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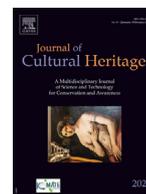
Original article

Potential and limitations of adhesive identification on museum curated metal objects

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ABSTRACT

In Europe, adhesives were produced and employed from the Middle Palaeolithic onwards. In the earlier periods, adhesives were used predominantly for hafting tools and weapons, but their functionality evolved with the advent of ceramic technologies, with use widening to pottery repair and ornamentation. Limited attention has been directed towards their application in metalwork. It is unclear whether the scarcity of adhesives described in association with metal is due to preservation factors, such as corrosion-related issues, or to a research emphasis on other materials associated with metalwork such as coral, amber, and glass. To address this issue, we conducted chemical analyses including gas chromatography – mass spectrometry on 18 adhesive residues present on 15 objects from France and England dated from the mid first millennium BCE to the first century CE. These artefacts include jewellery, vessels, harness fittings and weaponry components. Our findings suggest that a range of adhesives were employed in assembling and applying decoration to diverse types of metal objects. These include birch tar and conifer resins, also bitumen and possibly beeswax, which have not been reported before. However, the application of waxes in past conservation practices introduces challenges that can potentially constrain the interpretation of molecular analyses. Our results have implications for the understanding of the adhesive technologies, and illustrate the potential of identifying adhesives linked to metal ornamentation. They further demonstrate the widening application of long-established adhesive technologies within the framework of increasingly complex craft specialisms.

Introduction

Adhesives are the first synthetic material made by humans attested in the archaeological record [1–4]. Their application range varies depending on region and period. The adhesive most frequently encountered archaeologically in Europe is birch bark tar (hereafter birch tar), a product obtained through distillation of birch bark. It's prominence in the archaeological record is likely due to its preferential use for its adhesive strength [5], and greater resistance to taphonomic processes compared to other adhesives [6]. To a lesser extent, conifer resins [7], or bitumen [8], beeswax [9] or hide glue have been found [10]. Addition of inorganic materials to adhesives has been evidenced in some cases (for example ochre, [11]), and shown to modify adhesive properties [12].

Archaeological evidence attests to a diversification of adhesive function likely linked to concurring inventions such as composite tool, ceramic and metal technologies. Hafting of stone or bone tools is well documented for the Mesolithic and Neolithic [13–18]. For these, the composition of the adhesives is revealed through chemical analyses [14,18] and their performance reconstructed through mechanical testing [5,12,19,20]. With the onset of ceramic technologies, evidence of ceramic repair or decoration becomes frequent [18,21–24].

Few studies have examined adhesive use on metal objects. Chemical data from artefacts from Iron Age Europe evidence the use of birch tar [25–27], in some cases possibly mixed with conifer resin [28,29]. Birch tar was used to affix decorations on harness fit-
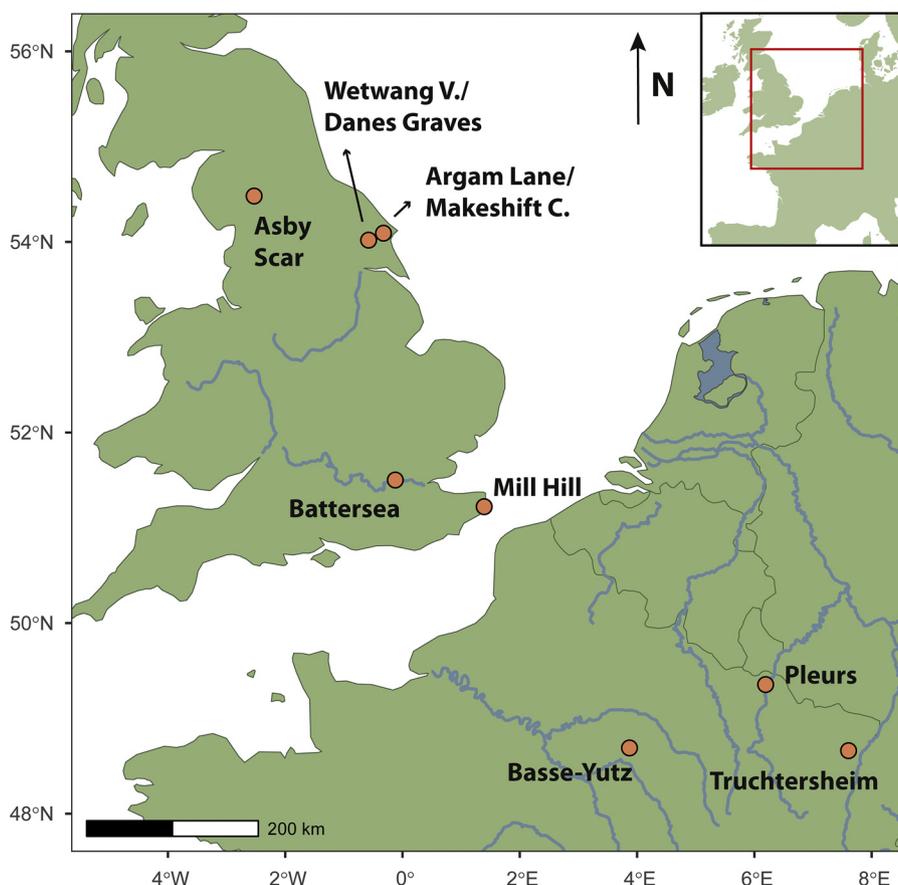
Fig. 1. Map of site locations. Site locations that are very close to each other are represented by the same point. Base map made with Natural Earth (free vector map data @naturalearthdata.com).

tings [25,29] and brooches [30], glue tin strips onto ceramic pots [22], on sword sheaths [26,27] and has been found within a bronze pendant [28]. Birch tar was used until the Roman period in western Europe [31] and in the early medieval period in the United Kingdom [32]. It is unknown whether the lack of adhesive evidence in Europe on metal is due to a research bias in the study of the metal objects themselves, decreased preservation on metal as opposed to stone and ceramic, or whether adhesives were simply not used for all types of metalwork.

To investigate these aspects, we studied a range of metal artefacts in the collections of The British Museum, Hull and East Riding Museum in England, and the Institut national de recherches archéologiques préventives (Inrap) repository in Strasbourg (France). The objects include brooches, a pendant, a sword hilt, harness fittings, horse chariot terrets and a vessel (Table 1). These were selected due to the presence of black residues visible on the metal surfaces or at the interface between different materials on composite objects. Both copper alloy and iron artefacts were included. The objects originate from ten different Iron Age sites in northern and south-eastern England and north-eastern France, dated between the fifth century BCE to first century CE (Fig. 1). Two well-known composite objects from the British Museum collections were also examined: the Battersea shield found in the Thames river in London, England [33], and one of the Etruscan style flagons from Basse-Yutz, France [34].

This work has three research aims. First, to identify whether adhesive residues are preserved on different metal objects. Second, to identify the chemical composition and, hence, the nature of these residues to understand how adhesives were used in metal technologies. And thirdly, to assess the potential impact of past sur-

face treatments and conservation interventions on the composition and condition of ancient adhesives associated with metal objects. For this, 18 residues were analysed from the 15 objects using gas chromatography – mass spectrometry (GC–MS). The objects have different ornamentations, such as studs and inlays made of coral, red glass, shell or amber. The adhesives on two of the artefacts have been studied before but to varying degrees of detail. For example, the composition of the copper alloy and the glass have been analysed and published for the Battersea shield [33]. However, the adhesive is only briefly mentioned in the unpublished scientific report where the use of bitumen for ornamentation is noted but no chemical characterisation was reported [35]. Birch tar was identified on the Mill Hill, Deal strap union [36,37] and bitumen as the material underlying domed pins on the Asby Scar sword guard [38]. We reanalysed the data by Stacey [37] and Stead [38] to compare the results with the objects in this study. Our results allow for a holistic perspective of adhesive technologies in the Iron Age, currently known predominantly for its use on ceramics. This has implications for our understanding of the respective adhesive technologies and their entanglement with metal technology and ornamentation.

Research aims

This study aims at 1) identifying whether organic adhesives preserve on metal objects curated in museum environments; 2) characterising the chemical composition to identify the nature of these adhesives, which will allow us to illustrate the range of applications that adhesives were used for and to understand combined adhesive and metal technologies; 3) highlighting the poten-

Table 1

List of sites as shown in Fig. 1 and respective objects sampled for organic residue analysis. BM = British Museum, HER = Hull and East Riding Museum, INRAP = Institut national de recherches archéologiques préventives; UK = United Kingdom, FR = France. Material types based on previous publications or internal museum records.

Site	County/Dept., country	Chronology	Museum or collection: ID	Sample IDs	Objects	Metal type	Inlay/stud type	Conservation treatment
Argam Lane	East Yorkshire, UK	c. 400–150 BCE	BM: 1991,1001.25	AL02	Brooch	Fe/Cu alloy	Glass	No record of conservation undertaken at the BM
Makeshift Cemetery	East Yorkshire, UK	c. 400–150 BCE	BM: 1975,0401.36 BM: 1975,0401.27	MC01 MC02	Brooch Brooch?	Bronze Fe/Cu alloy	Glass Glass and coral	No record of conservation undertaken at the BM
Wetwang Village	East Yorkshire, UK	c. 400–150 BCE	BM: 2001,0401.9 BM: 2001,0401.18	WW01S1 WW01S2	Strapfitting Strapfitting	Cu alloy Fe	Coral Coral	PB72 PB72
			BM: 2001,0401.4	WW01T2	Terret	Fe/Cu alloy	Coral	PB72
			BM: 2001,0501.5	WW01T3	Terret	Fe/Cu alloy	Coral	PB72
			BM: 2001,0401.7	WW01T5	Terret	Fe/Cu alloy	Coral	PB72
Danes Graves	East Yorkshire, UK	c. 400–150 BCE	HER: KINCM:1946.65.2.1 (same ID) (same ID)	Danes_01 Danes_02 Danes_06	Brooch (same) (same)	Cu alloy Cu alloy Cu alloy	Tufa? Amber? (dentalium) shell?	HMG, Incralac
Battersea	Greater London, UK	c. 350–50 BCE	BM: 1857,0715.1 (same ID)	BS01 BS02	Shield (same)	Bronze	Glass Glass	PB72, HMG
Mill Hill, Deal	Kent, UK	c. 250–100 BCE	BM: 1990,0102.27	DL01	Strap fitting	Cu alloy	Coral	PB72, HMG
Asby Scar	Cumbria, UK	c.1–100 CE	BM: 1994,0204.1	AS01	Sword	Tin bronze	–	PB72, HMG, Araldite epoxy
Pleurs	Marne, FR	c. 450–320 BCE	BM: ML.1631	Pleurs01	Brooch	Cu alloy	Coral	No record of conservation undertaken at the BM
Basse-Yutz	Moselle, FR	c. 420–360 BCE	BM: 1929,0511.2	BYu01	Flagon	Cu alloy	Coral?	No record of conservation treatments of the inlays undertaken at the BM
Truchtersheim	Bas-Rhin, FR	c. 625–550 BCE	INRAP: 016,885-MCU-606–004	TR01	Pendant?	Cu alloy	–	No treatment

tial of chemical analyses on metal objects but also the impact of conservation history on our interpretation of ancient adhesives.

Materials and methods

Materials

We sampled fifteen metal objects from ten Iron Age contexts from the collections of The British Museum, the Hull and East Riding Museum, including copper alloy and iron objects (Table 1 and Fig. 2; contextual information on each site and object in the SI). One object (016885-MCU-606–004) is curated at the Inrap repository in Strasbourg. Where possible, prior to sampling the adhesives, objects were examined and recorded in situ using a VHX Keyence digital microscope (Fig. 3 and SI). For most of the objects, the adhesives are underlying studs and/or inlays made of glass, coral, possibly dentalium shell and amber. In some cases, the inlays were not preserved but residues could be identified in the sockets. In two cases, the organic material is infilling hollow metal components: the Truchtersheim pendant and the Asby Scar sword. Museum conservation records show the treatment of some of the objects with Paraloid® B72, HMG®, Araldite® and Incralac® (Table 1).

Solvent extraction protocol and GC–MS analysis

Sample preparation and analyses of samples from museum objects were performed in the laboratories of the Department of Scientific Research of the British Museum. The sample taken from the Truchtersheim pendant was analysed at the Cepam laboratory in Nice, France. Samples were extracted and analysed based on previously established protocols [18,21,39]. The potential adhesive residues were solvent extracted and analysed using GC–MS (analytical details in the SI).

The analytical protocol of the AS01 extraction can be found in Stead [38], and extraction protocols from Stacey [37] of DL01 are noted in the SI. Identification was conducted with the free software AMDIS (Automated Mass Spectral Deconvolution and Identification System; http://chemdata.nist.gov/mass-spc/amdis), NIST library and published data [40–43]. Compound abundances are expressed in percentage and were calculated from the sum of the integrated areas of compounds belonging to the same chemical class normalised by the total area of identified compounds. All raw data are archived at the British Museum in the Department of Scientific Research Project Records (PRO 7711) and available on request to science@britishmuseum.org.

Results

Molecular profiles of birch tar

In twelve samples we identified triterpenoid compounds characteristic for birch tar (Table 2). These were completely soluble in DCM. The residues can be linked to their botanical origin based on the presence of specific biomarkers present in birch bark, such as betulin, lupeol and betulinic acid, and erythrodiol [40–42,44], see Fig. 4. Birch tar is characterised by the degradation products of these biomarkers forming during distillation. We identified the degradation markers lupa-2,20(29)-diene, lupa-2,20(29)–dien-ol, lupenone, betulone, allobetul-2-ene, allobetulin, and less frequently 28-oxoallobetul-2-ene and 3-oxoallobetulane. The infrequency of the latter two compounds is most likely due to coelution with other triterpenoid compounds, seen in samples WW01T3 and WW01T5. Although some of these markers can form through natural decay [40], their abundance increases during production and

Table 2
Summary of chemical classes identified in the sample set with adhesive interpretation and identification of conservation treatments. For detailed list of all compounds detected, see SI.

Sample ID	Fatty acids/Diacids	Even-numbered fatty alcohols	Odd-numbered n-alkanes	Long-chain even-numbered palmitic wax esters	Diterpenoids	Triterpenoids	Hopanes	Steranes	Interpretation of original adhesive	Conservation treatment identified
AL02	–	×	×	–	–	–	–	–	No clear result	Pthalates
MC01	×	–	–	–	×	×	–	–	Possibly birch tar, Pinaceae resin	Pthalates
MC02	×	×	–	×	×	×	–	–	Possibly wax	Pthalates
WW01S1	×	–	–	–	–	–	–	–	No clear result	None
WW01S2	×	–	–	–	×	×	–	–	Birch tar	None
WW01T2	×	–	–	–	×	×	–	–	Birch tar, Pinaceae resin	None
WW01T3	×	–	–	–	–	×	–	–	Birch tar	None
WW01T5	×	–	–	–	–	×	–	–	Birch tar	None
Danes_01	×	–	–	–	×	×	–	–	Birch tar, possibly Pinaceae resin	Pthalates
Danes_02	×	–	–	–	–	×	–	–	Birch tar	Pthalates
Danes_06	×	–	–	–	×	×	–	–	Birch tar, Pinaceae resin	Pthalates
BS01	×	×	–	×	×	×	–	–	Birch tar, possibly wax	Waxes?
BS02	×	–	–	×	–	×	–	–	Birch tar, possibly wax	Pthalates, waxes?
BYu01	×	–	–	×	–	×	–	–	Birch tar, possibly wax	Pthalates, waxes?
DL01	×	–	–	–	–	×	–	–	Birch tar	Pthalates
AS01	×	–	–	–	–	–	×	×	Bitumen	Pthalates
Pleurs01	×	–	–	×	–	×	–	–	Birch tar, possibly wax	None, waxes?
TR01	×	–	–	–	–	×	–	–	Birch tar	None

Fig. 2. Selected photographs of objects included in the study (image credits for 016885-MCU-606–004: T. Koch; for object 1946.65.2.1: © Hull and East Riding Museum; and for the remaining objects: © The Trustees of the British Museum). For details see Table 1 and SI.
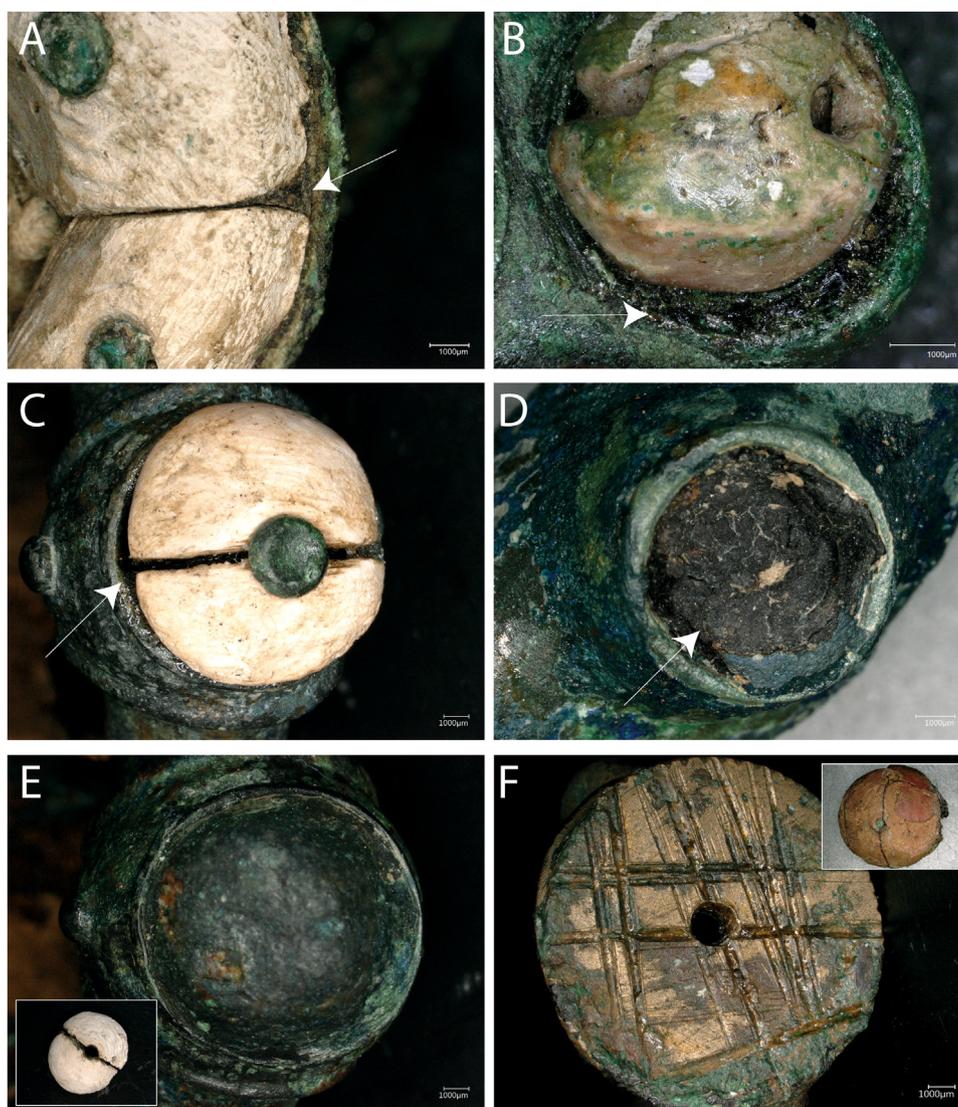
Fig. 3. Microscope images of selected adhesive residues (arrows indicate adhesive), A) between coral inlays on the brooch from Pleurs (BM registration ML.1631); B) underlying the studs on the Danes Graves brooch (HER registration KINCM:1946.65.2.1); C) underlying the coral studs (BM registration 2001,0401.7) and D) preserved in empty sockets on the Wetwang Village terrets (BM registration 2001,0501.5). Microscope image of empty cavities with E) no rivet puncture through the metal on a Wetwang Village terret (BM registration 1975,0401.36) and F) puncture related to the rivet on the brooch from grave R22 at Makeshift cemetery (BM registration 1975,0401.27). © The Trustees of the British Museum.

their presence with other degradation markers linked to manufacturing supports the interpretation of birch tar [39]. Many triterpenoids present in birch tar remain to be chemically identified. We therefore expect the real values of triterpenoid abundance to be higher than presented in Fig. 5. We identified saturated and unsaturated fatty acids, and diacids, which have been reported in previous studies on birch tar residues and may be released from suberin [41] during the production of birch tar [39]. The presence of betulin in samples MC02 without other bio- or degradation markers is insufficient for an interpretation as it also occurs in other angiosperms [44]. For a list of all detected compounds, see Table S1 of the SI.

Diterpenoid profiles of pinaceae-derived products

In addition to triterpenoid compounds, four samples also contained specific markers suggesting the presence of a conifer-derived substance. We identified dehydroabietic acid and its degradation product 7-dehydroabietic acid, which, are common markers for resins from the Pinaceae family [18,45] in samples WW01T2

and Danes_01. Sample MC01 also contains simonellite, which is another common biomarker derived from conifer products [46,47]. Sample Danes_06 features a fourth marker, pimaric acid. Compared to the area of triterpenoid molecules in these samples (see Fig. 5), the diterpenoid compounds are less abundant. We were unable to identify specific markers that would enable us to narrow down the botanical source to a genus level.

Wax-characteristic compounds

The molecular profile of beeswax is commonly characterised by a combination of long-chain even-numbered palmitic and 15-hydroxypalmitic wax esters, even-numbered fatty alcohols, long-chain fatty acids and odd-numbered *n*-alkanes [48–50]. We found some of these compounds in the samples taken from one of the brooches from the Makeshift Cemetery (MC02), the Pleurs brooch, the Battersea shield and the Basse-Yutz flagon (Table 2). Five samples taken from these objects show a molecular profile of wax esters with W40-W50, although W50 was absent in two samples (Pleurs01 and BYu01). In one of the samples taken from the Bat-
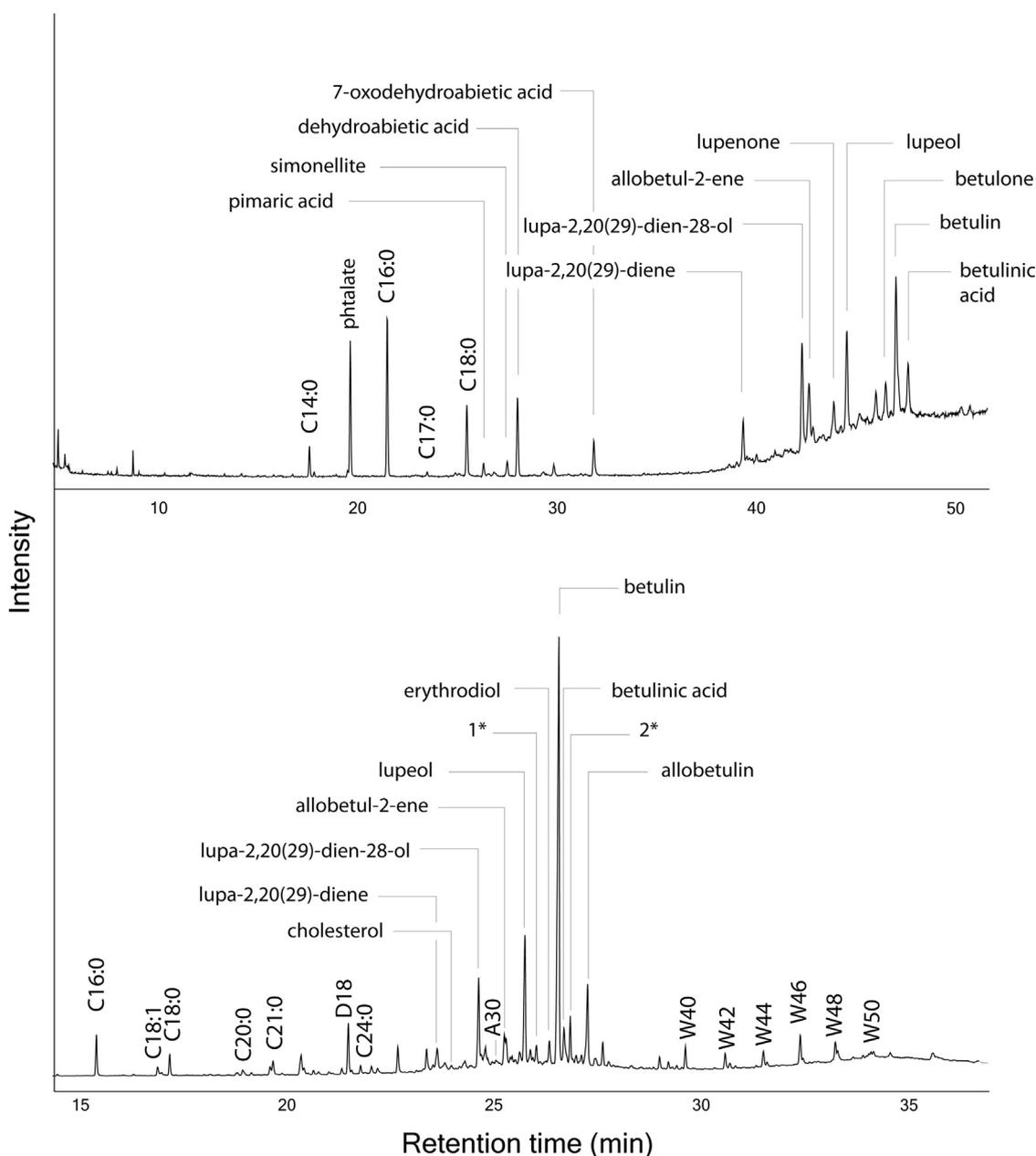
Fig. 4. A) Total Ion Chromatograms (TIC) of the residues from the Danes Graves brooch (Danes_06, top) and the Battersea Shield (BS01, bottom); CX:Y = fatty acid, DX = diacid, AX = alcohol, WX = wax ester, where X = number of carbon atoms, Y = number of double bonds on the aliphatic chain,; * = unidentified oxidised triterpenoids with mass spectra identical to (1) lupenone and (2) betulone.

tersea Shield (BS02) we detected only one wax ester (W46). To further investigate the composition of the wax esters, we extracted specific ion fragments related to different fatty acids (C14:0-C30:0, m/z = 229, 257, 285, 313, 241, 369, 397, 425, and 453). We found that palmitic wax esters are the predominant species (details are reported in the SI), these being characteristic markers for beeswax [49,50]. Even-numbered fatty alcohols (A24-A32) were present in sample MC02. Sample BS01 only contained A30. Odd-numbered *n*-alkanes were not identified in any of the samples that contained wax esters. Different long chain fatty acids (C24:0 and C30:0) were identified in samples BS01 and MC02. For a confident identification of beeswax, a complete set of wax esters with alcohols or alkanes is crucial, which is not the case for all our samples. We identified palmitic wax esters and even-numbered alcohols in sample BS01 and MC02, the latter also containing long chain fatty acids. The other three samples BS02, BYu01 and Pleurs01 only contain wax

esters without any traces of alcohols or *n*-alkanes. However, we note that the absence of *n*-alkanes in our samples could also be due to heating or natural degradation of beeswax [49].

Molecular profile of bitumen

The Asby Scar sample (AS01) contained a series of chemical classes characteristic of bitumen (Fig. 6): terpanes (C28-C29), steranes (C27-C29), and hopanes (29$\alpha\beta$H to 33$\alpha\beta$H). Steranes were characterised based on their $\alpha\alpha\alpha$ and $\alpha\beta\beta$ configuration which can be identified by their m/z 217 vs 218 ratio [51]. The $\alpha\alpha\alpha$ configuration is characterised by more abundant m/z 217, whereas $\alpha\beta\beta$ configuration by m/z 218. The simultaneous presence of these classes suggests that the residue is a petroleum product [52].
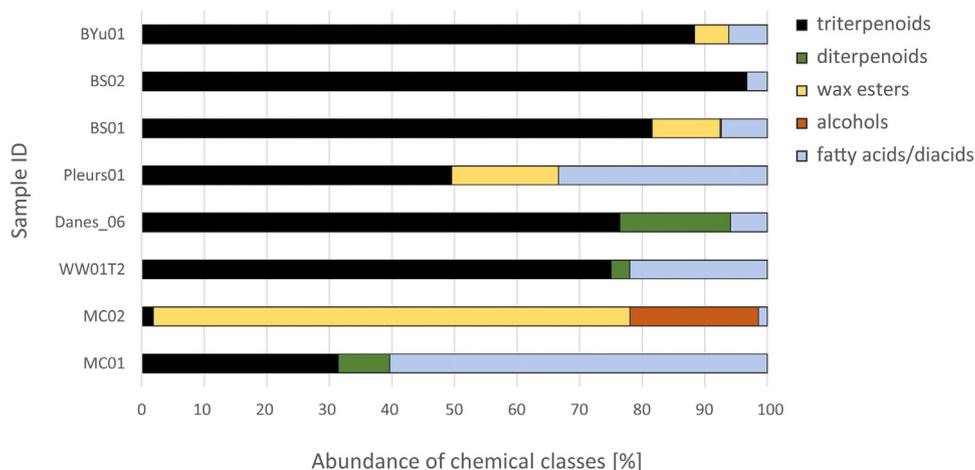
Fig. 5. Relative abundance of each major chemical class for samples with complex molecular compositions (as calculated from the sum of peak integrals per chemical class normalised by the sum of peak integrals from all identified compounds; unidentified peak areas were not taken into account).
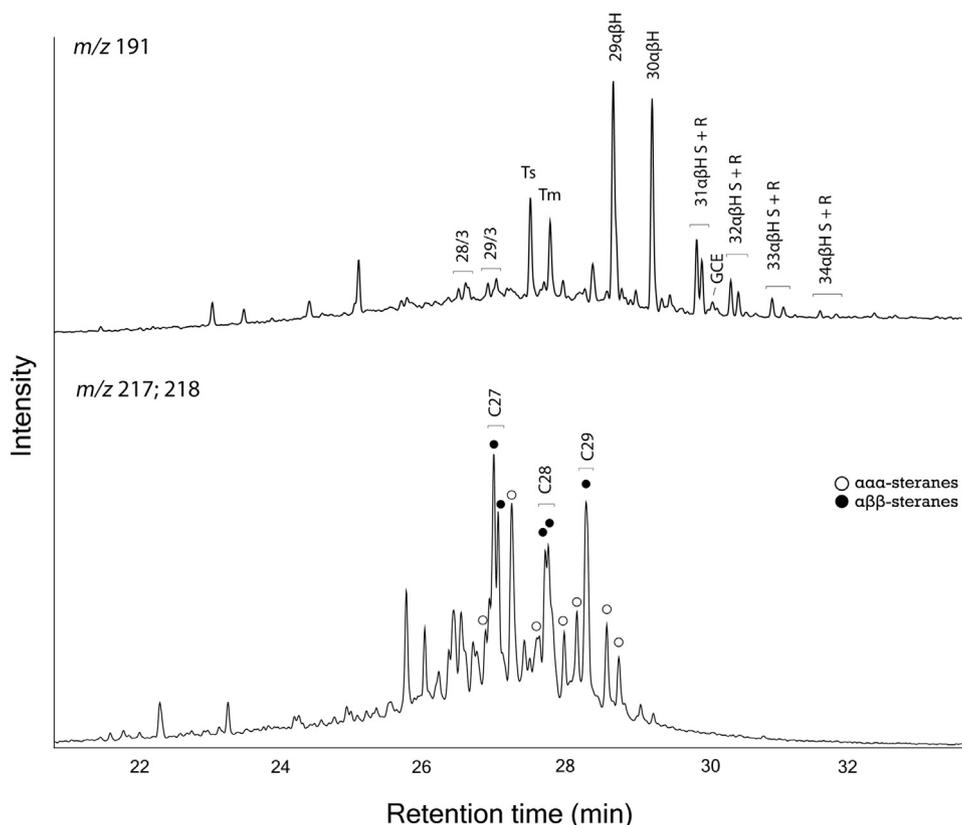
Fig. 6. Extracted Ion Chromatograms (EIC) of the bitumen residues on the Asby Scar sword sheath showing the distribution of terpanes (m/z 191, top) with tricyclic terpanes with n total carbon atoms (n/3), $17\alpha-22,29,30$-trisnorhopane (Tm), $18\alpha-22,29,30$-trisnorneohopane (Ts), Gammacerane (GCE), and $17\alpha,21\beta$-hopanes with n total carbon atoms (n $\alpha\beta$H) in both R and S configurations; and steranes (m/z 217 and 218, bottom) with long chain $\alpha\alpha\alpha$- and $\alpha\beta\beta$- steranes with n carbon atoms (Cn).

Non-identified residues

Sample WW01S1 contained diacids and fatty acids, but no characteristic compounds that would allow further interpretation, as these could also be linked to handling or sediment contamination. Several odd-numbered *n*-alkanes and even-numbered fatty alcohols are present in sample AL02, but the lack of beeswax-characteristic palmitic wax esters hinders clear identification.

Conservation treatment residues

The sample chromatograms were further investigated by extracting specific m/z values related to compounds applied for the conservation treatments listed in the objects' conservation records. Paraloid® B72, which is a copolymer of ethyl methacrylate and methyl acrylate [53], could not be chemically identified in any of the samples. We identified phthalates (based on the characteristic ion fragment m/z 149) in almost all samples, except for the Wet-

wang Village objects, the Truchtersheim pendant, and one of the Battersea Shield samples (BS01). These likely derive from plasticisers added to treatments or storage in plastic containers and wrappings.

Discussion

Implications of our data for adhesive diversity and functionality

Our results show the diverse use of adhesive substances for metal ornamentation and assembling. Birch tar being the main component in most samples is in line with previous studies on Iron Age adhesives on ceramic [21,22,54,55] and metal [28–30]. This suggests continuity and persistence of birch tar as an adhesive. Iron Age birch tar finds use in a wider range of applications and specialised crafts. This raises questions on combined technological expertise of adhesive technology and metallurgy. Based on our study and previous findings [28–30], we argue that metal as a substrate, or the corrosion thereof, does not hinder adhesive preservation. However, most objects in this study are copper alloys. It is unclear if adhesives survive on forged iron objects, whose often stronger corrosion could have a more significant impact on the preservation of adhesives. These might be dislodged or concealed by corrosion. We analysed only one iron object (WW01S2) which shows that adhesives can preserve. Still, the choice to include mostly copper alloy objects in this study could potentially have been biased by lack of visible adhesive residues on iron objects, an issue which remains to be further explored.

Current data ([28–30]; and this study) make clear that adhesive technologies are closely entangled with other material technologies. In this study, the manufacture of adhesives such as birch tar seems to be an integrated step in the finishing of metal objects, constituting a key component of a secondary metallurgical *chaîne opératoire* including other materials. Material acquisition (birch bark, resin, coral, shell, amber) and production (glass, birch tar, metal) might relate to specialised crafts, but the Danes Graves brooch shows that different materials may have sometimes been combined in a single object. The original publication of the brooch [56] proposes the beads were made of tufa (or a similar stone), amber (or similar resin) and dentalium shell, but scientific research is underway for accurate identifications [57]. The integration of multiple material *chaînes opératoires* highlights the degree of craft organisation played in wider production networks or *réseaux opératoires* (see [58]). Use of rivets to attach studs already held in place by an adhesive demonstrates how different material components are integrated, potentially in the same workshop. It is not clear why some studs are held in place only by adhesive whilst others are also attached with a rivet. The Danes Graves brooch, or the Battersea shield, show that the use of rivets was not always necessary. Similarly, the Wetwang Village terrets are decorated with coral studs that, when preserved, are attached with rivets. However, when the coral and rivets are not preserved, it becomes evident that the rivets do not always fully pierce into the underlying metal (Fig. 3e). This contrasts with the clear technical use of a rivet on one of the Makeshift cemetery brooches (Fig. 3f), where the rivet penetrates both the stud and the underlying metal. Here, the marking of narrow grooves into the surface of the metal before adding the adhesives may have aided adhesion. This questions the necessity of rivets: were they meant to hold the coral in place while the adhesive dried, or do they represent an older technology but are now purely decorative? For a more informed assessment of these technological choices, future experimental studies could help determine the functional necessity of combining adhesive (e.g., birch tar) and mechanical (e.g., rivets) joining techniques.

Adhesive function in securing and holding studs and inlays of different materials is clear for the ornamentation of brooches, harness fittings or the Battersea shield and the Basse-Yutz flagons. For example, the red glass decorating the Battersea Shield cannot be melted and fused into place by enamelling ([33], p. 49), which explains the need for an adhesive. Two of the objects analysed here, however, indicate the use of adhesive between metals without any other material components attached. The Truchtersheim half-sphere filled with a lump of birch tar is comparable to a previous discovery by Courel et al. [28]. The authors suggest that the adhesive is used to join two half-spheres to make a pendant. The guard and pommel of the Asby Scar sword is ornamented with multiple hollow domes that are filled with bitumen. Bitumen here serves both as an adhesive to aid the pin holding the dome in place, and as a filler of the hollow metal. We may hypothesise that this function is different from gluing studs into metal sockets, where no infill is required. It may be that bitumen presents a more suitable adhesive for this specific purpose, or it could be an opportunistic choice because bitumen was available, thus reflecting the craft specialism or workshop environment. Freshly collected bitumen is sticky but it has been shown to have no measurable adhesive strength, even after cooking [11]. However, air-dried bitumen's adhesive strength is comparable to cooked/reduced birch tar from double-pot distillation, and may be even slightly stronger (see [5,11]). This would explain the use of both materials for similar purposes.

In a previous study, Koch et al. [21] compared the molecular composition of birch tar samples on different ceramic objects, functioning as repair material, decoration or surface treatments. This comparison was made with samples from site locations in geographical and chronological proximity. In contrast, the objects presented here originate from different geographical contexts, which are not always clear or known. Chronological classification can also be vague for objects within the museum records, hindering direct temporal comparison. When possible, we encourage chemical comparison of birch tar function on ceramics versus metal objects from similar site contexts to assess whether any variation due to production or post-production processes can be identified. However, we do call for caution in the comparison of archaeological residues found on different substrates (i.e. metal versus ceramic) as the differential impact on degradation is not fully understood. Huber et al. [59] showed that (cedar oil-characteristic) molecules degrade differently based on the material they are adherent to. Studies of other archaeological residues associated with copper alloys have shown the occurrence of copper salt formation [60]. The organic acids detected here might therefore be present as metal complexes, as these are indistinguishable from free acids when analysed as TMS derivatives. This phenomenon has not yet been examined for archaeological resins and tars, meaning the impact on preservation and molecular profiles is unknown.

Intentional use of pinaceae resins or fuel-derived contamination?

We further found evidence of Pinaceae-derived products in four of the samples. Pinaceae resins have been identified at other Iron Age sites, for example Le Cailar (France) where Iron Age human heads were impregnated with a possibly heated Pinaceae-derived product for facial preservation or embalming [61]. The interior surface of an adult parietal fragment from Oram Arbour (UK) was covered in a residue ([62], p. 205) likely a pine resin [63]. The exterior of this bone showed evidence of scorching, suggesting either its use as a potential vessel (a skull cup), or post-mortem mortuary rites [63] which fit a wider range of Iron Age technologies [64]. Previous studies have shown that Pinaceae resins were used in combination with birch tar to attach coral studs to the Wetwang terrets [29] and assemble the Eckwertsheim pendant [28]. We did not identify any molecular component of a resin added to the Truchtersheim artefact. This might relate to a hypothesis

proposed by Courel et al. [28] that the presence of resin is due to contamination. The three samples from different inlay locations of the Danes Graves brooch show that adhesive compositions can also vary on the same object. Besides birch tar, two of the samples taken from the brooch contained diterpenoids. A possible explanation for this is that the mixture was not physically homogenous, resulting in samples containing topical varying amounts of molecular markers which might skew molecular characterisation. Or, small amounts of diterpenoid compounds could come from nearby fires using conifer woods as fuel. Multiple conifer specific compounds are also present in smoke from biomass burning, for example dehydroabietic, pimaric, abietic acid and retene [65]. This was also evidenced by the diterpenoid markers found in ceramic pots fired using pine wood [66]. Incidentally produced wood tar has also been shown to form on flint tools if deposited in fire places [67]. For these reasons, we cannot be certain of the origin of these markers. This is especially so if they are present as minor components in an archaeological material which required fire to produce (here, the production of birch tar). Low abundances of diterpenoids have been identified in experimentally made birch tar [16]. The samples in this study contain only few diterpenoids, whereas a full sequence of diterpenoid markers would provide more convincing data for the intentional use of conifer products (as suggested in [68]).

Limitations in interpretation due to museum conservation practices

Past conservation treatments may have had an influence on the organic composition of the residues sampled. Conservation records at the British Museum note different treatments on some of the objects (Table 1). Paraloid® B72 is an acrylic resin that has been used in conservation practices to restore paintings [69] or consolidate glass [53,70]. It is known to have a weak adhesion to inorganic materials and poor water resistance [53], which may have influenced its preservation over time and explain the absence of Paraloid-related residues. Paraloid® does not specifically require a plasticiser [71], explaining their absence in some samples treated with it. Incralac® is an acrylic resin that is commonly used in bronze and copper coatings [72]. Given that acrylic resins are mainly composed of synthetic polymers, the absence of these compounds might be due to limitations in our methodology (artworks are more commonly tested for acrylic resins using pyrolysis coupled with GC–MS, see [73,74]).

Cellulose nitrate is the polynitrate ester of cellulose commonly used in art conservation [75]. Combined with plasticisers to soften it, it is used for repair in museum conservation [75,76]. We found phthalates in almost all samples. However, there is no apparent correlation between the presence of phthalates and the recorded use of nitrate cellulose. The only objects with known treatment of HMG® are the Battersea Shield and the Asby Scar sword. In these two cases the phthalates are likely linked to conservation treatments. For the other objects, they may be linked to plastic bags or storage containers. Although no further records are known of specific conservation, we cannot exclude that further treatment was undertaken. This is especially the case for older museum acquisitions or objects that have a long history between discovery and museum acquisition, such as the Danes Graves brooch, the Battersea Shield, the Basse-Yutz flagons and the Pleurs brooch. We also acknowledge a certain limitation of our study in identifying conservation-related materials without analysing the reported conservation treatments for direct comparison. We therefore encourage future to include chemical characterisations of modern substances, if these are available for analysis.

A case point is the Battersea Shield, which arrived at the Museum in 1857 [77] and was almost entirely reconstructed. Technical examination reports describe the adhesives used to fix the glass inlays as "bituminous cement not to be confused with the bitumen which has been used for modern repairs" [35]. This relates to a prior interpretation of the original adhesive as well as a record of conservation treatment. Our chromatographic data of the adhesive does not indicate any presence of bituminous materials. This inconsistency is probably due to previously undefined terminology, with the terms pitch, tar and bitumen being used interchangeably for black substances [78]. Or, it could relate to a sampling bias, if different adhesives were used in different locations. To our knowledge, birch tar has not been used in conservation practices or for modern repair in museums, leading us to conclude that it is the original adhesive used to ornament the shield.

Oils, fats, lacquer and wax were, however, common substances used in artefact conservation ([79], p. 279). Details of the specific composition of these varnishes and adhesives are not always recorded and the definition for specific terms may vary. Plenderleith [[79], pp. 179–180] describes bleached beeswax as an effective finish on metal objects to prevent corrosion. This raises the concern that the wax-characteristic markers identified on some objects could be related to conservation using waxy substances. Previous analyses on the contents of the Basse-Yutz flagon found that it contained waxy and resinous residues ([34], p. 75). The wax residues found in the adhesive from the outside of the flagon could hence originate from the vessel content. No tar, resin or bitumen was identified in sample MC02, and the wax-characteristic markers more likely represent the main adhesive component. On the other objects, wax-characteristic markers are less abundant compared to triterpenoids (see Fig. 5). Plenderleith [[79], pp. 179, 359] notes the use of Paraffin wax to enhance the appearance of artefacts and exclude moisture. Paraffin waxes can be characterised by long homologous series of even and odd-numbered *n*-alkanes [80]. No *n*-alkane was identified on the Basse-Yutz flagon, the Battersea Shield or the Pleurs brooch, making Paraffin as a conservation substance unlikely. One of the technical examination reports on the Battersea Shield notes a sealing wax being added to one of the roundels [35]. It is not clear whether this relates to wax typically used for seals, possibly to replicate the red glass inlays. The wax composition is not reported but it might be an explanation for the presence of wax-characteristic markers on the shield, and possibly, on the other objects. This highlights that distinguishing between ancient use of beeswax as an adhesive and modern beeswax for conservation is especially challenging on museum-curated objects.

Previous studies have tested whether the process of lost-wax casting can be evidenced through biomarkers preserving in clay cores [81]. The authors note, however, that high temperatures during the casting process would strongly alter the beeswax compounds. While they might survive the casting process in the ceramic moulds (during dewaxing), it is very unlikely that wax esters preserve on the cast metal itself. Rather, the residues originate from (bees)wax used with birch tar as the original adhesive, or from modern conservation.

Conclusion

Previous studies have shown that birch tar and other adhesive substances were used in composite tool hafting technologies, in ceramic repair, and decoration. Less attention has been given to the use of adhesives to ornament metal objects. Our results broaden understandings of combined metal and adhesive technologies, highlighting the continuity of birch tar use and its diverse range of applications on metal objects. We demonstrate that birch tar was used for the attachment of coral and amber studs onto brooches and harness fittings, of glass inlays on the Battersea Shield and coral inlays on the Basse-Yutz flagons, and the infill in the Truchtersheim pendant. Adhesive use is not limited to birch tar, as bitumen is shown to be used as an infill on the guard of the

Asby Scar sword. Based on the success of our analysis we propose that future studies offer real potential for identification of organic residues associated with metal objects. Identification of Pinaceae-derived compounds is in line with previous research, though we stress that low abundances might originate from the tar production environment. The potential for the preservation and analysis of archaeological adhesives may be affected by surface treatments and past conservation practices, and it is vital to consider past treatments that have been carried out on the artefacts. Confident identification of molecular compounds may be hindered when treatments have not been reported or recorded in the past, particularly those applied to the object prior to assessment by a conservator and museum acquisition. Ideally, analysis would be undertaken prior to any treatment, soon after excavation. Nonetheless, our study demonstrates that even for metal objects held in museum collections for decades, with only small amounts of adhesive preserved, there exists potential to identify the original adhesive. Future extension of this work offers promise for understanding the full significance of adhesives in their craft and cultural contexts.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2024.12.013.

References

[1] J.M. Grünberg, H. Graetsch, U. Baumer, J. Koller, Untersuchung der mittelpaläolithischen "Harzreste" von Königsaue, Ldkr.Aschersleben-Staßfurt, Jahresschrift für mitteldeutsche Vorgeschichte 81 (1999) 7–38.

[2] P. Mazza, F. Martini, B. Sala, M. Magi, M. Colombini, G. Giachi, F. Landucci, C. Lemorini, F. Modugno, E. Ribechini, A new Palaeolithic discovery: tar-hafted stone tools in a European Mid-Pleistocene bone-bearing bed, J. Archaeol. Sci. 33 (2006) 1310–1318.

[3] M.J.L.T. Niekus, P.R.B. Kozowyk, G.H.J. Langejans, D. Ngan-Tillard, H. van Keulen, J. van der Plicht, K.M. Cohen, W. van Wingerden, B. van Os, B.I. Smit, L.W.S.W. Amkreutz, L. Johansen, A. Verbaas, G.L. Dusseldorp, in: Middle Palaeolithic complex Technology and a Neandertal tar-Backed Tool from the Dutch North Sea, 116, Proceedings of the National Academy of Sciences, 2019, pp. 22081–22087.

[4] P. Schmidt, T.J. Koch, M.A. Blessing, F.A. Karakostis, K. Harvati, V. Dresely, A. Charrié-Duhaut, Production method of the Königsaue birch tar documents cumulative culture in Neanderthals, Archaeol. Anthropol. Sci. 15 (2023) 84.

[5] P. Schmidt, T.J. Koch, C. Berthold, F. Lauxmann, K.G. Nickel, The evolution of strength, elasticity and rupture behaviour of birch tar made with 'double-pot' techniques during tar cooking, Archaeometry. (2022) 1–14.

[6] P. Kozowyk, A. Gijn, G. Langejans, Understanding preservation and identification biases of ancient adhesives through experimentation, Archaeol. Anthropol. Sci. (2020) 12.

[7] I. Degano, S. Soriano, P. Villa, L. Pollarolo, J.J. Lucejko, Z. Jacobs, K. Douka, S. Vitagliano, C. Tozzi, Hafting of middle paleolithic tools in latium (central Italy): new data from Fossellone and Sant'Agostino caves, PLoS. One 14 (2019) e0213473.

[8] F. Nardella, C. Duce, E. Ribechini, Analytical pyrolysis and thermal analysis to chemically characterise bitumen from Italian geological deposits and Neolithic stone tools, J. Anal. Appl. Pyrolysis. 158 (2021) 105262.

[9] A. van Gijn, J. Boon, Birch bark tar, in: L.P.L. Kooijmans, P.F.B. Jongste (Eds.), Analecta Praehistorica Leidensia 37/38 /Schipluiden : A Neolithic Settlement on the Dutch North Sea Coast c. 3500, CAL BC. Leiden University, 2006, pp. 262–266.

[10] N. Bleicher, C. Kelstrup, J.V. Olsen, E. Cappellini, Molecular evidence of use of hide glue in 4th millennium BC Europe, J. Archaeol. Sci. 63 (2015) 65–71.

[11] P. Schmidt, R. Iovita, A. Charrié-Duhaut, G. Möller, A. Namen, E. Dutkiewicz, Ochre-based compound adhesives at the Mousterian type-site document complex cognition and high investment, Sci. Adv. 10 (2024) eadl0822.

[12] P.R.B. Kozowyk, G.H.J. Langejans, J.A. Poulis, Lap shear and impact testing of ochre and beeswax in experimental middle stone age compound adhesives, PLoS. One 11 (2016) e0150436.

[13] A. Aleo, P.R.B. Kozowyk, L.I. Baron, A. van Gijn, G.H.J. Langejans, The dynamic lives of osseous points from Late palaeolithic/early mesolithic doggerland: a detailed functional study of barbed and unbarbed points from the Dutch North Sea, PLoS. One 18 (2023) e0288629.

[14] J. Kabaciński, A. Henry, É. David, M. Rageot, C. Cheval, M. Winiarska-Kabacińska, M. Regert, A. Mazuy, F. Orange, Expedient and efficient: an Early Mesolithic composite implement from Krzyż Wielkopolski, Antiquity. 97 (2023) 295–313.

[15] T.J. Koch, D. Groß, B.T. Måge, A. Little, Hafting of a Neolithic leister: identification of adhesives from Lolland (Denmark), Danish J. Archaeol. 13 (2024) 1–8.

[16] T.J. Koch, J. Kabaciński, A. Henry, B. Marquebielle, A. Little, R. Stacey, M. Regert, Chemical analyses reveal dual functionality of Early Mesolithic birch tar at Krzyż Wielkopolski (Poland), J. Archaeol. Sci.: Reports 57 (2024) 104591.

[17] G. Osipowicz, J. Orłowska, M. Bosiak, M.A. Manninen, P. Targowski, J. Sobieraj, Slotted bone point from Tłokowo – rewritten story of a unique artefact from Mesolithic Poland, Praehistorische Zeitschrift 95 (2020) 334–349.

[18] M. Rageot, C. Lepère, A. Henry, D. Binder, G. Davtian, J.-J. Filippi, X. Fernandez, J. Guilaine, F. Jallet, G. Radi, E. Thirault, X. Terradas, M. Regert, Management systems of adhesive materials throughout the Neolithic in the North-West Mediterranean, J. Archaeol. Sci. 126 (2021) 105309.

[19] T.J. Koch, P. Schmidt, Adhesive strength and rupture behaviour of birch tars made with different stone age methods, J. Paleolit. Archaeol. 6 (2023) 8.

[20] P. Kozowyk, J.A. Poulis, G.H.J. Langejans, Laboratory strength testing of pine wood and birch bark adhesives: a first study of the material properties of pitch, J. Archaeol. Sci.: Reports 13 (2017) 49–59.

[21] T.J. Koch, M. Saurel, H. Bocquillon, D.F. Pisani, L. Bonnabel, A. Little, R. Stacey, M. Rageot, M. Regert, Differences in birch tar composition are explained by adhesive function in the central European Iron Age, PLoS. One 19 (2024) e0301103.

[22] L.F. Morandi, S.N. Porta, E. Ribechini, Evidence for birch bark tar use as an adhesive and decorative element in early iron age central Italy: technological and socio-economic implications, Archaeometry. 60 (2018) 1077–1087.

[23] M. Regert, S. Vacher, C. Moulherat, O. Decavallas, Adhesive production and pottery function during the iron age at the site of grand aunay (Sarthe, France)*, Archaeometry. 45 (2003) 101–120.

[24] D. Urem-Kotsou, S. Mitkidou, E. Dimitrakoudi, N. Kokkinos, M. Ntinou, Following their tears: production and use of plant exudates in the Neolithic of North Aegean and the Balkans, Quaternary Int. 496 (2018) 68–79.

[25] J. Langlois, M. Rageot, M. Regert, Approche archéométrique des harnais, in: H. Lepaumier (Ed.), Environnement Archéologique d'une Tombe à Char, Édition Presses universitaires de Rennes, 2023, pp. 232–235.

[26] M. Regert, C. Rolando, Identification of archaeological adhesives using direct inlet electron ionization mass spectrometry, Anal. Chem. 74 (2002) 965–975.

[27] E. Ribechini, M. Bacchiocchi, T. Deviese, M.P. Colombini, Analytical pyrolysis with in situ thermally assisted derivatisation, Py(HMDS)-GC/MS, for the chemical characterization of archaeological birch bark tar, J. Anal. Appl. Pyrolysis. 91 (2011) 219–223.

[28] B. Courel, P. Schaeffer, C. Féliu, Y. Thomas, P. Adam, Birch bark tar and jewellery: the case study of a necklace from the Iron Age (Eckwersheim, NE France), J. Archaeol. Sci.: Reports 20 (2018) 72–79.

[29] R. Stacey, Evidence for use of birch-bark tar from Iron Age Britain, The Newsletter of the Prehistoric Society, 2004 Number 47.

[30] Z. Zlámalová Cílová, V. Čisťakova, V. Brychová, L. Lapčák, G. Březinová, T. Kmječ, Š. Matoušková, H. Čižmářová, Non-metallic decorative inlays in La Tène jewellery - contribution of archaeometry to the understanding of production technologies, Archaeol. Anthropol. Sci. 16 (2024) 60.

[31] Regert, M., Rodet-Belarbi, I., Mazuy, A., Dantec, G., Dessì, R.M., Henry, A., Rageot, M., Briz, S., 2019. Birch bark tar in the Roman world: the persistence of an ancient craft tradition. Antiquity.. 93.

[32] R.J. Stacey, J. Dunne, S. Brunning, T. Devièse, R. Mortimer, S. Ladd, K. Parfitt, R. Evershed, I. Bull, Birch bark tar in early Medieval England – continuity of tradition or technological revival? J. Archaeol. Sci.: Reports 29 (2020) 102118.

[33] I.M. Stead, The Battersea Shield, Published for the Trustees of the British Museum by British Museum Publications, London, 1985.

[34] Megaw, J.V.S., Megaw, M.R., 1990. The Basse-Yutz find: masterpieces of celtic art : the 1927 discovery in the British museum. Soc. Antiquaries London.

[35] Plenderleith, H.J., Maryon, H., 1953. The Battersea Shield (No. P.1083/A/257). British Museum, London.

[36] K. Parfitt, Iron Age Burials from Mill Hill, Deal. British Museum Press, London, 1995.

[37] R. Stacey, Analysis of a Black Adhesive Used on an Iron Age Strap Fitting (1990,0102.27) from Deal, Kent, UK (No. CSR Analytical Request no. Ar2012-86), Department of Conservation and Scientific Research, London, 2013.

[38] I.M. Stead, British Iron Age Swords and Scabbards, The British Museum Press, London, 2006.

[39] M. Rageot, I. Théry-Parisot, S. Beyries, C. Lepère, A. Carré, A. Mazuy, J.-J. Filippi, X. Fernandez, D. Binder, M. Regert, Birch bark tar production: experimental and biomolecular approaches to the study of a common and widely used prehistoric adhesive, J. Archaeol. Method. Theory. 26 (2019) 276–312.

[40] E. Aveling, C. Heron, Identification of birch bark tar at the mesolithic site of star carr, Anc. Biomol. 2 (1998).

[41] R. Ekman, The suberin monomers and triterpenoids from outer bark of Betula verrucosa Ehrh, Holzforschung. 37 (1983) 205–211.

[42] E.W.H. Hayek, P. Krenmayr, H. Lohninger, Identification of archaeological and recent wood tar pitches using gas chromatography/mass spectrometry and pattern recognition, Anal. Chem. 62 (1990) 2038–2043.

[43] M. Rageot, Les Substances Naturelles En Méditerranée nord-Occidentale (VIe-Ie Millénaire BCE) : Chimie Et Archéologie Des Matériaux Exploités Pour Leurs Propriétés Adhésives Et Hydrophobes (Doctorat), Université Nice Sophia Antipolis, 2015.

[44] E.W.H. Hayek, U. Jordis, W. Moche, F. Sauter, A bicentennial of betulin, Phytochemistry 28 (1989) 2229–2242.

[45] K. Helwig, V. Monahan, J. Poulin, The identification of hafting adhesive on a slotted antler point from a southwest Yukon Ice Patch, Am. Antiq. 73 (2008) 279–288.

[46] Y. Hautevelle, R. Michels, F. Malartre, A. Trouiller, Vascular plant biomarkers as proxies for palaeoflora and palaeoclimatic changes at the Dogger/Malm transition of the Paris Basin (France), Org. Geochem. 37 (2006) 610–625.

[47] B.G.K. van Aarssen, R. Alexander, R.I. Kagi, Higher plant biomarkers reflect palaeovegetation changes during Jurassic times, Geochim. Cosmochim. Acta 64 (2000) 1417–1424.

[48] R.P. Evershed, S.J. Vaughan, S.N. Dudd, J.S. Soles, Fuel for thought? Beeswax in lamps and conical cups from Late Minoan Crete, Antiquity. 71 (1997) 979–985.

[49] M. Regert, S. Colinart, L. Degrand, O. Decavallas, Chemical alteration and use of beeswax through time : accelerated ageing test and analysis of archaeological samples from various environmental contexts, Archaeometry. 43 (2001) 549–569.

[50] M. Roffet-Salque, M. Regert, R.P. Evershed, A.K. Outram, L.J.E. Cramp, O. Decavallas, J. Dunne, P. Gerbault, S. Mileto, S. Mirabaud, M. Pääkkönen, J. Smyth, L. Šoberl, H.L. Whelton, A. Alday-Ruiz, H. Asplund, M. Bartkowiak, E. Bayer-Niemeier, L. Belhouchet, F. Bernardini, M. Budja, G. Cooney, M. Cubas, E.M. Danaher, M. Diniz, L. Domboróczki, C. Fabbri, J.E. González-Urquijo, J. Guilaine, S. Hachi, B.N. Hartwell, D. Hofmann, I. Hohle, J.J. Ibáñez, N. Karul, F. Kherbouche, J. Kiely, K. Kotsakis, F. Lueth, J.P. Mallory, C. Manen, A. Marciniak, B. Maurice-Chabard, M.A. Mc Gonigle, S. Mulazzani, M. Özdoğan, O.S. Perić, S.R. Perić, J. Petrasch, A.-M. Pétrequin, P. Pétrequin, U. Poensgen, C. Joshua Pollard, F. Poplin, G. Radi, P. Stadler, H. Stäuble, N. Tasić, D. Urem-Kotsou, J.B. Vuković, F. Walsh, A. Whittle, S. Wolfram, L. Zapata-Peña, J. Zoughlami, Widespread exploitation of the honeybee by early Neolithic farmers, Nature 527 (2015) 226–230.

[51] Connan, J., 2012. Le Bitume Dans L'antiquité. Éditions Errance.

[52] P. Burger, R.J. Stacey, S.A. Bowden, M. Hacke, J. Parnell, Identification, geochemical characterisation and significance of bitumen among the grave goods of the 7th century mound 1 ship-burial at Sutton Hoo (Suffolk, UK), PLoS. One 11 (2016) e0166276.

[53] S. Chapman, D. Mason, Literature review: the use of paraloid B-72 as a surface consolidant for stained glass, J. Am. Inst. Conserv. 42 (2003) 381–392.

[54] Rageot, M., Fernandez, X., Filippi, J., Sarrazin, E., Pêche-Quilichini, K., Py, V., Delhon, C., Regert, M., 2010. Du Brai De Bouleau En Corse à l'âge du fer ; Nouvelles Données chimiques, Environnementales Et Archéologiques. Liège.

[55] M. Rageot, A. Mötsch, B. Schorer, A. Gutekunst, G. Patrizi, M. Zerrer, S. Cafisso, J. Fries-Knoblach, L. Hansen, R. Tarpini, D. Krausse, T. Hoppe, P.W. Stockhammer, C. Spiteri, The dynamics of Early Celtic consumption practices: a case study of the pottery from the Heuneburg, PLoS. One 14 (2019) e0222991.

[56] C.F.C. Hawkes, An unpublished Celtic brooch from Danes' Graves, Kilham, Yorks, Antiquaries J. 26 (1946) 187–191.

[57] Adams, S., Giles, M., Cartwright, C., Koch, T.J., Stacey, R.J., In prep. The Danes Graves Brooch: buried, bequeathed and borrowed. Antiquaries J..

[58] S. Croix, M. Neiß, S.M. Sindbæk, The réseau opératoire of urbanization: craft collaborations and organization in an early medieval workshop in Ribe, Denmark, Cambridge Archaeol. J. 29 (2019) 345–364.

[59] B. Huber, D.G. Vassão, P. Roberts, Y.V. Wang, T. Larsen, Chemical modification of biomarkers through accelerated degradation: implications for ancient plant identification in archaeo-organic residues, Molecules. 27 (2022) 3331.

[60] R.J. Stacey, The composition of some Roman medicines: evidence for Pliny's Punic wax? Anal. Bioanal. Chem. 401 (2011) 1749–1759.

[61] S. Ghezal, E. Ciesielski, B. Girard, A. Creuzieux, P. Gosnell, C. Mathe, C. Vieillescazes, R. Roure, Embalmed heads of the Celtic Iron Age in the south of France, J. Archaeol. Sci. 101 (2019) 181–188.

[62] S.S. King, What Makes War? Assessing Iron Age warfare Through Mortuary Behaviour and Osteological Patterns of Violence. Unpublished PhD Thesis, University of Bradford, 2012.

[63] I. ArmitJ. Bradbury, C. Scarre (Eds.), The visible dead: ethnographic perspectives on the curation, display and circulation of human remains in Iron Age Britain, Engaging With the Dead, Studies in Funerary Archaeology (2017) 163–173.

[64] M. Giles, Bog bodies: Face to Face With the Past, Manchester University Press, 2020.

[65] B.R.T. Simoneit, Biomass burning — a review of organic tracers for smoke from incomplete combustion, Appl. Geochem. 17 (2002) 129–162.

[66] E.A. Reber, M.T. Kerr, H.L. Whelton, R.P. Evershed, Lipid residues from low-fired pottery, Archaeometry. 61 (2018) 131–144.

[67] D. Cnuts, S. Tomasso, V. Rots, The role of fire in the life of an adhesive, J. Archaeol. Method. Theory. 25 (2017) 839–862.

[68] S. Croft, A.C. Colonese, A. Lucquin, O.E. Craig, C. Conneller, N. Milner, Pine traces at Star Carr: evidence from residues on stone tools, J. Archaeol. Sci.: Reports 21 (2018) 21–31.

[69] P. Schossler, I. Fortes, J.C.D. Júnior, F. de, F. Carazza, L.A.C. Souza, Acrylic and vinyl resins identification by pyrolysis-gas chromatography/mass spectrometry: a study of cases in modern art conservation, Anal. Lett. 46 (2013) 1869–1884.

[70] A. Vinçotte, E. Beauvoit, N. Boyard, E. Guilminot, Effect of solvent on PARALOID® B72 and B44 acrylic resins used as adhesives in conservation, Herit. Sci. 7 (2019) 42.

[71] S. Koob, The use of paraloid B-72 as an adhesive: its application for archaeological ceramics and other materials, Studies in Conservation 31 (1986) 7–14.

[72] Wolfe, J., Grayburn, R., Khanjian, H., Heginbotham, A., Phenix, A., 2017. Deconstructing Incralac: a formulation study of acrylic coatings for the protection of outdoor bronze sculpture.

[73] G. Chiavari, I. Ioele, S. Prati, P. Santopadre, Py-GC-MS of the synthetic polymers used in past restorations on Giotto's mural paintings at the Scrovegni Chapel (Padova), Chromatographia 56 (2002) 763–767.

[74] L. Osete-Cortina, M.T. Doménech-Carbó, Characterization of acrylic resins used for restoration of artworks by pyrolysis-silylation-gas chromatography/mass spectrometry with hexamethyldisilazane, J. Chromatogr. A 1127 (2006) 228–236.

[75] C. Selwitz, Cellulose nitrate in conservation, Research in Conservation (1988).

[76] E. Noake, D. Lau, P. Nel, Identification of cellulose nitrate based adhesive repairs in archaeological pottery of the University of Melbourne's Middle Eastern archaeological pottery collection using portable FTIR-ATR spectroscopy and PCA, Herit. Sci. 5 (2017) 3.

[77] J.W. Brailsford, Notes on the battersea shield and two iron age helmets from Britain, Tirada a Parte de La Crónica Del IV Congreso Internacional de Ciencias Prehistóricas y Protohistóricas, Zaragoza, Madrid, 1956 1954.

[78] A. Kurzweil, D. Todtenhaupt, Technologie der Holzteergewinnung, Acta praehistorica et archaeologica 23 (1991) 63–91.

[79] H.J. Plenderleith, The Conservation of Anttiquities and Works of art. Treatment, repair, and Restoration, Oxford University Press, London, 1956.

[80] E. Waś, T. Szczęsna, H. Rybak-Chmielewska, Application of gas chromatography with the mass detector (GC-MS) technique for detection of beeswax adulteration with paraffin, J. Apicultural Sci. 59 (2015) 143–152.

[81] Z. Wang, L. Yan, Y. Ma, A. Shao, J. Mei, K. Chen, Pilot study on the lipid residues in the clay core of Lost-wax process, J. Archaeol. Sci.: Reports 49 (2023) 103990.