Journal of Archaeological Science: Reports 17 (2018) 650–656

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: www.elsevier.com/locate/jasrep

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

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ARTICLE INFO

Keywords:
Mesolithic
Hunter-gatherers
Haematite
Ochre
Reflected visible light microscopy
Raman microspectroscopy

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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https://doi.org/10.1016/j.jasrep.2017.12.002
Received 15 August 2017; Received in revised form 30 November 2017; Accepted 4 December 2017

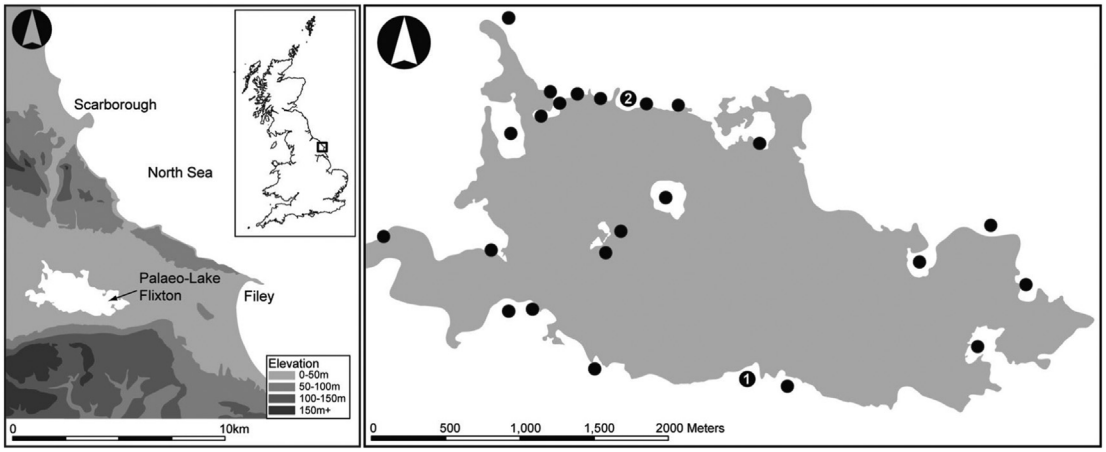

Fig. 1. Location of Palaeo-lake Flixton (left) with areas of Mesolithic occupation marked by black dots (right). Sites from which the objects were found are numbered.

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).

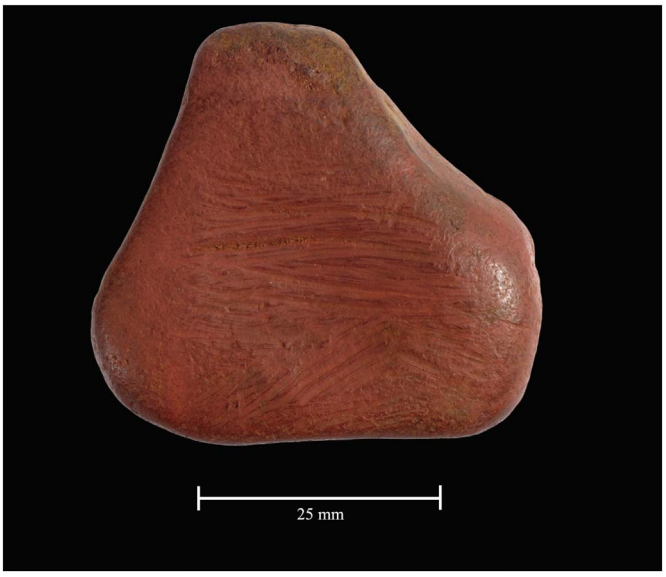

Fig. 2. Pebble FSH09 2870 with anthropogenic grooves from Flixton School House Farm.

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

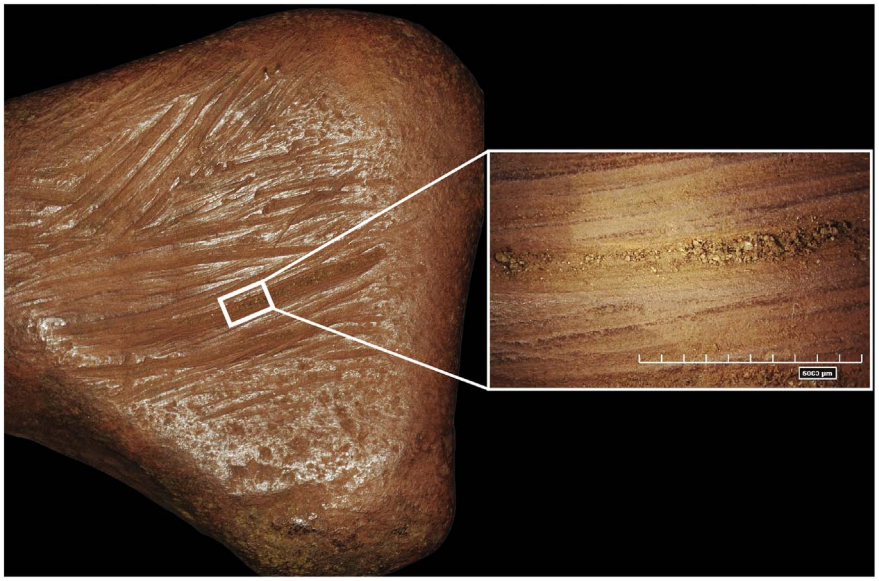

Fig. 3. Microphotograph showing the morphology of one of the grooves.

Fig. 4. Crayon SC83 9366 (2018) CXX1 from Seamer Carr showing a surface with parallel grooves and associated polished areas (darker red), and faceted end (left). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Raman spectra, based on the mass of the atoms, their geometric arrangement, and the types of chemical bonds present in the molecule (Larkin, 2011, 2). The sample is irradiated with a visible or near-IR monochromatic laser, and the resulting scattered radiation is measured with a spectrometer (Skoog et al., 2007). An unknown molecule can be identified because it exhibits a unique spectroscopic pattern of frequencies, or 'fingerprint', (Koenig, 2000, 16) that can be recognised by comparison with spectral libraries and published literature or based on direct calculations of the Raman bands using polarisability theory.

A HORIBA Jobin Yvon Xplora confocal Raman microscope with LabSpec (version 6) and IGOR Pro software for peak analysis was used to collect and evaluate eight spectra from the pebble and three spectra from the crayon. The instrument was calibrated using pure silica prior to collecting these spectra. Long working distance microscope objectives were used to prevent crushing the sample. A green Nd:YAG diode laser was operated at a wavelength of 532 nm, and a laser size of nominally 1 μm was used for spot micro-analysis with 10 × and 50 × large working distance objectives. The maximum laser power used was 20 mW and in none of the investigated samples laser induced modifications of the material was detected. The acquisition time was in the range of 20–30 s with 10–20 accumulations per scan using a 2400 T grating, which provides the highest spectral resolution of 1 cm^{-1}. Polynomial baseline corrections were applied to all Raman spectra using LabSpec6 software. This correction was applied to subtract background noise and illustrate a better signal-to-noise ratio. This corrected data was plotted using Origin 2016 software and then labelled. The Raman spectra band positions of the collected spectra were compared to spectral database reference libraries, as well as published literature, to identify the material.

4. Results

4.1. Pebble FSH09 2870

Microscopic observations indicate that pebble FSH09 2870 has been subject to multiple phases of anthropogenic modification and can be described as a palimpsest of working traces enacted over an unknown duration. In this context, a 'phase' can variously refer to a shifting of the orientation of the tool, reflecting a momentary pause before continuing work, through to a protracted hiatus in activity before recommencing at a later time. The capacity to discern temporality and distinct working phases can be assessed to an extent through observing changes in the nature and orientation of working.

The grooves evident on the pebble have a flat base and wide edges at a shallow angle, with multiple smaller striations evident within grooves along the bottom and edges. This profile shape is consistent with a scraping action using a stone tool, probably a scraper (d'Errico et al., 2012; Rifkin, 2012; Fig. 1), and possibly using a back and forth motion. Alternately, it has also been suggested by Isbister (2009) that Mesolithic ochre pieces from Sand, Scotland, could have been scraped with bevel-ended tools. While such tools have not been recovered from the site, this method of working remains a possibility. To reflect the nature of working, grooves were loosely grouped based on their orientation, with multiple grooves sharing an orientation taken to represent a phase of working. Based on groove orientation, three main groups (A, B and C) were identified (Fig. 5). The intersection of grooves from different groups was used to ascertain the chronology of working. On this basis, group A is the oldest phase, followed by group B, with group C being the youngest, and with the latter phases largely obliterating group A. The nature of working does not significantly vary between groups, with each produced by scraping, and possibly some incising in the very deep grooves associated with group B. Given the concave shape of the surface and partial obliteration of group A, it is likely that additional phases of working were once present but have been completely obliterated by more recent working phases.

A location on the back of the pebble with no striations was chosen for investigation with micro-Raman. The spectra collected from the

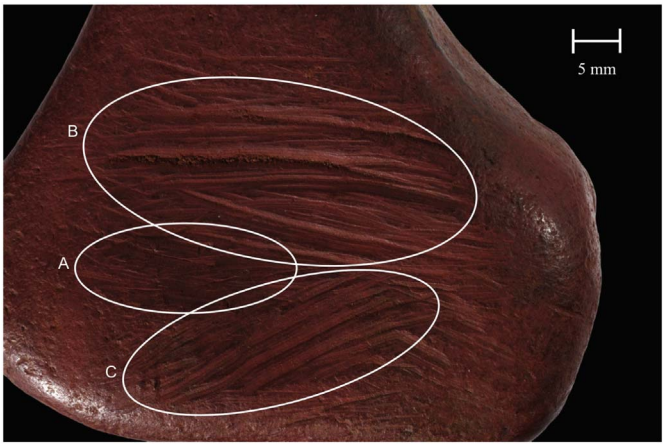

Fig. 5. Pebble FSH09 2870 with working phases identified in the text highlighted.

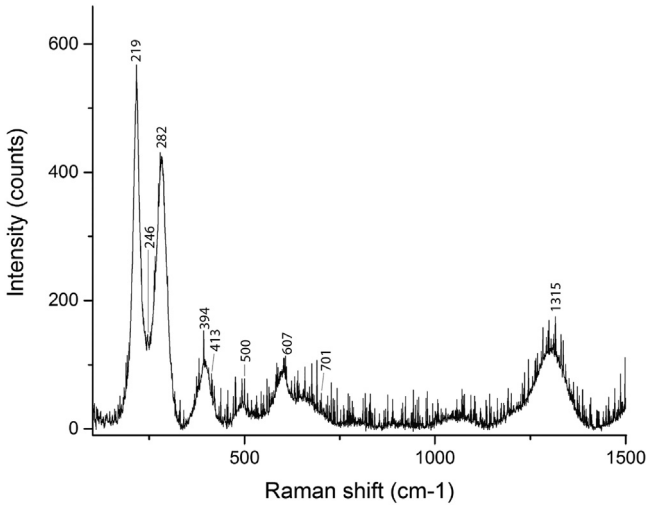

Fig. 6. Raman spectrum (with polynomial baseline correction) collected from the back corner surface of pebble FSH09 2870.

pebble are consistent with iron oxide α-Fe_2O_3 (haematite); the wavenumbers (cm^{-1}) and number and intensity of peaks match published examples (Beattie and Gilson, 1970; Ohtsuka et al., 1986; de Faria et al., 1997; de Faria and Lopes, 2007; Oh et al., 1998; Burgio and Clark, 2001; Mortimore et al., 2004; Legodi and de Waal, 2007; Froment et al., 2008; Courtin-Nomade et al., 2009; Das and Hendry, 2011). Major features include peaks at 219 cm^{-1} (assigned to A_{1g} Fe—O symmetric stretching), 282 cm^{-1} (assigned to E_g Fe—O symmetric bending), and a band at 394 cm^{-1} (assigned to E_g Fe—O symmetric bending) (Fig. 6). Additionally, the large feature at 1315 cm^{-1} seen in the pebble spectra is consistent with the two-magnon scattering reported in haematite at 1320 cm^{-1} discussed by de Faria et al. (1997, 875). Table 1 presents the relationship between Raman band features seen in the spectra collected from the pebble and crayon with published reference values for iron oxide and their assignments.

4.2. Crayon SC83 9366

Examination of the sides and ends of the elongate piece (SC83 9366) from Seamer Carr with reflected visible light microscopy allowed the depth of the striations and extent of polish to be assessed. The object is fragile and powdery, and excavation damage was noted in the form of three nick marks on the ends of the piece, which revealed fresh bright red colouration distinct from the surrounding surface. This damage allowed the internal structure to be examined. The crayon did not

Table 1
Raman wavenumbers (cm^{-1}) and assignment of pebble FSH09 2870 and crayon SC83 9366 results compared to haematite reference values.

Pebble (FSH09 2870)	Crayon (SC83 9366)	α-Fe2O3 haematite Beattie and Gilson, 1970	α-Fe2O3 haematite de Faria et al., 1997	α-Fe2O3 haematite Oh et al., 1998	haematite Mortimore et al., 2004	α-Fe2O3 haematite de Faria and Lopes, 2007	α-Fe2O3 haematite Legodi and de Waal, 2007	haematite Courtin-Nomade et al., 2009	α-Fe2O3 haematite de Tercero et al., 2014	Assignment (de Faria et al., 1997; Legodi and de Waal, 2007)
219	218	226	220	226	226	227	226	221	224	A_{1g} (Fe—O sym. Str)
246	246	245	237	245		246			243	E_g (Fe—O sym. Bend)
282	285		283							E_g (Fe—O sym. Bend)
	294	293	295	292	292	293	292	290	291	E_g (Fe—O sym. Bend)
298	299	298							298	
394	394		396							
413	413	413		411	407	412	406	404	408	E_g (Fe—O sym. Bend)
500		500	492	497	498	498	495	490	500	A_{1g} (Fe—O sym. Str)
607	603	612	596	612	609	610	600		610	E_g (Fe—O sym. Bend)
					659			655		
701							700			A_{1g} (Fe—O sym. Str)
								1072		
1315	1315		1320		1312	1322		1306	1317	2-magnon scattering

Fig. 7. Crayon SC83 9366 showing pointed end, grooves and polished area following the long axis.

display a laminar sheet crystal structure as might be expected in naturally formed haematite, but appeared powdery and contained small hard mineral inclusions. The shape of the elongate piece is an improbable natural formation habit of haematite. Each long surface contains deep elongate striations, occurring at locations roughly parallel to the long axis of the piece and an associated area of polish (Fig. 7). One end of the piece exhibits fine striations in one direction on one surface, and striations on another face. The grooves and striations on the crayon could possibly be traces of use of the piece against granular surfaces.

A location on the flat surface of the crayon was chosen for investigation. The major features present in Raman spectra collected were also consistent with iron oxide α-Fe_2O_3 (haematite) (Table 1). As can be seen in Fig. 8, peaks at 218 cm^{-1} (assigned to A_{1g} Fe—O *sym*metric stretching), 285 cm^{-1} (assigned to E_g Fe—O symmetric bending), and a band at 394 cm^{-1} (assigned to E_g Fe—O *sym*metric bending) are prominent. Like the pebble, a large feature at 1315 cm^{-1} was also seen in the crayon spectra, and is consistent with two-magnon scattering in haematite (de Faria et al., 1997, 875).

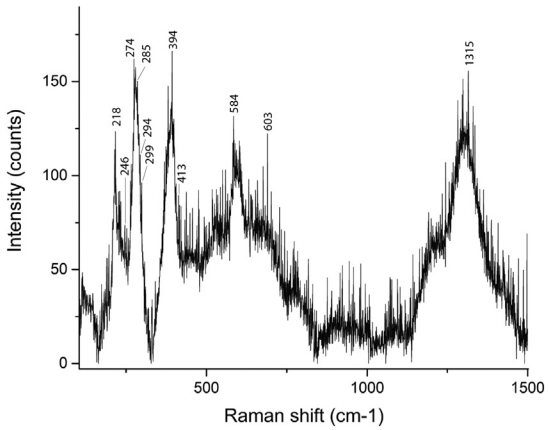

Fig. 8. Raman spectrum (with polynomial baseline correction) collected from crayon SC83 9366.

4.3. Comparison of pebble FSH09 2870 and crayon SC83 9366 Raman spectra results

Both the pebble and the crayon spectra do not match with expected clay minerals that typically compose ochre, such as kaolinite and vermiculite, but further work may illuminate these constituents. The spectra also do not contain dolomite, which was heavily dominant (~80%) in ochre samples reported by Sajó et al. (2015). There are some minor differences between the Raman spectra collected from the pebble and crayon, possibly reflecting the use of different haematite sources by Mesolithic hunter-gatherers. As can be seen in Table 1, some of the differences noted were: 1) the crayon spectrum contained a peak at 294 cm^{-1} (assigned to E_g Fe—O *sym*metric bending), that was not found within the pebble spectrum; 2) the pebble contained a small peak at 500 cm^{-1} (assigned to A_{1g} Fe—O symmetric stretching), not present in the crayon; 3) the pebble contained a peak at 701 cm^{-1} (assigned to A_{1g} Fe—O symmetric stretching), not present in the crayon. Additionally, the spectra collected from the crayon were 'noisier' and showed more peaks between 0 and 200 cm^{-1} and ~220–285 cm^{-1}. In the pebble, the major peak at 219 cm^{-1} is a more intense peak relative to the next major peak at 282 cm^{-1}, whereas in the crayon 218 cm^{-1} is less intense than the next major neighbouring peak at ~274–285 cm^{-1}. We hypothesise that the microscopic crystalline structure of iron oxide minerals slightly differs depending on the location of haematite formation. Thus, micro-Raman could potentially be an important analytical technique when attempting to source ochre because it is sensitive to small structural differences in materials and offers the potential of site-specific analysis at the micrometre level.

5. Discussion

5.1. Working ochre at Palaeo-Lake Flixton

The pebble and crayon are anthropogenically modified, evidencing diverse ochre working strategies during the Mesolithic at Palaeo-Lake Flixton. Deep groove marks are present on only a single surface of the pebble, which is inconsistent with taphonomic modification. Furthermore, the pebble has been used so intensively that the working surface has become concave. The characteristics of the shape and pattern of grooving exhibit striking similarities to published ochre artefacts (d'Errico et al., 2012; Henshilwood et al., 2001, 432) and experimental material (Rifkin, 2012, 187), with the concave shape of the pebble resembling objects produced by scraping (Henshilwood et al., 2001, 432; Rifkin, 2012, 187). The pebble is comparable to a deeply grooved ochre piece (KRM10) from Klasies River Cave 1 (d'Errico et al. (2012, 949), in which the lines were attributed to scraping with a flint tool to extract powder.

The elongate shape and four rough sides of the crayon does not conform to natural crystal formation habits of haematite. The most common crystal habit of haematite is flat tabular hexagonal plates, while fibrous, massive, oolitic, and botryoidal forms are also known (Gribble and Hall, 1985, 161; Nesse, 1986, 125; Bishop et al., 1999, 45; Rafferty, 2012, 267), all of which differ significantly from the crayon. The piece is a faceted elongate rod with a pointed end, a morphology that might suggest that humans deliberately moulded it and used it as a pigment stick. Alternatively, and perhaps more likely, the ochre crayon could have been collected in a rough natural shape such as a lump, with extensive subsequent use shaping the piece, resulting in the formation of four facets and a pointed working end. The object also has elongate grooves and associated polish roughly parallel to the long edges of the facets, likely the product of anthropogenic working. The method of working haematite can impact upon the properties of the powder produced, such as chroma or grain size (Rifkin et al., 2015) and this may be a factor in the diverse working strategies evident in ochre working and use at sites surrounding Palaeo-Lake Flixton.

The consideration of the *chaîne opératoire* of ochre working in the

region is ongoing. Recently, iron (III) oxide deposits were identified *in situ* on stone tools from Star Carr using micro-Raman (Croft, 2017). However, these red-orange concretions formed due to natural pedogenic processes in the soil. The case of the iron oxide deposits on tools is clearly different than the objects presented here, since the deposits are microscopically amorphous and lack granularity. It is therefore important not to assume that the presence of red-orange deposits is evidence for the preparation or application of powdered ochre. Recent consideration of beads (Needham et al., in press) and a pendant (Milner et al., 2016) at Star Carr found these objects to be free of ochre. The specific uses of these two ochre objects are different, but some suggestions can be made. The deep grooves lacking any apparent artistic design on the pebble suggests it was used to harvest red pigment powder. The sharp edges with striations in multiple directions might indicate the elongate shaped piece was used as a drawing and colouring tool, perhaps in a similar way to a contemporary pencil or crayon.

5.2. Micro-Raman and the study of ochre

Micro-Raman has seen increasing use in recent years across a diverse range of archaeological investigation, from the analysis of bitumen residues on stone tools (Monnier et al., 2013), to anthropogenic pyrite traces on flint fire-strikers (Lombardo et al., 2016). In the Palaeo-Lake Flixton region, micro-Raman was recently used to identify naturally formed authigenic pyrite microcrystals on the surfaces of an engraved Mesolithic shale pendant from Star Carr (Milner et al., 2016). There are three major benefits to micro-Raman: 1) it allows a chemical characterisation of materials with a high degree of molecular specificity; 2) it is minimally invasive and is considered a non-destructive technique, with a comparably small laser spot size of approx. 1 μm illuminated by the incident laser beam during analysis; 3) residues can be analysed *in situ* on the non-uniform surfaces of the object with no sample preparation required.

Haematite has been identified with micro-Raman in various rock art pigments (Bonneau et al., 2017; Gomes et al., 2013; Prinsloo et al., 2013; Stuart and Thomas, 2017; Ospitali et al., 2006), and on human skeletal remains (Edwards et al., 2001), but this is the first time micro-Raman has been used to identify and confirm that haematite was used to create artefacts in the Mesolithic of Britain. Elemental microanalysis of objects by energy dispersive X-ray spectroscopy conducted within the chamber of scanning electron microscopes (SEM-EDS, also known as SEM-EDX and SEM-EDAX) has been used previously to identify haematite on Mesolithic artefacts (Cristiani et al., 2009; Cristiani et al., 2014). However, new analytical techniques can improve the specificity, and thus confidence, of identification achievable with archaeological materials. EDS is perhaps best used as a preliminary test suitable to provide basic information to guide further chemical analyses. EDS analysis of emitted X-rays identifies the main element ratios present in the sample, but does not identify how elements are combined into specific molecules. Thus, EDS does not provide a chemical 'fingerprint'. This 'fingerprint' would be necessary in, for example, attempts to source ochre. In the current study, the chemical information provided by micro-Raman suggests that subtly different types of ochre were used in distinct ochre working strategies, and likely with the intent to provide diverse outputs at different sites around Palaeo-Lake Flixton. Future work could examine the haematite/clay ratio in various ochres and their mineral crystal sizes, which may be distinctive. Use of XRD on ochre sources may be helpful to answer these questions, but its application to archaeological artefacts is more problematic since the technique requires destructive sampling.

6. Conclusion

The analytical technique chosen to investigate the artefacts – micro-Raman – specifically and unambiguously identified pebble FSH09 2870 and crayon SC83 9366 as containing haematite (α-Fe_2O_3). Both objects show wear inconsistent with taphonomic action, but rather have striations on their surfaces occurring in roughly parallel groups. FSH09 2870 represents an utilised piece implicated in red pigment harvesting and SC83 9366 is consistent with use as a possible crayon, evidencing multiple working strategies across different sites around Palaeo-Lake Flixton. The specific usage of ochre in the region remains elusive, though recorded applications of ochre powder include the production of art (Prinsloo et al., 2013), body paint (Rifkin et al., 2015), decoration (Cristiani et al., 2014), hafting (Wadley, 2005), sunscreen (Rifkin et al., 2015), medicine (Velo, 1984), and to seal joints in water craft when combined with a mastic (Clarke and Waddington, 2007, 119). More research on the site-specific gathering and processing sequence of ochre is needed to explore these possibilities further within the vicinity of Palaeo-Lake Flixton.

As the preliminary micro-Raman data revealed, the pebble and crayon are broadly similar, though with slight differences evident in the haematite contained within the ochre artefacts. Due to these differing chemical compositions, slight variances in the properties of the ochreous material might be expected. Mesolithic hunter-gatherers may have been sensitive to these properties and harnessed them for different tasks. Using micro-Raman and its capacity to chemically 'fingerprint' samples, it may be viable in future studies to identify and locate the different ochre sources used by hunter-gatherers during the early Mesolithic.

Acknowledgements

We thank Ed Blinkhorn, Ben Elliott, Nick Overton and Dennis Rowland for insightful discussion, Matthew Von Tersch and Helen Goodchild for technical support, Nicky Milner, Matthew Collins and Rachel Shield for reading an earlier draft, Paul Shields for artefact photography, and Daniel Deocampo and Emily Beverly for helpful discussions about haematite. Excavations at FSH were in part supported by the AHRC in association with Barry Taylor's PhD research (AHRC Doctoral Award 2007/135399) and radiocarbon dating was supported by NERC (Grant NF/2009/1/20). We thank Carole and George MacDuff for permission to excavate and the excavators of FSH '08 and '09. We thank Andy Howard and two anonymous reviewers for really helpful comments that have improved the final paper.

References

Beattie, I.R., Gilson, T.R., 1970. The single-crystal Raman spectra of nearly opaque materials. Iron (III) oxide and chromium (III) oxide. J. Chem. Soc. A 1, 980–986.
Berridge, P., Roberts, A., 1994. The Mesolithic decorated and other pebble artefacts. In: Quinnell, H., Blockley, M.R. (Eds.), Excavations at Rhuddlan, Clwyd: 1969–73 Mesolithic to Medieval. Council for British Archaeology, York, pp. 115–131.
Bishop, A., Woolley, A., Hamilton, W., 1999. Cambridge Guide to Minerals, Rocks and Fossils. Cambridge University Press, Cambridge.
Bonneau, A., Moyle, J., Dufourmentelle, K., Arsenault, D., Dagneau, C., Lamothe, M., 2017. A pigment characterization approach to selection of dating methods and interpretation of rock art: the case of the Mikinak site, Lake Wapizagonke, Quebec, Canada. Archaeometry. http://dx.doi.org/10.1111/arcm.12289.
Burgio, L., Clark, R.J., 2001. Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. Spectrochim. Acta A Mol. Biomol. Spectrosc. 57 (7), 1491–1521.
Clark, J.G.D., 1954. Excavations at Star Carr: An Early Mesolithic Site at Seamer near Scarborough, Yorkshire. Cambridge University Press, Cambridge.
Clarke, A., 2014. Stainton West: Ochre and Haematite. Unpublished Report.
Clarke, A., Waddington, C., 2007. Bevelled pebbles, coarse stone tools and Ochreous material. In: Waddington, C. (Ed.), Mesolithic Settlement in the North Sea Basin. A Case Study from Howick, North-East England. Oxbow Books, Oxford.
Clarke, A., Vila-Mitjà, A., Estévez Escalera, J., Hardy, K., 2012. The tie that binds? An incised Mesolithic bevelled pebble from Camas Daraich, Skye. Mesolithic Miscellany 22 (1), 3–9.
Conneller, C., Schadla-Hall, R.T., 2003. Beyond star Carr: the Vale of Pickering in the tenth millennium BP. Proc. Prehist. Soc 69, 85–105.
Courtin-Nomade, A., Grosbois, C., Marcus, M.A., Fakra, S.C., Beny, J.-M., Foster, A.L., 2009. The weathering of a sulfide orebody: speciation and fate of some potential contaminants. Can. Mineral. 47, 493–508.
Cristiani, E., Pedrotti, A., Gialanella, S., 2009. Tradition and Innovation between the Mesolithic and Early Neolithic in the Adige Valley (northeast Italy). New data from a

functional analysis of trapezes from the Gaban rock-shelter. Documenta Praehistorica XXXVI, 191–205.
Cristiani, E., Živaljević, I., Borić, D., 2014. Residue analysis and ornament suspension techniques in prehistory: cyprinid pharyngeal teeth beads from Late Mesolithic burials at Vlasac (Serbia). J. Archaeol. Sci. 46, 292–310.
Croft, S. (Ed.), 2017. Lithic Residue Analysis at Star Carr. University of York (Unpublished PhD Thesis).
Das, S., Hendry, M.J., 2011. Application of Raman spectroscopy to identify iron minerals commonly found in mine wastes. Chem. Geol. 290, 101–108.
Edwards, H.G.M., Farwell, D.W., de Faria, D.L.A., Monteiro, A.M.F., Afonso, M.C., De Blasis, P., Eggers, S., 2001. Raman spectroscopic study of 3000-year-old human skeletal remains from a sambaqui, Santa Catarina, Brazil. J. Raman Spectrosc. 32, 17–22.
Elias, M., Chartier, C., Prévot, G., Garay, H., Vignaud, C., 2006. The colour of ochres explained by their composition. Mater. Sci. Eng. B 127, 70–80.
d'Errico, F., García Moreno, R., Rifkin, R.F., 2012. Technological, elemental and colorimetric analysis of an engraved ochre fragment from the middle stone age levels of Klasies River Cave 1, South Africa. J. Archaeol. Sci. 39, 942–952.
de Faria, D.L.A., Lopes, F.N., 2007. Heated goethite and natural hematite: can Raman spectroscopy be used to differentiate them? Vib. Spectrosc. 45, 117–121.
de Faria, D.L.A., Venâncio Silva, S., de Oliveira, M.T., 1997. Raman microspectroscopy of some iron oxides and oxyhydroxides. J. Raman Spectrosc. 28, 873–878.
Froment, F., Tournié, A., Colomban, P., 2008. Raman identification of natural red to yellow pigments: ochre and iron-containing ores. J. Raman Spectrosc. 39, 560–568.
Gomes, H., Rosina, P., Holakooei, P., Solomon, T., Vaccaro, C., 2013. Identification of pigments used in rock art paintings in Gode Roriso-Ethiopia using Micro-Raman spectroscopy. J. Archaeol. Sci. 40, 4073–4082.
Gribble, C.D., Hall, A.J., 1985. A Practical Introduction to Optical Mineralogy. Allen and Unwin, London.
Henshilwood, C.S., Sealy, J.C., Yates, R., Cruz-Uribe, K., Goldberg, P., Grine, F.E., Klein, R.G., Poggenpoel, C., van Niekerk, K., Watts, I., 2001. Blombos cave, southern cape, South Africa: preliminary report on the 1992–1999 excavations of the middle stone age levels. J. Archaeol. Sci. 28, 421–448.
Hose, H.R., 2016. Bauxite mineralology. In: Donaldson, D., Raahauge, B. (Eds.), Essential Readings in Light Metals: Alumina and Bauxite. Springer, Gewerbestrasse, pp. 21–29.
Isbister, A., 2009. Pigment resources report: excavations at Sand, Applecross, 2000. In: Wickham-Jones, C., Hardy, K. (Eds.), Mesolithic and Later Sites around the Inner Sound, Scotland: The Work of the Scotland's First Settlers Project 1998–2004. Scottish Archaeological Internet Reports, pp. 322–325.
Koenig, J.L., 2000. Infrared and Raman Spectroscopy of Polymers, Rapra Review Reports: Expert Overviews Covering the Science and Technology of Rubber and Plastics. Smithers Rapra Press, Belfast.
Larkin, P., 2011. Infrared and Raman Spectroscopy; Principles and Spectral Interpretation. Elsevier, Oxford.
Larsson, L., 1988. The Skateholm Project I. Man and Environment. Almqvist and Wiksell, Stockholm.
Legodi, M.A., de Waal, D., 2007. The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste. Dyes Pigments 74, 161–168.
Lombardo, T., Grolimund, D., Kienholz, A., Hubert, V., Wörle, M., 2016. The use of flint-stone fragments as “fire-strikers” during the Neolithic period: complementary micro-analytical evidences. Microchem. J. 125, 254–259.
Milner, N., Bamforth, M., Beale, G., Carty, J., Chatzipanagis, K., Croft, S., Conneller, C., Elliott, B., Fitton, L., Knight, B., Kröger, R., Little, A., Needham, A., Panter, I., Robson, H.K., Rowley, C., Taylor, B., 2016. A unique, engraved pendant from the Early Mesolithic site of Star Carr, UK. Internet Archaeology 41. http://dx.doi.org/10.11141/ia.40.8.
Mioč, U.B., Colomban, P., Sagon, G., Stojanović, M., Rosić, A., 2004. Ochre decor and cinnabar residues in Neolithic pottery from Vinča, Serbia. J. Raman Spectrosc. 35, 843–846.
Monnier, G.F., Hauck, T.C., Feinberg, J.M., Luo, B., Le Tensorer, J.-M., Sakhel, H., 2013. A multi-analytical methodology of lithic residue analysis applied to Paleolithic tools from Hummal, Syria. J. Archaeol. Sci. 40, 3722–3739.
Mortimore, J.L., Marshall, L.-J.R., Almond, M.J., Hollins, P., Matthews, W., 2004. Analysis of red and yellow ochre samples from Clearwell Caves and Çatalhöyük by vibrational spectroscopy and other techniques. Spectrochim. Acta A Mol. Biomol. Spectrosc. 60, 1179–1188.
Needham, A., Little, A., Conneller, C., Pomstra, D., Croft, S., Milner, N., 2018. Beads. In: Milner, N., Conneller, C., Taylor, B. (Eds.), Star Carr: 2004–2015. White Rose University Press, York (in press).
Nesse, W.D., 1986. Introduction to Optical Mineralogy. Oxford University Press, Oxford.
Oh, S.J., Cook, D.C., Townsend, H.E., 1998. Characterization of iron oxides commonly formed as corrosion products on steel. Hyperfine Interact. 112, 59–65.
Ohtsuka, T., Kubo, K., Sato, N., 1986. Raman spectroscopy of thin corrosion films on iron at 100 to 150 C in air. Corrosion 42, 476–481.
Ospitali, F., Smith, D.C., Lorblanchet, M., 2006. Preliminary investigations by Raman microscopy of prehistoric pigments in the wall-painted cave at Roucadour, Quercy, France. J. Raman Spectrosc. 37, 1063–1071.
Pomiés, M.-P., Menu, M., Vignaud, C., 1999. Red Palaeolithic pigments: natural hematite or heated goethite? Archaeometry 41, 275–285.
Pradeau, J.-V., Binder, D., Vérati, C., Lardeaux, J.-M., Dubernet, S., Lefrais, Y., Regert, M., 2016. Procurement strategies of Neolithic colouring materials: territoriality and networks from 6th to 5th millennia BCE in North-Western Mediterranean. J. Archaeol. Sci. 71, 10–23.
Prinsloo, L.C., Tournié, A., Colomban, P., Paris, C., Bassett, S.T., 2013. In search of the optimum Raman/IR signatures of potential ingredients used in San/Bushman rock art paint. J. Archaeol. Sci. 40, 2981–2990.
Rafferty, J.P., 2012. Minerals, Geology: Landforms, Minerals, and Rocks. Britannica Educational Publishing, New York.
Rifkin, R.F., 2012. Processing ochre in the middle stone age: testing the inference of prehistoric behaviours from actualistically derived experimental data. J. Anthropol. Archaeol. 31, 174–195.
Rifkin, R.F., Dayet, L., Queffelec, A., Summers, B., Lategan, M., d'Errico, F., 2015. Evaluating the Photoprotective effects of ochre on human skin by *In Vivo* SPF assessment: implications for human evolution, adaptation and dispersal. PLoS One 10 (9) (DOI: 10.1371.journal.pone.0136090).
Sajó, I.E., Kovács, J., Fitzsimmons, K.E., Jáger, V., Lengyel, G., Viola, B., Talamo, S., Hublin, J.-J., 2015. Core-Shell processing of natural pigment: upper Palaeolithic red ochre from Lovas, Hungary. PLoS One 10 (7). http://dx.doi.org/10.1371/journal.pone.0131762.
Skoog, D.A., James Holler, F., Crouch, S.R., 2007. Principles of Instrumental Analysis. Cengage Learning, Boston.
Smith, R.A., 1934. Examples of Mesolithic art. Br. Mus. Q. 8, 144–145.
Smith, G., Harris, D., 1982. The excavation of Mesolithic, Neolithic and Bronze Age settlements at Poldowrian, St. Keverne, 1980. In: Cornish Archaeology. 21. pp. 23–62.
Stuart, B.H., Thomas, P.S., 2017. Pigment characterisation in Australian rock art: a review of modern instrumental methods of analysis. In: Heritage Science. 5. pp. 10.
Taylor, B., Gray Jones, A., 2009. Definitely a pit, possibly a house? Recent excavations at Flixton School House Farm in the Vale of Pickering. Mesolithic Miscellany 20 (2), 21–26.
de Tercero, M.D., Röder, C., Fehrenbacher, U., Teipel, U., Türk, U., 2014. Continuous supercritical hydrothermal synthesis of iron oxide nanoparticle dispersions and their characterization. J. Nanopart. Res. 16, 2350. http://dx.doi.org/10.1007/s11051-014-2350-1.
Velo, J., 1984. Ochre as medicine: a suggestion for the interpretation of the archaeological record. Curr. Anthropol. 25 (5), 674.
Wadley, L., 2005. Putting ochre to the test: replication studies of adhesives that may have been used for hafting tools in the middle stone age. J. Hum. Evol. 49, 587–601.
Wadley, L., Hodgskiss, T., Grant, M., 2009. Implications for complex cognition from the hafting of tools with compound adhesives in the Middle Stone Age, South Africa. Proc. Natl. Acad. Sci. 106, 9590–9594.
Zagorska, I., 2008. The use of ochre in Stone Age burials of the East Baltic. In: Fahlander, F., Oetigaard, T. (Eds.), The materiality of Death, Bodies, Burials, Beliefs. BAR International Series 1768, Oxford, pp. 115–124.
Zilhão, J., Angelucci, D.E., Badal-García, E., d'Errico, F., Daniel, F., Dayet, L., Douka, K., Higham, T.F.G., Martínez-Sánchez, M.J., Montes-Bernárdez, R., Murcia-Mascarós, S., Pérez-Sirvent, C., Roldán-García, C., Vanhaeren, M., Villaverde, V., Wood, R., Zapata, J., 2010. Symbolic Use of Marine Shells and Mineral Pigments by Iberian Neandertals. 107. Proc. Natl. Acad. Sci., pp. 1023–1028.