Complicating the debate

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Complicating the debate: Evaluating the potential of gas-chromatography-mass spectrometry for differentiating prehistoric aceramic tar production techniques

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ABSTRACT

Birch bark tar was used extensively throughout human history. While later ceramic-based production technologies are known, prehistoric aceramic techniques leave little to no archaeological evidence. Experimental tar production attempts to fill this gap and suggest potential techniques. However, their archaeological relevance is unclear. Through an in-depth biomolecular analysis using Gas Chromatography-Mass Spectrometry, this study attempts to differentiate tars produced using four experimental aceramic techniques: condensation, ash mound, pit roll, and raised structure. In doing so we publish the largest collection of GC-MS results of aceramic birch tars. The results show that pentacyclic triterpenoids, characteristic of birch bark, vary between the production techniques in relation to heating exposure and perhaps the tar collection method. This allows for a tentative identification of tars produced through the condensation and ash mound techniques, which were formed consistently using short periods of heating and collected systematically by scraping. In contrast, tars produced using the pit roll and raised structure techniques do not have consistent molecular signatures. Despite the partial success of Gas Chromatography-Mass Spectrometry, the archaeological relevance is questioned because this technique is only applicable to samples from optimum lipid preservation conditions when a high number of pentacyclic triterpenoids are preserved. Therefore, using Gas Chromatography-Mass Spectrometry to determine the transformation methods of organics, like birch bark, may not be an appropriate standalone technique to fairly discuss the technological capabilities of past populations.

1. Introduction

Birch bark tar and adhesive production are central in research aimed at understanding the technological capabilities of past populations (Hoffecker, 2018; Niekus et al., 2019; Roebroeks and Soressi, 2016; Schmidt et al., 2023; Wadley, 2013; Wragg Sykes, 2015). The use of such tars is attested indirectly by archaeological residues. The oldest birch bark tar dates as far back as nearly 200,000 years ago in Europe, where it was used by Neanderthals as an adhesive on stone tools (Mazza, et al., 2006). Other residues show that birch bark tar continued to be used until the Middle Ages for a variety of purposes, including as a sealant, decoration in pottery, hafting adhesive, and chewing gum (Aveling and Heron, 1998; Charters et al., 1993; Chen et al., 2022; Langejans et al., 2022; Little et al., 2023; Lucquin et al., 2007; Osipowicz et al., 2020; Rageot et al., 2021; Regert, 2004; Regert et al., 2019; Regert et al., 2003; Stacey et al., 2020; Urem-Kotsou, et al., 2002; Van Gijn and Boon, 2006).

Experimental archaeology is frequently applied to reconstruct how ancient tars were produced (Kozowyk, et al., 2017; Osipowicz, 2005; Rageot et al., 2019; Schenck and Groom, 2016; Schmidt et al., 2019). Based on experimental methods, archaeologists can assess the complexity of these technologies and sometimes make cognitive inferences drawing from, for instance, cognitive evolutionary frameworks and computer science (Fajardo, et al., 2023; Kozowyk et al., 2023c; Schmidt, 2021). This can be supplemented by the chemical and spectrographic characterization of archaeological tars, using methods like Fourier Transform Infrared Spectroscopy (FTIR) and Gas-Chromatography Mass-Spectroscopy (GC-MS) (Egenberg, et al., 2003; Rageot et al., 2019; Regert, 2004; Schmidt et al., 2023). In this

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paper, we aim to contribute to the growing body of experimental knowledge on the characterization of birch tars, and we present the results of a biomolecular approach to identify aceramic birch tar production processes.

Archaeological research frequently suggests that birch tar is produced by heating bark to a high temperature in a reduced oxygen environment (Rageot, et al., 2019), although tar can also be produced with ease in open-air settings (Schmidt, et al., 2019). During pyrolysis the bark is transformed into liquids and volatiles that, together with a solid fraction, form a black plastic-like material, which ranges in viscosity from liquid to putty-like to a hard mass. Birch tar can be made using an allothermic system through an indirect transfer of heat to the bark (Kurzweil and Todtenhaupt, 1991). In later periods, this can be achieved through the use of fire-proof containers made from pottery and metal. In these examples, tar can be produced using a single receptacle; here the end product is not separated from the reaction material. Tar can also be produced *per descensum* in two containers using a separation system (Rageot, et al., 2019). These are also respectively referred to as the single- and double-pot (Rageot, et al., 2019). Tar production techniques that employ vessels can be reconstructed based on vessel morphology and the presence of adhering residues (Dal Ri and Tecchiati, 2003), and, relying on similar concepts, other built production features were identified in historic periods (Hennius, 2018; Orengo et al., 2013; Pietrzak, 2012; Snitker et al., 2022). In addition, recent studies show that the ceramic based single- and double-pot production techniques can be differentiated based on molecular analysis using GC-MS (Rageot, et al., 2021; Rageot et al., 2019). This relies on variations in the molecular signature of birch bark that occur due to the differences in the intensity and length of heating required to produce tar in each technique (Rageot, et al., 2019).

For prehistoric periods, before the invention of pottery, there is little direct archaeological evidence for aceramic methodologies as stone cobbles and pits used during tar production are difficult to identify (Hjulström, et al., 2006; Kozowyk et al., 2023b, Langejans et al., in press), limiting the discussion of the related technological complexity. This represents a major lacuna in archaeological research as the majority of the human past predates the use of ceramics. Examples of potential allothermic aceramic techniques include the ash mound (above ground and single system), pit roll, and raised structure (below ground and double systems) techniques (Kozowyk, et al., 2017; Osipowicz, 2005; Schenck and Groom, 2016). Autothermic open-air techniques, referred to as the condensation and cobble-groove methods, were also proposed as possibilities among aceramic populations (Koch and Schmidt, 2022; Schmidt et al., 2019); in these techniques, the reaction material is not mixed with the end product similar to the double-pot system.

Recent work has attempted to identify aceramic techniques using infrared spectroscopy, and through this, a method to separate between tars produced using above and below ground techniques was suggested (Schmidt, et al., 2023); these results were supplemented through the GC-MS analysis of two tars produced using the raised structure and condensation techniques (Schmidt, et al., 2023). In an attempt to increase this resolution, the present study applied GC-MS to a set of 29 experimental tars formed using the condensation, ash mound, pit roll, and raised structure techniques. This represents so-far the largest collection of published aceramic tars analyzed using this method. GC-MS was used to identify their molecular signature, and statistical analysis was applied to identify whether production techniques could be differentiated following the logic outlined by Rageot (et al., 2019) in his study on ceramic-based tar production technology. The archaeological applicability and the wider significance of this method are then discussed.

2. Materials and methods

2.1. Materials

We analyzed 29 experimental samples (SI1) produced in the Vlaardingen (Vla) and Horsterwold (HOR) open-air experimental centers, located in The Netherlands. This includes three previously published (HOR_AM3, Vla_PR11.2, and Vla_ROS2.2) (Kozowyk, et al., 2023a; Kozowyk et al., 2023b) experiments. The 29 samples were made using four different techniques (Fig. 1): 1) condensation, 2) ash mound, 3) pit roll, and 4) raised structure (Kozowyk, et al., 2017; Schmidt et al., 2019). The protocols are summarized as follows.

1) Condensation (N = 9) – Small amounts of birch bark were burned next to a near vertical stone surface. The smoke condensed on the stone, leaving a tar residue, which was scraped off with a flint flake.
2) Ash mound (N = 4) – A roll of birch bark was covered in hot ash and embers. The residual heat was used to form tar inside the bark roll. The tar was collected by unrolling the bark and scraping it with a flint flake or wooden stick.
3) Pit roll (N = 9) – A small pit was dug, and a birch bark cup was placed at the bottom. A roll of birch bark was placed into the hole, and hot embers were placed over and around the roll of bark. When heated, the tar dripped down into the pit, but some remained in the bark roll. Tar was collected from the cup in the pit and by scrapping the bark roll.
4) Raised structure (N = 7) – A small pit was dug, and a birch bark cup was placed at the bottom. A screen of twigs was placed over the pit. On top of this screen, round pebbles were placed, and a roll of birch bark was placed on top of the pebbles. The entire system was covered by a mud dome, and a fire was lit all around for several hours. The tar dripped down and was collected from the birch bark cup.

2.2. Methods

Sub-samples of the tars weighing approximately 4 mg were collected for analysis. Following established protocols (Regert, et al., 2006), 4 mL of dichloromethane (DCM) (HPLC grade) were added, and the lipid components were extracted by ultrasonication for 30 min. A 200 μL aliquot of the supernatant was dried under nitrogen at 30 °C. The extracts were derivatized using 50 μL of bis(trimethysilyl)trifluoroacetamide containing 1% trimethylchlorosilane, 10 μL of DCM, and 5 μL of pyridine. The reaction took place at room temperature for 20 min. Samples were then dried under a nitrogen stream at 30 °C and reconstituted with DCM.

GC-MS analysis was performed on an Agilent 7890B GC system with a split/splitless inlet, coupled with an Agilent 5977B EI MSD interface and a FID. The GC was fitted with a nonpolar Agilent J&W DB5 MS column (30 m × 0.25 mm i. d.; 0.25 μm film thickness). The samples were split equally between the FID and MSD and introduced in splitless mode at 300 °C, with a septum purge flow of 3 mL min^{-1}. The oven temperature was held isothermally for 2 min at 50 °C, ramped at 10 °C

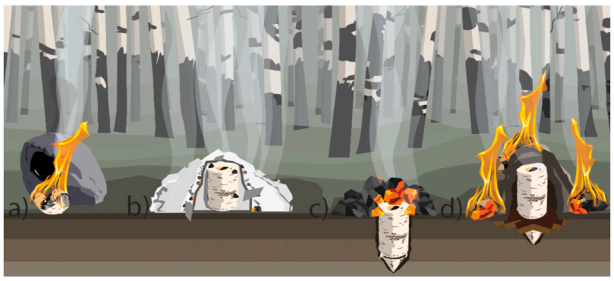

Fig. 1. Illustration of the studied tar production techniques: a) condensation; b) ash mound; c) pit roll; d) raised structure.

min^{-1} to 150 °C, ramped at 4 °C min^{-1} to 320 °C, and held at that temperature for 20 min. The analysis was conducted using helium as the carrier gas at a constant flow of 1.6 mL min^{-1} (average velocity 32.146 cm s^{-1}). The temperature of the FID was set at 340 °C, and the hydrogen flow was 30 mL min^{-1}, the synthetic air flow was 400 mL min^{-1}, and the nitrogen flow was 30 mL min^{-1}. The temperatures of the ion source and transfer line were set at 230 °C and 280 °C respectively. The mass spectrometer was monitored to scan 35–950 m/z with an ionizing voltage of 70 eV.

The resulting chromatograms were interpreted using the National Institute of Standards and Technology (NIST) library and reference mass spectra (Aveling and Heron, 1998; Charters et al., 1993; Rageot, 2015; Reunanen et al., 1993). The identification targeted fatty acids, dicarboxylic acids, and pentacyclic triterpenoids. Long-chain fatty acids and dicarboxylic acids may originate from the degradation of suberin (Kolattukudy, 2001), a biopolymer characteristic of birch bark (Gandini, et al., 2006; Pinto et al., 2009; Ribechini et al., 2015). When analyzing archaeological material with GC-MS, they are commonly the only surviving traces of the original suberin molecules. Phenols, another aliphatic monomer composing suberin, although identified (SI1), were not considered because they are highly subject to biodegradation (Agarry, et al., 2008) and unlikely to survive archaeological timescales. Pentacyclic triterpenoids, a core component of birch bark (Jäger, et al., 2009; Krasutsky, 2006), were also identified. Following the logic of a prior study on ceramics (Rageot, et al., 2019), the terpenoids were divided into biomarkers and soft and strong heating markers (Table 1). Biomarkers are pentacyclic triterpenoids found naturally in birch bark in high abundances: Lupeol, Erythrodiol, Betulin, and Betulinic acid. The heating markers are found naturally in birch bark and are also formed through the degradation of the biomarkers during the tar formation process. Soft heating markers are said to form when the bark is heated gradually to just below 400 °C, while strong heating markers form when there is a longer heating time and a fast increase in temperature to over 400 °C (Rageot, 2015; Rageot et al., 2019).

To evaluate the differences between production processes, bivariate and multivariate analysis were conducted in R (Version 4.2.2). Bivariate analysis included forming scatter plots depicting the relationship between two variables, namely the percentage of biomarkers versus the percentages of soft and strong heating markers. Multivariate analysis included PCA; this was conducted using the prcomp function in R, which relies on singular value decomposition (SVD). These results were compared to birch bark tars similarly extracted from archaeological material in a prior study (Aleo, et al., 2023) to test its archaeological significance in light of degradation.

Table 1
Pentacyclic triterpenoids identified in the birch bark tar samples classified using published information and organized in order of retention time (Rageot, et al., 2019).

Biomarkers	Soft heating markers	Strong heating markers		Unknown
		Double degraded pentacyclic triterpenoids	Hydrocarbon pentacyclic triterpenoids	
Lupeol	Lupa-2,20 (29)-diene	α-Allobetulin	α-Lupane (B337)	Lupenone[a]
Erythrodiol	α-Betulin I	Allobetul-2-ene	α-Lupane (B360)	B432
Betulin	Lupa-2,20 (29)-dien-28-ol (B395)	3-Oxoallobetulin[a]		B422
Betulinic acid	Lupa-2,20 (29)-dien-28-ol (B396)			
	Olean-2,11-dien-28-oic acid			
	Betulone[a]			
	Allobetulin			
	Betulinic acid, 28-acetate			

[a] Oxidation products.

3. Results

3.1. GC-MS

3.1.1. Fatty acids

While fatty acids can be identified in a wide range of organic materials (Pollard and Heron, 2008), in birch tar, long-chain saturated and unsaturated fatty acids may relate to the degradation of suberin (Kumar, et al., 2022). Their presence has been used in the past to identify tar production methods, with these considered suggestive of the double-pot production technique (Rageot, et al., 2019). The identified fatty acids in our results are primarily saturated, ranging from $C_{7:0}$–$C_{22:0}$, with a predominance of long-chain even-numbered variants (Fig. 2). Unsaturated fatty acids are less abundant and include $C_{16:1}$, $C_{18:1}$, $C_{18:2}$, $C_{20:1}$, and $C_{22:1}$ (Fig. 2). Several tars produced by the ash mound, pit roll, and raised structure techniques contain no or few fatty acids (*e.g.* Fig. 2b–d). The ash mound technique is further unique, with just $C_{16:0}$ and $C_{18:0}$ and no unsaturated fatty acids. However, the variability within the pit roll and raised structure samples prevent this from being an accurate measure.

3.1.2. Dicarboxylic acids

A series of long-chain dicarboxylic acids, ranging from $C_{16:0}$–$C_{24:0}$, are produced from the degradation of suberin in birch bark (Gandini, et al., 2006; Pinto et al., 2009; Ribechini et al., 2015). As with fatty acids, their presence and absence has been used to suggest different tar production methods, including in particular the double-pot and underground aceramic methods (Rageot, et al., 2019; Schmidt et al., 2023). In our samples long-chain dicarboxylic acids are identified only in tars produced by condensation; however, this is restricted to hexadecanedioic acid, and as such, there is no clear signature related to suberin, and dicarboxylic acids cannot be used to differentiate the tar production techniques.

3.1.3. Terpenoids

Twenty pentacyclic triterpenoids were identified in the samples (Fig. 3; Table 1), with little qualitative variation between tars produced by different techniques. However, some variability was noted within the identified biomarkers. Erythrodiol is absent from tars produced using the raised structure technique, and Betulinic acid is identified less frequently in tars produced from the pit roll and raised structure techniques (Fig. 3c and d). In addition, Betulinic acid, 28-acetate, a soft heating marker, was not identified in condensation produced tars (Fig. 3a).

Quantitative analysis (Fig. 4; Table 2) was conducted using the indexes proposed by Rageot (et al., 2019). The median is given here to represent what is 'typical' of a production technique rather than the mean as the results do not follow a perfect normal distribution. The standard deviation (stdev) was also calculated. The level of natural biomarker degradation was measured using the index of degradation (ID). ID is equal to [Lupa-2,20(29)-dien-28-ol + Betulone]/Betulin; the abundance of Lupa-2,20(29)-dien-28-ol and Betulone are considered in favor of other molecules because, while they can be formed during the tar production process, they also form from natural decay within the sedimentary matrix.

The results show that typically the ash mound and pit roll techniques alters the Betulin content the least (median ID 0.1 and stdev 0.1). The condensation (median ID 0.3 and stdev 0.1) and raised structure techniques (median ID 0.4 and stdev 0.1) degrade Betulin the most. This pattern is refined by the overall percentage of biomarkers in each sample (Fig. 4a and b; Table 2); condensation (median 64% biomarkers and

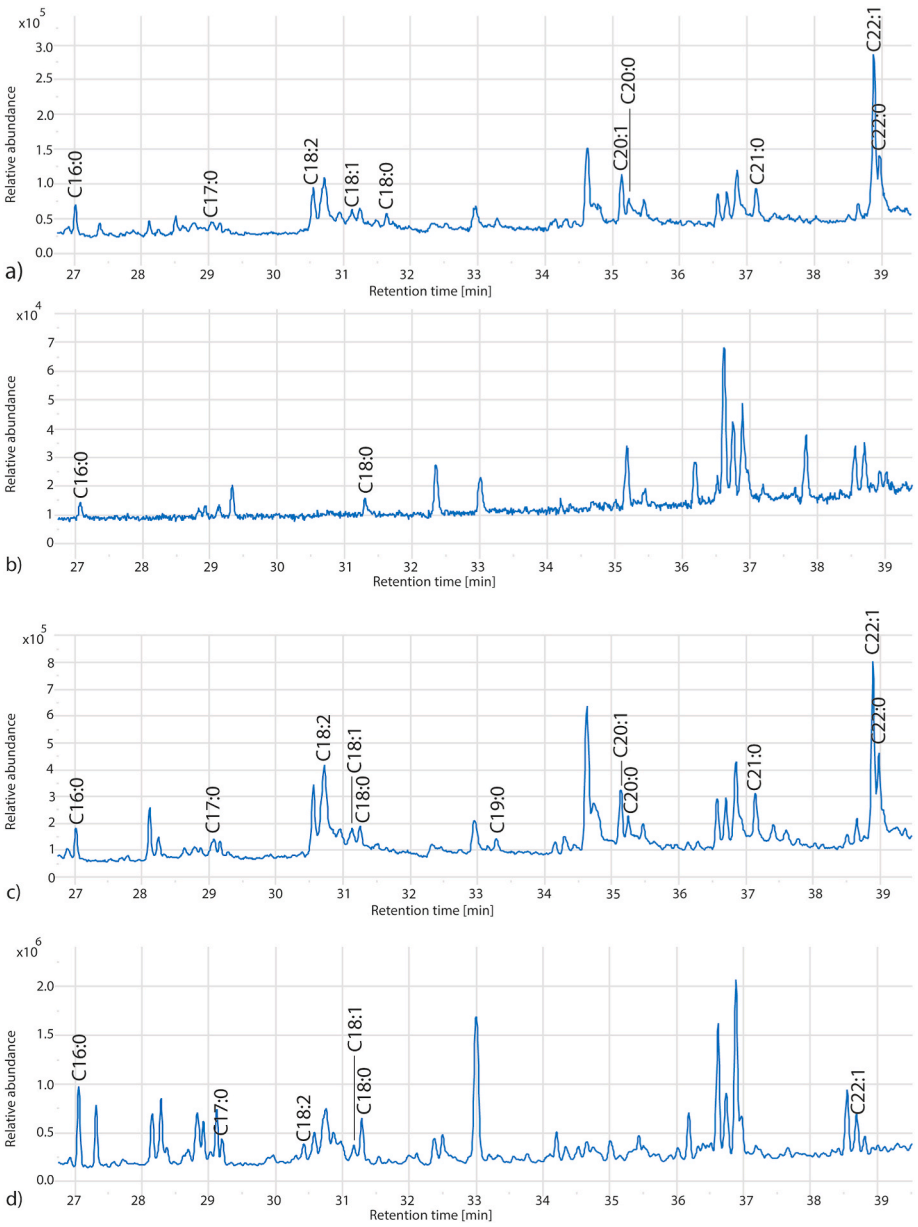

Fig. 2. Partial total ion chromatogram displaying fatty acids analyzed as TMS derivatizes from solvent extracted tars produced using the following techniques: a) Condensation (Vla_C04.1); b) Ash mound (HOR_AM3); c) Pit roll (Vla_PR09.1); d) Raised structure (Vla_RS02.2).

stdev 5%), ash mound (median 89% biomarkers and stdev 10%), and pit roll tars (median 75% biomarkers and stdev 13%) have a greater preservation of Lupeol, Erythrodiol, Betulin, and Betulinic acid, while these are more thoroughly degraded in tars produced in raised structures (median 31% biomarkers and stdev 13%). The wide range of variation though in each technique prevents the ID and percentage of biomarkers from being effective metrics.

The percentage of soft heating markers, formed at lower temperatures, also displays unclear divisions (Fig. 4c). The median is 31% for condensation (stdev 4%), 9% for ash mound (stdev 7%), 19% for pit roll (stdev 12%), and 35% for raised structure (stdev 8%). The indirect heating involved in the raised structure technique may explain the high amount of soft heating markers; however, the high amount of soft heating markers in the tars produced by condensation is unusual as the bark was exposed to direct heat. Therefore, the definition of soft heating markers should be reconsidered or expanded to relate to the length of heating as these are likely simply just the first degradation products formed.

Double degraded pentacyclic triterpenoids (DPT) and hydrocarbon pentacyclic triterpenoids (HPT) are considered strong heating markers. These form with long and fast heating to high temperatures from cycloisomerization and alcohol degradation (Rageot, 2015; Rageot et al., 2019). In the studied samples (Fig. 4d–e; Table 2), tars produced by condensation have consistently low amounts of strong heating markers (median DPT 2.5% and stdev 1%; median HPT 1.4% and stdev 0.5%). Tars produced by the ash mound technique however have almost no strong heating markers (median DPT 1.5% and stdev 1.2%; median HPT 0.3% and stdev 0.2%). The amount of strong heating markers produced by the pit roll technique is variable, although generally low (median DPT 3.5% and stdev 9.4%; median HPT 1.2% and stdev 1.5%). Tars produced using raised structures consistently have high amounts of strong heating markers (median DPT 25% and stdev 5.9%; median HPT 4% and stdev 2.7%).

The amounts of strong heating markers can be explained by the length of heating time. In the condensation technique, while each experiment lasted an extended period of time (16–185 min), the tar was

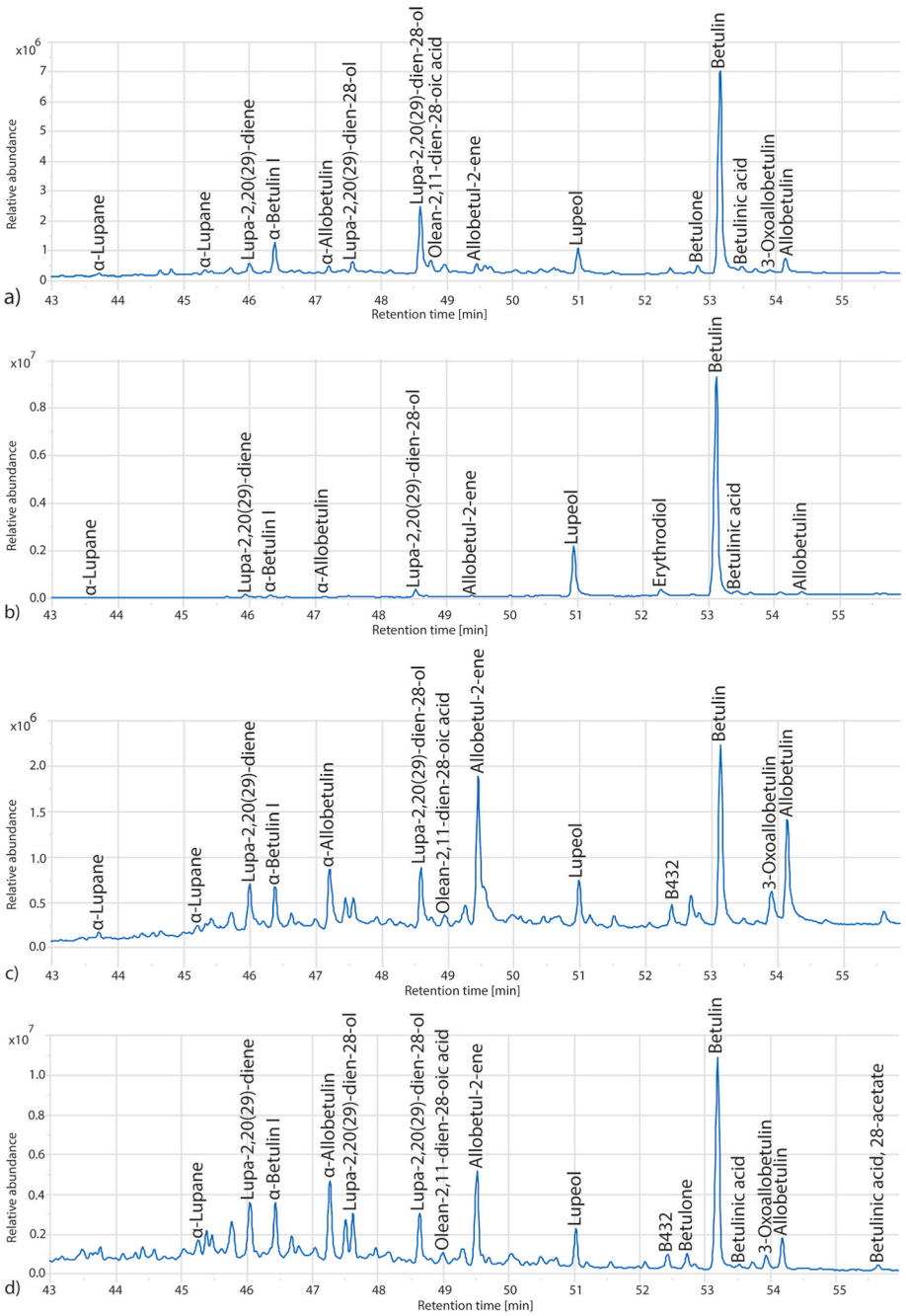

Fig. 3. Partial total ion chromatogram displaying terpenoids analyzed as TMS derivatizes from solvent extracted tars produced using the following techniques a) Condensation (Vla_C02.1); b) Ash mound (HOR_AM2.1); c) Pit roll (Vla_PR03.1); d) Raised structure (Vla_RS02.2).

collected periodically throughout the process minutes after fresh bark was added to the fire, so the tar and bark were exposed to heat for short periods of time. Bark in the ash mound technique was also heated for a short duration (19–32 min). This worked to minimize chemical alteration and the formation of strong heating markers. On the opposite end of the spectrum, in the raised structure technique, the bark was heated for the longest duration (413–485 min), and correspondingly these samples have high amounts of strong heating markers. The pit roll samples display high variability in the amount of degradation products, and while further controlled experimentation is required to support this, it may relate to the variability in heating time (25–168 min). The relationship to the rate of temperature increase (Rageot, et al., 2019) is unlikely as the bark in the condensation technique heats to the maximum temperature the fastest, yet it has low frequencies of DPT and HPT.

3.2. Statistical analysis

These patterns can be confirmed by a bivariate analysis of the percentage of biomarkers, soft heating markers, and strong heating markers. Plotting the percentage of biomarkers against the percentage soft heating markers shows that as the biomarkers degrade, soft heating markers are produced (Fig. 5a). Soft heating markers however stop being produced in abundance once the percentage of biomarkers reaches approximately 50%. Instead, at this stage strong heating markers are produced. In tars with over 50% of the biomarkers preserved, the percentage of strong heating markers is negligible, but with extended heating, the percentage of strong heating markers increases sharply, as

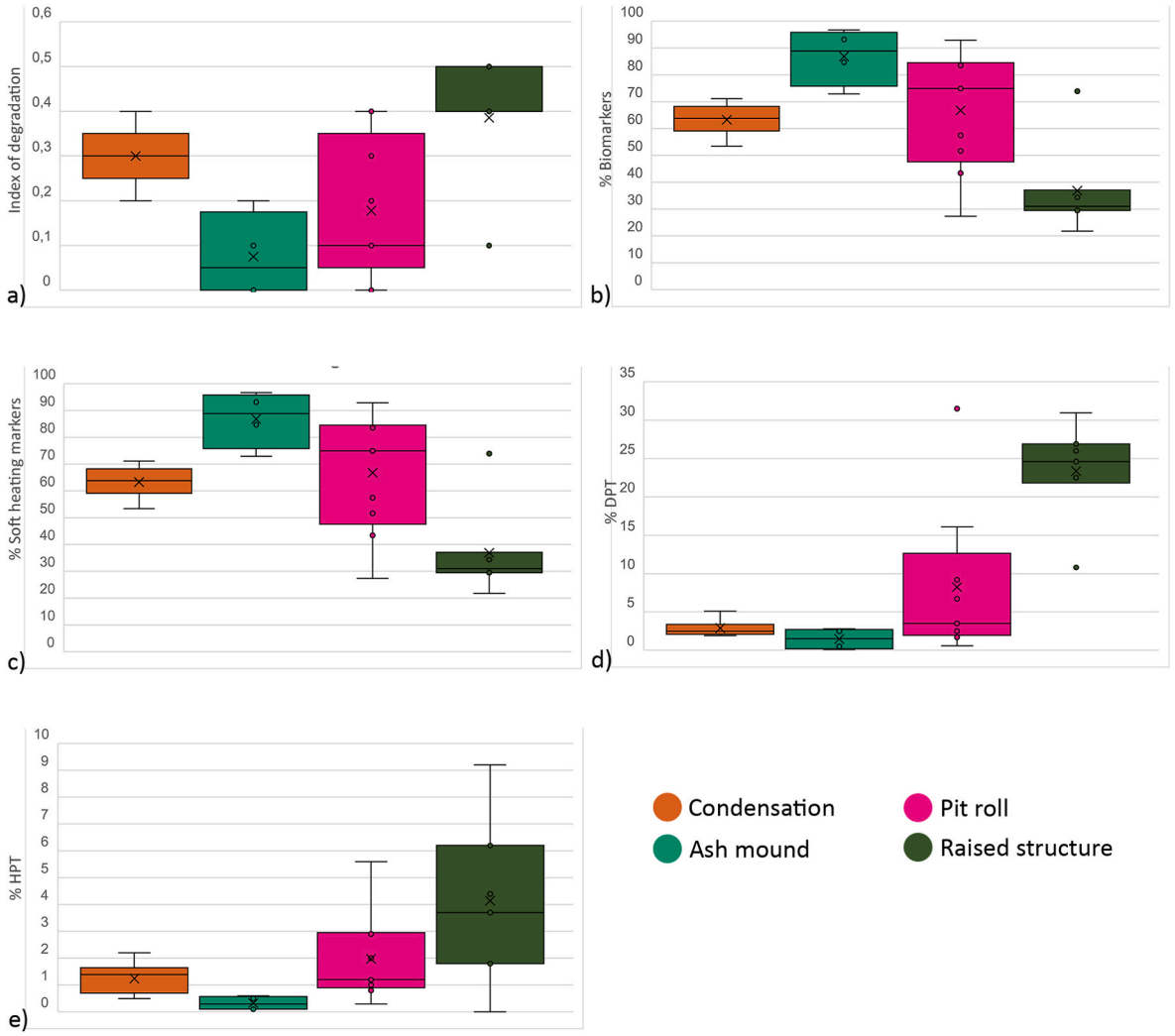

Fig. 4. Box and whisker plots showing the distribution of the: a) index of degradation; b) percentage of biomarkers; c) percentage of soft heating markers; d) percentage of double degraded pentacyclic triterpenoids; e) percentage of heterocyclic pentacyclic triterpenoids.

observed in most raised structure tars and some pit roll tars (Fig. 5b).

Principle component analysis was then conducted to identify whether these variables can be used to accurately cluster the tars based on the production technique. Following initial PCA of the relative contributions of the pentacyclic triterpenoids (Fig. 6a), PCA was conducted on the indexes (the percentages of biomarkers and soft and strong heating markers) used in the biplots (Fig. 6b). In the first method, principle components 1 and 2 explain 59% of the variation, while in the second method, principle components 1 and 2 explain 93% of the variation. This difference shows that while the definition of these indexes is complicated, grouping molecules into these is valid.

In both methods, two primary clusters are observed: condensation and ash mound. Condensation is off-set by a high amount of soft heating markers (Lupa-2,20(29)-dien-28-ol (B396), Olean-2,11-dien-28-oic acid, and Betulone) as well as the high preservation of biomarkers. This can be explained by the short heating time the bark undergoes. Ash mound tars are off-set by their abundance of biomarkers – Betulin, Lupeol, and Erythrodiol and correspondingly their absence of degradation biproducts. The explanation for this is two-fold. First, as in condensation, the bark is heated for shorter periods of time. Second, while further experimentation is required to support this, to collect the tar, the bark is scrapped with a flint or wooden tool, thereby potentially collecting unaltered residues from the bark itself.

However, the reliability of these groupings must be questioned as some of the pit roll and raised structure samples plot similar to the ash mound and condensation tars. Tars produced from these techniques are spread throughout the plot based on their varying levels of biomarker preservation. In the case of the pit roll samples, this may relate to the variation in heating time (25–168 min) or the tar collection method, which sometimes mixed tar from the collection cup with tar scrapped off of the bark roll. The variability within the raised structure samples may be attributed to their long heating process and advanced stage of degradation.

3.3. Case study

Applying this knowledge to archaeological material can provide some valuable insight. Comparisons were made to three Mesolithic bone points from the now submerged Doggerland area of the Dutch North Sea, dated to between 13,000 and 5000 cal. BP (Aleo, et al., 2023; Amkreutz and Spithoven, 2019). The residues were extracted and analyzed using methods parallel to this study, but the pentacyclic triterpenoids were identified primarily relying on NIST.

Of the three bone points, one contained exclusively α-Lupane (Aleo, et al., 2023); while this likely originated from birch bark tar, α-Lupane alone is not enough to discuss the production technique as it differs from all known patterns, so this sample will not be discussed further. The residues on the other two bone points contained biomarkers (Betulin,

Table 2
Overview of the indexes used to assess birch bark biomarker degradation during tar formation.

Sample	Production technique	ID	% Biomarkers	% Soft heating markers	Strong heating markers	
					% DPT	% HPT
Vla_C02.1	Condensation	0.4	53.4	37.8	5.1	2.2
Vla_C03.1	Condensation	0.3	66.3	30.2	1.9	1.4
Vla_C04.1	Condensation	0.3	60.0	33.4	3.3	1.7
Vla_C05.1	Condensation	0.3	64.3	31.3	2.3	1.0
Vla_C06.1	Condensation	0.2	71.2	25.8	2.5	0.5
Vla_C07.1	Condensation	0.2	70.2	26.1	2.1	0.5
Vla_C08.1	Condensation	0.3	63.8	31.2	3.5	1.6
Vla_C16.1	Condensation	0.4	58.2	36.3	3.2	0.9
Vla_C17.1	Condensation	0.3	62.4	31.9	2.1	1.4
HOR_AM01	Ash mound	<0.1	96.8	3.1	0.1	0.1
HOR_AM02	Ash mound	<0.1	93.2	6.1	0.5	0.1
HOR_AM03	Ash mound	0.2	72.9	20.8	2.8	0.6
HOR_AM04	Ash mound	0.1	84.7	12.3	2.5	0.5
Vla_PR01.1	Pit roll	0.2	43.5	34.8	16.1	5.6
Vla_PR02.1	Pit roll	0.1	85.2	10.7	2.5	1.0
Vla_PR03.1	Pit roll	0.4	27.4	37.4	31.5	2.0
Vla_PR04.1	Pit roll	<0.1	83.6	13.2	2.2	1.0
Vla_PR07.1	Pit roll	0.1	84.1	12.7	1.7	0.8
Vla_PR08.1	Pit roll	<0.1	93.0	6.0	0.6	0.3
Vla_PR09.1	Pit roll	0.4	51.7	37.6	6.7	3.0
Vla_PR11.1	Pit roll	0.3	57.5	28.9	9.2	2.9
Vla_PR11.2	Pit roll	0.1	75.0	19.0	3.5	1.2
Vla_RS01.1.1	Raised structure	0.1	74.0	13.6	10.8	0.0
Vla_RS01.1.2	Raised structure	0.4	31.0	38.1	21.8	6.2
Vla_RS02.1	Raised structure	0.5	30.8	37.5	26.0	3.7
Vla_RS02.2	Raised structure	0.4	34.4	34.7	24.6	4.4
Vla_RS02.1.1	Raised structure	0.4	21.8	34.7	31.0	9.2
Vla_RS02.1.2	Raised structure	0.4	37.1	33.5	22.5	3.7
Vla_RS02.1.3	Raised structure	0.5	29.5	36.7	26.9	1.8

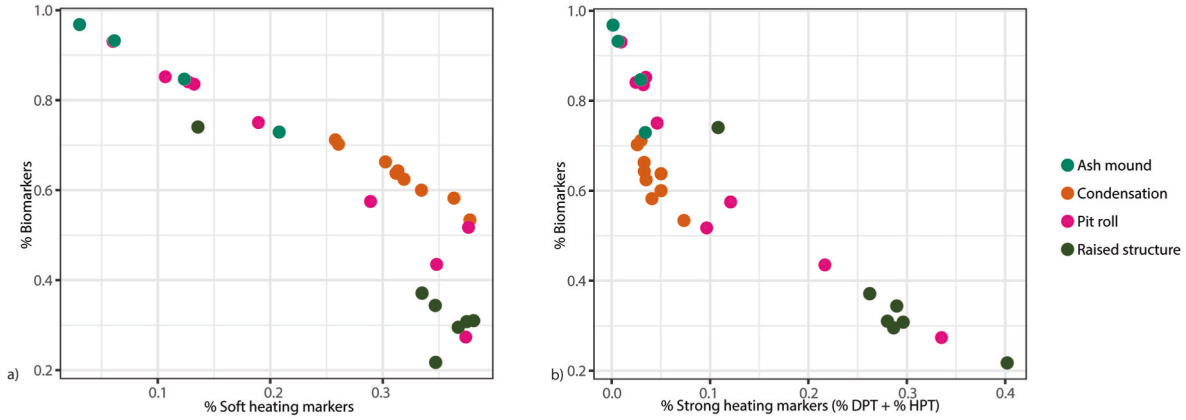

Fig. 5. Biplot of the percentage of a) soft heating markers and biomarkers; b) strong heating markers and biomarkers identified in the experimentally produced tars.

Betulinic acid, and Lupeol), soft heating markers (Lupa-2,20(29)-diene, α-Betulin I, Betulone, and Allobetulin), and strong heating markers (α-Lupane, α-Allobetulin, and Allobetul-2-ene) (Aleo, et al., 2023). The biomarkers are very abundant, so when plotted with PCA, the results are similar to the ash mound technique (Fig. 7). However, reanalysis of the tars and comparison to published reference mass spectra (Aveling and Heron, 1998; Charters et al., 1993; Rageot, 2015; Reunanen et al., 1993) led to the identification of additional molecules – Lupa-2,20 (29)-dien-28-ol (B395 and B396), Olean-2,11-dien-28-oic acid, 3-Oxoallobetulin, and Lupenone. The signature is well preserved, with an ID of 0.2 (NSM1) and 0.3 (NSM10) (SI1); this relates to the anaerobic deposition context these were recovered from. With the adjusted relative abundances, the PCA results shift and are more similar to condensation (Fig. 7). In reality however, with both the old and new data, the bone points do not perfectly match either the ash mound or condensation samples. What the results imply is that the tars were produced with a method that heats the bark for a short period of time similar to these techniques, but the exact method is unknown.

4. Discussion

Birch bark tar is identified in the archaeological record by the presence of key biomarkers and their degradation products. This study shows based on experimental analysis that a high number of molecules is required to identify the tar production technique. From the GC-MS results, it can be observed that the molecular signature of tar varies according to the length the bark is heated for. In tars heated for shorter periods of time, as in the condensation and ash mound techniques, there are higher abundances of biomarkers and soft heating markers. However, once the bark is heated for longer periods of time, as in the pit roll and raised structure techniques, soft heating markers stop being produced and instead more strong heating markers are produced. Despite these patterns, the archaeological applicability of these results must be questioned for two reasons.

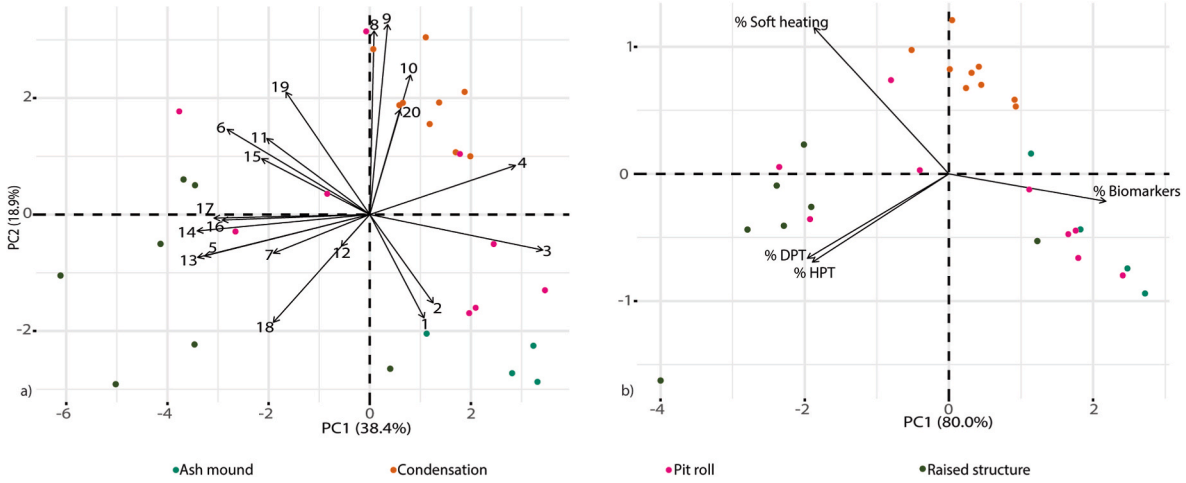

Fig. 6. a) PCA plot of the experimentally produced tars using the relative abundances of pentacyclic triterpenoids and the loading scores of each variable displayed as a number: 1) % Lupeol; 2) % Erythrodiol; 3) % Betulin; 4) % Betulinic acid; 5) % Lupa-2,20(29)-diene; 6) % α-Betulin I; 7) % Lupa-2,20(29)-dien-28-ol (B395); 8) % Lupa-2,20(29)-dien-28-ol (B396); 9) % Olean-2,11-dien-28-oic acid; 10) % Betulone; 11) % Allobetulin; 12) % Betulinic acid, 28-acetate; 13) % α-Allobetulin; 14) % Allobetul-2-ene; 15) % 3-Oxoallobetulin; 16) % α-Lupane (B337); 17) % α-Lupane (B360); 18) % Lupenone; 19) % B432; 20) % B422; b) PCA plot of the experimentally produced tars using summarizing indexes and their loading scores.

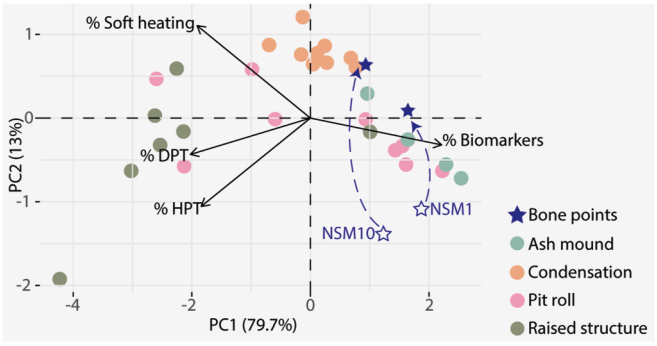

Fig. 7. PCA plot of Mesolithic bone points against the experimentally produced tars using the summarizing indexes. The filled stars represent material analyzed as part of this study, while unfilled stars represent data from the previous study. The arrows show the transformation of the bone points' results interpretation after publication when additional molecules were identified during the reanalysis.

First, the identified molecules are directly correlated with the post-depositional conditions. Lipids preserve best in acidic and anaerobic environments where they are subject to less microbial degradation (Evershed, 1993; Moucawi et al., 1981). For example, as many as 12 pentacyclic triterpenoids, including a predominance of biomarkers (Betulin, Betulinic acid, Lupeol, Erythrodiol, Oleanolic acid, Oleanolic acid 3-acetate, and β-amyrin) and soft heating markers (Lupa-2,20 (29)-diene, α-Betulin I, Lupa-2,20(29)-dien-28-ol, Olean-2, 11-dien-28-oic acid, Betulone, and Betulinic acid, 28-acetate) and lower amounts of strong heating markers (Allobetulin, 3-Oxoallobetulin) and other pentacyclic triterpenoids (Hydroxy-allobetulin, Lupenone, and Betulinic aldehyde), were identified in birch tar remains dated to the Middle Paleolithic and Mesolithic and recovered from peat bogs (Aveling and Heron, 1998; Kabaciński et al., 2023; Koller et al., 2001), which have an acidic pH. These results are similar to the tars produced using the condensation and ash mound techniques, so it can be suggested that they were produced using a short heating period. In contrast, only Betulin, Lupeol, Lupa-2,20(29)-diene, Lupa-2,20(29)-dien-28-ol, and Betulone were identified in a Middle Paleolithic tar recovered from a clay pit covered in sand at the Campitello Quarry in Italy (Mazza, et al., 2006). The alkaline clay and sand support microbial activity, which promotes the degradation of the original tar molecular signature. These less favorable conditions, in which only the biomarkers are likely to survive in high amounts, would generate a potentially false positive identification of the condensation or ash mound technique, similar to the tars recovered from the peat bogs. One way to differentiate these two situations might be using the ID, which assesses the effect of sedimentary degradation. In the experimental samples (Table 2), the ID ranges from <0.1 to 0.5, with an average and median of 0.3; the lower extremity is represented by the ash mound tars, which potentially have a naturally low ID due to the collection method. The next step would be to see how archaeological samples from different contexts compare to this and use that to create a cut-off point for 'well-preserved.' For example, the two bone points discussed in this study have an ID of 0.2 and 0.3, which fall within the range of the experimental samples. If the ID is too low or cannot be calculated due to the absence of biomarkers (as in the case of the third bone point), the tar production technique cannot be reliably assessed. By applying this ID cut-off, erroneous identifications can be minimized.

A second issue to consider is that the number of successfully identified peaks may bias the results. Reliance on general mass spectral libraries like NIST will allow for the confident identification of a limited number of peaks, including primarily the biomarkers. However, there are additional mass spectra that can be identified by comparing to published results (Aveling and Heron, 1998; Charters et al., 1993; Rageot, 2015; Reunanen et al., 1993), and there are others whose identifications are still unknown and require further evaluation of the fragmentation pattern. As such, the identified molecular signature is not absolute, and correspondingly the percentages of the pentacyclic triterpenoids and the PCA results are liable to change. For example, in the detailed case study on the Doggerland bone points, we identified in the reanalysis five additional soft and strong heating markers, causing the molecular signature to shift and become more similar to the condensation technique instead of the ash mound technique. This shows that new identifications of unidentified peaks, which are omnipresent and inevitable, can drastically change the results. This is true for archaeological samples as well as experimental reference material.

Given all these issues, it stands to question if tar production techniques can ever be reliably identified with a higher level of confidence using GC-MS. To progress toward this goal, the experimental dataset should be expanded to include tars from each method that were degraded in diverse deposition contexts; this will allow us to understand how the molecular signature changes due to post-depositional processes.

In addition, the experiments should be expanded to include tars made from birch bark originating from different environments as the molecular signature of bark from different trees can vary based on sedimentary and climatic differences (Guo, et al., 2023; Holonec et al., 2012; Yin et al., 2015). The simplest way to achieve this is through promoting increased data accessibility and collaboration. Aceramic replicas of birch bark tar are being formed by several research groups (Blessing and Schmidt, 2021; Groom et al., 2013; Koch and Schmidt, 2022; Schenck and Groom, 2016; Schmidt et al., 2019), but the raw data is unfortunately unavailable. A more open access approach to data management would quickly expand and diversify the dataset.

In addition, caution must be applied when attempting to assign a tar production technique to archaeological residues. While GC-MS paired with PCA can differentiate to some extent different tar production techniques, or more accurately, the relative length of the tar production process, the state of residue preservation must first be assessed. Because only certain environments and deposition conditions provide adequate preservation, results from one site or a small area can only reliably be used to make inferences about that specific site and its occupants. Sweeping statements about the technological capabilities of past populations should be treated with caution. In addition, it is highly likely that other tar production techniques existed, and these could produce similar results. Therefore, generalized suggestions are more useful and reliable to assess the archaeological record than specific statements. For example, instead of concretely saying based on PCA (Fig. 7) that the Mesolithic population in the Netherlands used the condensation and/or ash mound techniques to produce hafting adhesives, it would be more appropriate to state that the adhesives were produced using a method that heats the bark softly for short periods of time, similar to the condensation and ash mound techniques.

5. Conclusions

In this paper we presented the largest collection of GC-MS results of aceramic birch tars, and we demonstrated the usefulness of combining biomarkers and heating markers in a statistical approach to differentiate different tar production techniques. However, our results also show that identifying tar production techniques using GC-MS is complicated. The percentages of pentacyclic triterpenoid biomarkers, soft heating markers, and strong heating markers, vary between each production technique and are likely linked to the length of the heating process and the tar collection method. However, the overlap between the molecular signatures of the techniques and the variability within each technique prohibit confident identification. In the case of the experimental samples, this variability may relate to known inconsistencies in tar production, *e.g.* how the tar was collected, the length and rate of heating, the maximum temperature, the type and quantity of bark used. In archaeological contexts, these variables would increase as there is an infinite number of ways to produce tar if idiosyncrasies are considered. Despite these difficulties, there is still value in attempting to descriptively characterize techniques used in the past based on the molecular signatures of archaeological tar samples as they vary in relation to specific actions part of the production process.

Data availability

The data that support the findings of this study are openly available in the 4TU.ResearchData repository: "Gas Chromatography-Mass Spectrometry data used to identify ancient aceramic birch tar production methods". https://doi.org/10.4121/87cdb877-3757-4e05-8618-906140752a83.

CRediT authorship contribution statement

Rivka Chasan: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Liliana Iwona Baron:** Formal analysis, Methodology, Resources, Writing – review & editing. **Paul R.B. Kozowyk:** Conceptualization, Investigation, Visualization, Writing – review & editing. **Geeske H.J. Langejans:** Conceptualization, Funding acquisition, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Geeske H.J. Langejans reports financial support was provided by European Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jas.2024.105960.

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