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The preservation of archaeological brain remains in a human skeleton

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The identification of biomass within the cranial cavity of a waterlogged human skeleton inside a fish-tailed wooden coffin from a nineteenth century burial has been confirmed as brain tissue. A comparison is made between the Raman spectra obtained in the current study with those from an Iron Age brain found in an isolated cranium dating from about 500 years BCE, the only other Raman spectroscopy study made of human brain recovered from waterlogged, archaeological excavations. The spectra give some surprisingly detailed information about the state of preservation of brain tissue in both burials, especially when it is realized that, unlike preserved bog bodies, no other soft tissue has survived. The biosignatures of proteinaceous brain material are well characterized. The presence of spectral signatures from extraneous cyanobacterial colonization in the depositional site of the Iron Age brain had been construed to be responsible in part for the unusual preservation of brain tissues in the waterlogged environment, but they were not detected in the current study of the nineteenth century brain. The challenges for Raman spectroscopic analysis of biomaterials under these conditions are reviewed in the light of the successful outcome of the experiments.

This article is part of the themed issue 'Raman spectroscopy in art and archaeology'.

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1. Introduction

The successful application of Raman spectroscopy for the analysis of archaeological artefacts is now well established [1] and can be attributed to several factors, including the ability to interrogate non-destructively fragile objects wholly or partially without the necessity of undertaking prior mechanical or chemical pretreatment, sectioning, polishing or desiccation, the identification of characteristic signatures from both organic and inorganic components together without resorting to multiple techniques and the effective separation of materials, thereby losing information that can be gleaned from a study of their relative spatial interactions in the specimens under study.

Following the first Raman spectroscopic studies [2–7] of human skin, nails and hair from which assignments were made of key spectral bands arising from proteins keratins, lipids and chemical functionalities such as the C–S and C–S–S–C bonds in cysteine and cysteic acid, the Raman spectroscopic characterization of human skin tissue from an archaeological source was reported: namely, that of Otzi, the Alpine Iceman, who died some 3200 years BCE and whose remains were preserved by natural freeze-dried mummification [8–10]. Later comparisons could be effected between natural mummification of human skin and nails and mummification through the application of exogenous materials by the Raman spectroscopy of a Greenland ice-mummy (600 years BP) and the Egyptian 12th Dynasty mummies of Khnum-Nakht and Nekht-Ankh (4100 years BP) from Petrie's excavations at Der Rifeh in the Nile valley [11,12]. Raman spectra of human hair and bone from archaeological excavations from a variety of sites [13–16], including waterlogged wooden coffin and dry coastal stone cist burials, enabled assessments to be made about biological degradation, protein tertiary structural destruction and the provision of evidence of the incorporation of compounds from the depositional environment, such as newberyite and cerussite.

A major advantage for the adoption of Raman spectroscopy for archaeological specimens [17] is the low sensitivity of the technique to the presence of water and moisture, which means that specimens need not be dried or desiccated before analytical procedures can commence; hence, recent interest has been shown in the information that can be derived from artefacts excavated from sub-aqua environments and the feedback given to underwater archaeological site examination. Examples include biomaterials from bottles in sixteenth and eighteenth century medicine chests from naval warships, whose integrity had been compromised by leakage of seawater [18–20].

Parallel interdisciplinary studies of biosignatures from epilithic and endolithic lichens and cyanobacteria [21–23] and the protective chemicals these organisms produce as defence against predators and extremes of environment such as temperature, radiation insolation and chemical toxicity for survival of the colonies have established an increasing database for their characterization in complex biosystems. Hence, the presence of *Natromonas pharoahinis* in an Egyptian mummy probably sourced from biologically contaminated natron used in the mummification ritual and which contributed to the degradation of the mummy was demonstrated first by Raman spectroscopy [24].

The preservation of brain tissue in otherwise skeletalized remains is rare but not unheard of where burial has taken place rapidly and in a wet, anoxic and often clay-rich environment [25–29].

The only study thus far reported of the Raman spectroscopic analysis of human brain tissue recovered from skeletalized remains is that of the brain from a cranium found in a waterlogged, Iron Age pit in Heslington, Yorkshire, UK [29]. Perimortem damage to cranium and associated vertebrae showed that the individual had been hanged and decapitated. The brain remains were greatly shrunken, odourless, soft and hydrated, their smooth surfaces retaining recognizable neural folds. Fractures revealed the brain's interior to be a tan coloured, tofu-like material. Raman spectroscopy revealed the presence of decayed protein and little fat. Most interestingly, key spectral biosignatures of cyanobacterial colonization were found in the material from the waterlogged cranial cavity and it was theorized that the bacteria had perhaps acted in a preservational role for the underlying brain tissue [30].

In this paper, we report the Raman spectroscopic study of a second example of preserved brain tissue from a skeletalized human in a waterlogged burial site, but here the remains are only two centuries old and not 26 centuries as in the previously cited case. Also, in the Iron Age burial the decapitated cranium was found alone, whereas in the case studied here the brain was located inside the cranium of a complete skeleton which had been placed in a wooden coffin, which itself contained the remains of degraded associated clothing, sawdust and wood shavings [31].

2. Experimental set-up

(a) Skeletal remains: the archaeological site

A project to create a pedestrianized area near St John the Evangelist Church in Blackpool, Lancashire, UK, necessitated the excavation of parts of the churchyard, which had apparently been cleared in 1927, but which revealed the presence of several remaining burials. A team of archaeologists from Oxford Archaeology North was commissioned to exhume and examine the human remains before re-interment. One of these burials comprised a well-preserved, wooden fish-tailed coffin (burial 116/skeleton 117) from the nineteenth century containing a complete skeleton, buried within very heavy clay (figures 1 and 2). The use of oak (approx. 10 mm thickness) instead of elm indicated the high social status of the deceased, a female in her mid to late twenties. Five pieces of tinned iron coffin furniture were recovered but were too badly corroded to reveal the identity of the occupant. The coffin was full of trapped rain water and several skeletal elements were displaced in the fine silt that had infiltrated the coffin. Although the wood of the coffin and its packing of wood shavings were well preserved, there was no surviving soft tissue or hair on the skeleton and none was recovered from the silt fill. It seemed all the more surprising, then, that a mass of biomaterial was found inside the cranium (figures 3 and 4). Examination by Sonia O'Connor confirmed that, although shrunken, it had retained the overall shape and neural folds of the brain and that the material closely resembled in colour, morphology and texture the brain remains recovered at Heslington and the other published examples of brains recovered from inhumations in anoxic, waterlogged burial environments. Because the brain was still inside the intact skull, a specimen was extracted from the cranium (figure 5) for Raman spectroscopic analysis; no specimen preparation was involved and the sample was examined as provided in a wet state, no desiccation being undertaken.

(b) Raman spectroscopy

A DeltaNu Advantage prototype Raman spectrometer unit operating at 1064 nm with a spectral footprint of about 50 µm diameter was used to interrogate the specimen using a few milliwatt laser power at source. Although of more limited spectral wavenumber range than its laboratory benchtop FT Raman counterpart, this being effectively 200–2000 cm^{-1}, here the long wavelength CCD detector was able to acquire spectral data very rapidly (approx. one acquisition every second); this coupled with its superior fluorescence rejection capability over visible wavelength CCD devices facilitated the recording of Raman bands with little general background emission. This aspect of the long wavelength laser excitation and instrumentation was important for archaeological artefacts, as has been demonstrated hitherto. The inferior spectral resolution of 10 cm^{-1} of the miniaturized portable prototype instrument compared with the normal operating spectral resolution of the FT instrument was not found to be a significant issue for the recording of definitive Raman spectra and the identification of key biomolecular spectral features was not compromised.

Generally, up to 10 spectra were accumulated at each datum point for each replicate sampling footprint and spectral averaging was undertaken to give improved signal-to-noise ratios. Calibration of the instrument was effected using a polystyrene standard and wavenumbers found to be accurate to approximately $\pm 1\,cm^{-1}$, which was considered adequate for the assignment

Figure 1. Fish-tailed coffin 116 preserved in anoxic waterlogged, clay-rich sediments (permission of Oxford Archaeology North). (Online version in colour.)

Figure 2. Skeleton 117 *in situ* in coffin 116 (permission of Oxford Archaeology North). (Online version in colour.)

of spectral features to biochemical and mineral functionalities. For diagnostic and identification purposes, spectral band wavenumbers were compared with those in our laboratory Raman database for archaeological biomaterials, much of which has appeared in the literature.

Figure 3. The skull of skeleton 117 (S.O'C.). (Online version in colour.)

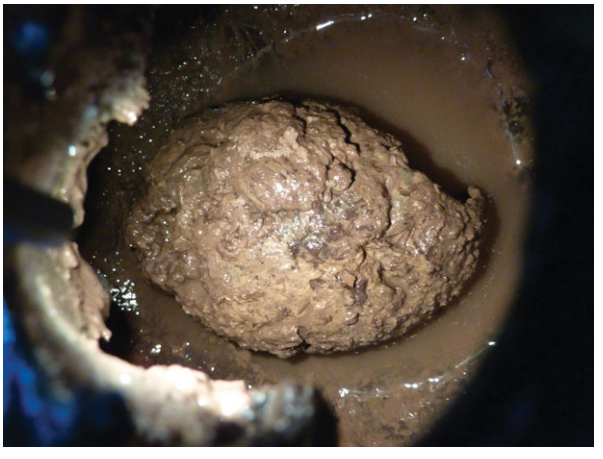

Figure 4. Surviving brain mass seen through the foramen magnum of the skull (S.O'C.). (Online version in colour.)

3. Results and discussion

The specimen was examined spectroscopically over 20 replicate footprints, each one of these being about 50 µm in diameter; all spectra were essentially the same and exhibited similar spectral features, with the major difference being small changes in relative intensity of the Raman bands reflecting compositional variation between sampling points. The laser power was kept low to

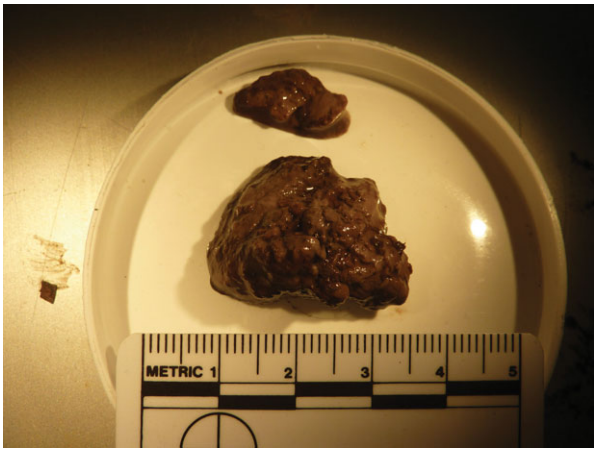

Figure 5. Samples from the brain taken for analysis (S.O'C.). (Online version in colour.)

minimize the possibility of inducing specimen degradation, which usually becomes manifest with the observation of the D (sp^3) and G (sp^2) amorphous carbon signals at about 1350 cm^{-1} and 1580 cm^{-1}, respectively [32,33]; archaeological biomaterials are particularly prone to this thermal damage, especially those that have been excavated from burial sites from which colourants and exogenous materials have been extracted from the depositional environment. An example of this was reported in the literature with the Raman spectroscopic study of human hair from a skeleton in a waterlogged wooden coffin and in which the distinctive Raman signatures of cerussite were observed; the conclusion resulting from this was that the skeletal remains had originally occupied a lead coffin which was found elsewhere in the archaeological burial site [14].

The Raman spectra obtained from the specimen found in the cranium of skeleton 117 found inside coffin 116 at the St John the Evangelist site confirmed the forensic pathology that it was indeed organic material consistent with its attribution to brain tissue.

Figure 6 gives the Raman spectrum recorded from the brain specimen using 1064 nm excitation; there are some clear Raman features superimposed upon a broad emission background and these can be tentatively assigned as follows. The weak and rather broad features at 1648 cm^{-1} and 1610 cm^{-1}, respectively, are ascribed to degraded α-helical protein, now better described as beta-sheet and random coil conformational structures, whereas the bands at 1563 and 1517 cm^{-1} are assignable to aromatic ring breathing modes based on C=C and C=N skeletons, respectively. The stronger band centred at 1452 cm^{-1} is probably a CH_3/CH_2 deformation and that at 1327 cm^{-1} is a CCN fused ring stretching vibration. At 1265 and 1208 cm^{-1}, we have NH deformational modes, along with CC stretching modes at 1167 and 1107 cm^{-1}. At 1086 cm^{-1}, there is a band assignable to the CO symmetric stretch of the carbonate ion in calcite or aragonite; supportive evidence for the differentiation between these is unfortunately lost in the background noise around 700 cm^{-1} and 200 cm^{-1}, but it is reasonable to suppose that the presence of detritus in the coffin surrounding the skeleton would perhaps be a source of limestone fragments. The 1066 cm^{-1} band is ascribed here to a CO stretch and the band at 1001 cm^{-1} to either aromatic amino acid residues such as tryptophan or phenylalanine or possibly to unsaturated CH_3–C=C groups akin to degraded carotenoid structures. At 955 cm^{-1}, we note the presence of a band which is distinctive for a phosphate PO stretching mode or alternatively this could be ascribed along with the band at 890 cm^{-1} to CH_3–C methyl rocking features. The bands at 690 and 620 cm^{-1} we have noted hitherto in degraded human skin, where they have been assigned to CS stretching modes from degraded CSSC cross-linked protein strands occurring at cysteine residues, where the formation of cysteic acid had occurred through biological degradation. The presence of a weak feature at 1729 cm^{-1} is indicative confirmation of a carboxylic acid which could possibly arise from this source.

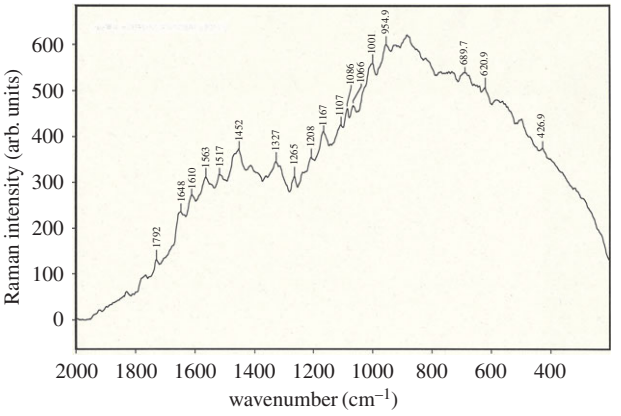

Figure 6. Raman spectrum of the brain recorded using 1064 nm excitation (H.G.M.E.). (Online version in colour.)

Although the specific band assignments are necessarily rather tentative in what must be viewed as a complex specimen, it is nevertheless reasonable to propose that the Raman spectroscopic data support the assertion that the specimen is in fact human brain, although this has been degraded somewhat in the burial environment. The surprising outcome of this study is that the brain has survived at all over some 160 years; there is now a growing body of support in the literature from archaeological excavations for the survival of brain tissue with associated skeletal remains, particularly in wet, anoxic environments such as that noted here. In the case of the Iron Age brain from Heslington, the presence of cyanobacterial biosignatures were evident in the Raman spectrum both of the brain itself and in the black sludge occupying the cavity between the brain and the cranium [30]. It was concluded that possibly the cyanobacteria had been a contributing factor in the preservation of the brain tissue over many centuries. Here, in contrast, there is no evidence at all for the presence of cyanobacteria in the Raman spectra of the brain specimen. It could be construed that a different survival mechanism may be responsible, despite the common features between the two studies, such as their physical appearance and the clay-rich, waterlogged depositional environment in which the skeletal remains rested. However, it must also be considered that the cyanobacteria detected in the Iron Age brain represented an incidental colonization that did not influence its survival. The individual from Blackpool was interred as a complete body but the head from Heslington was detached from the body before burial providing opportunity for microbial contamination of the intercranial space which might not otherwise have occurred.

4. Conclusion

The Raman spectrum of archaeological soft human tissue investigated here has confirmed its attribution to brain which has survived some 160 years in a waterlogged burial environment, albeit with evidence in the spectra of some protein structural degradation having taken place. This is the second Raman spectroscopic study undertaken and reported on archaeological brain and differs from that previously reported in that cyanobacterial signatures were not observed here. Hence, a previous suggestion that the presence of cyanobacterial colonization of the biological tissue was responsible for its preservation in an archaeological environment cannot apply here. Studies of future finds may clarify if more than one survival mechanism is indicated. It is clear from this and the previous study that Raman spectroscopy provides an excellent first-pass, non-destructive analytical interrogation of putative brain remains from archaeological contexts.

Authors' contributions. S.O'C. conceived the project, recorded and sampled the brain, contributed to the initial paper and undertook its revision. H.G.M.E. helped draft the manuscript, provided the interpretation of the

Raman spectral data and the comparison with the previous study of the Heslington brain. E.M.A.A. was responsible for the acquisition of the Raman spectral data and instrument expertise. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.

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