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The application of micro-Raman for the analysis of ochre artefacts from Mesolithic palaeo-lake Flixton

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ABSTRACT

Ochre is an important mineral pigment used by prehistoric hunter-gatherers across the globe, and its use in the Mesolithic is no exception. Using optical microscopy and Raman spectroscopy with micrometre spatial resolution (micro-Raman), we present evidence that confirms unambiguously the use of ochre by hunter-gatherers at Mesolithic sites surrounding Palaeo-Lake Flixton, Vale of Pickering, North Yorkshire, UK. Our results suggest that people collected ochre and processed it in different ways, likely for diverse purposes. The quality and specificity of chemical characterisation possible with micro-Raman facilitates new avenues for further research on ochreous materials in Britain, including provenancing through chemical 'fingerprinting'.

1. Introduction

There are several minerals that have been used as red colourants at prehistoric archaeological sites: haematite (iron (III) oxide, α-Fe2O3), maghemite (iron (II) oxide, γ-Fe_2O_3), cinnabar (mercury (II) sulfide, HgS), litharge (lead (II) oxide, PbO), realgar (ruby sulfur, α-As_4S_4), red lead (lead (II), (IV) oxide, Pb_3O_4), and bauxite (composed gibbsite (Al $(OH)_3$), boehmite (γ-AlO(OH)), and diaspore (α-AlO(OH)), mixed with variable amounts of kaolinite, halloysite, goethite, haematite, magnetite, anatase, quartz, and some phosphatic and magniferous minerals) (Gomes et al., 2013; Hose, 2016; Mioč et al., 2004; Ospitali et al., 2006; Pomiés et al., 1999; Pradeau et al., 2016; Zilhão et al., 2010). Several analytical techniques have been used to differentiate among these red minerals and rocks, including X-ray powder diffraction (XRD), Raman microspectroscopy, infrared spectroscopy (IR), and transmission electron microscopy (TEM). Ochre containing haematite is commonly identified archaeologically, but its structure and composition is variable depending on the site of collection and how it is treated, for instance by heating or grinding. A recent XRD study by Sajó et al. (2015) of three samples of ochre from an Upper Palaeolithic mining pit revealed that the ochre samples were comprised of only ~5% haematite, with the remainder composed of dolomite, quartz, and kaolinite. Although mineral haematite is responsible for imparting the intensive red colour when ochre is rubbed on surfaces, only a small quantity is needed to act as an effective source of pigment. There are two types of artefacts related to ochre: (1) cohesive objects that are made out of ochre, and (2) objects that have ochre traces on them, such as non-cohesive powder (Pradeau et al., 2016, 12). Here we present two objects that fit into the first category, a pebble with grooves across its surface and a 'crayon' with striations and grooves. Both objects were found around Palaeo-Lake Flixton in the Vale of Pickering (North Yorkshire, UK), a landscape now blanketed in peat and known for its rich record of Mesolithic occupation, including the famous site of Star Carr (Fig. 1). We hypothesised that these objects contain haematite and were anthropogenically modified, evidencing collection and use of red pigments.

Ochre exploitation in the Mesolithic is an important activity to explore because it was likely used in diverse cultural activities. However, methods of exploitation and use of ochre have received only cursory consideration in the study area (Clark, 1954, 167). While it is common to interpret Mesolithic ochre powder to be of symbolic or ritual significance based on its frequent occurrence in burials, for instance Skateholm I and II in Sweden and Zvejnieki in Latvia (Larsson, 1988; Zagorska, 2008), patterns of ochre working at sites in the vicinity of Palaeo-Lake Flixton could broaden understanding of its use as human burial is entirely lacking in the region.

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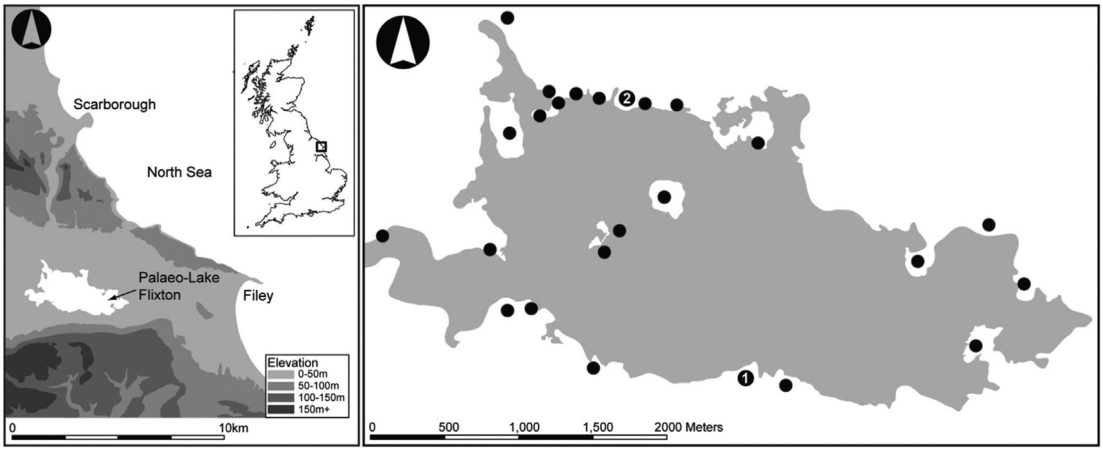

Fig. 1. Location of Palaeo-lake Flixton (left) with areas of Mesolithic occupation marked by black dots (right). Sites from which the objects were found are numbered.

2. Samples and sites

2.1. Flixton school house farm: FSH09 2870

A red pebble that is possibly ochreous, FSH09 2870 (Fig. 2) was recorded at Flixton School House Farm on the southern shore of Palaeo-Lake Flixton (Fig. 1, location 1). The pebble was recorded from an occupation horizon containing diagnostically Early and Late Mesolithic material culture, adjacent to a sequence of pits and associated stake and postholes (Taylor and Gray Jones, 2009). The pit sequence is sealed by a layer dated to the mid-7th Millennium cal BC (7867 ± 40 BP; OxA-22,211), proving a potential *terminus post quem* for activity at the site.

Similar grooved pebbles are rare within the Mesolithic of Britain, though examples have been found recently at Stainton West and Mussleburgh (Clarke, 2014). The pebble measures 45 mm long, 43 mm wide and 16 mm deep at maximum extent and has a smooth, well-rounded shape, with a fine grain size. The material is hard, in marked contrast to published descriptions of ochre pieces from the nearby site of Star Carr (Clark, 1954, 167). The colour of the pebble is deep red to brown, suggesting it contains iron and thus it could consist of haematite within ochre (Elias et al., 2006; Wadley et al., 2009). It is likely that the piece was collected from a secondary context, based on its rounded shape and weathered, pitted surface. These features are consistent with a beach pebble or a rolled pebble derived from glacial till. The object is marked by deep grooves running roughly parallel to one another, in groups with differing orientations. The deep striations are concentrated to a single surface and in a localised area, indicating they are of probable anthropogenic origin (Fig. 3). The surface of the pebble is concave in the area of the grooving, suggesting extensive working. The grooves are unlikely to reflect artistic expression, differing appreciably from known British Mesolithic engravings, which typically feature geometric patterns (Berridge and Roberts, 1994; Clarke et al., 2012; Milner et al., 2016; Smith, 1934; Smith and Harris, 1982).

Fig. 2. Pebble FSH09 2870 with anthropogenic grooves from Flixton School House Farm.

2.2. Seamer Carr site C: Crayon SC83 9366

Crayon SC83 9366 was found during excavations at Seamer Carr Site C, on the northwest shore of Palaeo-Lake Flixton (Fig. 1, location 2). Activity at the site consists of diagnostically Terminal Upper Palaeolithic and Early Mesolithic lithic scatters, and small quantities of animal bone (Conneller and Schadla-Hall, 2003). Though lithic scatters of different date tend to be spatially discrete, the relationship between these and the object cannot be established. The artefact may belong to either phase of occupation, though a Mesolithic association is perhaps more likely given its prevalence at the site. The elongate object measures 22 mm long, 7 mm wide and 6 mm deep at maximum extent and has a sub-rounded cross section with four long, relatively flat surfaces and a pointed end. There are long, parallel grooves evident on each surface, and polished areas associated with grooves on two surfaces. The object is rounded to one end and faceted to the other, likely reflecting use (Fig. 4).

3. Methods

The two objects were analysed first with a low-power reflected visible light stereomicroscope at magnifications from × 6.3–× 50 (Leica MZ75) with Schott KL1500 LCD swan neck lights. In order to explore how the grooves were made on the pebble, observations of groove shape and relative order were made using a VHX-100 Keyence microscope with S5 transmitted light stage working between × 25 and × 175 magnification with visible light. This technique had the advantage of allowing manipulation of the microscope to explore the morphology of grooves by changing its position and angle relative to the object. It can also create 3D models of grooves and capture microphotographs, supported *via* dedicated software.

Confocal micro-Raman was used to determine the specific composition of each object and if they represented different minerals. Raman spectroscopy measures the interactions between photons and lattice or molecular vibration modes. It can be used to identify inorganic and organic molecular species of solid, liquid, or gas samples (Larkin, 2011, 55). A unique 'fingerprint' of a specific molecule is provided by IR and