measuring the outer Schreger angles, they are unable to distinguish between Indian and African elephant ivory using this method. Other archaeological ivories, such as hippopotamus and pig lower canine, cannot reliably be distinguished on their fine structure alone but sometimes overall size and shape or the way that an object has physically changed, cracked or exfoliated can provide the identification required.

Ivory is the generic term for exoskeletal tooth (or "tusk") formations associated with a limited group of terrestrial and marine mammalian species which includes the African and Asian elephants, sperm whale, narwhal, hippopotamus, walrus, wart hog, pig and mammoth. In common with teeth from other animal species, ivory consists of osteons comprising a matrix of hydroxyapatite with proteinaceous collagen. The composition of the inorganic and organic components of ivory varies with the enamel, dentine or pulp regions of the tusk; this is illustrated in Fig. 1 where the enamel, dentine and pulpal cavity regions are clearly seen for a walrus tusk.

Identification of large ivory pieces, especially in sections, is generally fairly straightforward when there are good surfaces or complete tusks available for examination and the characteristic pattern of tusk construction is usually definitive for the attribution of ivory to the mammalian species; the observation of Schreger line angles [5] on polished sections is a normal forensic protocol for the discrimination between elephant ivories and mammoth ivory. However, the recognition of genuine ivory and its assignment to an individual species is rendered extremely difficult for small fragments or for highly carved artefacts.

In many cases, however, it is not possible to say any more than that an object is clearly dentine rather than bone, even after extensive microscopic examination. Where sampling is permissible, thin sectioning or the use of scanning electron microscopy, particularly back-scattered electron imaging, could be used to gain a positive identification where non-destructive light microscopy fails. Scanning electron microscopy has proven useful in the study of mineral-preserved organic remains from the corrosion of metal objects, but, commonly, destructive sampling is not an option. DNA and many chemical analytical techniques which might aid identification also involve destructive sampling.

The identification of such ivories can have a direct effect on the interpretation of the archaeological context. The status of a burial and its cultural origins, the economic significance of a settlement and the trade routes being exploited have been inferred by the presence or absence of these materials. It is of primary importance then that the materials are correctly identified, that the techniques and criteria applied in their identification are reliable and clearly stated in publications in support of their identifications.

The application of Fourier-transform Raman spectroscopy (FTRS) for the molecular characterisation of biomaterials has demonstrated the versatility and capability for the non-destructive analysis of sensitive specimens, including the skin tissue of mummified remains [6,7], hair [8], teeth [9,10] and bone [11]. The use of long wavelength excitation or FTRS for the identification of modern specimens of animal ivories including those of African and Asian elephants, mammoth, narwhal, sperm whale, hippopotamus, walrus and wart hog has been proposed [12,13]. The results were encouraging and provided the basis of material identification by examination of small band relative intensity changes which occur in the $300–1800\,cm^{-1}$ wavenumber region of the vibrational spectrum; in this work, the application of chemometrics and cluster analysis [14,15] has been found to be of critical importance for mammalian source ivory identification.

A particular advantage of FTRS over the complementary infrared technique is the ease of sample presentation to the spectrometer for analysis; no mechanical or chemical pre-treatment is required and flat, polished surfaces are unnecessary. Coupled with the low sensitivity of response in the Raman spectra to water and –OH groups, this means that FTRS has great potential for application to archaeological artefacts, particularly those which are fragile and for which removal of even small samples would be denied on the grounds of disfigurement. This approach has special merit for the examination of small samples or shards of ivory and bone from waterlogged sites, for which even partial desiccation would not be acceptable to archaeologists or conservators because of disintegration of the specimen.

In this paper we present the FTRS analysis of several specimens of osseous materials from archaeological sites; the protocol and criteria for material identification proposed on the basis of contemporary specimens of similar material have been applied to identify objects which cannot be distinguished by microscopy alone. Test samples of archaeological specimens of

Early Bronze Age, Roman, Saxon and 18th century periods of established site provenance and taphonomic history, including conserved and unconserved items, have been considered for the present work.

2. Samples

2.1. Pig tusk from Tell es-Sa'idiyeh, Jordan

This unworked fragment of a lower pig canine (24 mm × 10 mm) is by far the earliest object in the test group and derives from a floor deposit within the Early Bronze Age housing complex of the lower Tell at Tell es-Sa'idiyeh in the central Jordan valley [16]. The site is situated on fertile alluvial soils adjacent to a wadi from which water could have been drawn for the cereal cultivation and the watering of sheep, goats, cattle and pigs, which made up a proportion of the economic basis of the settlement. Today, the region experiences winter rainfall but in the hot dry summers irrigation for crops and pastures is essential. The size and curvature of the tooth, the transverse undulations of the surface, the triangular cross-section and the macro-structure of the dentine revealed by the broken surfaces, together confirm the identification of the specimen as pig tooth. Apart from washing and drying, the pig tusk has received no post-conservation treatment. It is very white and brittle and has a tendency to crack at the boundaries between incremental growth layers within the dentine, which can be seen microscopically as nested triangles in the cross-section.

2.2. Ivory die from Frocester Court Roman Villa, Gloucestershire

Frocester Court was a 4th century villa [17] built on lime-rich gravels; not only were the osseous materials from this site well preserved but objects in copper alloy and even those in iron were found in remarkable condition. The ivory die comes from a mid-to-late 4th century occupation deposit in Room 11, which has been identified as an office. The die was found amongst the back-fill of a strong box sunken into the floor of this room. The die is an approximately 15 mm cube of a non-vascular, osseous material. The surfaces of the die have only been roughly finished and the surviving saw marks make observation and micro-photography of the structure of the material difficult. However, the material has cracked, producing layers curved in one plane, reflecting a cone within cone structure. Following excavation, the die separated into a number of curved segments which were stuck together with an unknown adhesive, probably the polyvinyl acetate-based "Durafix".

Using low power microscopy, fine layers of mineralised material can be seen parallel to the cracks. Such structures are common to ivories from many sources, and there are no other distinguishing features visible. The die was originally examined by Dr Juliet Cutton-Brock of the British Museum of Natural History, and it was published as being "ivory of uncertain source but probably hippopotamus" [17]. In this object, where fine layering is clearly visible, the absence of Schreger lines can confidently be taken to show that this is not elephant ivory. Unfortunately

from the structures visible it is not possible to positively identify this as being hippopotamus ivory.

2.3. Boar Tusk Buckle from 7th century grave at Castledyke, Humberside. Grave 91, site reference CS90 SK1334, recorded find 1337

The human burials at Castledyke, excavated by the Humberside Archaeology Unit, were cut into a well-drained calcareous soil over chalk rubble and a fractured chalk surface. Most of the skeletons were complete but fragmentation of the ribs, longbone and skulls was frequent, while only 53% of adults had retained a vertebral column complete enough for analysis. The teeth were generally in good condition, although the upper and lower jaw bones had sometimes disintegrated. The grave from which the buckle derived had possibly been disturbed. It was filled with a soft sandy loam, and the skeleton was incomplete and poorly preserved. There were only two other finds, one each in iron and copper, both with associated mineral-preserved organic remains.

The buckle is an oval frame type measuring 20.7 mm × 28.7 mm and 6.8 mm thick. It has copper alloy folded plates and a copper alloy pin. The ivory frame has an uneven brown colouration, probably due to groundwater staining. There is a whiter, rectangular strip of enamel below the pin tip on the outer edge of the frame and, on the inner surface of the same side, there is a line of minute black dots, also running parallel to the long axis of the object. The frame is split longitudinally in several places; the underside is polished and well preserved, while the upper surface is badly degraded and friable. In the end sections the lamellae formed by the cracking are arranged in concentric triangles around an angled crack. These features can be found in dentine from the lower canines of both hippopotamus and pig. Although the enamel had been worked it was possible to observe faint, transverse undulations in the surface which suggested that this a pig source rather than hippopotamus. A study of the organisation of the dentinal tubules in specimens of both pig and hippopotamus was undertaken. These structures were visible in places on the surface of the buckle and matched those of pig. From the taper indicated by the lamination, the relative position of the line of black dots (the commissure or heartline), and the position of the surviving enamel it was concluded that this object was cut from a lower left canine.

During conservation, the buckle was cleaned using industrial methylated spirits and consolidated with Primal WS 24, a colloidal dispersion of an acrylic resin in water. The adhesive HMG, a solution of cellulose nitrate, was also used to reattach fragments of both the copper alloy fittings and the osseous material.

The origin of ivory found in pagan Anglo-Saxon graves has in recent years been the object of much discussion. During the Roman occupation of Britain, both African and Asian elephant ivory was traded throughout the Empire. In the post-Roman period, little ivory reached Northern Europe and this has given rise to the conjecture that finds from this period can be attributed to mammoth or walrus ivory [18]. A problem associated with ivory in Anglo-Saxon grave sites is the burning of the material

– it has been argued that while this certainly results in fragmentation and distortion of specimens, it can also assist in the definition of the surface morphological features such as transverse herringbone arc patterns which are also characteristic of elephant or mammoth ivories.

2.4. Comb-making debris from two post-mediaeval sites in York

Deposits from two excavations in the Coffee Yard (1987.1, context 2006) and Forsselius Garage (1991.11, context 2008), York, have produced evidence of comb-making in the form of small, roughly rectangular, worked plaques of ivory. These are all longitudinal, tangential plates of ivory with their top and bottom edges providing transverse sections between 43 and 30 mm in height and 1.5–2 mm in thickness. They seem to have been discarded at various stages in the comb-making process; it could be that from the quality of the workmanship these pieces were cut from scrap ivory which was unsuitable for the production of saleable items. The material from both sites is well-preserved although since excavation some further longitudinal cracking has been observed. The Coffee Yard material was from a levelling deposit of loose mortar with occasional fragments of tile, brick and plaster. The Forsselius Garage pieces were from a rubbish-filled feature mixed with grey-brown silt and sand at the base of which were pebbles covered by sand and cinders. The deposits immediately surrounding this feature were of clay, sand and silt with quantities of brick, mortar, tile, pebble, shell and bone.

Five objects were selected for Raman spectroscopic analysis. One piece, small find number 44 (labelled E) was selected from the Coffee Yard finds. This had previously been identified as hippotamus ivory (O'Connor, unpublished); when examined using reflected light microscopy, this plaque was very finely lamellar and had been cut obliquely across the commissure of the tusk and a seam of dark stained lines appeared running from one face to the other. Although these features are common to both pig and hippotamus canines, the piece under study here is too large to have been cut from the former. The other specimens were from the Forsselius Garage, small find number 38; seven pieces fit together to form the remains of four separate objects which had also been identified by O'Connor using reflected light microscopy—three of these (labelled A, B and C) showed the Schreger line patterns and one or more other feature(s) characteristic of elephant ivory but the fourth (labelled D) did not. This latter piece was clearly lamellar and had been cut parallel to a fairly diffuse commissure seen as dark lines running across one face of the plaque. This was then tentatively identified as hippotamus ivory on the same basis as the plaque from the Coffee Yard. It should be pointed out that the visual observations and expert opinions on the sourcing of these specimens were withheld until the results of the Raman spectroscopic analyses were made public.

3. Experimental

Raman spectra were obtained using a Bruker IFS 66 instrument with FRA 106 Raman module attachment. Excitation was effected using 1064 nm radiation from an Nd^{3+}/YAG laser with a sample spot diameter (footprint) of 100 μm. Spectral data over the wavenumber region 200–3500 cm^{-1} were obtained using 4 cm^{-1} spectral resolution and typically 2000 scans accumulation. Band wavenumbers are accurate to better than $\pm 1\,cm^{-1}$ and spectra were corrected for white light background. A typical example of a fluorescence-free Raman spectrum of an archaeological specimen of ivory is shown in Fig. 2.

Sample spectra were obtained at several spots on each specimen; normally, at least five spectral sampling positions were selected and in some cases, for example the elephant tusk ivory standards, up to 32 different sampling positions were analysed for seven different specimens of the same mammalian species.

The spectra of artefacts and standards are presented in the form of a stack-plot over pre-selected wavenumber ranges for ease of visual comparison. It should be noted that some of the spectra look very similar superficially and this is perhaps to be expected since generically all the specimens being studied are
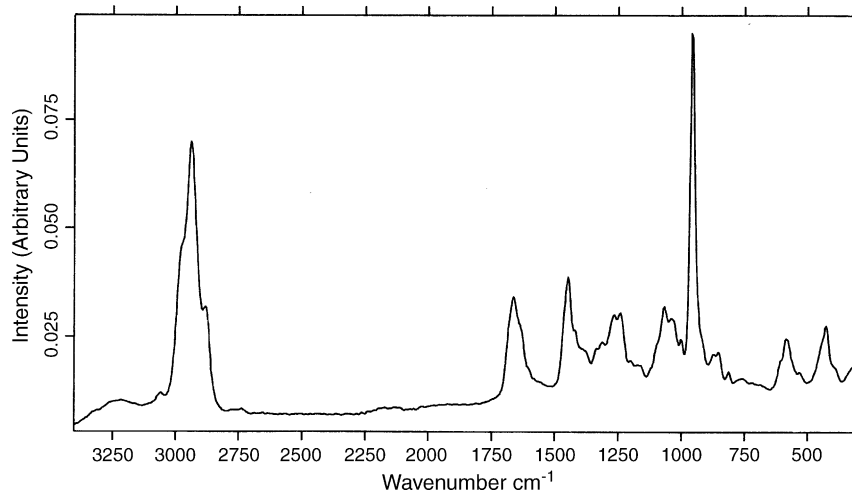

Fig. 2. Example of a fluorescence-free Raman spectrum of archaeological ivory; fragment 4 of post-mediaeval ivory comb from excavations at York.
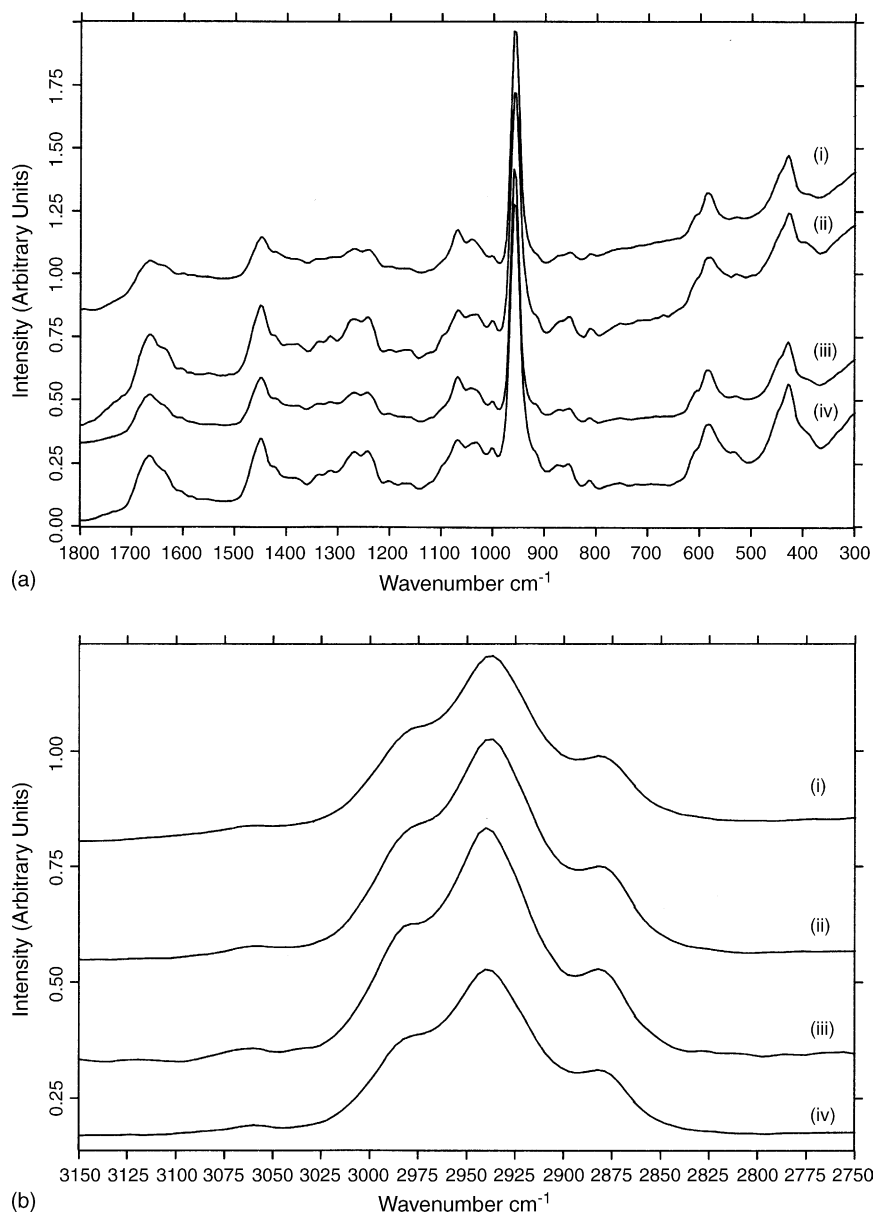
Fig. 3. (a) Comparison of the FT-Raman spectra of the Roman die (i) with specimens of African elephant (ii), sperm whale (iii) and hippopotamus ivory (iv) over the wavenumber region 300–1800 cm^{-1}; 1064 nm excitation. (b) Specimens of ivory as defined in (a) over the wavenumber region 2750–3150 cm^{-1}.

"ivory". However, it must be stressed that the small spectral differences that are highlighted and discussed below are nevertheless reproducible and form the basis of the spectroscopic differentiation.

4. Results and discussion

4.1. Archaeological ivory samples

The Raman spectra of the archaeological ivory samples are shown in a series of stack-plots as follows: Roman die, along with modern specimens of African elephant, sperm whale and hippopotamus ivory (Fig. 3); Bronze age pig tusk, along with contemporary pig tusk, mammoth and wart hog tusk ivories (Fig. 4); Saxon boar tusk buckle, along with modern

wart hog and contemporary pig tusks (Fig. 5); post-mediaeval comb fragments, along with modern hippopotamus and elephant ivories (Fig. 6). To reflect small compositional differences in these specimens in the differentiation of mammalian species ivory it is vital that the spectral quality is high. The spectral stack-plots have been divided into two wavenumber regions, namely 300–1800 and 2750–3150 cm^{-1}, which cover the skeletal stretching and bending regions and the CH stretching regions, respectively.

The Raman spectra of mammalian ivories have been characterised in previous publications from our laboratories [1,14] and the vibrational features identified using a collagen sample for the representation of the organic component of the ivory matrix. In Fig. 3a (ii), for example, the Raman spectrum of African elephant ivory consists of a strong vibrational band at 960 cm^{-1} character-
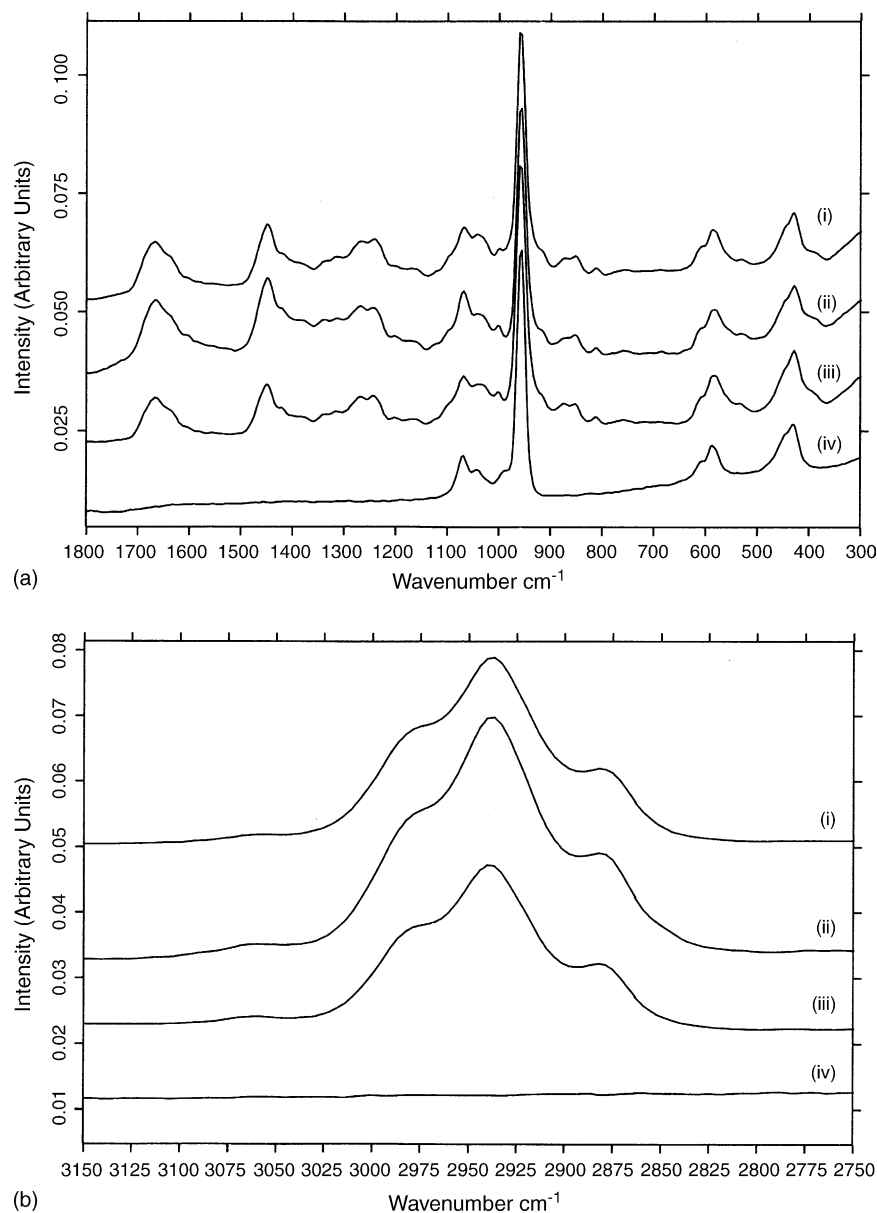
Fig. 4. (a) Comparison of the FT-Raman spectra of the Bronze Age pig tusk (iv) with specimens of mammoth (i), wart hog (ii) and modern pig ivory (iii) over the wavenumber region 300–1800 cm^{-1}. (b) Specimens of ivory as defined in (a) over the wavenumber region 2750–3150 cm^{-1}.

istic of the PO symmetric stretching mode of the hydroxyapatite inorganic matrix component. The weaker multiplet bands near 440 and 590 cm^{-1} can be assigned to PO deformation modes of the hydroxyapatite. In a previous study [19] we have shown that a weak shoulder at ~400 cm^{-1} is a characteristic of mammalian ivory, which is absent from the spectra of bone and false ivories. The quartet of bands between 1000 and 1100 cm^{-1} is a complex feature which contains bands arising from both organic and inorganic components of ivory; the strongest band at 1070 cm^{-1} is of inorganic origin and has been assigned to a carbonated hydroxyapatite [9,10], whereas that at ~1040 cm^{-1} is an asymmetric PO stretching mode of the phosphatic matrix. The weak band at 1003 cm^{-1} in contrast is assignable to the collagen component of the ivory, and probably arises from aromatic ring stretching modes in aminoacids such as phenylalanine and tyrosine.

Other features in the spectra between 1200 and 1700 cm^{-1} are assignable exclusively to collagen, being the amide I CONH stretching modes near 1660 cm^{-1}, the NH deformation modes near 1450 cm^{-1} and the amide III CH$_2$ bending modes near 1260 cm^{-1}. Fig. 3b (ii) shows the Raman spectrum of elephant ivory over the wavenumber range 2750–3150 cm^{-1} and consists of predominantly three CH stretching bands from CH$_2$ and CH$_3$ groups with a weaker feature near 3060 cm^{-1} characteristic of aromatic ring C=CH unsaturation.

The four ivories studied in Fig. 3 have very similar spectra in the 2750–3150 cm^{-1} region which means that this wavenumber region is only of minor relevance for adoption in the spectroscopic differentiation of specimen mammalian species; it is significant, however, that the spectra in this region show no evidence of either a thermal background arising from sam-
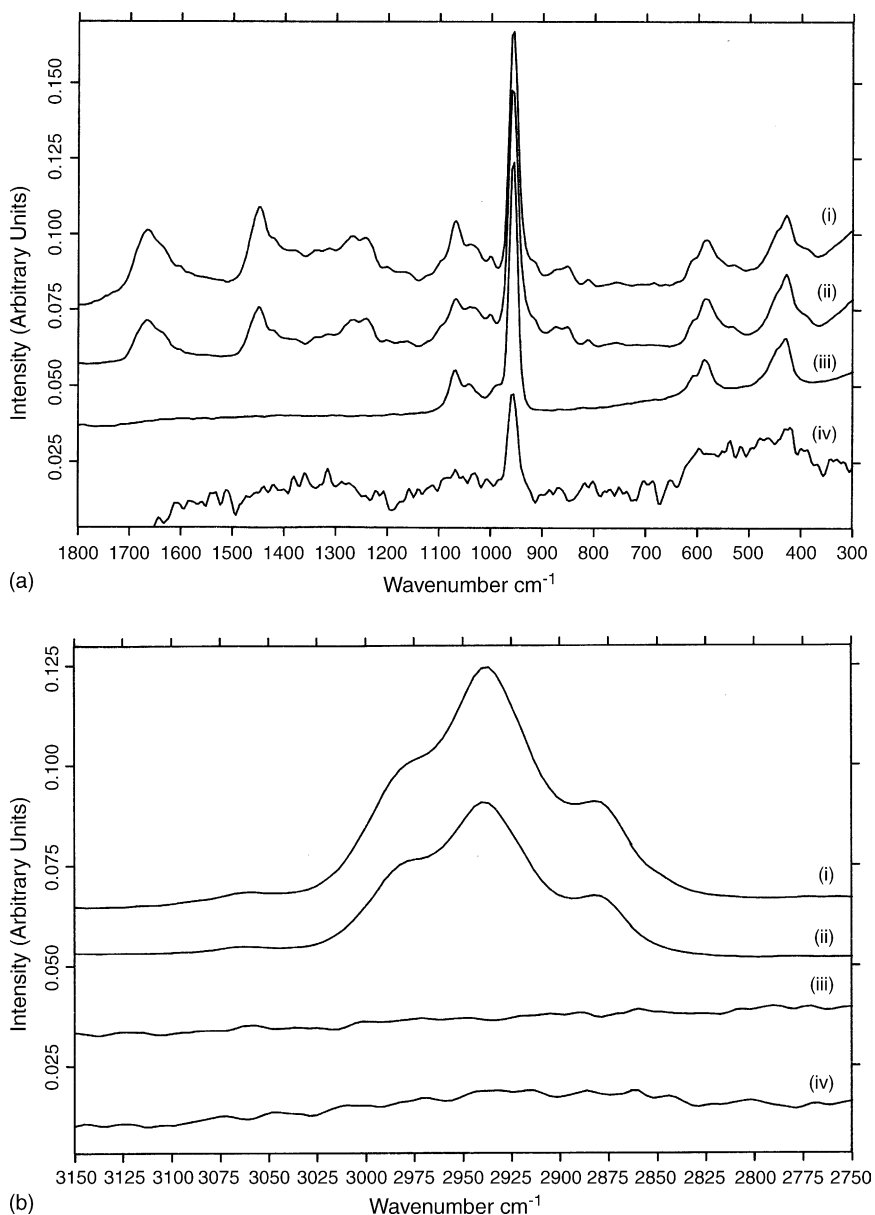
Fig. 5. (a) Comparison of the FT-Raman spectra of the Saxon buckle (iv) with specimens of modern wart hog (i), modern pig (ii) and Bronze Age pig tusk ivory (iii) over the wavenumber region 300–1800 cm^{-1}. (b) Specimens of ivory as defined in (a) over the wavenumber region 2750–3150 cm^{-1}.

ple degradation under 1064 nm laser radiation or a fluorescence emission emanating from the uptake of materials from the burial environment or from treatment in storage. A similar situation pertains for the other archaeological and museum samples reported here. We have found that this is not always the case and that some archaeological specimens do exhibit a fluorescence emission which can be troublesome as it results in a deterioration of the spectral quality of the Raman spectra and in some cases can even mask the Raman spectrum completely.

A visual comparison of the Roman die with specimens of Africa elephant, sperm whale and hippopotamus ivory in Fig. 3a indicates that it is not possible to unambiguously match the archaeological ivory specimen with the modern standards. In previous work [19] protocols for the identification of mam-

malian ivory from their Raman spectra have been proposed based on the patterns of relative intensities on the wavenumber range 300–1800 cm^{-1}, especially for the complex feature between 1000 and 1100 cm^{-1} and the asymmetry of the band profile of the amide I mode near 1660 cm^{-1}. Adoption of the protocols has been instrumental in the identification of modern ivory species, where confirmation of the onset of specimen degradation is provided by the weakness in relative intensity of the low wavenumber bands at 400 and 540 cm^{-1} and by the relative intensities of the CH$_2$ band near 1260 cm^{-1} and NH$_2$ band near 1440 cm^{-1}. These are shown clearly in Fig. 3b, from which it is seen that the spectra can have little visual diagnostic differentiation; the adoption of chemometric techniques has, however, been successfully demonstrated for this application.
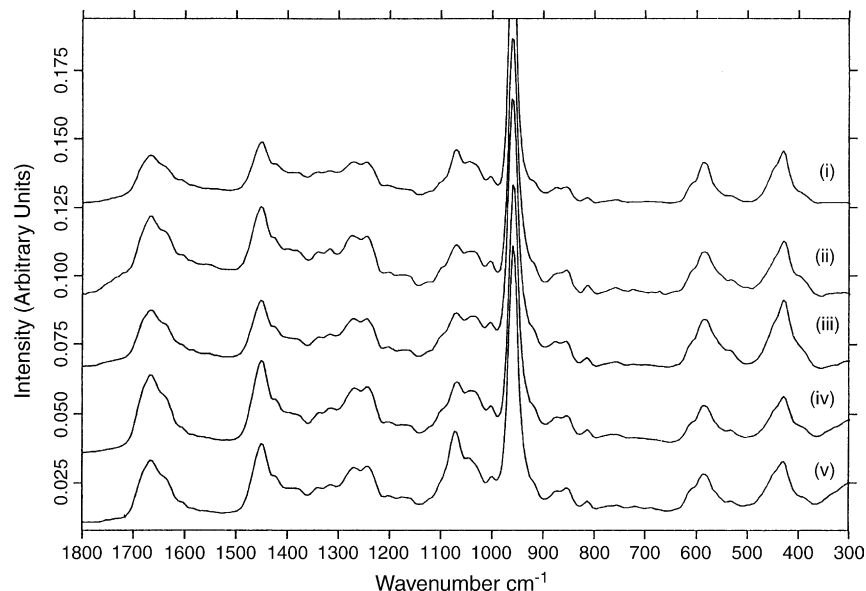
Fig. 6. Comparison of the FT-Raman spectra of the post-mediaeval comb fragments D (iv) and E (v) with sperm whale (i), African elephant (ii) and hippopotamus ivory (iii) over the wavenumber region 300–1800 cm^{-1}.

4.2. Archaeological pig tusk

In Fig. 4a and b are shown the Raman spectra over the wavenumber regions 300–1800 and 2750–3150 cm^{-1}, respectively, for the archaeological material believed to be pig tusk from Tell es-Sa'idiyeh, Jordan, and contemporary specimens of mammoth, wart hog and pig ivory tusk for comparison. Clearly, the Jordanian archaeological sample spectrum is very different from the other mammalian ivories; all spectral components ascribed to collagen, for example the amide I band at 1660 cm^{-1}, are missing and only the hydroxyapatite bands remain. This situation can be ascribed to extensive degradation of the specimen under the desert burial conditions from which the tusk was recovered. Although the Jordanian sample dates from the Bronze Age, ca. 4000 years BP, the degradation indicated from the Raman spectrum cannot merely be a function of time alone since the Roman die, dating from ca. 2000 years BP, shows little evidence of this. The mammoth ivory spectrum shown in Fig. 4(i), which dates from about 10,000 years BP when the animals became extinct, shows no evidence of significant degradation of the organic collagen component; it seems likely therefore that there are several different environmental degradative effects operating on buried materials in that the mammoth ivory has been preserved from decay in permafrost whereas the Jordanian ivory sample has been subjected to a hot desert, corrosive climatic environment which was not conducive to survival of the organic molecules in the matrix and this is confirmed by the sample's brittleness and friability unlike the mammoth ivory which is still capable of being carved and worked.

Fig. 5a and b shows stack-plots over the same wavenumber regions of the Tell es-Sa'idiyeh pig tusk and contemporary wart hog and pig ivories along with the 7th century Saxon buckle. The FTRS of the buckle is of mediocre quality and only the 960 cm^{-1} band due to hydroxyapatite is apparent, with very weak phosphate deformations occurring near 450 and 600 cm^{-1}.

Again, there is supporting archaeological evidence for poor environmental burial conditions which could be responsible for degradation of this fragile specimen and the associated skeletal remains were found to be in a severely decomposed state. Unlike the Raman spectra of early mediaeval human teeth from well-preserved skeletal remains which have been recorded in our laboratories [9] the Raman spectrum of the Saxon buckle does not contain sufficient spectral data to enable an unambiguous identification to be made.

4.3. Mediaeval comb fragments

In Fig. 6 the Raman spectra of the mediaeval comb fragments from the York excavations are presented and compared with the Raman spectra from modern African elephant and hippopotamus ivories and a sperm whale tooth; here, the results are of excellent quality and facilitate the identification of the mammalian ivories concerned. The five fragments presented for analysis may be classified into two groups on the basis of their Raman spectra:

- Fragments A, B and C, represented by spectrum (iv) in Fig. 6, have Raman spectra which are clearly assignable to hippopotamus ivory. This was in agreement with the expert identification made from studies of their macroscopic and microscopic structures and which was revealed after the spectral identification had been made.
- Fragments D and E, represented by spectrum (v) in Fig. 6, have Raman spectra which are assignable to sperm whale ivory; however, the macroscopic and microscopic analysis of these fragments favour an assignment to an African elephant.

The ability to identify two different mammalian sources namely hippopotamus and sperm whale for ivory fragments from the same archaeological burial site represents considerable suc-

cess for non-destructive analytical spectroscopy which will be clearly applicable to other similar situations.

5. Conclusions

This paper addresses the application of non-destructive Raman spectroscopy for the evaluation of excavated archaeological ivories; the specimens were fragmented and could not be prepared for analysis using chemical or mechanical techniques. Comparison of the ancient ivories with contemporary specimens has been affected and it can be concluded that the degradation processes which affect the collagenic component in archaeological specimens results in significant difficulties in some cases for the unambiguous differentiation between mammalian species. The various burial environments play a key role in the survival capabilities of the organic moieties in the ivories and the length of time spent in the depositional environment is not necessarily a factor for the resulting spectral quality. Despite this setback, it has still been possible to effect a partial discrimination between marine and terrestrial ivories which provides some information for specimen identification. For example, in some similar unpublished work [20] carried out in our laboratories some 15 fragments from a 1st century Romano-British burial excavation were believed to be ivory; Raman spectroscopy demonstrated that 13 of the specimens were ivory—probably African elephant—whereas two specimens were not ivory at all but marble chips stained with iron deposits from the depositional environment. In future studies we intend to explore a wider range of archaeological ivories, and also other osseous and keratinous hard tissues such as bone, antler and horn, and to examine further the effects of diagenesis on these important artefacts which have found application for utility and decorative items historically in many cultures.

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