Proc. Univ. Bristol Spelaeol. Soc., 2016, 27 (1), 81-93

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

by

GEORGE NASH, SARA GARCÉS, HUGO GOMES, PIERLUIGI ROSINA, MARIA NICOLI, LISA VOLPE and CARMELA VACCARO

ABSTRACT

Recent investigations within Cathole 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 palaeozoomorphic 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 (Fe203) 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

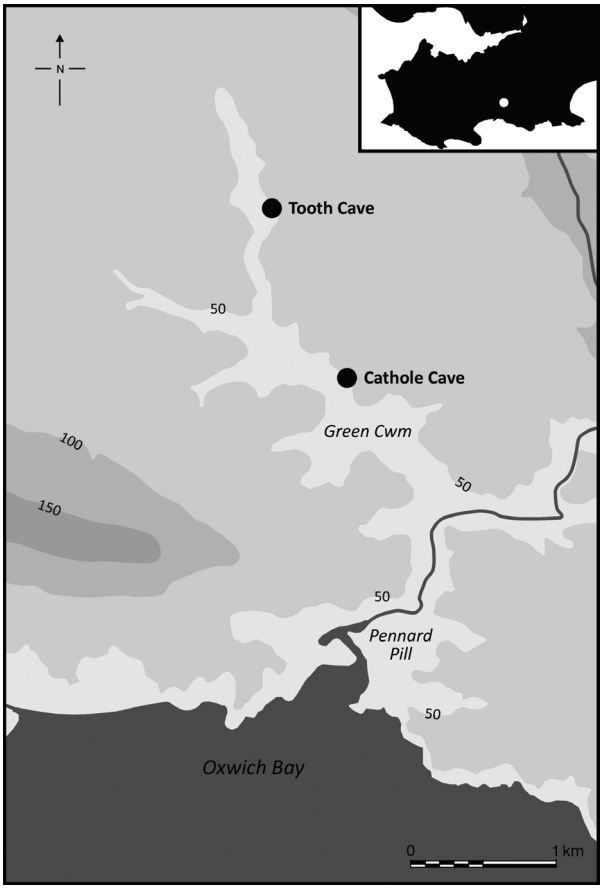

Figure 1. *Map showing the location of Cathole Cave, Gower.*

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.

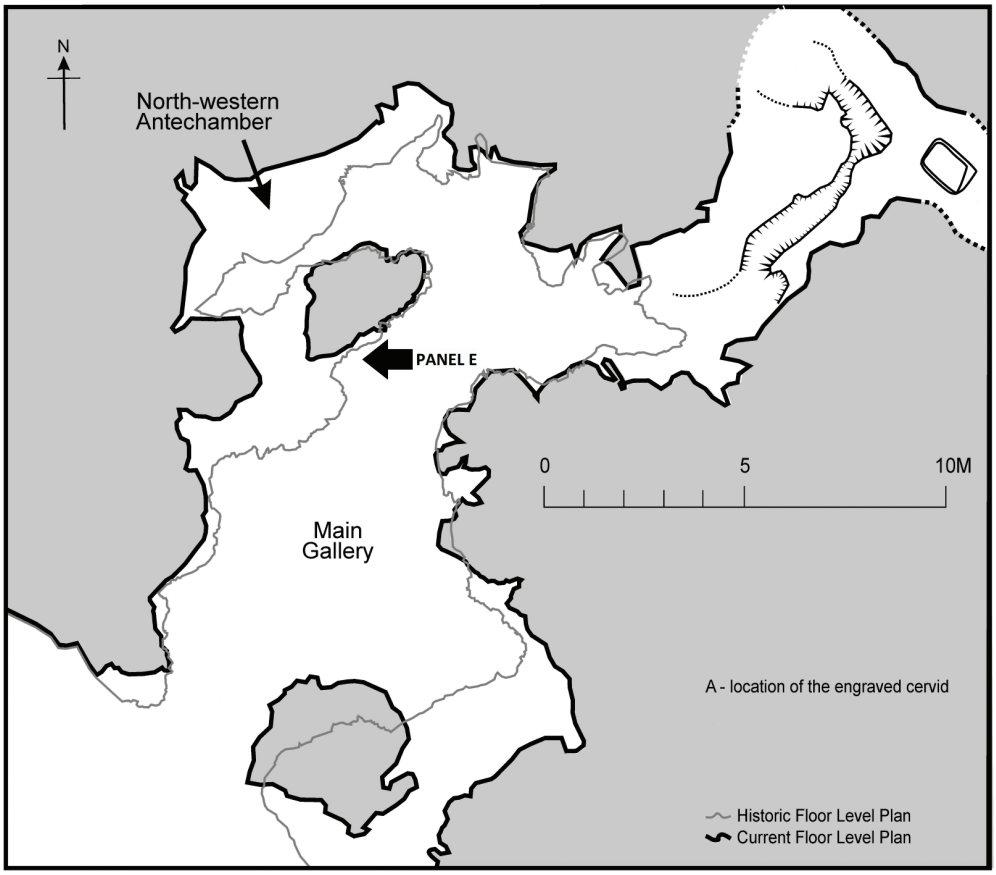

Figure 2. *Plan of Cathole (after Nash and Beardsley 2013)*.

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)?

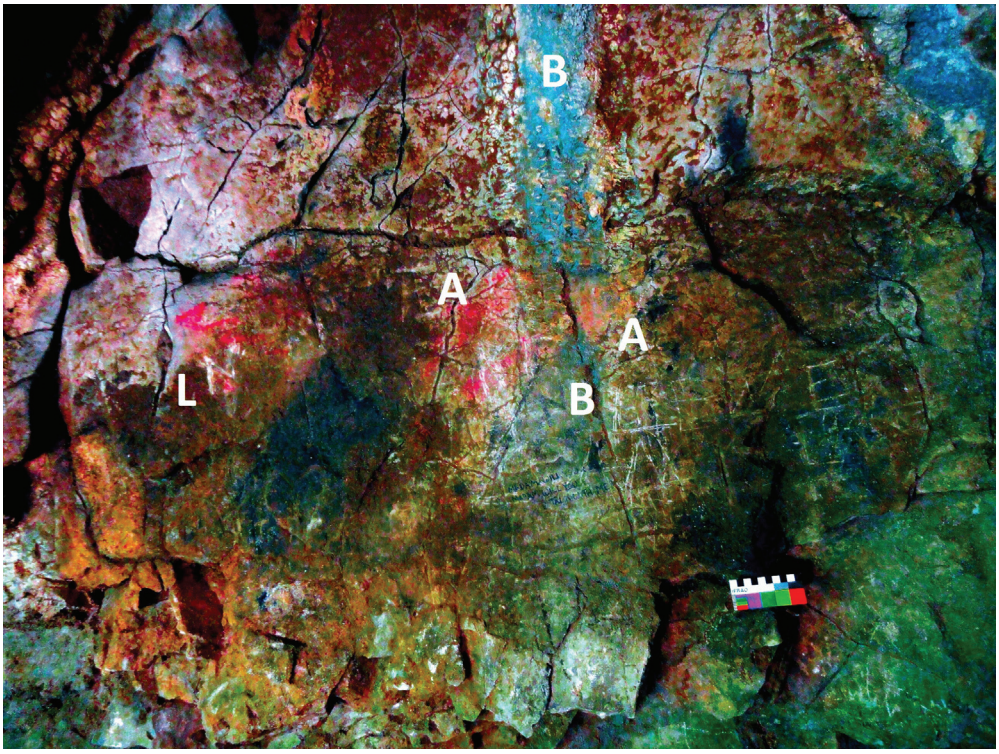

Figure 3. *Panel E, showing pigmentation enhanced using "D-Stretch" software. For details see text.*
Image: © G.H. Nash

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.[2] 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).[3] 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).*

Photo: © G.H. Nash.

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 SZ6745TRstereo 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

---

[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}.

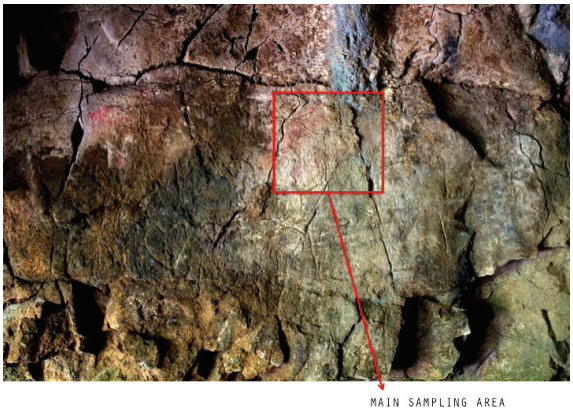

Figure 5. *The area sampled on panel E.*

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 ~610 and ~660 cm^{-1}, and a slight shift to a lower wave number of the peak at ~410 cm^{-1}.

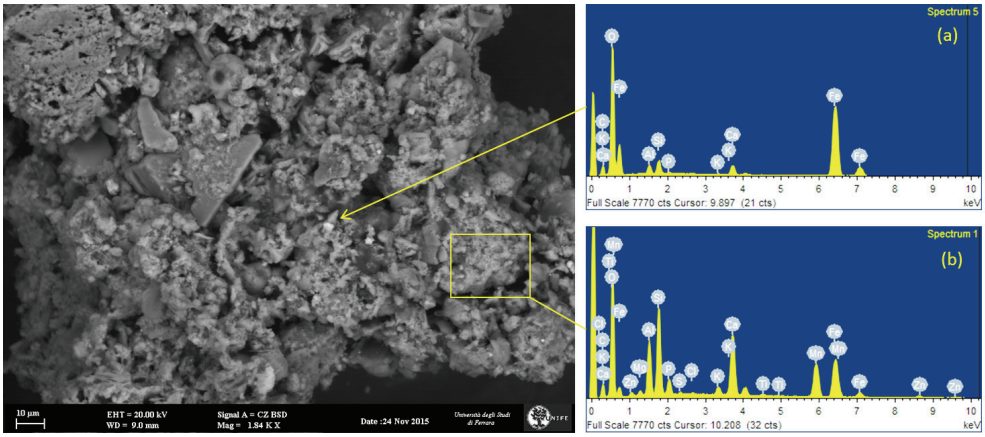

Figure 6a and 6b. *SEM/EDS analyses on a sample of red pigment: semi-quantitative chemical analyses on a grain of iron oxide (a) and within the matrix of the sample (b).*

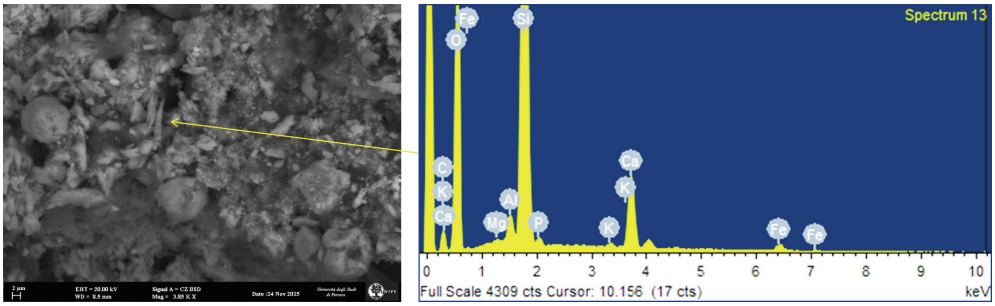

Figure 7. *SEM/EDS analysis on a clay mineral platelet within the matrix*

In previous laboratory programmes using identical samples, several researchers have given different interpretations for the peak at ~660 cm^{-1}. De Faria *et al.* (1997), for example, reported the Raman band at ~660 cm^{-1} could be related to the presence of the mineral magnetite (Fe304). 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 ($Al_2Si_2O_5(OH)_4$) 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 ~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 ~660 cm^{-1} in the haematite spectrum is a disorder in the

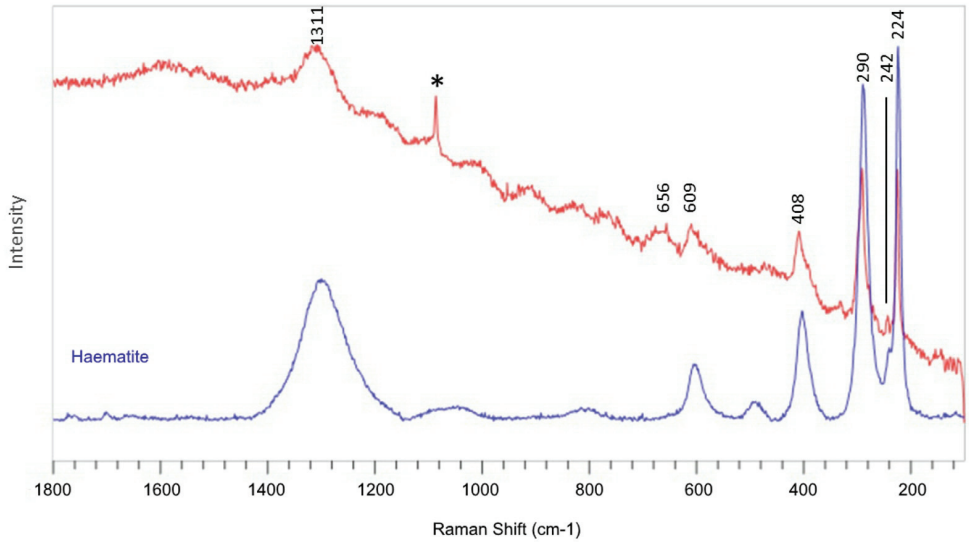

Figure 8. *Raman spectrum of Hematite from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line). The marked peak (*) is attributable to the carbonatic group CO_3^{2-}, probably due to the presence of calcite.*

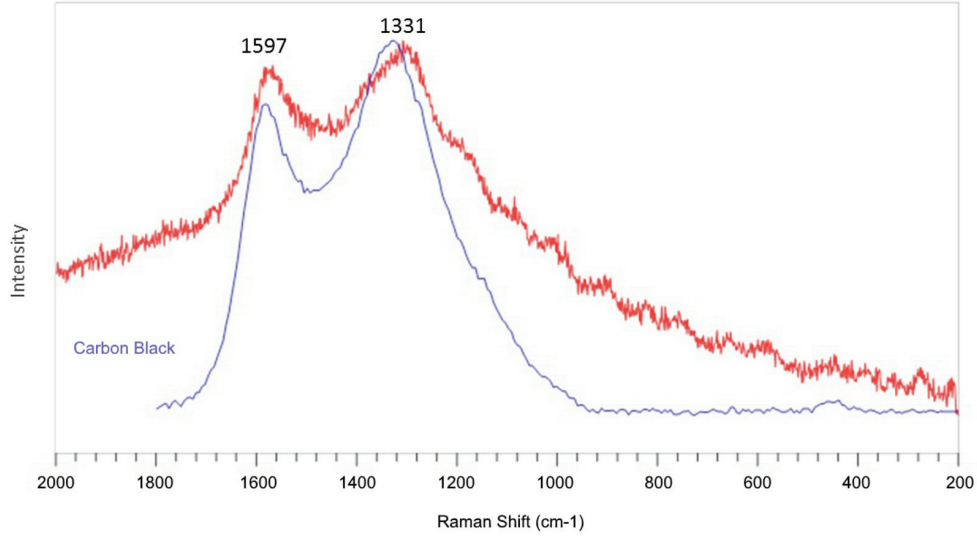

Figure 9. *Raman spectrum of amorphous carbon from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line).*

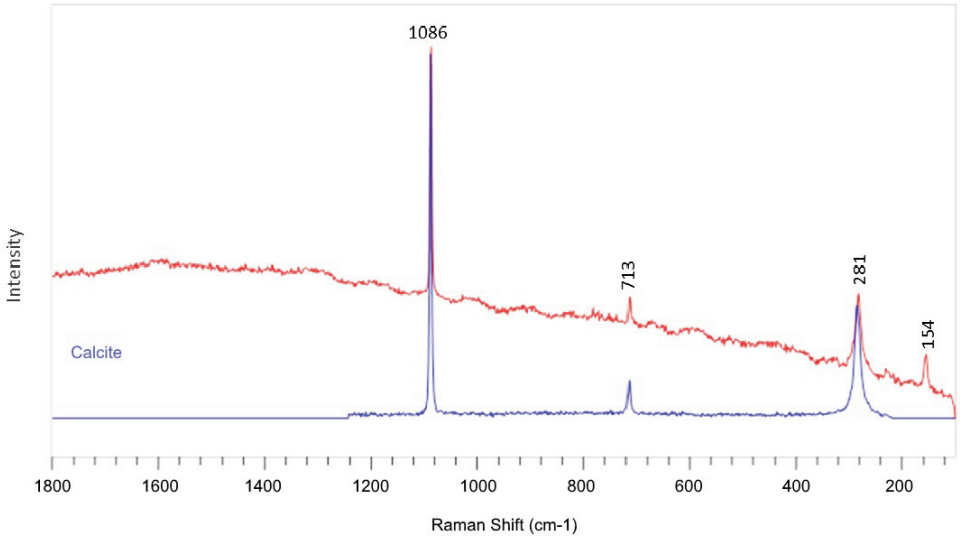

Figure 10. *Raman spectrum of Calcite from the sample (red line) compared with the reference spectrum from the LabSpec 5 database (blue line).*

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 (CaCO3) 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.

ACKNOWLEDGEMENTS

The authors would like to thank the following individuals and organisations for their assistance. Firstly, thanks to Sara Garcês of the Instituto Terra e Memória, Mação (Portugal) and Nadine Oliverira of Prehistoric Skills Limited who provided logistical support during the fieldwork element of the project. Thanks also to the Welsh Government heritage agency Cadw who kindly provided an essential grant to undertake fieldwork and laboratory analysis. Finally, thanks to the Tilley Foundation for providing a small grant towards publication.

REFERENCES

ACTON, Q.A. 2013. *Issues in Geology and Mineralogy*. Scholarly Editions.

BAHN, P. and PETTITT, P. 2009. *Britain's Oldest Art: The Ice Age Cave Art of Creswell Crags.* English Heritage.

BIKIARIS, D., DANIILIA S., SOTIROPOULOU, S., KATSIMBIRI, O., PAVLIDOU, E., MOUTSATSOU, A.P. and CHRYSSOULAKIS, Y. 1999. Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece. *Spectrochim. Acta A*. **56**. 3-18.

CAMPBELL, J. B. 1977. *The Upper Palaeolithic of Britain. A Study of Man and Nature in the Late Ice Age*. Oxford. Clarendon Press.

DE FARIA, D.L.A. and LOPES, F.N., 2007. Heated goethite and natural Haematite: can Raman spectroscopy be used to differentiate them? *Vibrational Spectroscopy.* **45.** 117–121.

DE FARIA, D. L. A., VENÂNCIO SILVA, S. and DE OLIVEIRA, M. T., 1997. Raman microspectroscopy of some iron oxides and oxyhydroxides. *J. Raman Spectrosc.* **28.** 873–878.

EASTAUGH, N., WALSH, V., CHAPLIN, T. and SIDDALL, R. (eds.) 2008. *Pigment Compendium: A Dictionary and Optical Microscopy of Historic Pigments*. Elsevier.

GARROD, D.A.E., 1926. *The Upper Palaeolithic Age in Britain*. Oxford. Clarendon.

GOMES, H., 2015. *Archaeometry of rock art pigments. Mineralogical characterization and production techniques in schematic rock art in western Iberian peninsula*. Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal. Unpublished PhD Thesis.

HERNANZ, A., MAS, M., GAVILÁN, B. and HERNÁNDEZ, B. 2006a. Raman microscopy and IR spectroscopy of prehistoric paintings from Los Murciélagos cave (Zuheros, Córdoba, Spain). *J. Raman Spectrosc.* **37.** 492–497.

HERNANZ, A., GAVIRA-VALLEJO, J. M. and RUIZ-LÓPEZ, J. F., 2006b. Introduction to Raman microscopy of prehistoric rock paintings from the Sierra de las Cuerdas, Cuenca, Spain. *J. Raman Spectrosc.* 37.1054–1062.

HERNANZ, A., GAVIRA-VALLEJO, J. M., RUIZ-LÓPEZ, J. F. and EDWARDS, H. G. M. 2008. A comprehensive micro-Raman spectroscopic study of prehistoric rock paintings from the Sierra de las Cuerdas, Cuenca, Spain. *J. Raman Spectrosc.* **39.** 972–984.

HERNANZ, A., RUIZ-LÓPEZ, J. F., GAVIRA-VALLEJO, J. M., MARTIN, S. and GAVRILENKO, E., 2010. Raman microscopy of prehistoric rock paintings from the Hoz de Vicente, Minglanilla, Cuenca, Spain. *J. Raman Spectrosc*. **41.** 1394–1399.

HERNANZ, A., GAVIRA-VALLEJO, J. M., RUIZ-LÓPEZ, J. F., MARTIN, S., MAROTO-VALIENTE, Á., DE BALBÍN-BEHRMANN, R., MENÉNDEZ, M. and ALCOLEA-GONZÁLEZ, J. J. 2012. Spectroscopy of Palaeolithic rock paintings from the Tito Bustillo and El Buxu Caves, Asturias, Spain. *J. Raman Spectrosc.* **43.** 1644–1650.

IRIARTE, M., HERNANZ, A., RUIZ-LÓPEZ, J. F. and MARTÍN, S., 2013. μ-Raman spectroscopy of prehistoric paintings from the Abrigo Remacha rock shelter (Villaseca, Segovia, Spain). *J. Raman Spectrosc*. **44.** 1557–1562.

LOFRUMENTO, C., RICCI, M., BACHECHI, L., DE FEO, D. and CASTELLUCCI, E. M., 2012. The first spectroscopic analysis of Ethiopian prehistoric rock painting. *J. Raman Spectrosc*. **43.** 809–816.

McBURNEY, C.B.M. 1959. Report on the first season's fieldwork on British Upper Palaeolithic cave deposits. *Proceedings of the Prehistoric Society* **. 25**. 260-9.

NASH, G.H., 2015. Further possible discoveries of engravings within Cathole Cave, Gower, Swansea. *Proceedings of the University of Bristol Speleological Society*. **26.** 3. 229-238.

NASH, G.H. and BEARDLSEY, A. 2013. The Survey of Cathole Cave, Gower Peninsula, South Wales. *Proceedings of the University of Bristol Speleological Society*. **26.** 1. 73-83.

NASH, G.N., VAN CALSTEREN, P., THOMAS, L. and SIMMS, M.J. 2012. A discovery of possible Upper Palaeolithic parietal art in Cathole cave, Gower Peninsula, South Wales. *Proceedings of the University of Bristol Speleological Society*. **25.** 3. 327-336.

OLDHAM, A.D. 1978. *The Caves of Gower*. Privately printed.

OSPITALI, F., SMITH, D. C. and 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.

PIKE, A.W.G., GILMOUR, M., PETTITT, P., JACOBI, R., RIPOLL, S., BAHN, P. and MUÑOZ, F. 2005. Verification of the age of the Palaeolithic rock art at Creswell**.** *Journal of Archaeological Science*. 32**.** 1649–1655.

ROBERTS, J. 1887. Cats Hole Cave. *Annual report and Transactions of the Swansea Scientific Society*. 15-23.

SIMMS, M. 2011. *Report on a Parkmill Cave, Parkmill Valley, Gower* (unpublished report).

VAN DER WEERD, J., SMITH, G.D., FIRTH, S. and CLARK, R.J.H., 2004. Identification of black pigments on prehistoric Southwest American potsherds by infrared and Raman microscopy. *Journal of Archaeological Science*. **31.** 1429-1437.

WAINWRIGHT, I.N.M., HELWIG, K., ROLANDI, D.S., GRADIN, C., PODESTÁ, M.M., ONETTO, M. and ASCHERO, C.A., 2002. *Rock Paintings Conservation and Pigment Analysis at Cueva de las Manos and Cerro de los Indios, Santa Cruz (Patagonia)*, Argentina. 3rd. triennial meeting e Rio de Janeiro preprint, vol. II.

WALKER, A.E., CASE, D., INGREM, C., JONES J.R. and MOURNE R., 2014. Excavations at Cathole Cave, Gower, Swansea. *Proceedings of the University of Bristol Speleological Society.* **26.** 2. 131-169.

WRIGHT, V.P., 1986. Facies sequences on a carbonate ramp: the Carboniferous Limestone of South Wales. *Sedimentology*. 33, pp. 221-241.

George Nash
Department of Archaeology & Anthropology
University of Bristol, England

Sara Garcés
Grupo de Quaternário e Pré-História do Centro de Geociências
CGeo Instituto Terra e Memória, ITM, Portugal

Hugo Gomes
Grupo de Quaternário e Pré-História do Centro de Geociências
CGeo; Instituto Terra e Memória, ITM, Portugal

Pierluigi Rosina
Grupo de Quaternário e Pré-História do Centro de Geociências
CGeo; Instituto Terra e Memória, ITM, Portugal

Maria Nicoli
TekneHub laboratory
Techbopole of Ferrara University, Italy

Carmela Vaccaro
Department of Physics and Earth Science
University of Ferrara, Italy

Lisa Volpe
TekneHub laboratory
Department of Physics and Earth Science, University of Ferrara, Italy