ASSESSING THE GEOCHEMISTRY OF POSSIBLE INORGANIC APPLIED PIGMENTS WITHIN CATHOLE CAVE, GOWER PENINSULA, SOUTH WALES

by

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ABSTRACT

Recent investigations within Cat hole Cave have revealed several rock engravings that date from the Upper Palaeolithic including a stylised cervid, possibly a reindeer and, as yet indistinguishable engravings above and below the cervid. In advance of the erection of a protective steel grille in 2014, several archaeological trenches revealed evidence of anthropogenic and palaeozoosporopic activity which probably dates from a period when much of the northern and western parts of the British Isles was covered by ice. In November 2010, one of the authors (GHN) discovered the presence of a possible haematite (Fe2O3) spread that occupied a small section of the western wall of the main gallery of the cave. This spread was either the result of natural secretion from the substrate or it was applied via human agency. No other possible haematite spreads existed within this particular cave, although haematite is common throughout the limestone caves of the Gower Peninsula. In 2015 the Welsh heritage agency Cadw awarded a generous grant for the possible haematite spread to be sampled and chemically analysed, and for an overlying speleothem coat to be dated using uranium-series disequilibrium methods. This paper reports on the fieldwork and the first phase of laboratory research that included Raman Spectrometry, Scanning Electron Microscope analysis (SEM) and thin-section analysis on samples of loose substrate. The results of this phase of work confirm that the samples taken from Cathole Cave may be the result of pigment application.

INTRODUCTION

Rock art confirmed as dating from the Upper Palaeolithic has been found in two sites in Britain, both of which contain engravings; Church Hole Cave (Creswell Crags), located along the Derbyshire/Nottinghamshire border (Bahn and Pettitt 2009; Pike et al. 2005) and Cathole Cave, on the Gower Peninsula in South Wales (Nash et al. 2010). The engravings in each cave comprise naturalistic and stylised animal figures and geometric forms. Cathole Cave, in which a possible cervid engraving was discovered in 2010, stands at about 30 m above sea level on the north-east side of a dry limestone valley, approximately 2 km north of the present coastline (Figure 1). The cave comprises several principal components, a wide passage with a largely flat undulating roof and tall, narrow, joint-influenced rifts that rise several metres above the general roof level (Simms, 2011). The cave has two entrances, the southern entrance leads to a large low-roofed gallery extending about 11 m to the north-east. On either side of the main gallery are side-chambers; the northern side-chamber diverts westwards to an antechamber and, beyond this is a second blocked entrance (Oldham 1978). To the northeast of the main gallery is another gallery that extends a further c. 8.3 m. This section of the cave is difficult to access and, as far as the author is aware, was not fully investigated until recently (Nash and Beardsley 2013).

Cathole Cave has been the focus of a number of investigations over the past 150 years (summarised in Green and Walker, 1991). The first of these was undertaken around the (upper) cave floor in 1864 by a Colonel E. R. Wood, who recovered a small assemblage of lithic
material, several metal implements and pottery dating to the Bronze Age, as well as a significant Pleistocene faunal assemblage, which was later summarised by Garrod (1926). Despite the absence of chronometric dating of these remains, the presence of such animals indicated a cooler climate than present, probably coinciding with the interstadial and stadial regimes between 13,000 and 11,000 years BP. This dating range roughly coincided with the uranium-series disequilibrium dating results at Church Hole Cave and Cathole Cave (Pike et al. 2005; Nash et al. 2012). In 1958, Charles McBurney excavated four small rectangular trenches within the entrance area of the cave and recovered a significant lithic assemblage, a good proportion of it diagnostically similar to the tool industry found at a number of Creswellian sites (McBurney 1959). In 1968 John Campbell excavated a small trench within the entrance area of the cave, the results of which largely substantiated McBurney’s previous interpretation of the stratigraphy (Campbell, 1977, 58). The only intrusive investigations that have occurred since 1968 is the limited trenching that was undertaken in advance of the installation of a steel grille and gate (Walker et al. 2014).

In early 2011, accessible sections of the cave were surveyed using 3D laser technology (Nash and Beardsley, 2013). Use of this data has enabled the team to produce an accurate floor plan, constructed using nine laser scan targets that were positioned at key positions within the cave (Figure 2). The laser scanning project identified a number of natural anomalies that could not be mapped using conventional survey equipment, in particular the contour complexity of the roof and the relationship between the main gallery and the various side niches.

A survey of the cave, carried out in July 2012 alongside the exploratory excavations undertaken by the National Museum of Wales, identified further possible engravings (referred to as Panels B to D) and a haematite spread, labelled Panel E (Nash, 2015). The panel on which the haematite spread was present stood immediately north of a linear trench (Trench A) excavated in advance of the installation of a steel grille (Walker, et al. 2014). Unfortunately, unlike the figure found in September 2010 (Panel A) no direct chronometric dating for these
newly discovered engraved panels could be obtained, nor could the style and form from each engraving be clearly distinguished. Panel E contained both engraved and possible painted forms. The engravings are all considered to be modern, reflecting personal names, tagging and insignia.

Figure 2. Plan of Cathole (after Nash and Beardsley 2013).

Panel E is located within the far-western section of the main galley and is now secured behind the metal grille. Prior to the installation of the grille, this panel and much of the main galley were subjected to periodic graffiti events, some of which is dated. Panel E, standing approximately 1.2 m above the current floor level and 0.70 m above the pre-1864 excavation cave floor measures c. 1.25 m x 1.10 m and comprises a plethora of modern graffiti (Figure 3). The graffiti is mainly textual and abstract motifs/patterns and has been applied using a variety of techniques including spray can, alcohol-based permanent marker pens, incisions and scratches, and lipstick (Figure 3, labelled L). As part of the analytical process, one of the authors employed a desk-based colour spectrum program called D-Stretch (Nash 2015). This program digitally enhanced the base image to reveal a potential underlying haematite spread and a damaged flowstone (speleotherm). The haematite spread had, in places, been cut into by
the modern textual graffiti (Figure 3, labelled A). At the time discovery, it is not clear if this spread was natural or of human agency. Covering part of this spread is a fragmented (damaged) flowstone sheet which extended from the ceiling to within 0.90 m of the cave floor (Figure 3, labelled B). It should be noted that previous inspections of the cave had revealed no other haematite spreads. Therefore, could this small area of the cave be a natural ochre secretion or was it the result of human agency (i.e. applied haematite onto the substrate)?

**Figure 3.** Panel E, showing pigmentation enhanced using “D-Stretch” software. For details see text.

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**FIELDWORK METHODS**

In December 2014, Scheduled Monument Consent (SMC) was obtained from the Welsh Heritage Agency Cadw to sample both the haematite spread and the speleotherm. Supported by a generous grant from Cadw, the first part of the sampling programme was undertaken in May 2015.¹

Prior to the fieldwork and following a successful application for SMC, the team provided Cadw with a detailed project design, showing the areas that were to be sampled and the size of the sample to be taken. The field team sampled the possible haematite spread

¹ Fieldwork followed the end of the bat roosting season.
underlying the graffiti on Panel E in four strategic locations, using where possible non-contact ethical extraction techniques. The rationale of the sampling strategy was to ascertain whether or not the spread was haematite. Each sample, weighing between 10 and 100 mg was extracted in areas of the panel where pigment was visible (Figure 5). Each sample was obtained using a sterilized tungsten scalpel and inserted in a 0.5 ml microcentrifuge tube (e.g. Wainwright et al., 2002). In order to protect the visual integrity of the haematite spread, pigment samples were either scraped from rock cracks or from the densest layer/deposit.

Figure 4. Inspecting the panel before sampling. This shows the unenhanced colour as compared with Figure 3 (above).

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LABORATORY METHODS

The laboratory element of the project was undertaken by colleagues from TekneHub - Physics and Earth Science Department of the University of Ferrara, Italy. The four micro-samples of pigment were first observed under a stereomicroscope and then analysed by SEM-EDS and Raman spectroscopy. The first observation was made using an Optika SZ6745TR stereo microscope in order to define the areas of interest for the following analysis.

SEM-EDS analysis highlighted the morphology and chemical characterization of each sample without destroying it. The analysis and measurement of each sample was undertaken

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2 Applying the code of ethics and guidelines for practice of American Institute for Conservation.

3 Samples also contained visible rock substrate.
using a SEM ZEISS EVO MA15-HR with OXFORD Smartmap EDS INCA Energy 250 X-Act for EDS chemical microanalysis.

Micro-Raman spectroscopy was the preferred methodology in order to determine the mineralogical components within the samples and to characterize the pigment-type used. Raman measurements were performed with a HORIBA JobinYvonLabRam HR800 spectrometer, matched with an Olympus BXFM optical microscope and equipped with an air-cooled CCD detector (1024 x 256 pixels), set at -70° C. This instrumentation worked with a He-Ne laser source with a wavelength set at 632.81 nm. The spectrometer had a focal length of 80 mm and it was geared with two gratings (600 and 1800 groove/mm). The laser beam diameter was around 1 mm and the spectral resolution was about 2 cm⁻¹. The laser potency was kept between 0.2 and 10 mW and the exposure time varied between 5 and 16 seconds with 5-11 scans. The analysis was performed using 50x and 10x microscope objective, calibrating and checking the spectrometer with silicon standard at 520 cm⁻¹.

To make the spectra interpretations we used reference spectra from the LabSpec 5 spectral reference library and we referred to the scientific/specific bibliography.

**OBSERVATIONS AND RESULTS**

Samples of red pigment were analysed by Scanning Electron Microscope (SEM) equipped with an EDS microprobe. In the SEM images, white microcrystals were dispersed among a darker matrix. Their size is variable but less then 10μm, as observed in pigments taken from other prehistoric rock art sites (e.g. Hernanz et al. 2008, 2012). Not surprisingly, the EDS spectra of these crystals reveal a high Fe and O content and therefore it was possible to assess the presence of small and irregular grains of iron oxides (Figure 6a). Further EDS analyses at high magnification on the darker matrix (Figure 6b) reveal signals of Ca, Si, Al, O, Mg, K, Fe, C suggesting the presence of calcite, quartz and clay minerals associated with the tiny white grains previously described. In Figure 7 the typical layer structure of sheet silicate was shown and the composition of clay minerals is recorded in the EDS spectrum. The particle size, the irregular shape and the presence of impurities, such as clay minerals [platelets] and quartz, suggest the natural origin of the pigment enriched in iron oxides and is typical of ochre deposits found elsewhere (e.g. Eastaugh et al. 2008; Hernanz et al. 2010; 2012).

Further μ-Raman analyses were performed in order to characterise the mineralogical phases in the specimens. Raman spectra of red grains (Figure 8) show typical Raman bands of haematite at 224, 242, 290, 408, 609, 656 and 1311 cm⁻¹. This mineral is commonly used as the base material in prehistoric rock art pigmentation recipes (Gomes 2015; Hernanz et al. 2006a; 2006b; 2008; 2010; 2012; Iriarte et al. 2013). The spectra show two remarkable features: the
presence of a doublet in the 520-740 cm\(^{-1}\) spectral region, with peaks at \(\sim 610\) and \(\sim 660\) cm\(^{-1}\), and a slight shift to a lower wave number of the peak at \(\sim 410\) cm\(^{-1}\).

**Figure 6a and 6b.** SEM/EDS analyses on a sample of red pigment: semi-quantitative chemical analyses on a grain of iron oxide (a) and within the matrix of the sample (b).

**Figure 7.** SEM/EDS analysis on a clay mineral platelet within the matrix.

In previous laboratory programmes using identical samples, several researchers have given different interpretations for the peak at \(\sim 660\) cm\(^{-1}\). De Faria et al. (1997), for example, reported the Raman band at \(\sim 660\) cm\(^{-1}\) could be related to the presence of the mineral magnetite (Fe3O4). Iron oxide can occur in natural ochre deposits and, when weathered, it can undergo oxidation to become haematite (Acton, 2013). Moreover, De Faria et al. (1997) shows that magnetite can undergo the same transition after exposure to heat (via a naked flame). Alternatively, Bikiaris et al. (1999) note that the characteristic peak of the layered silicate clay mineral kaolinite (\(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\)) is at 658 cm\(^{-1}\). The presence of clay minerals in the samples may also explain the fluorescence background detected in the spectra during Raman analyses (Hernanz, et al. 2008; 2010; 2012). Thus the peak at \(\sim 660\) cm\(^{-1}\) can be assigned both to the presence of magnetite and kaolinite because these minerals can occur in association with haematite in natural red earths (Eastaugh et al. 2008; Lofrumento et al. 2012). Another explanation for the presence of such a peak at \(\sim 660\) cm\(^{-1}\) in the haematite spectrum is a disorder in the
Figure 8. Raman spectrum of Hematite from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line). The marked peak (*) is attributable to the carbonatic group CO$_3^{2-}$, probably due to the presence of calcite.

Figure 9. Raman spectrum of amorphous carbon from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line).
Figure 10. Raman spectrum of Calcite from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line).

lattice structure of this mineral. Such disorder has been detected by Hernanz et al. (2012) in prehistoric pigments and in natural ochre.

Many factors can give rise to the disordered structure of the haematite such as temperature, grinding, biodegradation and weathering processes (De Faria et al. 2007). The slight shift to lower wave-numbers (400-407 cm\(^{-1}\)) and the broadening of the Raman band at \(~410\) cm\(^{-1}\) could suggest either a disordered structure of the haematite and a structural state that is intermediate between goethite (FeO(OH)) and Haematite. Indeed, goethite, an iron oxide present in natural red earth, easily dehydrates to form Haematite, giving rise to an intermediate mineralogical phase. The spectrum of this intermediate phase shows a slight shift to a lower wave-number of the peak at \(~410\) cm\(^{-1}\) and the presence of the peak at \(~660\) cm\(^{-1}\) (e.g. Ospitali et al. 2006).

When using Raman spectroscopy it is not possible to differentiate between disordered haematite and heated goethite (De Faria and Lopes, 2007). The presence of very small particles of amorphous carbon dispersed within the samples may reinforce the hypothesis of a pigment preparation through heating. Figure 6b shows the broadband spectrum of between 1331 and 1597 cm\(^{-1}\) and is typical of disorganised carbonaceous materials (Hernanz et al., 2006b). Those remaining particulates can be interpreted as organic matter that includes charcoals of vegetal origin and soot. It is considered by the team that the presence of such organic matter could be the result of recipe additions to the pigment rather than the result of residues from historic fires within the cave (see Hernanz et al. 2012; Iriarte et al. 2013, Ospitali et al., 2006). We postulate this based on the fact that the charcoal and soot residues were embedded throughout the samples, rather than incorporated into the surface matrix.

In addition to minerals and residues already mentioned, calcite crystals (CaCO\(_3\)) were also detected in the samples and probably originate from the limestone substrate from which the cave was formed (e.g. Wright 1986; Walker et al. 2012). In Figure 6c, the characteristic Raman
bands of calcite are visible at 154, 281, 713 and 1086 cm⁻¹ (see also Weerd et al. 2004; Hernanz et al. 2006a, 2010, 2012). Calcite is the main component of carbonate rock but small crystals of that mineral can be also detected in natural red ochre (Eastaugh et al. 2008).

RESULTS

From each sample taken from panel E in Cathole Cave, crystals of haematite were detected using SEM/EDS and μ-Raman spectroscopy. Intermediate size and irregular shape of the grains, together with the presence of clay platelet minerals as impurities suggest that the sampled material may be natural ochre (Eastaugh et al. 2008; Hernanz et al. 2010; 2012). This hypothesis is supported by the Raman spectrum of the haematite that is attributable to a disordered lattice of this mineral. This occurrence is common in the recipes used in pigments in the production of prehistoric rock painting (Hernanz et al. 2012; Iriarte et al. 2013). Amorphous carbon was also detected as small particles that were dispersed among the haematite crystals. This material also commonly occurs in natural ochre (Eastaugh et al. 2008); however, the presence of charcoal or soot as well could suggest that these constituents could well have been part of pigment recipe and would have allowed the artist to make the pigment darker (Hernanz et al. 2012; Iriarte et al. 2013). The presence of amorphous carbon particulates can also indicate the possible heating process of the pigment (Ospitali et al. 2006). However, we express caution to any one interpretation given the fact that the cave has been subjected to fire vandalism in recent years (see Hernanz et al. 2006b).

The results from the samples taken from Panel E are consistent with results obtained by several other projects focusing on the pigmentation chemistry of prehistoric rock art (Hernanz et al. 2006a; 2006b; 2008; 2010; 2012; Iriarte et al. 2013). Considering the history of the cave and the presence of other rock art evidence (Nash et al. 2012; 2015), the red pigmentation spread could be interpreted as a natural red pigment, enriched in iron oxides, but alternatively it could have also been applied by human agency. As a result of the indeterminate results, further conformation in the form of lipid analysis (to determine the presence of an organic binder) and substrate composition will confirm whether or not this haematite spread was the result of human agency.

CONCLUSIONS AND FURTHER RESEARCH

This interim paper presents the results of the first part of the Cathole Cave project in which the geochemistry of a suspected haematite spread has been sampled and analysed. The results are as yet inconclusive. However, laboratory analysis shows that the dark red deposit on Panel E is haematite. Further analysis, using SEM EDS indicates that charcoal and soot may have been used in order to darken the haematite pigment. These ingredients were common in the production of pigment recipes during the prehistoric period. Future laboratory research using lipid analysis will confirm whether or not the spread was applied by human agency. Due to the poor state of preservation of the haematite spread, it is difficult to discern if a pictorial image is present; however, it should be noted that this haematite spread is the only one present in Cathole Cave.

In terms of future research, the team will be undertaking lipid analysis on the extracted samples which will be supported by further SEM EDS investigations. In addition, uranium-series disequilibrium dating will be applied to two samples taken from the overlying flowstone.
For the dating element, the fieldwork and analysis will be undertaken by a team led by Dr David Richards from the School of Geographical Sciences, University of Bristol. This element of the project will also be supported by a generous grant from Cadw.

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REFERENCES


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