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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.

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.

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., 2011a, 2011b; 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., 2013, 2016), and bitumen (Boëda et al., 1996, 2002, 2008; 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).

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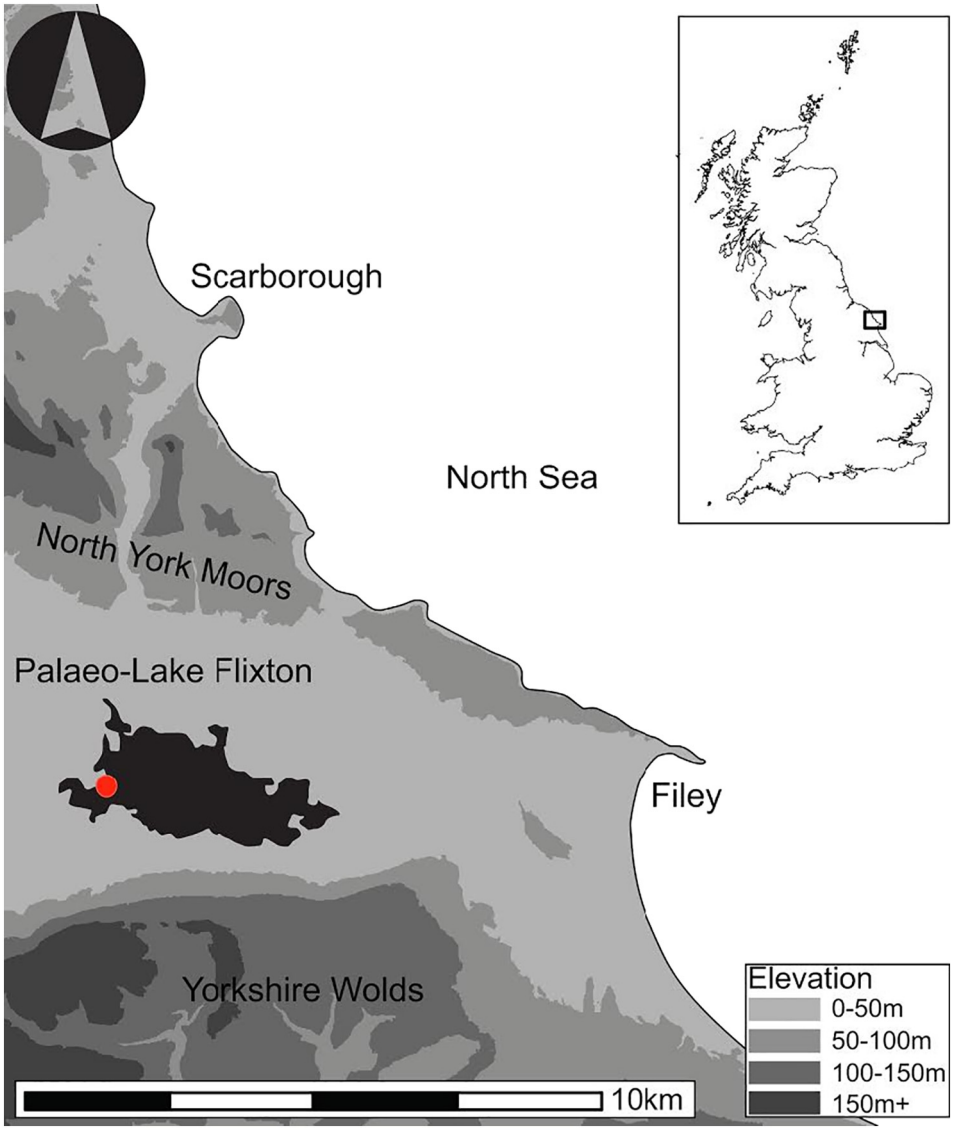

Fig. 1. Location of the site of Star Carr in North Yorkshire, UK.
(Sourced from Milner et al., 2016, *Internet Archaeology* licenced under CC-BY 2.0.)

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 (1954) original excavations. 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, 1999, 2000; 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.

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