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Chemical analyses reveal dual functionality of Early Mesolithic birch tar at Krzyż Wielkopolski (Poland)

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ABSTRACT

Birch bark tar played an important role as an adhesive in the European Middle Palaeolithic and Mesolithic with key practical functions. For the Mesolithic in northern Europe, tar is suggested to have a variety of functions, including decorative, on various artefacts such as amber beads, antler and bone objects. However, no chemical characterisation has been conducted to confirm the organic composition of such decorations. To address this gap, we conducted organic residue analysis on archaeological samples taken from three artefacts excavated at the Early Mesolithic site Krzyż Wielkoposki (Poland). These include a wooden shaft, an antler point, and a perforated antler object with ornamental engravings. We further replicated two potential aceramic birch bark tar production techniques and employed Principal Component Analysis (PCA) for molecular differentiation. Our results show that birch bark tar served a dual functionality in tool hafting and ornamentation at Krzyż. We found compositional differences among archaeological samples, but comparing these results to experimental data presents significant challenges. Our findings shed light on birch bark tar versatility, and imply more widespread use of birch bark tar as a decorative element in the European Mesolithic than has hitherto been recognised.

1. Introduction

Birch bark tar (hereafter referred to as birch tar) is a material used for a variety of everyday purposes throughout prehistory. It is the earliest known human-made adhesive, employed by Neanderthals in the Middle Palaeolithic (Grünberg et al., 1999; Mazza et al., 2006; Niekus et al., 2019). In these early contexts, the use of other adhesive materials, for example bitumen, both in Europe (Schmidt et al., 2024) or in the near East (Boëda et al., 2008; Hauck et al., 2013), and Pinaceae resin in central Italy (Degano et al., 2019), is also evidenced. In subsequent periods, birch tar is continuously found in archaeological contexts up to the Medieval period (Hayek et al., 1990; Urem-Kotsou et al., 2018; Regert et al., 2019; Stacey et al., 2020; Rageot et al., 2021; Little et al., 2022; Bernardini et al., 2023; Ren et al., 2023; Koch et al., 2024b). This wider distribution of birch tar may partly be due to its strong adhesive properties (Kozowyk et al., 2017a; Schmidt et al., 2021, 2022; Koch and Schmidt, 2023), excellent preservation (Kozowyk et al., 2020) and hydrophobic properties (Kabaciński et al., 2023). The oldest pieces of birch tar were used for the backing of stone tools (Mazza et al., 2006; Niekus et al., 2019; Schmidt et al., 2023), but it gained a more diverse functionality during the Mesolithic, notably in northern Europe (for an overview, see Little et al., 2022).

Mesolithic uses of birch tar include hafted composite tools and nondescript lumps, some bearing tooth imprints often interpreted as chewing marks (Aveling and Heron, 1999; Kashuba et al., 2019). Chemical analyses confirmed the use of birch tar as the hafting adhesive on osseous points (Aleo et al., 2023; Kabaciński et al., 2023), for flint inserts on bone (Vahur et al., 2011; Bjørnevad et al., 2019; Osipowicz et al., 2020) or wooden projectile points (Larsson et al., 2016). However, birch tar has been suggested not only to have a utilitarian purpose, but also to have been used as a decorative element. This suggestion has been made for various types of artefacts, such as amber beads, antler axes, bone axes, and daggers (for an overview, see Little et al., 2022). More specifically, multiple pieces of antler are reported as being decorated

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with a black resinous/tarry substance. This black residue sometimes fills an ornamental pattern engraved into the antler (Malmer and Magnusson, 1955, and references therein; Trąbska and Trybalska, 2017). Certain authors suggest birch tar to be the material filling these engravings. Only a small number of chemical characterisations were conducted on the preserved residues to identify their nature. Trąbska and Trybalska (2017) attempted to identify the dark black substance filling an ornamental pattern on an antler artefact from Rusinowo, dating to the Late Palaeolithic (~10700 BCE), using infrared spectroscopy followed by elemental analyses. The results, however, did not allow any organic adhesive material to be detected, and the residue was interpreted as ash remains. Sulgostowska (1997) reports spectral analyses on a black antler decoration, possibly indicating a wood tar of birch origin, however, details on the analysis or results are not given. Despite the growing corpus of accounts mentioning black decorative infills on different types of Mesolithic artefacts in northern Europe, there remains an absence of information on the origin and nature of the material used to enhance these engravings.

To address this gap, we conducted gas chromatgography – mass spectrometry (GC–MS) on residues sampled from four artefacts discovered at the Early Mesolithic site Krzyż Wielkopolski, Poland (from here on referred to as Krzyż, see Fig. 1). The site is located on the lower northern terrace of the Noteć River with artefacts being recovered from its sandy terraces. The site has excellent organic preservation due to waterlogged conditions. Previous studies have already shown that birch tar was employed for hafting purposes at this site (Kabaciński et al., 2023). The discovery of additional artefacts with residues from the same site context, recovered during the 2019 excavation campaign, provides the opportunity to test whether birch tar was consistently used, and served more than hafting purposes. Black residues were identified on a wooden shaft, and antler point and a perforated antler object. The latter bears engraved patterns infilled with a black residue. In a first step, all three objects were sampled to identify the adhesive's composition and shed light on adhesive use and function in relation to different artefact types. Secondly, we compared the tar's molecular signatures with experimentally produced birch tar samples made with aceramic techniques. Regarding the latter, previous studies have found molecular differences using ceramic production techniques (Rageot, 2015; Rageot et al., 2019), however, applying chemical analyses to aceramic production methods has shown significant challenges (Kozowyk et al., 2023; Schmidt et al., 2023; Chasan et al., 2024).

To better understand possible aceramic production processes, we replicated two of the most frequently discussed aceramic production methods: the condensation method (Schmidt et al., 2019; Blessing and Schmidt, 2021) and the raised structure (Kozowyk et al., 2017b; Schenck and Groom, 2018). We did this to narrow down the production technique that might have been employed at Krzyz, while also assessing any potential differences in production linked to the adhesive function, i.e. hafting versus decoration.

2. Materials and methods

2.1. Archaeological samples

We sampled three artefacts discovered during the 2019 excavation at the site Krzyż Wielkopolski 7 in western Poland (Fig. 1), dated to the late Preboreal-Boreal period. A more detailed description of the site context is given in the supplementary material. Two artefacts are likely components of composite tools or weapons. These include a wooden pine (*Pinus* subg. *Pinus*) shaft with black residue towards its proximal end (KRZYZ-7–2019/23, depicted in Fig. 2b), and an antler point covered by a thicker black substance, primarily on its proximal end (KRZYZ-7–2019/86). The latter bears a flat impression on one side, suggesting it might have been hafted (left image in Fig. 2a). On the opposite side of the antler point, the residue reveals evenly spaced imprints on its surface (right image in Fig. 2a). The point and shaft discussed here were discovered in different and distant trenches, hence certainly relate to different objects. The third sample was taken from a perforated object

Fig. 1. Map indicating site location of Krzyż Wielkopolski (credit: J. Kabaciński).

Fig. 2. Artefacts with visible residue from Krzyż. (a) Antler point with residues and possible ligature imprint on one side (KRZYZ-7–2019/86); (b) wooden shaft with residues on its proximal end (KRZYZ-7–2019/23); (c) fragment of perforated antler object, decorated with engraved patterns that are filled with a black residue (KRZYZ-7–2019/178, the close-up image is to scale, the smaller image of the entire artefact is not).

crafted from deer antler, featuring ornamental incisions filled with black residue (KRZYZ-7–2019/178, Fig. 2c). For details on the wood and osseous technology, see the supplementary material. To assess the preservation of biomarkers we sampled bark from a birch trunk recovered in trench T1/2022, dated to the Boreal period, and compared it to a modern bark sample (*Betula pendula*) (for photographs, see Fig. S5 of the supplementary material). To permanently record the shape of the antler artefact and the ornamental pattern, it was scanned using a 3D Artec Spider and 3D models were created using Artec Studio v.16. The scan is publicly available at the data repository NAKALA (https://doi.org/10.34847/nkl.0e8as770).

2.2. Experimental samples

We conducted an experimental program with the aim of comparing two aceramic birch tar production methods and their molecular signature. For this, we produced 20 reference samples with the two most frequently discussed aceramic birch tar production techniques: the raised structure (Osipowicz, 2005; for details on the production method, see Kozowyk et al., 2017b; Schenck and Groom, 2018) and the condensation method (for details on the production method, see Schmidt et al., 2019). Although more production methods are currently debated (Kozowyk et al., 2017b; Koch and Schmidt, 2022; Chasan et al., 2024), these two have very opposite production parameters that may result in the most significant influence on molecular composition. This is because the raised structure tar is produced in oxygen-depleted, allotherm conditions, whereas tar obtained through condensation is produced autotherm and in open air. In brief, the condensation method consists of directly burning birch bark next to a tilted river cobble onto which the tar then condenses. The raised structure consists of a two-chamber set-up. An upper, earthen dome contains birch bark, and a fire is lit around this sealed dome. Below this, a second underground chamber with a receptacle serves to contain the tar that drips down during the process. Ten samples were produced with each method. Details and images of the tar production can be found in the supplementary material. The raised structures were conducted simultaneously with the aim to reduce variability, with the temperature monitored in 3 of the setups.

2.3. Gas chromatography – Mass spectrometry

The sampled residues were analysed following established methods for archaeological adhesives (Rageot et al., 2019, 2021; Koch et al., 2024b). Samples were crushed and weighed. Tetratriacontane (*n*-C34, 10 μL of 2 mg/mL cyclohexane solution) served as the first internal standard. Sample powders underwent solvent extraction using dichloromethane (DCM) at a ratio of 2–3 mg/mL and two 15-minute sonication cycles. A DCM blank sample was included to check for in-laboratory contamination. A 100 μL aliquot was taken from each sample and dried under nitrogen flow. Each subsample was then derivatized using 50 μL of N,Obis(trimethylsilyl)trifluoroacetamide (BSTFA), 10 μL of DCM, and 2 μL of pyridine (heated for 60 min at 70° C). After drying the aliquot under nitrogen flow, 90 μL DCM were added. Hexadecane (*n*-C16, 10 μL of a 0.2 mg/mL cyclohexane solution) was added as the second internal standard before injection into an Agilent J&W HP-5MS GC Column 30 m x 0.32 mm x 0.25 μm film thickness). The inlet temperature was set at 300° C. The oven temperature was programmed to increase from 50° C (with a 2-minute hold time) to 150° C at a rate of 10° C/min and then directly raised to 320° C at a rate of 4° C/min, maintaining this temperature for 15 min. GC–MS analyses used a Shimadzu GC 2010 PLUS in splitless injection mode with a column flow of 6 mL/min. Mass spectra were recorded with a Shimadzu QP2010 ultra (electron ionization at 70 eV, *m/z* range 50–950). Compound identification was done through comparison with the NIST library and published data (Ekman, 1983; Hayek et al., 1990; Aveling and Heron, 1998; Rageot, 2015). Internal standards were only added to the experimental samples. The raw GC–MS files of the archaeological and experimental reference samples are publicly available at the data repository NAKALA (https://doi.org/10.34847/nkl.0e8as770).

2.4. Statistical analysis

The peak integrals of all identified molecular compounds were extracted from the total ion chromatograms of the archaeological and reference tar samples. The relative abundance of each molecule was calculated to the sum of peak integrals of all identified compounds (for the main compound families detected, see Table 1). The relative abundances served as variables for Principal Component Analysis (PCA). Four different PCA's were made using different combinations of variables: 1) birch tar bio- and degradation markers and fatty acids/diacids (n = 20), 2) birch tar bio- and degradation markers (n = 11), 3) only birch tar degradation markers (n = 7) and 4) only fatty acids/diacids (n = 9). The compound categories used for PCA are listed in Table 1.

Table 1
Compound categories as used for statistical analysis (PCA). A full list of compounds identified in the archaeological and experimental samples can be found in the supplementary material.

Birch tar biomarkers	Birch tar degradation markers	Fatty acids/diacids
Betulin	Betulone*	Azelaic acid
Lupeol	Lupenone*	Hexadecanoic acid
Betulinic acid	Lupa-2,20(29)-diene	Heptadecanoic acid
Erythrodiol	Lupa-2,20(29)-dien-28-ol	*trans*-9-Octadecenoic acid
	Allobetulin	Octadecanoic acid
	28-oxoallobetul-2-ene	Eicosanoic acid
	Allobetul-2-ene	Heneicosanoic acid
		cis-13-Docosenoic acid
		Docosanoic acid

*also natural degradation markers found in minor amounts in birch bark, but increased amount through oxidation during birch tar production

3. Results

3.1. Chemical identification of archaeological samples

All archaeological samples yielded molecular constituents characteristic of birch tar. The residues from the antler point, wooden shaft and antler decoration contained varying combinations of triterpenoid compounds, including bark biomarkers betulin and lupeol, as well as natural degradation markers associated with oxidation, such as betulone. Lupenone is biomarker, but its amount can increase through oxidation during birch tar production (Ekman, 1983). Degradation markers specifically linked to the production of tar from birch bark, 28-oxo-allobetul-2-ene and allobetulin, align with prior identifications of birch tar (Rageot et al., 2019). Our samples contained a range of saturated and unsaturated fatty acids and diacids, which might be related to the decomposition of suberin during the production (Ekman, 1983). However, the exact origin of these acids and diacids remains unclear for now. Minor traces of diterpenoid compounds (<1% of all identified compounds) including dehydroabietic acid, abietic acid, tetrahydroretene and retene, were identified in all archaeological samples. In addition, we found cholesterol and two derivatives (cholesta-3,5-dien-7-one and cholesta-4,6-dien-3-ol) in the sample taken off the antler decoration (Fig. 3). This sample has a lower abundance of triterpenoid compounds (73 %) and a higher abundance of fatty acids (17 %) compared to the other archaeological tars (Table 2). Cholesterol and its degradation markers might indicate the presence of a fatty substance of animal origin. We further note the presence of a homologous compound series (indicated through asterisk in Fig. 23, mass spectra of each compound in Fig. S4 of the supplementary material). These elute at retention times 36.04, 37.82 and 39.23, with a possibly related compound eluting at 30.67. The *m/z* 204 and 217 are characteristic for sugar compounds, possibly derived from cellulose (Bae et al., 2012). Levoglucosan, for example, has previously been identified in experimentally made birch tar samples, and could hence be linked to the production process (Kozowyk et al., 2023). The chromatograms for samples KRZYZ-7–2019/86 and KRZYZ-7–2019/23, and a list of identified compounds can be found in the supplementary material.

3.2. Chemical signatures of Boreal versus modern bark

The chromatograms of both bark samples are shown in Fig. S5 of the supplementary material. The modern bark sample (*Betula pendula*)

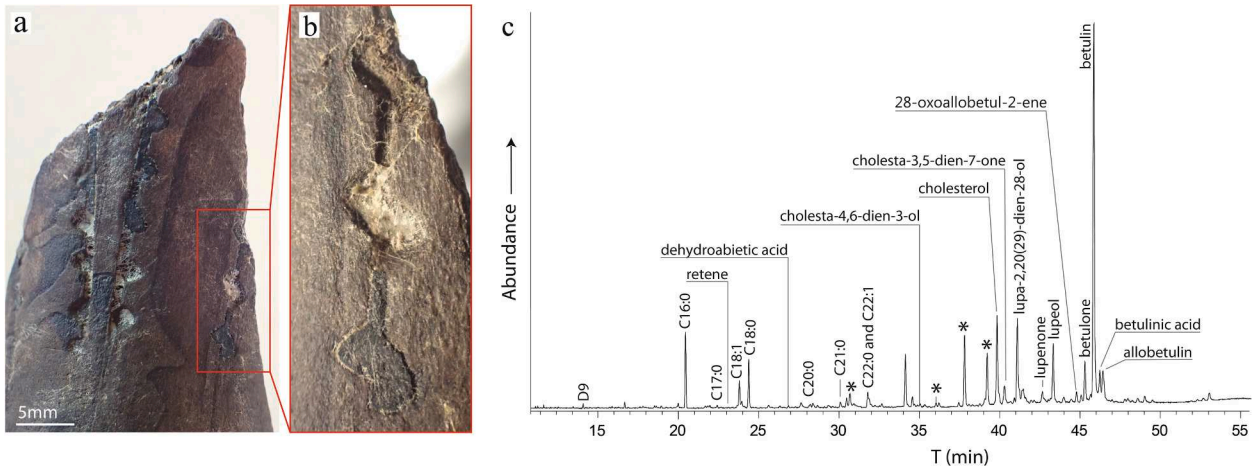

Fig. 3. Results obtained from the black residue filling the engraved decorative pattern on the antler object (KRZYZ-7–2019/178). (a) Photograph of the decorative pattern with black residue filling some of the elements (red frame indicates sampling location before sampling). (b) Close up photograph of the sampled location after sampling (residue was taken from upper half circles). (c) Chromatogram of black substance filling the decorative pattern on the antler. DX = Diacids (X = carbon n), CX:Y = Fatty acids (X = carbon n, Y = n of unsaturations). Asterisk indicates an unidentified homologous compound series (for mass spectra see Figure S4 in the Supplementary Information). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Relative percentages of main molecular families identified in archaeological samples and experimental samples (the latter show average values for each set of 10 experiments). Note that unidentified compounds are not included in the calculation. Lab ID (for the archaeological samples) refers to the sample ID used in the laboratory, but the sample ID is used throughout this study.

Samples	Lab ID	Triterpenoid markers [%]	Fatty acids/diacids [%]	Diterpenoid markers [%]	Cholesterol + derivatives [%]
KRZYZ-7–2019/86 (antler point)	TK8360	97	2	< 1	0
KRZYZ-7–2019/23 (wooden shaft)	TK8363	98	2	< 1	0
KRZYZ-7–2019/178 (antler decoration)	TK8362	73	17	< 1	10
Condensation method	CM01-10	91	8	0	0
Raised structure	RS01-10	85	14	0	0

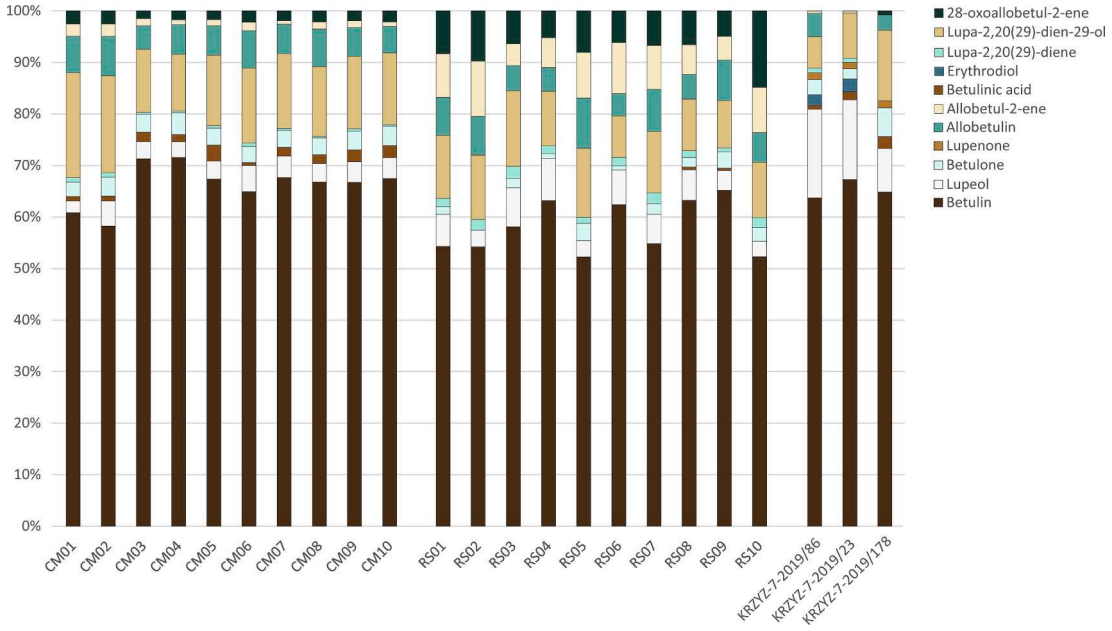

Fig. 4. Relative percentages of birch tar related compounds (as of the sum of all birch tar bio- and degradation markers). CM = Condensation method tar, RS = Raised structure tar, KRZYZ-7–2019/86 = Antler point tar, KRZYZ-7–2019/23 = Wooden shaft tar, KRZYZ-7–2019/178 = Antler decoration tar.

consists in the majority of the biomarkers betulin and lupeol, and to a lesser extent betulinic acid. We further detected betulone, which forms through oxidation from betulin, and sitosterol. This is in line with previous analyses of modern birch bark (Ukkonen and Erä, 1979; Aveling and Heron, 1998). The bark recovered from the Boreal layer in Krzyż shows the presence of the same biomarkers (betulin, lupeol and betulinic acid), and the oxidised products betulone and lupenone (oxidation product forming from lupeol). The commonly referenced biomarker erythrodiol (for example in Ekman, 1983) could not be identified, and lupa-2,20(29)-dien-28-ol (previously mentioned by Aveling and Heron, 1998) was not detected. Ekman (1983) reports erythrodiol as a biomarker of birch bark, but as shown by two previous studies (Hayek et al., 1990; Aveling and Heron, 1998) and the results of this study, it is not always present in modern, or archaeological birch bark. It remains unclear if the absence of some biomarkers is due to environmental influences, degradation, or to the genus, which we could not identify for the Boreal bark.

3.3. Experimental aceramic tar

The temperature measured in three of the raised structures is shown in Fig. S2 of the supplementary material (one structure was measured in both the upper and lower container). All experimentally made birch tar samples contain most of the commonly found bio- and degradation markers of birch tar (Fig. 4). We could not identify erythrodiol in any of the tars made with the raised structure (RS) or condensation method (CM). We found that it should elute at a similar retention time as 28-oxallobetul-2-ene, which is present in all samples and a higher abundance might obscure the presence of erythrodiol. Lupenone is equally absent in tars made with both methods. Betulinic acid was detected in all CM tar, but only as minor traces in two of the RS tars. Varying combinations of saturated and unsaturated fatty acids, as well as diacids, were detected in all samples. Azelaic acid was found more frequently in the CM samples (9 of 10) than the RS (1 of 10), whereas eicosanoic acid was found more frequently in the RS tar (9 of 10, CM samples: 4 of 10). Traces of one alkane (n-C_{21}) were found in one of the RS samples. We further identified levoglucosan in all experimental samples, which is coherent with previous studies (Kozowyk et al., 2023). Details on all compounds detected in our experimental samples are listed in Table S2 of the supplementary material.

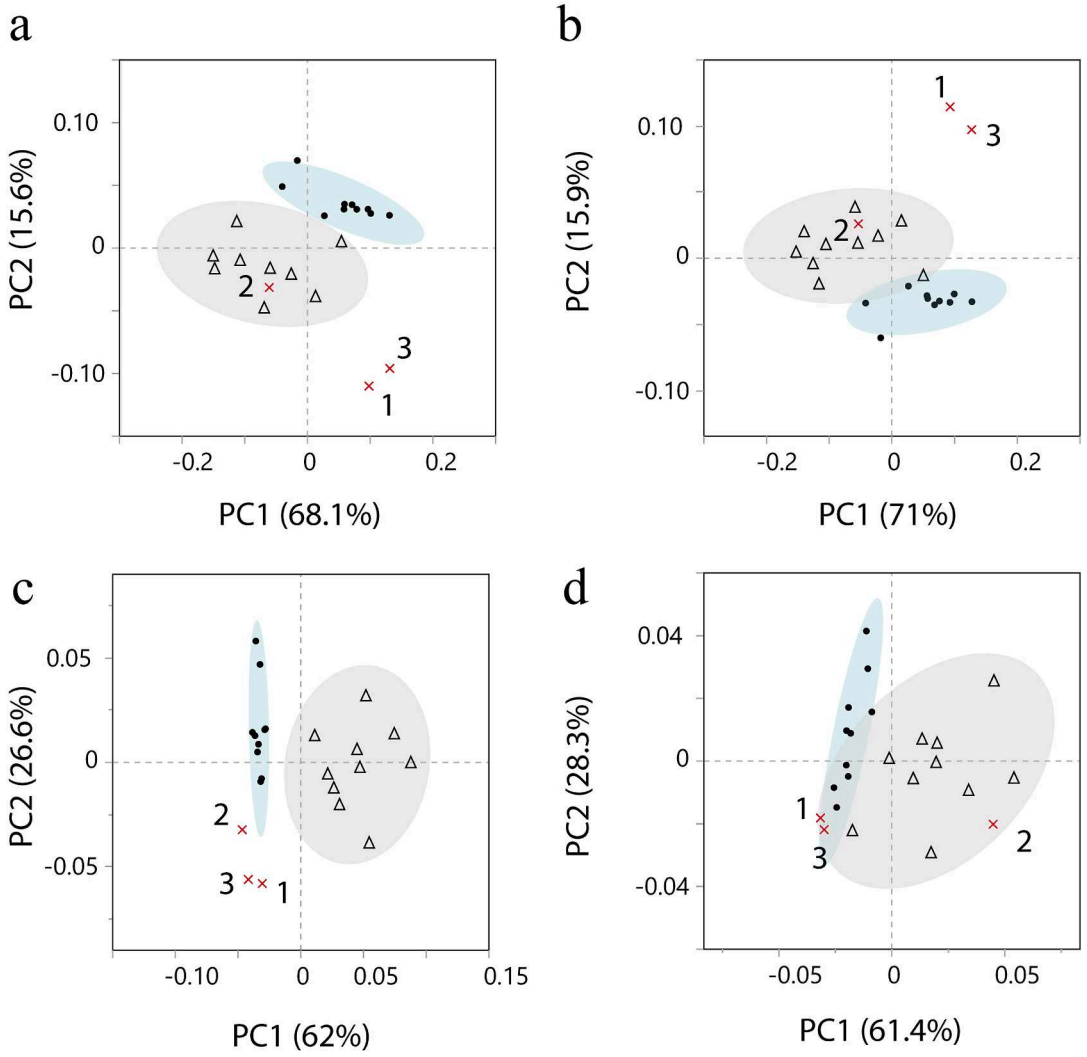

Fig. 5. PCA plots showing the molecular variation (as calculated from relative abundances) among experimental and archaeological samples using different sets of variables: a) all birch tar bio and degradation markers + fatty acids/diacids (n = 20) b) all birch tar bio- and degradation markers (n = 11), c) natural and anthropogenic birch tar degradation markers (n = 7) and d) fatty acids/diacids (n = 9). Experimental samples: ● = Condensation method, Δ = Raised structure. × (red) = Archaeological samples: 1 = KRZYZ-7–2019/86 (antler point), 2 = KRZYZ-7–2019/178 (antler decoration), 3 = KRZYZ-7–2019/23 (wooden shaft). Ellipses show 95 % confidence intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Statistical comparison (PCA)

PCA allowed us to identify differences between the two experimentally reproduced tar types (CM and RS). The two groups form distinct clusters indifferent to which of the four sets of variables was used to perform the analyses (Fig. 5). RS tar and CM tar can thus be differentiated using birch tar bio- and degradation markers and the fatty acid/diacid profile, or only one of these compound groups. Fig. 5a-b shows a similar differentiation of the archaeological samples in regards to the two experimental groups based on the complete set of triterpenoids and fatty acids/diacids (Fig. 5a) and only the triterpenoid compounds (Fig. 5b). Here, the tar sample from the antler decoration plots with the RS whereas the other two samples from the antler point and wooden shaft are grouped together but apart from the experimental samples. However, when using only the degradation markers found in the birch tars, the opposite can be observed. Fig. 5c shows the tar from the antler decoration plotting slightly closer with the CM. If we use only the fatty acid/diacid profile to differentiate our samples, the reference samples still form clusters but the confidence ellipses slightly overlap. The antler tar lies within the RS and the other two archaeological tars lie in the interface of the two groups. These plots show that depending on which molecular groups (different molecular families but also within triterpenoids) are used for PCA, a different result is obtained. A trend can be seen within the archaeological samples, always differentiating between the antler decoration tar versus the antler point and wooden shaft tars. The latter two plot together indifferently of the variables used, suggesting they are molecularly more similar to each other than to the antler tar. In three of the PCA's (Fig. 5a-c), the two hafting tars plot entirely outside of the confidence intervals of either of the production method clusters. This means that they do not fall within the range of variation of both methods.

4. Discussion

4.1. Limitations and perspectives in molecular differentiation of birch tar production methods

Based on a set of experimental birch tar samples using production methods with ceramics (double-pot and single pot), previous studies showed that specific molecular markers are only found in *per descensum* production systems (Rageot, 2015; Rageot et al., 2019). Three recent studies have tested whether this difference can be found in aceramic birch tar production methods relying on similar principles (Kozowyk et al., 2023; Schmidt et al., 2023; Chasan et al., 2024), but characteristic markers are either not present in the experimental samples or their abundance is too variable to be confidently used for differentiation. This limitation in aceramic conditions hence calls for a different approach. Kozowyk et al. (2023) applied PCA to differentiate four aceramic production methods using a sample set of 7 samples. The authors state that the sample size is likely the reason for inter- and intra-method variation for most compounds, limiting the differentiation between production methods relying on similar principles. Our results, using an increased sample size per method, also show that the CM and RS can be reliably differentiated using different sets of variables (e.g. biomarkers, degradation markers, fatty acids/diacids). Albeit increasing the sample size, we also observe a higher variability in the RS samples (as already shown by Kozowyk et al., 2023). Still, the molecular difference between these methods should be sufficient to identify an archaeological sample if it was made with a similar method. In a recent study, Chasan et al. (2024) showed that when comparing the aceramic methods with the molecular signature of archaeological samples, the choice of variables significantly influenced the outcome of a PCA. Our results stand in line with this finding. By using fatty acids and triterpenoid compounds (Fig. 5a), only triterpenoids (Fig. 5b) or only fatty acids/diacids (Fig. 5d), it seems that the antler decoration tar is molecularly similar to the RS. However, if plotted only with triterpenoid degradation markers (Fig. 5c), it clusters closer to the CM. Similarly, the hafting tars seem to plot entirely separate from both techniques, which might suggest a completely different method to having been used. Their fatty acid/diacid signature, however, more closely aligns with the CM (Fig. 5d). As a result, we argue that modern experimentally produced birch tar samples can be differentiated, because these have been produced in similar conditions and have undergone only limited post-production degradation caused by natural or anthropogenic factors. It seems all the more challenging to compare archaeological samples to these experimentally replicated tars. This is partly due to anthropogenic alteration of tar through cooking and reuse, but also the unknown degree of degradation over thousands of years through environmental influences and diagenetic processes. Such effects can alter the molecular signature to a point where it no longer resembles its original composition. A recent study using spectroscopic methods to differentiate aceramic tar production, based on molecules that only undergo limited taphonomic processes (in birch tar: suberin), showed that Palaeolithic tar at Königsaue was made in an underground, oxygen-depleted condition (Schmidt et al., 2023). Using infrared spectroscopy, in addition to molecular characterisation, may provide a promising approach to fully characterise archaeological birch tar artefacts.

Besides these limitations, our study provides insight into the compositional differences between archaeological samples. We argue that it may be possible to compare archaeological samples with each other using a molecular approach, given that these have likely undergone similar environmental changes, or originate from the same or similar archaeological contexts. This being the case for the three birch tar samples identified here, hafting tars are more similar to each other but different from the tar used for decorative purposes. The differentiation between the samples can be related to both presence and absence, as well as the varying abundances of specific triterpenoid bio- and degradation markers, and fatty acids/diacids. It remains unclear why the abundances vary; it might be due to factors such as the initial production conditions of the tars or post-production treatments, such as cooking or rendering the tar into a more liquid state. For example, it is known that hafting tar requires specific mechanical properties which can be enhanced through cooking (Schmidt et al., 2022). Kabaciński et al. (2023) compared the composition of hafting birch tar (also from Krzyż) to an experimentally made birch tar in slow heating conditions (max. 350° C), which would, according to previous experimentations (Rageot et al., 2019, 2021) produce a liquid tar with low viscosity. It is unclear whether such tar would suffice for hafting purposes and if it does not, it may explain the use of ligatures for additional binding of composite tools at Krzyż. As an alternative explanation, Kabaciński et al. (2023) propose the use of birch tar for its hydrophobic properties (i.e. waterproofing the tool), which might be especially useful if used in aquatic environments (Koch et al., 2024a). Tar which is not used for hafting but only for decoration, may not require the same mechanical properties, as it "only" needs to adhere to the object. Due to the small sample size of archaeological material in this study, we cannot predict whether the same molecular difference would be observed in a larger sample set. What our data allows is to provide a new working hypothesis. A future study on additional decorated and hafted artefacts, from the same contexts/site and other northern European Early Mesolithic sites, is needed to test this assumption.

4.2. Our results in line with previous data on Mesolithic hafting adhesives

Previous chemical analyses on a bone implement discovered at Krzyż found that birch tar was used as a hafting agent to attach a bone point to a wooden shaft, strengthened by bast ligatures (Kabaciński et al., 2023). Birch tar as a hafting adhesive is known from multiple Mesolithic contexts across northern Europe. These hafting contexts may vary, as some objects consist of different component materials, such as bone, wood or stone (Aveling and Heron, 1998; Vahur et al., 2011; Larsson et al., 2016; Bjørnevad et al., 2019; Osipowicz et al., 2020; Aleo et al., 2023; Kabaciński et al., 2023). Our findings of birch tar on an antler point and

wooden shaft therefore fall in line with current knowledge of Mesolithic adhesives in composite hafting technologies. In our case, the point and wooden shaft were found in distant trenches and certainly represent different artefacts, however, they could be linked to the same time period (late Preboreal-Boreal). Ligatures are underlying the birch tar on the implement presented in Kabaciński et al. (2023), and we may hypothesise that the parallel grooves left in the thick tar layer on the point (Fig. 3a and Fig. S7a-b) could also be left behind by ligatures attaching two components, in this case however, on top of the tar. Similar composite tools are reported at the contemporary site Friesack in northern Germany (Gramsch, 1991, 2000). The latter have not yet been subjected to chemical analyses but the use of birch tar for hafting purposes at Krzyż (Kabaciński et al., 2023; and this study) helps strengthen our understanding of the use of the same organic adhesive (birch tar in particular) and hafting technologies in the Early Mesolithic of the north European Plain.

In our samples, we further detected minor traces which might be indicative of a conifer resin/tar (<1%), but we cannot exclude contamination from fire fuel using pine wood. Use of conifer resin is known from earlier (see Degano et al., 2019) and later contexts (Mitkidou et al., 2008; Rageot et al., 2019), but clear evidence from the Mesolithic is lacking (see Croft et al., 2018 for an exception). The North European Plain during the Early Holocene was covered by birch and pine forests with some deciduous trees, including elm and hazel (Ralska-Jasiewiczowa et al., 2004), suggesting an availability of pine resin. This is also supported by the numerous finds of pine wood artefacts at Krzyż (Kabaciński et al., 2023). Nevertheless, our results, along with the prevalent evidences of birch tar in Mesolithic Europe, suggest that birch tar was preferred over conifer resins, possibly due to its strong adhesive properties and hydrophobicity, as suggested by Kabaciński et al. (2023).

4.3. Implications of our data for decorative residues observed in Mesolithic contexts

Decorated objects, often made of antler or bone, but also amber beads, are well-known in Mesolithic contexts, characterised through geometrical patterns or scenes engraved into the artefact's surface. Multiple studies mention the presence of a resinous or tar-like substance filling these decorative engravings (Malmer and Magnusson, 1955, and references therein; Sulgostowska, 1997; Petersen, 2013; Molin et al., 2014; Toft and Petersen, 2016; Trąbska and Trybalska, 2017; Little et al., 2022). As a consequence, determining whether a residue was purposefully used to infill decorative engravings is challenging. Płonka (2003) suggests that the dark infill was used to highlight the ornamental patterns on antler objects. An alternative hypothesis, in at least some cases, is that hafting material remained stuck within the incised grooves, as suggested for the bone dagger from Motala, Sweden (Molin et al., 2014). Petersen (2013) mentions birch tar to fill engraved decorations on an amber pendant of the Maglemose culture in Denmark, but no specifics on the analyses undertaken are provided. Other studies have identified a residue as ash remains (Trąbska and Trybalska, 2017). The perforated antler from Krzyż, along with similarly decorated bone and antler artefacts dated to the Mesolithic (a similar decorated antler is presented in Sulgostowska, 1997), presents a more homogenous filling of the engraved lines and half-circles (see Fig. 3b and Fig. S7c-d). Furthermore, no indication of hafting or residue on other parts of these decorated antlers are visible. To our knowledge, we provide the first clear chemical identification confirming the use of birch tar for ornamental purposes on antler in the Mesolithic.

It remains unclear, based on our analyses, whether the relatively high amount of cholesterol and its degradation markers in our sample might suggest an intentional mixture with an animal-derived fat or animal glue. Their absence in the antler point's tar make it unlikely that these components originate from the antler itself. Animal glues (made from bone or hide collagen) are rarely discovered in archaeological contexts, likely due to their water solubility (Kozowyk et al., 2020). The mixture with birch tar might enhance its preservation, as can be hypothesised for DNA preservation in archaeological birch tar (Jensen et al., 2019; Kashuba et al., 2019). At the Neolithic site La Draga, Spain, Rageot et al. (2021) found a similar signal of cholesterol and one of its degradation markers in combination with birch tar. At La Draga it was found on a marble bracelet, but it is not clear whether its function was to assemble or decorate the object. Some additives, for example beeswax, are known to act as a plasticiser (Gaillard et al., 2015) and, if added to plant-based adhesives, it was shown to increase the adhesive's mechanical strength (Kozowyk et al., 2016). In the case of the antler piece here, adding an animal fat could have provided a more malleable glue which could facilitate the filling of the engravings and also enhance its visual appearance. A thorough investigation on the molecular signature of experimentally composed glues (birch tar with animal fat, or glue), together with tests on its adhesive properties and water-solubility will help us understand the meaning behind these findings in archaeological samples. Our findings provide a promising outlook for future analyses on engraved artefacts recovered from Mesolithic contexts, whilst confirming birch tar was used for ornamental purposes as early as the Early Mesolithic. This yields potential to evaluate the chronological persistence of birch tar use as a decorative element from the Mesolithic onwards, up to the roman antiquity (Regert et al., 2019).

5. Conclusion

While previous studies have shown that birch tar was used as a hafting agent at Krzyż, our results broaden this understanding of birch tar functionality to encompass use as a decorative element. This finding is significant because it encourages a closer look for similar decorated objects of the Mesolithic. If a stronger research focus is put on identifying decorative residues, and analytical methods are applied for their characterisation, we can broaden our understanding of birch tar use in the European Mesolithic beyond strictly utilitarian functions. Identifications of birch tar with evidence of animal fat or glue might further allow us to differentiate between adhesive technologies, and identify the advantages such a mixture yields. We show the limitations for the use of biomolecular approaches to characterise archaeological birch tar artefacts in relation to their production techniques. We advocate for caution when comparing the molecular composition of modern experimental tar samples to archaeological ones, especially considering the taphonomic influences are likely to be different or unknown. We propose, however, that a comparison might be possible between archaeological artefacts from the same site or if their archaeological context is similar. Our results have revealed molecular differences between birch tar used for hafting purposes and tar used for decoration. Such variation in function needs to be further tested in future studies drawing on larger sample sets. We argue that a deeper knowledge of the diversity of uses of tar within the Mesolithic material world has real potential to provide new insight into the technological, as well as artistic, choices people made in the production and use of birch tar.

CRediT authorship contribution statement

Tabea J. Koch: . **Jacek Kabaciński:** Writing – review & editing, Resources, Investigation, Funding acquisition. **Auréade Henry:** Writing – review & editing, Visualization, Investigation. **Benjamin Marquebielle:** Writing – review & editing, Visualization, Investigation. **Aimée Little:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Rebecca Stacey:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Martine Regert:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data will be publicly accessible on an online data repository.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2024.104591.

References

Aleo, A., Kozowyk, P.R.B., Baron, L.I., van Gijn, A., Langejans, G.H.J., 2023. 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, e0288629.

Aveling, E., Heron, C., 1998. Identification of Birch Bark Tar at the Mesolithic Site of Star Carr. Anc. Biomol. 2.

Aveling, E., Heron, C.P., 1999. Chewing tar in the early Holocene: an archaeological and ethnographic evaluation. Antiquity 73, 579–584.

Bae, M.-S., Lee, J.Y., Kim, Y.-P., Oak, M.-H., Shin, J.-S., Lee, K.-Y., Lee, H., Lee, S.Y., Kim, Y.-J., 2012. Analytical Methods of Levoglucosan, a Tracer for Cellulose in Biomass Burning, by Four Different Techniques. Asian J. Atmos. Environ. 6, 53–66.

Bernardini, F., Vaccari, L., Zanini, F., Bassetti, M., Degasperi, N., Rottoli, M., Micheli, R., 2023. Production and use of birch bark tar at the Neolithic pile-dwelling of Palù di Livenza (North-Eastern Italy) revealed by X-ray computed micro-tomography and synchrotron Fourier-transform infrared spectroscopy. Archaeometry 65, 897–907.

Bjørnevad, M., Jonuks, T., Bye-Jensen, P., Manninen, M.A., Oras, E., Vahur, S., Riede, F., 2019. The Life and Times of an Estonian Mesolithic Slotted Bone "Dagger". Extended Object Biographies for Legacy Objects. Estonian Journal of Archaeology. 2, 103–125.

Blessing, M.A., Schmidt, P., 2021. On the efficiency of Palaeolithic birch tar making. J. Archaeol. Sci. Rep. 38, 103096.

Boëda, E., Bonilauri, S., Connan, J., Jarvie, D., Mercier, N., Tobey, M., Valladas, H., Al, H., Sakhel, 2008. New evidence for significant use of bitumen in middle palaeolitic technical systems at Umm El Tlel (Syria) Around 70,000 BP. Antiquity 34, 67–83.

Chasan, R., Baron, L.I., Kozowyk, P.R.B., Langejans, G.H.J., 2024. Complicating the debate: Evaluating the potential of gas-chromatography-mass spectrometry for differentiating prehistoric aceramic tar production techniques. J. Archaeol. Sci. 164, 105960.

Croft, S., Colonese, A.C., Lucquin, A., Craig, O.E., Conneller, C., Milner, N., 2018. Pine traces at Star Carr: Evidence from residues on stone tools. J. Archaeol. Sci. Rep. 21, 21–31.

Degano, I., Soriano, S., Villa, P., Pollarolo, L., Lucejko, J.J., Jacobs, Z., Douka, K., Vitagliano, S., Tozzi, C., 2019. Hafting of Middle Paleolithic tools in Latium (central Italy): New data from Fossellone and Sant'Agostino caves. PLoS One 14, e0213473.

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

Gaillard, Y., Chesnaux, L., Girard, M., Burr, A., Darque-Ceretti, E., Felder, E., Mazuy, A., Regert, M., 2015. Assessing Hafting Adhesive Efficiency in the Experimental Shooting of Projectile Points: A new Device for Instrumented and Ballistic Experiments. Archaeometry 58.

Gramsch, B., 2000. Mesolithic bone points: hunting weapons or fishing equipment. Anthropologie Et Préhistoire. 111, 109–113.

Gramsch, B., 1991. Friesack Mesolithic Wetlands. The Wetland Revolution. Proceedings of a conference hyld by and WARP at the . 65–72.

Grünberg, J.M., Graetsch, H., Baumer, U., Koller, J., 1999. Untersuchung der mittelpaläolithischen "Harzreste" von Königsaue. Ldkr. Aschersleben-Staßfurt. Jahresschrift Für Mitteldeutsche Vorgeschichte. 81, 7–38.

Hauck, T.C., Connan, J., Charrié-Duhaut, A., Le Tensorer, J.-M., Sakhel al, H., 2013. Molecular evidence of bitumen in the Mousterian lithic assemblage of Hummal (Central Syria). J. Archaeol. Sci. 40, 3252–3262.

Hayek, E.W.H., Krenmayr, P., Lohninger, H., 1990. Identification of Archaeological and Recent Wood Tar Pitches Using Gas Chromatography/Mass Spectrometry and Pattern Recognition. Anal. Chem. 62, 2038–2043.

Jensen, T.Z.T., Niemann, J., Iversen, K.H., Fotakis, A.K., Gopalakrishnan, S., Vågene, Å. J., Pedersen, M.W., Sinding, M.-H.-S., Ellegaard, M.R., Allentoft, M.E., Lanigan, L.T., Taurozzi, A.J., Nielsen, S.H., Dee, M.W., Mortensen, M.N., Christensen, M.C., Sørensen, S.A., Collins, M.J., Gilbert, M.T.P., Sikora, M., Rasmussen, S., Schroeder, H., 2019. A 5700 year-old human genome and oral microbiome from chewed birch pitch. Nat Commun. 10, 5520.

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

Kashuba, N., Kırdök, E., Damlien, H., Manninen, M.A., Nordqvist, B., Persson, P., Götherström, A., 2019. Ancient DNA from mastics solidifies connection between material culture and genetics of mesolithic hunter–gatherers in Scandinavia. Communications Biology. 2.

Koch, T.J., Groß, D., Måge, B.T., Little, A., 2024a. Hafting of a Neolithic leister: Identification of adhesives from Lolland (Denmark). Danish Journal of Archaeology. 13, 1–8.

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

Koch, T.J., Schmidt, P., 2022. A new method for birch tar making with materials available in the Stone Age. Sci. Rep. 12.

Koch, T.J., Schmidt, P., 2023. Adhesive Strength and Rupture Behaviour of Birch Tars Made with Different Stone Age Methods. Journal of Paleolithic Archaeology. 6, 8.

Kozowyk, P.R.B., Langejans, G.H.J., Poulis, J.A., 2016. Lap Shear and Impact Testing of Ochre and Beeswax in Experimental Middle Stone Age Compound Adhesives. PLoS One 11, e0150436.

Kozowyk, P.R.B., Baron, L.I., Langejans, G.H.J., 2023. Identifying Palaeolithic birch tar production techniques: challenges from an experimental biomolecular approach. Sci. Rep. 13, 14727.

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

Kozowyk, P., Soressi, M., Pomstra, D., Langejans, G., 2017b. Experimental methods for the Palaeolithic dry distillation of birch bark: implications for the origin and development of Neandertal adhesive technology. Sci. Rep. 7.

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

Larsson, L., Sjöström, A., Heron, C., 2016. The Rönneholm Arrow : A Find of a Wooden Arrow-tip with Microliths in the Bog Rönneholms Mosse, Central Scania. Southern Sweden, Lund Achaeological Review, p. 22.

Little, A., Needham, A., Langley, A., Elliott, B., 2022. Material and Sensory Experiences of Mesolithic Resinous Substances. Camb. Archaeol. J. 1–30.

Malmer, M., Magnusson, E., 1955. Mesolithische Harzornamentik. Ein Fund aus dem Lyby-Moor, Schonen. Meddelanden Fran Lunds Universitets Historika Museum. 4, 81–104.

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

Mitkidou, S., Dimitrakoudi, E., Urem-Kotsou, D., Papadopoulou, D., Kotsakis, K., Stratis, J.A., Stephanidou-Stephanatou, I., 2008. Organic residue analysis of Neolithic Pottery from North Greece. Microchim. Acta 160, 493–498.

Molin, F., Gruber, G., Hagberg, L., 2014. Motala—a north European focal point. In: Riede, F., Tallavaara, M. (Eds.), Lateglacial and Postglacial Pioneers in Northern Europe. Archaeopress, Oxford, pp. 91–102.

Niekus, M.J.L.T., Kozowyk, P.R.B., Langejans, G.H.J., Ngan-Tillard, D., van Keulen, H., van der Plicht, J., Cohen, K.M., van Wingerden, W., van Os, B., Smit, B.I., Amkreutz, L.W.S.W., Johansen, L., Verbaas, A., Dusseldorp, G.L., 2019. Middle Paleolithic complex technology and a Neandertal tar-backed tool from the Dutch North Sea. Proc. Natl. Acad. Sci. 116, 22081–22087.

Osipowicz, G., 2005. A method of wood tar production, without the use of ceramics. Reconstr. Exp. Archaeology EuroREA. 2, 11–17.

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

Petersen, P.V., 2013. Amber pendants, bears and elks. Bernsteinanhänger. Bären Und Elche. Die Kunde. 64, 2019–2237.

Płonka, T., 2003. The portable art of Mesolithic Europe. Wydawnictwo Universytetu Wroclawskiego, Wrocław.

Rageot, M., Théry-Parisot, I., Beyries, S., Lepère, C., Carré, A., Mazuy, A., Filippi, J.-J., Fernandez, X., Binder, D., Regert, M., 2019. Birch Bark Tar Production: Experimental and Biomolecular Approaches to the Study of a Common and Widely Used Prehistoric Adhesive. J. Archaeol. Method Theory 26, 276–312.

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

Rageot, M., 2015. 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.

Ralska-Jasiewiczowa, M., Latałowa, M., Wasylikowa, K., Madeyska, E., Wright, H.R., Turner, C., 2004. Late Glacial and Holocene History of Vegetation in Poland Based on Isopollen Maps.
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.
Ren, M., Yang, Y., Rao, H., Gu, A., Lei, Y., Yang, Y., 2023. Birch bark tar ornaments: identification of 2000-year-old beads and bracelets in southwest China. Archaeol. Anthropol. Sci. 15, 186.
Schenck, T., Groom, P., 2018. The aceramic production of Betula pubescens (downy birch) bark tar using simple raised structures. A viable Neanderthal technique? Archaeol. Anthropol. Sci. 10, 19–29.
Schmidt, P., Blessing, M., Rageot, M., Iovita, R., Pfleging, J., Nickel, K.G., Righetti, L., Tennie, C., 2019. Birch tar production does not prove Neanderthal behavioral complexity. Proc. Natl. Acad. Sci. 116, 17707–17711.
Schmidt, P., Blessing, M.A., Koch, T.J., Nickel, K.G., 2021. On the performance of birch tar made with different techniques. Heritage Science. 9, 140.
Schmidt, P., Koch, T.J., Berthold, C., Lauxmann, F., Nickel, K.G., 2022. The evolution of strength, elasticity and rupture behaviour of birch tar made with 'double-pot' techniques during tar cooking. Archaeometry 1–14.
Schmidt, P., Koch, T.J., Blessing, M.A., Karakostis, F.A., Harvati, K., Dresely, V., Charrié-Duhaut, A., 2023. Production method of the Königsaue birch tar documents cumulative culture in Neanderthals. Archaeol. Anthropol. Sci. 15, 84.
Schmidt, P., Iovita, R., Charrié-Duhaut, A., Möller, G., Namen, A., Dutkiewicz, E., 2024. Ochre-based compound adhesives at the Mousterian type-site document complex cognition and high investment. Sci. Adv. 10, eadl0822.
Stacey, R.J., Dunne, J., Brunning, S., Devièse, T., Mortimer, R., Ladd, S., Parfitt, K., Evershed, R., Bull, I., 2020. Birch bark tar in early Medieval England – Continuity of tradition or technological revival? J. Archaeol. Sci. Rep. 29, 102118.
Sulgostowska, Z., 1997. Examples of the application of wood tar during the mesolithic on polish territory. In: Piotrowski, W.B., W. (Eds.), Proceeding of the First International Symposium on Wood Tar and Pitch. State Archaeological Museum, Warsaw.
Toft, P.A., Petersen, E.B., 2016. Five Thousand Years of Decorated Amber Pendants from the Danish Mesolithic. Die Kunde. 64, 197–217.
Trąbska, J., Trybalska, B., 2017. The residue filling the lines of the ornament. In: Płonka, T., Kowalski, K. (Eds.), Rusinowo. University of Wrocław, Institute of Archaeology, Wrocław, The Symbolic Culture of Foragers in the Late Palaeolithic and the Early Mesolithic, pp. 147–161.
Ukkonen, F.K., Erä, V., 1979. Birch Bark Extractives. Kemia-Kemi. 5, 217–220.
Urem-Kotsou, D., Mitkidou, S., Dimitrakoudi, E., Kokkinos, N., Ntinou, M., 2018. Following their tears: Production and use of plant exudates in the Neolithic of North Aegean and the Balkans. Quat. Int. 496, 68–79.
Vahur, S., Kriiska, A., Leito, I., 2011. Investigation of the adhesive residue on the flint insert and the adhesive lump found from the Pulli early Mesolithic settlement site (Estonia) by micro-ATR-FT-IR spectroscopy. Estonian Journal of Archaeology. 15, 3–17.