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Pine traces at Star Carr: evidence from residues on stone tools

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ABSTRACT

The combined use of microscopy and organic residue analysis on stone tools from the Early Mesolithic site of Star Carr, England, has tentatively identified residues consistent with pine (Pinaceae family) tree compounds. Microscopic residues from nine stone tools, originating from several locations and dated between ca 9300–8500 cal BC, were found to contain traces of diterpene compounds, consistent with dehydroabietic acid (DHA), 7-oxo-dehydroabietic acid (7-oxo-DHA), and dehydro-7-dehydroabietic acid (dehydro-7-DHA) through analysis by GC-MS. Sediment samples taken directly underneath each tool did not contain any of the above compounds associated with Pinaceae. The results suggest the use of Pinaceae resin by Early Mesolithic hunter-gatherers in this region.

Keywords:
Residue analysis; stone tools; reflected visible light microscopy (VLM); gas chromatography-mass spectrometry (GC-MS); Mesolithic; Star Carr

HIGHLIGHTS

- First time conifer resins are directly associated with stone tools from Star Carr
- First use of GC-MS on stone tools with residues only visible at a microscopic scale
- Sediment samples from burial environment yielded no resin compounds
- Link suggested between stone tools and their use in Early Mesolithic Britain

1 Introduction

Star Carr is an important Early Mesolithic site in North Yorkshire, England, dating to ca 9300-8500 cal BC (Fig. 1). Recent excavations, undertaken since 2004, have made remarkable discoveries including substantial wooden platforms, evidence for

the earliest ‘house’ (Conneller et al., 2012) and the earliest example of Mesolithic portable art in Britain (Milner et al., 2016). A total of 614 stone tools and 614 sediment samples have been meticulously recovered from well-dated deposits using anti-contamination protocols, specifically for residue analysis (Croft, 2017). These remains allow an investigation of many aspects of lithic production, including microscopic organic residues potentially associated with usage and technology.

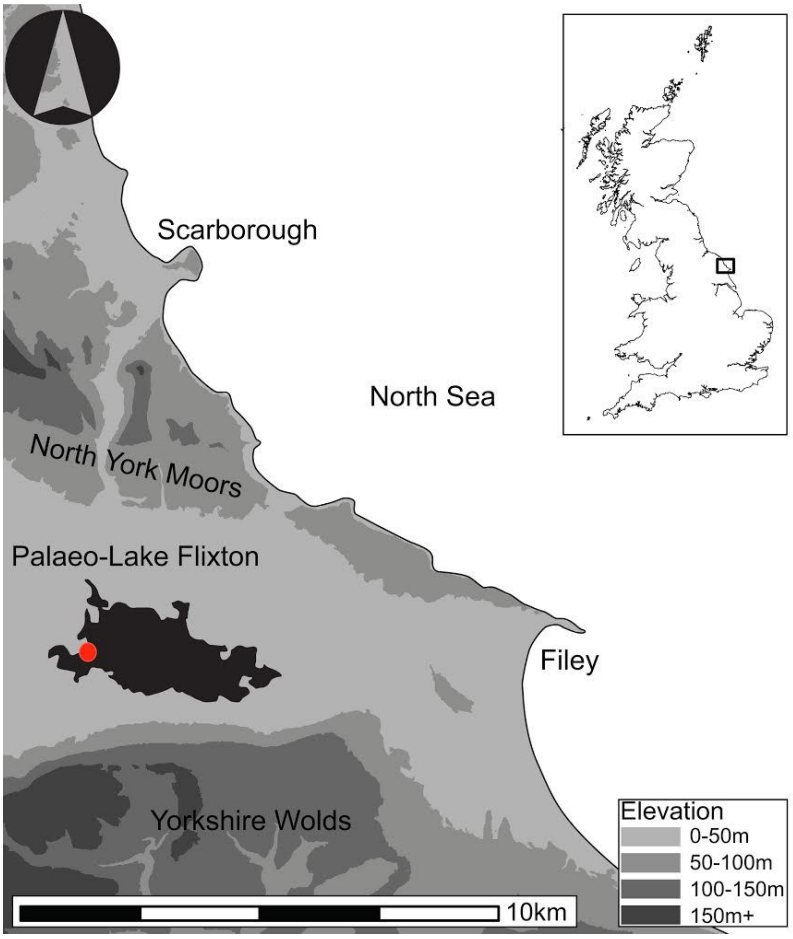

Fig. 1
Location of the site of Star Carr in North Yorkshire, UK. (Sourced from Milner et al. 2016, *Internet Archaeology* licenced under CC-BY 2.0).

Recent studies of stone tools from Star Carr identified residues microscopically and chemically characterised them using SEM-EDS, FTIRM, and micro-Raman spectroscopy (Croft, 2017; Croft et al., 2018). These analyses showed that most residues were not anthropogenic and likely originated from the changing chemical composition of the sediment (Boreham et al., 2011b, 2011a; Milner et al., 2011). Micro-Raman in particular was useful to determine residue origin. Amorphous red-orange deposits on stone tools were hypothesised to be resinous residues based on microscopic appearance, but when tested using micro-Raman spectroscopy were identified as iron (III) oxide (Croft et al., 2018), a material also identified from ochre artefacts at other Mesolithic sites near Star Carr (Needham et

al., 2018). Likewise, it was also determined using micro-Raman spectroscopy that lithic residues proposed as possible silica phytoliths or woody tissue were actually gypsum (Croft et al., 2018). Gold coloured crystals investigated with micro-Raman spectroscopy on an engraved shale pendant from Star Carr were revealed as pyrite framboids that form naturally in peat (Milner et al., 2016). Collectively, these results demonstrated that interpretation of residue identity based only on visible observations has the potential to be incorrect. As previously shown experimentally by Monnier et al. (2012), Pedergnana and Blasco (2016), Croft et al. (2016), and Croft (2017), there are often no diagnostic structures visible in crushed and smeared modern lithic residues, such as muscle and bone, when reflected visible light microscopy (VLM) and/or SEM are used. These studies have highlighted the issue of reliability of archaeological residue identification by visual means alone.

Gas chromatography coupled with mass spectrometry (GC-MS) has been previously used to characterise the chemical nature of amorphous organic residues on stone tools following solvent extraction, in many cases to investigate the origin of putative resinous and bituminous residues. Examples of resinous and bituminous residues on stone tools, identified using GC-MS, include birch bark tar (*Betula* sp.) (Mazza et al., 2006), conifer resin (*Podocarpus elongatus*) (Charrié-Duhaut et al., 2016, 2013), and bitumen (Boëda et al., 2008, 2002, 1996; Cârciumaru et al., 2012; Hauck et al., 2013) from the Palaeolithic; and birch bark tar and pine resin (Regert, 2004; Regert et al., 1998) from the Neolithic. In North America, GC-MS has identified spruce resin on several stone tools from sites in the Canadian Yukon stretching over a 6000 year period (Helwig et al., 2014).

Organic residue analysis was previously conducted at Star Carr by Aveling and Heron (1998) on one of the microliths with a lump of resin adhering to it and five ‘resin cakes’ – all found in Grahame Clark’s original excavations (1954). Their GC and GC-MS results clearly demonstrate the presence of manufactured birch bark tar at the site. However, during our excavations and examination of every piece of flint, no signs of residues were visible at the macroscopic level and no further ‘resin cakes’ were found. Lumps of birch bark tar found as both individual pieces and lithic residues have been unearthed at other Mesolithic sites in Northern Europe, identified by simple visual inspection (Bang-Andersen, 1989; Bokelmann et al., 1981; Gramsch and Kloss, 1989), and GC-MS and direct temperature resolved mass spectrometry (DTMS) (Aveling, 1998; Aveling and Heron, 2000, 1999; Roberts et al., 1998; Van Gijn and Boon, 2006). Here we present the first use of mass spectrometry techniques on stone tools where the residues were only visible at the microscopic scale.

This paper investigates the chemical signatures of visible amorphous residues preserved on nine Mesolithic stone tools from Star Carr. The residues were analysed

using GC-MS, which detected compounds typically attributed to Pinaceae resin. This is the first time that conifer resins are directly associated with stone artefacts at the site, suggesting a link between stone tool manufacture and use during the Early Mesolithic in Britain.

2 Methods

2.1 Sampling procedure

During excavations, a total of 614 stone tools and sediment samples were taken on site for residue analysis. In order to reduce potential modern contamination, the stone tools were carefully levered out of the sediment and placed in individual plastic zip-lock bags, without contact with hands. Associated sediment samples were taken directly underneath each stone tool and also placed into zip-lock bags. Of these, a subsample of 138 stone tools (~23%) were examined using reflected VLM (Croft, 2017).

Out of 138 stone tools, twelve pieces with amorphous dark deposits were selected for organic residue analysis by GC-MS. In addition, five negative controls (stone tools with no microscopically visible residues) were analysed. Chromatograms from all tools were examined first, then sediment sample controls (n = 9) for tools containing Pinaceae compounds and all negative controls were analysed.

Samples of sediment taken directly underneath each excavated tool were laid out on aluminium foil-lined trays, loosely covered with foil, and air dried at ambient temperature (~20 °C) to remove moisture. Each sediment sample was homogenized with an agate mortar and pestle rinsed with dichloromethane (DCM) between each sample. Homogenized samples were weighed to 1 g and placed in glass tubes containing 100 µl of the internal standard C_{34} alkane (at concentration of 1 µg/µl).

Powder and starch-free gloves (Semperguard®) were worn during handling and cleaning of stone tools, and gloves were changed between samples to avoid cross-contamination. Each stone tool was cleaned with deionized water and laid out to dry on trays lined with a new layer of cling film. For microscopic analysis, the stage was prepared in the same way as noted by Croft et al. (2016). Blu-Tack® was used to provide a moldable support base for each tool, which was overlaid with a new layer of plastic paraffin film (Parafilm M®) to create a fresh unused surface that separated the moldable Blu-Tack® from each stone tool. This prevented contamination and loss of residues. Each stone tool was placed on the microscope stage and manoeuvred using a new glove.

2.2 Reflected visible light microscopy (VLM)

Stone tools were first examined with reflected VLM (Leica DM1750 M). All edges as well as the dorsal and ventral surfaces of the tools were scanned using the 10x and 20x objectives and potentially resinous residues were located (Fig. 2). Microscopic visual characteristics recorded for each *in situ* residue included colour, shape, texture, brightness, reflectivity, transparency, structural patterns, presence of identifiable cell margins (where possible), presence of microcrystals and their colour and shape, nature of residue deposit edges (circular, ragged, angular, etc.). Residue locations were documented and z-stacked images taken using Leica Application Suite. After organic extractions, locations of the residue deposits were revisited with reflected VLM to confirm that the target residue had been removed by the solvent and sonication (see Fig. 3).

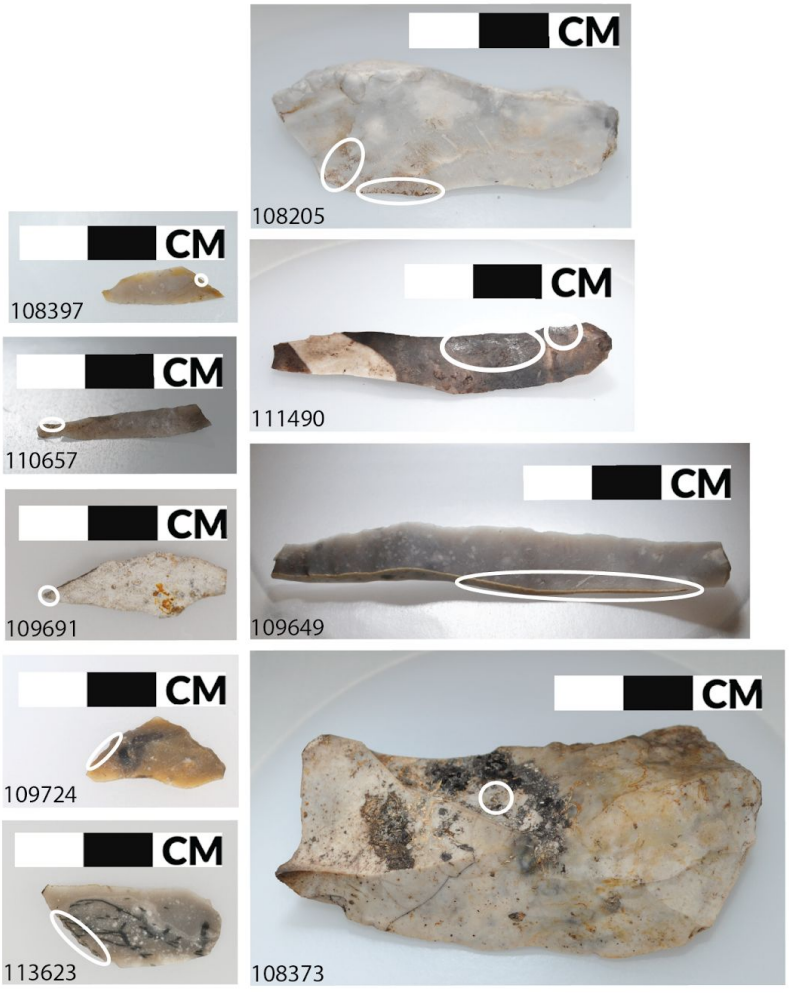

Fig. 2
The location of residues found on nine stone tools.

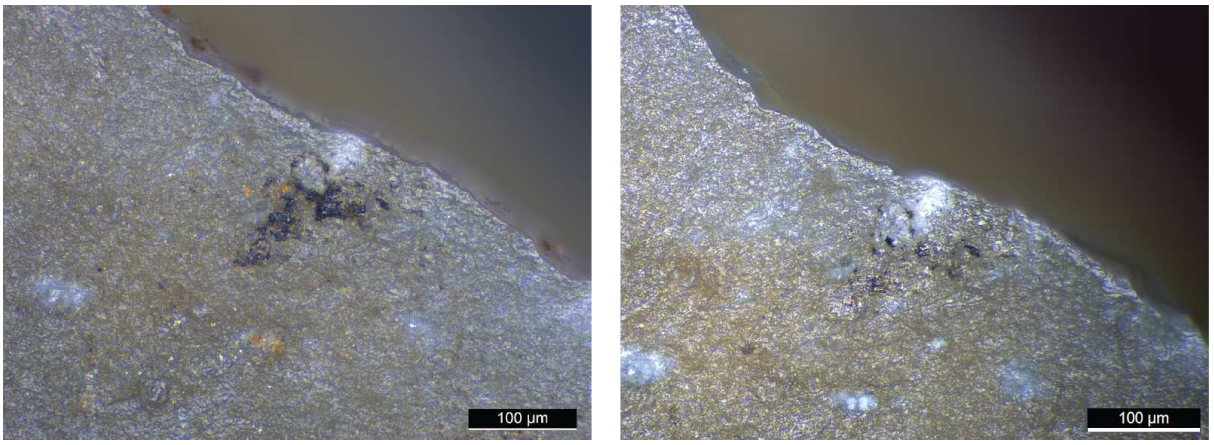

Fig. 3.
Left: Black amorphous residue located on microlith 108397, prior to solvent extraction and GC-MS. Right: Black residue deposit after GC-MS. Most of the deposit was removed but some residue still remains.

2.3 Organic residue analysis

Twelve stone tools containing amorphous dark coloured residues, and their associated sediment samples (controls to test the burial environment), were selected for lipid extraction and GC-MS analysis. These residues were hypothesised to be resinous based on their microscopic appearance.

Five additional tools and their associated sediments were selected to provide a negative control group. These tools lacked visible microscopic residues, thus no response for resin-related compounds was expected from the tools or associated sediments by GC-MS. All samples are listed in Table 1. Blank controls to test for lab contamination were included as standard protocol during preparation of samples and GC-MS.

Table 1

Sampled archaeological stone tools, negative controls, and sediment sample controls.

Number	**Type**	**Sample type**	**Context**	**Context description**
94554	Microlith fragment	Tool with residues	308	Grey/orange clay on dry land part of the site
95828	Burin	Tool with residues	310	Wood peat
94362	Flake	Tool with residues	310	Wood peat
108205	Burin	Tool with residues	312	Reed peat
108373	Blade	Tool with residues	337	Fill of small pit
108397	Microlith	Tool with residues	325	Upper fill of dark silty feature/structure
109649	Blade	Tool with residues	317	Detrital muds
109691	Microlith	Tool with residues	415	Small sandy lens in tree-bowl

109724	Microlith	Tool with residues	466	Possible fill of feature
110657	Bladelet	Tool with residues	301	Oxidised peat
111490	Bladelet	Tool with residues	310	Wood peat
113623	Microlith	Tool with residues	310	Wood peat
93593	Blade	Negative control	308	Grey/orange clay on dry land part of the site
98858	Bladelet	Negative control	317	Detrital muds
99276	Bladelet	Negative control	312	Reed peat
99851	Blade fragment	Negative control	312	Reed peat
108206	Scraper	Negative control	310	Wood peat
108205_S	–	Sediment sample control	312	Reed peat
108373_S	–	Sediment sample control	337	Fill of small pit
108397_S	–	Sediment sample control	325	Upper fill of dark silty feature/structure
109649_S	–	Sediment sample control	317	Detrital muds
109691_S	–	Sediment sample control	415	Small sandy lens in, tree-bowl
109724_S	–	Sediment sample control	466	Possible fill of feature
110657_S	–	Sediment sample control	301	Oxidised peat
111490_S	–	Sediment sample control	310	Wood peat
113623_S	–	Sediment sample control	310	Wood peat

Microsampling by drilling, use of tweezers, or swabbing with solvent, was not attempted because residues were too small and discontinuous, covering areas on each tool ranging from about 0.01 mm^2 to 100 mm^2 cumulatively. To ensure the target residues were removed, it was necessary for stone tools to be completely immersed in organic solvent and sonicated.

Each stone tool was immersed in 2:1 dichloromethane/methanol (DCM:MeOH; 3 x 30 ml) and 100 µl of the internal standard C_{34} alkane (at concentration of 1 µg/µl) was added, ultra-sonicated for 15 min and centrifuged at 3,000 RPM for 10 min. The supernatant was removed with a sterile pasteur pipette to a sterile glass tube. Lipid-soluble residues were solvent extracted from soils using the same protocol as stone tools. However, the sediment extracts had to be filtered through sterile glass pasteur pipettes stuffed with sterile glass wool to remove particulate matter.

All samples were transferred to sterile hydrolysis vials, evaporated under a gentle stream of N_2 on a heating block and stored in the freezer at -20 °C prior to derivatisation. Samples were silylated with 150 µl of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trichloromethylsilane (TCMS) at 70 °C for one hour. Samples were evaporated again under a gentle stream of N_2, transferred to GC vials and 10 µl of internal standard C_{36} alkane (at concentration of 1 µg/µl) was added to each sample. Samples were analysed using a 7890A Series chromatograph attached to a 5975C Inert XL mass-selective detector with a quadrupole mass analyser (Agilent Technologies, Cheadle, UK). The type of ionisation used was electron impact ionisation with an ionisation energy of 70 eV. The GC column used was a DB-5ms (5%-phenyl)-methylpolysiloxane column (30 m × 0.250 mm × 0.25 µm; J&W Scientific, Folsom, CA, USA) and helium was the carrier gas. The temperature for this column was set at 50°C for 2 min, rising by 10°C/min to 325°C, where it was maintained for 15 min. Data acquisition time was 44.5 min. The samples were injected with a splitless injector and the injector temperature was 300°C.

For data analysis, Agilent MSD Chemstation software (version G1701EA E.02.02.1431) was used. Compounds in spectra were identified by comparison with the National Institute of Standards and Technology (NIST) Library, published literature, and prepared modern resins. Peak areas were used for relative quantification by comparison with the known amount of the internal standard (C_{36} alkane).

3 Results

Nine of the twelve tools with dark coloured amorphous residues contained compounds consistent with Pinaceae tree resin: four microliths, two blades, two bladelets, and one burin. Although Pinaceae contains the genera *Abies, Cathaya, Cedrus, Keteleeria, Larix, Nothotsuga, Picea, Pinus, Pseudolarix, Pseudotsuga,* and *Tsuga,* only *Pinus* was present during the Early Mesolithic in the Vale of Pickering, where the Star Carr site is located. More specifically, resin originating from *Pinus sylvestris* (scots pine) is the most likely source based on palynological evidence from the Vale of Pickering. The five tools in the negative control group that contained no microscopic potentially resinous residues were negative for Pinaceae compounds.

The dark coloured amorphous residues found on tools did not appear to exhibit a regular pattern of occurrence on tool surfaces. Rather, these deposits were found in several locations on tools, including places not expected to be associated with hafting such as distal pointed tips and confined to the centre areas of tools. The

distribution of residue was also minimal, usually covering only a fraction along a tool edge. The microscopic nature of the residues and small sample size in this study makes interpretations of tool use speculative, however, some possibilities are discussed below.

The nine tools that contained compounds related to Pinaceae were recovered from both waterlogged and dry areas of Star Carr (Fig. 4). There is no apparent clustering spatially of these tools on site, but three tools were associated with the dry land structures.

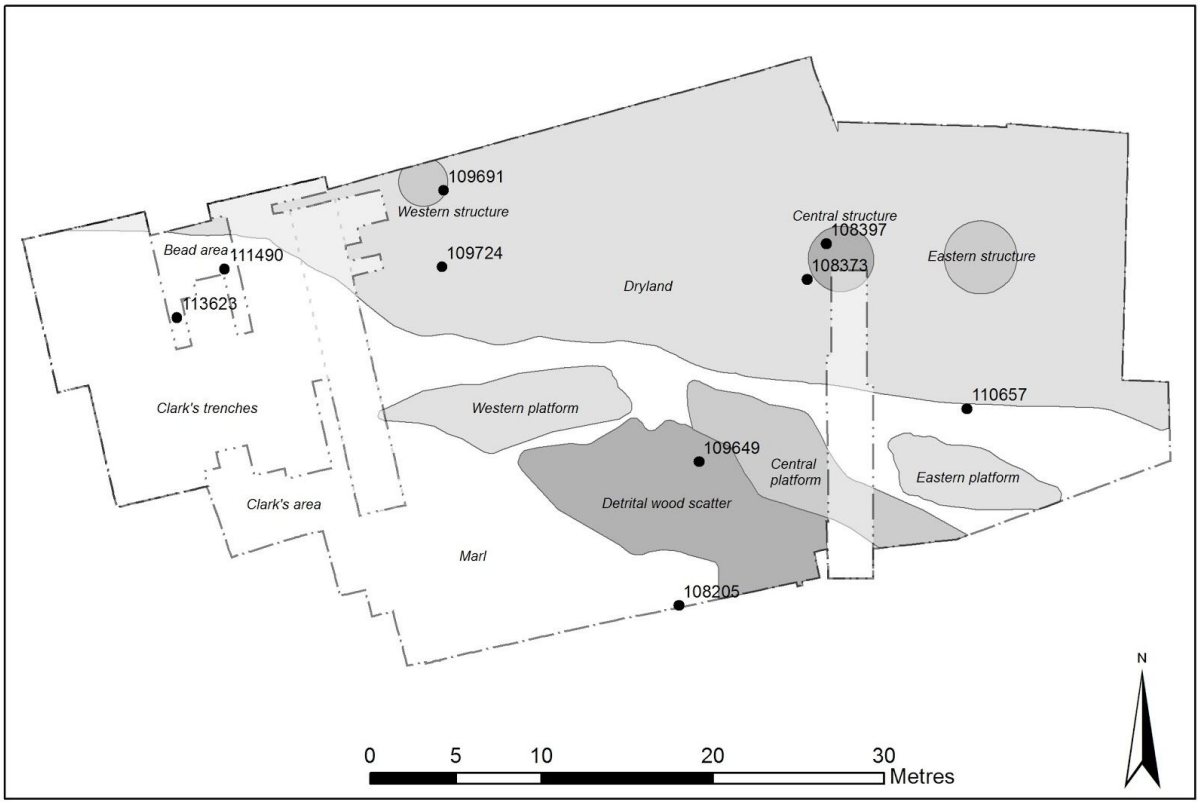

Fig. 4
Location of nine stone tools that contained organic residues with Pinaceae compounds.

A range of organic compounds were found, including saturated fatty acids (e.g. $C_{14:0}$ myristic acid, $C_{16:0}$ palmitic acid, $C_{18:0}$ stearic acid) and dicarboxylic acids (adipic acid, azelaic acid). Nine of the tool samples contained products related to common natural fatty acids found in plants and animals, with palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$), found in tool extract samples from 108205, 108373, 108397, 109649, 109691, 109724, 110657, 111490, and 113623. Palmitic acid and stearic acid were present in six of nine sediment sample controls. Both these compounds are ubiquitous and can originate from the flint, a resin, or transfer to stone tools from the sediment.

3.1 Diterpenoid compounds associated with Pinaceae *resin*

Three conifer-derived diterpenoid resin acids, considered as altered products of abietic acid, were identified: dehydro-7-dehydroabietic acid (Dehydro-7-DHA), dehydroabietic acid (DHA), and 7-oxo-dehydroabietic acid (7-oxo-DHA). Five tools contained three diterpenoid resin acids: Dehydro-7-DHA, DHA, and 7-oxo-DHA, and a further four tools contained two of these diterpenoids: Dehydro-7-DHA and DHA (Table 2). These diterpenoid resin acids have an abietane skeleton and have been reported in archaeological and historical samples as markers indicative of Pinaceae resin (Andreotti et al., 2006; Colombini et al., 2005; Evershed et al., 1985; Fox et al., 1995; Helwig et al., 2008; Hjulström et al., 2006; Mills and White, 1977, 2012; Pastorova et al., 1997; Pérez-Arantegui et al., 2009; Pollard and Heron, 2008; Proefke and Rinehart, 1992; Regert, 2004; Regert et al., 2005, 2003b; Regert and Rolando, 2002; Richardin, 1996; Robinson et al., 1987; Scalarone et al., 2002; Scalarone and Chiantore, 2009; Van den Berg et al., 2000, 2003). A chromatogram and mass spectra from one of the tools (burin 108205) containing Dehydro-7-DHA, DHA, and 7-oxo-DHA is presented in Fig. 5.

Table 2
Diterpenoids found on each tool.

Number	**Tool type/sediment sample**	**Context**	**Microscopic description of residues**	**Residue location**	**Pinaceae resin compounds**
108205	Burin	Reed peat	Black shiny deposits with bubbly smooth appearance	Dorsal left mid edge and dorsal centre distal, slightly left	DHA, Dehydro-7-DHA, 7-oxo-DHA
108205_S	Sediment sample control	Reed peat	N/A	N/A	–
108373	Blade	Fill of small pit	Black shiny deposit associated with microcharcoal, unburnt wood fragments, and sediment adhering	Dorsal surface, centre	DHA, Dehydro-7-DHA, 7-oxo-DHA
108373_S	Sediment sample control	Fill of small pit	N/A	N/A	–
108397	Microlith	Upper fill of dark silty feature/structure	Black amorphous deposit	Ventral proximal mid edge	DHA, Dehydro-7-DHA, 7-oxo-DHA
108397_S	Sediment sample control	Upper fill of dark silty feature/structure	N/A	N/A	–

109649	Blade	Detrital muds	Black granular deposits	Cortex surface, ventral left proximal edge. Same deposit type also along reverse edge of tool, dorsal right side, mid edge	DHA, Dehydro-7-DHA, 7-oxo-DHA
109649_S	Sediment sample control	Detrital muds	N/A	N/A	–
109691	Microlith	Small sandy lens in tree-bowl	Microcharcoal	Ventral distal tip	DHA, Dehydro-7-DHA
109691_S	Sediment sample control	Small sandy lens in tree-bowl	N/A	N/A	–
109724	Microlith	Possible fill of feature	Microcharcoal	Ventral left curved edge.Same deposit type also along reverse edge of tool, dorsal right edge	DHA, Dehydro-7-DHA
109724_S	Sediment sample control	Possible fill of feature	N/A	N/A	–
110657	Bladelet	Oxidised peat	Q black resinous deposit associated with white crystalline material (Q bone or Q mineral?)	Ventral right distal edge	DHA, Dehydro-7-DHA, 7-oxo-DHA
110657_S	Sediment sample control	Oxidised peat	N/A	N/A	–
111490	Bladelet	Wood peat	Black shiny material which appears cracked and platelike	Large areas of the ventral surface covered	DHA, Dehydro-7-DHA
111490_S	Sediment sample control	Wood peat	N/A	N/A	–
113623	Microlith	Wood peat	Black plant material, associated with iron oxide	Ventral left edge	DHA, Dehydro-7-DHA
113623_S	Sediment sample control	Wood peat	N/A	N/A	–
94362	Flake	Wood peat	Bright sparkly black deposits containing potential striations (Q tar, Q plant remains?)	Dorsal right mid and proximal edges	–
94554	Blade fragment	Grey/orange clay on dry land part of the site	Black spots, Q tar. Translucent residue along edge, contains black specks, Q charcoal frags?	Ventral distal edge	–

95828	Burin	Wood peat	Black spots, Q tar, Q charcoal. With polariser and analyser, bright white parts of the residue turn black	Dorsal right proximal edge	–
93593 negative control	Blade	Grey/orange clay on dry land part of the site	No potentially resinous residues	N/A	–
98858 negative control	Bladelet	Detrital muds	No potentially resinous residues	N/A	–
99276 negative control	Bladelet	Reed peat	No potentially resinous residues	N/A	–
99851 negative control	Blade fragment	Reed peat	No potentially resinous residues	N/A	–
108206 negative control	Scraper	Wood peat	No potentially resinous residues	N/A	–

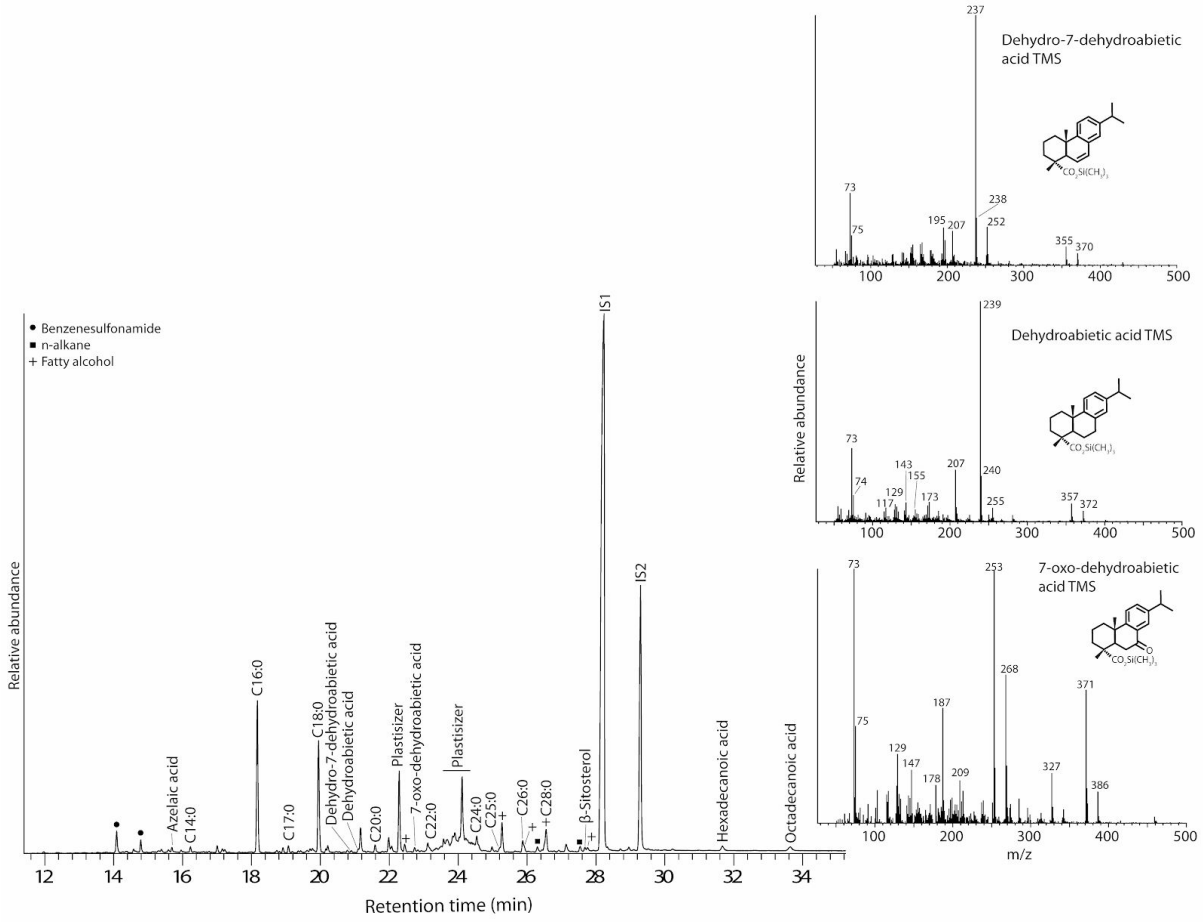

Fig. 5
Total ion chromatogram of the trimethylsilylated residue extract from burin 108205 containing trace amounts of Dehydro-7-DHA, DHA, and 7-oxo-DHA. $C_{n:x}$ indicates fatty acid with n carbon atoms and x double bonds, IS1 and IS2 indicates the internal standards C_{34} and C_{36} respectively. Inset: mass spectra of Dehydro-7-DHA, DHA, and 7-oxo-DHA.

Retene, a thermal alteration marker resulting from the strong heating of Pinaceae resin (Font et al., 2007; Modugno and Ribechini, 2009), was not present in any of the extracts from stone tool residues. Abietic acid was also not found in any tool samples. Perhaps this is not surprising since abietic acid is dominant in fresh (bleed) resin, but is transformed in atmospheric conditions into oxidised compounds (Beltran et al., 2016).

Despite the visual presence of black potentially resinous deposits on tools 94362, 94554, and 95828, no diterpenes were found in their extracts. This finding cautions that the visual identification of lithic residues can be misleading or exhibit high ambiguity, supporting the previous results of Monnier et al. (2012), Pedergnana and Blasco (2016), Croft et al. (2016), Croft (2017), and (Croft, 2017; Croft et al., 2018)).

3.2 Controls

Tool extracts were compared to their underlying sediment sample controls. By taking this step, the sediment as a possible contamination source on the stone tools could be excluded. DHA, 7-oxo-DHA, and dehydro-7-DHA were not present in any of the sediment extracts (Table 2). As a group, the sediment sample controls were typically characterised by the presence of saturated fatty acids, alkanes and alcohols, as well as plant sterols (Fig. 6).

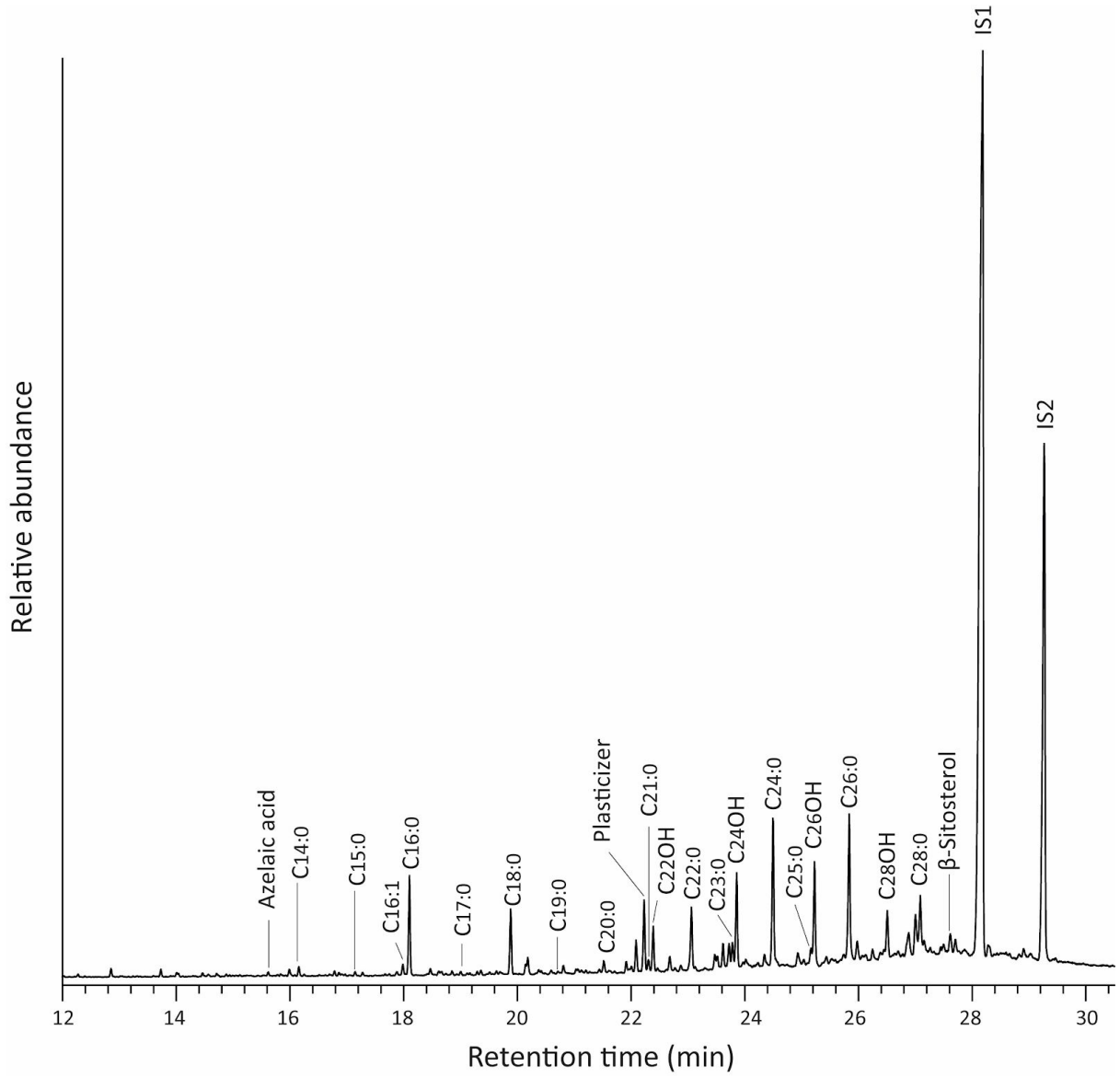

Fig. 6
Example of a sediment sample control total gas chromatogram collected underneath tool 108373. Note Dehydro-7-DHA, DHA, and 7-oxo-DHA are not present. Cn:x indicates fatty acid with n carbon atoms and x double bonds, CnOH indicates 1-alkanol with n carbon atoms, IS1 and IS2 indicates the internal standards C36 and C34 respectively.

The negative controls did not contain DHA, 7-oxo-DHA, or dehydro-7-DHA. Three of the twelve tools that were hypothesised to contain resinous residues based on microscopic observations did not contain them. This finding suggests that visual observations should be tested by chemical characterisation techniques. Modern contaminants (*m/z* ion 149, phthalic acid; (Ji et al., 2013; Li et al., 2013) were detected in both tools and sediments, most likely derived from the plastic zip lock bags used to collect stone tools and sediment samples, or cling film used as a clean surface for drying stone tools after cleaning.

4 Discussion

4.1 Natural or anthropogenic Pinaceae *diterpenoids?*

Pinaceae compounds dehydro-7-DHA, DHA, 7-oxo-DHA were found on nine stone tools. These could be the remains of archaeological Pinaceae resin residues or natural deposits from direct or indirect exposure to burning wood. The nature of the data is considered below.

Evidence of pine macrobotanical remains, such as wood, needles, or cones, at Star Carr to corroborate the chemical findings is lacking (Radini et al., 2018). However, Pinaceae resin could have been collected when people traveled outside of the immediate surroundings of Star Carr. It is also possible that tools with Pinaceae resin already on their surfaces were brought to the site from elsewhere.

It might be posited that the tools found to contain Pinaceae resin acids at Star Carr were heat treated in a fire containing embers of Pinaceae wood, and hence diterpenoid compounds from dripping resin could have transferred to the surfaces of the flint. Schmidt et al. (2016, 2015) proposed that heat treatment of silcrete was carried out at the Middle Stone Age site of Diepkloof Rock Shelter, South Africa, as evidenced by the similar presence and locations of black heat tempering-residues on both experimental and archaeological tools. Perhaps it is possible that Mesolithic people at Star Carr were heat treating the flint prior to knapping, but again there are no pine macrobotanical remains on site, so no evidence of fires with Pinaceae wood are present. Also, heat treatment does not make sense as a practical manufacturing choice for the flint artefacts found at Star Carr. The majority of stone tools from the site are made of a high quality cryptocrystalline glacial till flint, so fracturing properties would not be improved significantly by heating.

Diterpenoid resin acids can also be found within smoke particulates from burning conifer wood (Simoneit, 2002). Wood burning experiments by Simoneit et al. (2000) and Fine et al. (2002) showed that DHA and 7-oxo-DHA, among others, were found in smoke residues from two pine species (*Pinus elliottii* and *Pinus taeda*). The tool samples from Star Carr did contain DHA and 7-oxo-DHA, which were also found in particulates in smoke from modern *Pinus* wood campfires. However, other major markers of pine smoke (found in *Pinus elliottii* and *Pinus taeda*) reported by Simoneit et al. (2000) and Fine et al. (2002), including pimaric acid, isopimaric acid, sandaracopimaric acid, abietic acid, retene, levoglucosan (a product of cellulose pyrolysis), and lignin phenolics such as vanillic acid, were not found in any of the tool samples or sediment sample controls. Levoglucosan specifically should have been found in tool samples if the residues resulted from exposure to wood smoke, since it is the most abundant organic compound in both hardwood and softwood smoke by mass (Fine et al., 2002; Simoneit et al., 1999). Also, dehydro-7-DHA (found in some

tool samples), has not been detected in *Pinus* wood smoke, but has been reported in archaeological resin samples.

Refitting sequences evidence tool manufacture both on and off site (Conneller et al., 2018), so Pinaceae compounds originating from elsewhere must be considered. Because no macrobotanical pine remains have been securely identified at Star Carr, there are a number of scenarios which are less likely or difficult to support: 1) the tools found to contain Pinaceae resin acids were heat treated on site at Star Carr in a fire with Pinaceae wood embers, and further excavations may recover evidence of the Pinaceae wood, 2) tools were exposed to Pinaceae wood smoke following discard at Star Carr, and further excavations may recover the Pinaceae wood, 3) people made tools off site using a fire treatment with Pinaceae wood, although no heat tempering-residues like those Schmidt et al. (2016, 2015) reported were found, or 4) people made tools off site that were exposed to Pinaceae wood smoke that were brought to Star Carr.

Secondly, a clear and consistent connection between the microscopic appearance of dark coloured deposits and the positive identification of the Pinaceae resin acids in tool extracts could not be established. Rather, a variety of dark residue morphologies were seen on the tools from Star Carr, including granular, cracked, shiny and bubbly. Perhaps Pinaceae resin residues can exhibit multiple morphologies under the microscope; this appears to corroborate observations of *Pinus* resin during burial experiments by Croft et al. (2016). Experimentally buried *Pinus* resin residues examined by Croft et al. (2016) appeared variably granular, smooth, textured, amorphous, diffuse, shiny, opaque, and with colours ranging from white to red to brown/black. Aged Pinaceae residues from a Norman wig dated to AD 1123–895 from Romsey Abbey, Hampshire, UK, containing DHA (methyl ester), Dehydro-DHA (TMS derivative), DHA (TMS derivative), and 7-oxo-DHA (TMS derivative), identified with GC-MS were also a black colour (Cameron et al., 2017), but further microscopy or visual information was not available.

Thirdly, the Pinaceae resin-related peaks (alteration markers dehydro-7-DHA, DHA, and 7-oxo-DHA) in samples were small, in every case yielding signals lower in abundance than other fatty acids and plasticizers present in the chromatograms. The quantity of dehydro-7-DHA in tool samples was between 13–636 ng, DHA between 120–328 ng, and 7-oxo-DHA between 28–440 ng.

The low abundance of Pinaceae resin compounds present might suggest contamination of the samples, but lab contamination can be ruled out as the source of the diterpenoid markers since none of the Pinaceae compounds were found in the method blanks. Also, a sediment source of the Pinaceae compounds from environmental contamination of the flint can also be excluded, since no sediment

samples contained Dehydro-7-DHA, DHA, or 7-oxo-DHA. Recently, Costa et al. (2016) found that abietic acid and/or DHA are produced by ten types of prokaryotic cyanobacteria from marine, estuarine and inland habitats. Thus, the status of abietic acid and DHA as biomarkers specific to conifer plants has been called into question. If the DHA found here on stone tools originated from cyanobacterial contamination, it is reasonable to expect DHA to be present in the surrounding burial environment as well, but this was not the case. The minimal traces available for sampling in this study – microscopic residues – may have contributed to the finding of low concentrations of Pinaceae compounds.

It might be argued that the trace levels of Pinaceae resin acids present on the stone tools are too low for robust archaeological interpretations to be drawn. However, the levels are similar to those observed by Giachi et al. (2013) and Bianchin et al. (2009). Giachi et al. (2013) interpreted low concentrations of DHA and 7-oxo-DHA relative to the internal standard as indicating the presence of Pinaceae resin in a 2,000-year-old Etruscan medicine tablet. Similarly, Bianchin et al. (2009) found low concentrations of dehydro-DHA, DHA, and 7-oxo-DHA from an Italian Renaissance altarpiece painting, and considered this evidence of Pinaceae resin.

Fourthly, just three diterpenoids marker compounds were found in the tool samples. The identification of a full suite (five or more) of Pinaceae resin-related acids from historical and archaeological samples have been described (Bailly et al., 2016; Burger et al., 2013; Egenberg et al., 2002; Fox et al., 1995; Helwig et al., 2008; Hjulström et al., 2006; Modugno and Ribechini, 2009; Rageot et al., 2016; Regert, 2004; Regert et al., 2005; Ribechini et al., 2009, 2008), and such reports provide stronger evidence for the interpretation of ancient Pinaceae resin. Our results are similar to other findings that identify Pinaceae resin on the basis of two to four altered abietic acid marker compounds (Bianchin et al., 2009; Čukovska et al., 2012; Giachi et al., 2013; Pérez-Arantegui et al., 2009; Proefke and Rinehart, 1992).

4.2 The case for an anthropogenic origin of Pinaceae *resin*

Perhaps the strongest argument for an anthropogenic and intentional origin of Pinaceae compounds on stone tools from Star Carr is offered by pollen records. At Star Carr, scots pine (*Pinus sylvestris*) pollen is present throughout all the sequences taken from both the lake-edge (four monoliths) and from the lake centre (one monolith) of Palaeolake Flixton (Dark, 1998a, 1998b). Significantly, no other pollens from the Pinaceae genera (*Abies, Cathaya, Cedrus, Keteleeria, Larix, Nothotsuga, Picea, Pseudolarix, Pseudotsuga,* and *Tsuga*) have been found in these cores. The dates from the pollen cores taken by Dark relate to occupation at Star Carr, and also agree with a recent high-resolution dating programme at Star Carr

(Bayliss et al., 2018). Other pollen data by Innes et al. (2011) also supports the presence of scots pine in Dark's pollen cores (Dark, 1998a, 1998b). The continuous pollen curves for scots pine, in conjunction with pollen percentages of ca 10–20% and concentration curves that also suggest its pervasiveness indicate that scots pine was highly likely to have been present in the wider landscape during occupation of Star Carr.

Pine (*Pinus*) pollen is bisaccate (two air-filled sacs are attached to each pollen grain) and able to travel considerable distances from the tree, up to 100+ kilometers (Schuster and Mitton, 2000). However, in a study of scots pine pollen dispersal, Robledo-Arnuncio and Gil (2005) found the tree has an average pollen dispersal distance of 135 m, with only 7% of effective pollen moving beyond 200 m of the source tree. Even considering that a fraction of *Pinus* pollen can disperse great distances by wind currents, palynologists have still ascribed *Pinus* as present, although likely restricted to specific habitats, in Early Mesolithic environments near Star Carr.

The case for an anthropogenic origin of Pinaceae resin compounds on stone tools from Star Carr is also strengthened in an analogical way by ethnographic evidence. Among hunter-gatherers, *Pinus* resin is universally viewed as a valued resource. Its exploitation for utilitarian items, medicines, and even food, is well-documented and remains widespread. Thus, we suggest any *Pinus* resin available to Mesolithic people in Britain could have been put to myriad applications. *Pinus* resin use by native aboriginal groups in British Columbia, Canada (Turner, 1998, p. 91), California, USA (Balls, 1962, p. 29; Du Bois, 1935, p. 124; Laylander, 2000, p. 133, originally in Eastwood, 1924), Northern Mexico (Bennett and Zingg, 1935, p. 284), Mesoamerica (Langenheim, 2003, p. 296), Malaysia (Gianno, 1990, p. 94), Sweden, Norway, and Finland (Bergman et al., 2004) are noted in ethnographic accounts.

As Aveling and Heron (1998) showed, at least one plant-based adhesive, birch bark tar, was clearly used by the people visiting Star Carr. Contrary to expectation, and particularly considering the dark and shiny appearance of many residue deposits on artefacts, no chemical evidence of birch bark tar was found on tools, based on comparison with three different reference birch bark tars and the literature. However, the finding of compounds consistent with Pinaceae resin may have significant implications for our understanding of the hunter-gatherers that visited Star Carr.

For instance, confirmation of Pinaceae resin at Star Carr via other studies would further bolster the idea that in addition to wood used as construction material for structures and small artefacts (Bamforth et al., 2018; Taylor et al., 2018), Early Mesolithic people actively collected useful tree products such as resins and bark in the landscape (Aveling and Heron, 1998; Fletcher et al., 2018). Given that no

confirmed *Pinus* macrobotanical remains have been found on site, it might be suggested that people used or collected *Pinus* at off-site locations, perhaps at higher elevations. Since *Pinus* resin naturally exudes from the tree, it could have been collected by people casually on an encounter basis, when it was seen during travelling to or from Star Carr. Alternatively, perhaps resin production was made more predictable by purposeful scarification of pine trees, as a type of plant management practice.

The results presented here might also hint that a tradition of resin use existed. The nine tools containing Pinaceae resin compounds were scattered across the site and recovered from a range of contexts, suggesting some time depth in terms of use. It would not be surprising that Mesolithic people exploited any pine resin available. Ethnographic accounts of native peoples everywhere document the use of *Pinus* resin, and their intimate understanding of botanical resources within a network of traditional ecological knowledge (Turner, 2014).

5 Conclusion

This study is the first to report the presence of DHA, 7-oxo-DHA, and Dehydro-7-DHA, from the Early Mesolithic site of Star Carr. These three compounds are derivatives of abietic acid – a biomarker found in the resin of trees of the Pinaceae family. Although the results are preliminary, they are supported by the fact that the Pinaceae compounds found could not be traced to archaeological sediments or a modern contaminant source from the lab. Additionally, the negative control group of tools that contained no potentially resinous residues were negative for Pinaceae resin acids, as expected.

The resin acids were found on nine stone tools and most likely originate from scots pine, since pollen cores from Star Carr document the species as the only Pinaceae tree in the region. Our findings suggest that hunter-gatherers visiting Star Carr were using conifer resin in some way(s), however the precise nature of its exploitation is currently speculative.

Organic residue analysis of amorphous microscopic residues on stone tools can be a sensitive and effective means to test visual observations. Future organic residue analyses of lithic residue studies at Star Carr or other Mesolithic sites in the Vale of Pickering may build on our results and provide additional evidence of Pinaceae resin use.

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