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In situ characterization of prehistoric rock paintings: the Côa Valley (Portugal).

José Santiago Pozo-Antonio[1], Teresa Rivas[1], Pablo Barreiro[2], Vera Caetano[3], Fernando Carrera[4],
Lara Bacelar Alves[3]

[1] *CINTECX, GESSMin, University of de Vigo, 36310 Vigo, Spain. ipozo@uvigo.gal, trivas@uvigo.gal*
[2] *CINTECX, FA3 Novos materiais, University of de Vigo, 36310 Vigo, Spain. pbarreiro@uvigo.gal,*
[3] *Centro de Estudos em Arqueologia, Artes e Ciências do Património (CEAACP/FCT), University of Coimbra, 3004-531 Coimbra, Portugal*
vera.mcaetano@gmail.com; lara.b.alves@uc.pt
[4] *RAC, Rock Art Conservation and Management. Vigo, 36202, Spain*
rac.fcarrera@gmail.com

***Abstract* – This paper draws on the study of the prehistoric art complex of the Côa Valley in north-east Portugal. Its main goal was to apply an *in situ* methodology for characterising prehistoric rock paintings. Thus, panels exhibiting red motifs were analysed by colour spectrophotometry and portable Raman spectroscopy. Motifs, crusts developed on the decorated surfaces and the backdrop stones have been analysed. Motifs from four sites within this archaeological complex were grouped considering their CIELAB and CIELCH parameters L*, a*, b*, C^*_{ab} and h due to their different colours. Raman spectroscopy showed that hematite is the predominant pigment in the motifs. Goethite, quartz and feldspars have also been identified in some motifs; their presence may reveal the use of ochre but may also come from the backdrop.**

Keywords – rock art, non-invasive technique, portable technique, Raman spectroscopy, colour spectrophotometry, hematite, goethite.

I. INTRODUCTION

The environmental diversity to which engravings and rock paintings are subjected is reflected in the heterogeneity of alteration agents that affect these artworks. This causes a great diversity of degradation processes that hinder the conservation process. To design any conservation strategy for this tangible cultural heritage, it is essential to carry out a complete characterization of the paintings and the backdrop using techniques that allow us to work *in situ*.

Regarding prehistoric rock paintings, red-orange and black pigments were most likely mixed with organic binders of vegetable or animal origin [1-3]. In Iberia, black pigments were mainly produced from charcoal, and red pigments composed of iron oxides or oxyhydroxides such as hematite (Fe_2O_3) or goethite ($FeOOH$) mixed with clay but also with minerals such as quartz (SiO_2), feldspar ($(K, Na, Ca, Ba, NH_4)(Si, Al)_4O_8$), etc.[4,5]. When hematite is present, motifs used to show intense red colours whereas when goethite is predominant, the colouration is closer to orange-yellow [5,6].

Therefore, it is very important to know the composition of the rock paintings not only to design appropriate conservation strategies but also for the archaeological interpretation of the rock art, to consider issues like the process of imagery making, the sequence in which motifs were created on a particular rock surface or the possible origins of raw materials. However, the most used analytical techniques, i.e., petrographic and scanning electron microscopy modalities require the extraction of microsamples. In recent years, the techniques used in the laboratory to chemically and mineralogically characterize the samples, that is, Raman spectroscopy, Fourier transform infrared spectroscopy, X ray diffraction, etc., have undergone a relevant refinement as portable analysis techniques with the advantage of being able to be used *in situ*. Moreover, physical properties such as colour are not commonly measured to characterize rock paintings [7]. A combined characterisation of the chemical, mineralogical and physical properties allow us to identify deterioration forms affecting the structure of both the paintings and the backdrop, alteration agents such as water or biological colonisation, etc.[8].

As Raman and Fourier transform infrared spectroscopies have shown their portable modalities, several scientific works were found to have applied Raman spectroscopy *in situ* [8-12] to characterize prehistoric art. Moreover, colour spectrophotometry is another portable technique, which is not commonly used for the characterisation of prehistoric rock paintings, but it could be useful to perform aesthetical analyses of decorated surfaces, since colorimetric variations may indicate chemical and mineralogical alterations as was stated in [7,8].

This research describes the *in situ* application of an analytical protocol based on enhanced photographic images and vector drawings, colour spectrophotometry and Raman spectroscopy to prehistoric rock paintings from the Côa Valley (Portugal). Four sites with decorated panels were characterised. Motifs, crusts and backdrop stones were analysed.

II. MATERIALS AND METHODS

A. *The Côa Valley rock art (Trás-os-Montes and Alto Douro, Portugal)*

Amongst the rock art sites analysed, two of them - Ribeirinha and Lapas Cabreiras - are in the area of the Côa Valley archaeological park, and two others - Poço Torto and Colmeal - sit just outside its southern borders. The Côa Valley (Trás-os-Montes and Alto Douro, Portugal) archaeological park, included in the UNESCO World Heritage List due to the relevant petroglyphs from the Upper Paleolithic (~30,000–12,000 cal BP), is undoubtedly the most well-known.

The presence of Late Prehistoric rock paintings belonging both to a subnaturalistic style and to the Schematic Art tradition also stands out. In the current project "*LandCRAFT - the socio-cultural contexts of the Late Prehistory art in the Côa valley*", an interdisciplinary approach aims to conciliate the recording of the rock art with archaeological excavations, paleoenvironmental studies, conservation, physical and chemical analysis and ethnoarchaeology [13,14]. The Late Prehistoric rock art assemblage includes both carvings and paintings. The latter appear both in rock shelters and on exposed rocks along the river, constituting one of the largest concentrations of sites belonging to the period spanning from the end of the Upper Palaeolithic to the early 2nd millennium BCE in the Portuguese territory [14].

Biological colonization and crusts on the decorated surfaces are the most common deterioration forms in these rock art sites. Considering the susceptibility and vulnerability of rock paintings in particular, the study of their composition is essential to work towards the prevention of alterations and eliminate or minimize risks.

In the present study, motifs belonging to the Ribeirinha and Lapas Cabreiras panels on granite, Colmeal panels on quartzite and Poço Torto panels on schist were studied *in situ* (Fig. 1). In order to perform a suitable analysis, crusts found on the stone surfaces and the backdrop stones were also characterized. In the identifier of the motif, panels are indicated by P.

B. *In situ analytical methodology*

The first stage of the analytical protocol consisted of the photorealistic recording of the rock paintings based on orthophotos of the panels subjected to digital photographic enhancement. Digital photographs were taken with a Canon 5D Mark II. To better identify the number and morphological features of the painted motifs, the surfaces were imaged using DStretch (https://www.dstretch.com), a plugin for ImageJ developed by John Harman.

Once the motifs (in the identifier of the motif, motifs are indicated by m) were catalogued, both their colour and the colour of the backdrop stones (indicated by B from base) and the superficial crusts (C) in all panels from the four sites were analysed using spectrophotometry. The measurements were obtained with a portable spectrophotometer (Konica Minolta CM-700d) equipped with CM-S100w (SpectraMagicTM) software. The working conditions of the device were: area view (MAV) of 8 mm, CIE standard daylight Illuminant D65 and angle observer of 10°, with Specular Component Excluded (SCE) mode. The colour was measured in the CIELAB and CIELCH colour spaces [15]. The colour parameters measured were: L*, lightness, which varies from 0 (absolute black) to 100 (absolute white); a*, associated with changes in redness–greenness (positive a* is red and negative a* is green); and b*, associated with changes in yellowness–blueness (positive b* is yellow and negative b* is blue). Moreover, the chroma or intensity of the colour (C^*_{ab}) and the hue (h) were also measured. For each m, ten measurements were made. L*, a*, b*, C^*_{ab} and h means were analysed using a Principal Component Analysis (PCA) to group the motifs according to their colours.

Raman spectroscopy was used to detect the molecular composition of the pigments, the crusts and the outcrop stones. Raman spectroscopy was applied in the same place where colour measurements were taken. Excitation at 785 nm was provided by a continuous wave diode laser, coupled to an optical head. Individual areas of measurement were controlled with a light-emitting diode and a high-resolution colour camera. The scattered radiation was collected through the objective lens, passed through an edge filter that cut off Rayleigh scattering, and focused into an optical fibre that was fed into a compact spectrograph, equipped with a concave grating, providing spectral coverage in the 120–3395 cm^{-1} range at a spectral resolution of about 10–15 cm^{-1}. The detector, a Synapse™ CCD (1024 × 256 pixels), was Peltier-cooled and featured high sensitivity with low dark counts. During the analysis, the power delivered by the laser beam on the sample surface was adjusted to 30 mW, exposure time was 10 s and spectra corresponded to an average of 2–5 consecutive scans on the same point. Three Raman spectra were taken from each m (motifs), C (crusts) and B (backdrop stones).

III. RESULTS

A. *Motifs identification*

Based on digital photographs, enhanced photographic images and vector drawings, a preliminary rock art catalogue was produced prior to data collection by spectrophotometry and Raman spectroscopy. In some of the panels, crusts with different colourations and the backdrop stones were also documented.

At Lapas Cabreiras (Fig. 1a,b), there are red coloured motifs on four different surfaces being panel 1 (P1) the most relevant with 15 motifs measured. In this panel, two crusts with different colour (P1-Ca and P1-Cb) were identified - one whiter and one darker – as well as whitish deposits identified as speleothems (P1-Cc).

At Colmeal (Fig. 1c, d), there are 5 decorated panels in 3 sectors: sector 1 with 1 panel (S1P1), sector 2 with 2 panels (1 without motifs) (S2P1 and S2P2) and sector 3 with 3 panels (S3P1, S3P2 and S3P3). In the S1P1, 29 painted motifs were analysed. Moreover, 4 crusts with different colorations were recognised (S1P1-Ca… S1P1-Cd) with yellow, orange, red and brown tones respectively. In the S2P1, 2 motifs were identified and in the S2P2 (without motifs), 4 crusts with different colourations were detected (brown, black and white tones; S2P2-Ca…S2P2-Cd). In S3P1, one motif was found. In S3P2, 9 motifs were measured and in S3P3, there are 3 motifs painted in black.

In Ribeirinha (Fig. 1e), 2 panels were identified (P1, P2). In P1, 10 motifs were measured and in P2, measurements were obtained in 4 motifs.

In Poço Torto (Fig. 1f), 2 panels were identified (P1, P2). In P1, only 1 motif was recorded and in P2, 7 motifs were measured.

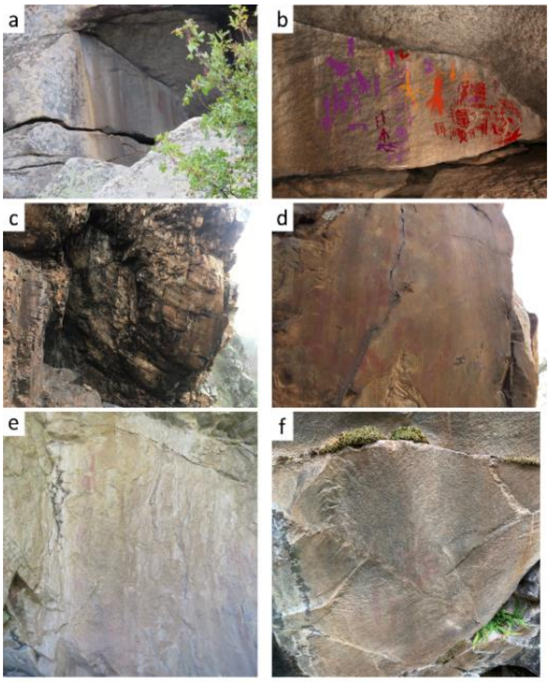

Fig. 1. General view of the decorated surfaces in the Côa Valley where the studied motifs are located. a: panel 1 (P1) in Lapas Cabreiras. b:motifs recorded in P1 from Lapas Cabreiras using DStretch. c: Colmeal (S1P1). d: motifs shown in b) with more detail. e: Ribeirinha (P1). F: Poço Torto (P2).

B. Colour characterization

Spectrophotometry allowed to identify that the colour parameters L*, a*, b*, C^*_{ab} and h measured in the motifs presented different values than those obtained in the stones and crusts on which they are found. Once the values of these parameters were obtained, the means were calculated and the PCA was performed (Fig. 2) in order to identify statistical similarities on colour data among the motifs and between these and the stone and crusts. Considering the large volume of processed data, we present in this paper 2 PCAs: one of them focuses on the comparison only between motifs from one panel and the other one considers motifs but also crusts and backdrop rocks.

At panel 1 of Lapas Cabreiras (Fig. 2a,b) the PCA reduces the number of variables (5, i.e. L*, a*, b*, C^*_{ab} and h) to 2 factors that together explain 92.09% of the variance of the data population. Factor F1 is defined by h coordinate, with a positive weight, and C^*_{ab} parameter, with the highest negative weight (Fig. 2a). Factor F2 is defined by h and L* with negative weight and a* with positive weight. The projection of the motifs on the space defined by F1-F2 factors (Fig. 2b) indicates that motifs m14, m15 and m13 are located in area of the factor F1 defined by h coordinate whereas m10 and m11 are grouped together around C^*_{ab} parameter. In addition, F2 separates m13, m10 and m15 motifs (grouped around a* coordinate) from m2 and m7 (associated with h and L* weights). The rest of the motifs are grouped in the central part of the projection indicating the similarity between them and the different colour regarding the rest. These results confirmed the grouping of motifs by different hue and chroma previously identified by means of DStretch (Fig. 2b): motifs m13, m14 and m15 have a dark but not very saturated violet colour while motifs m10 and m11, along with m9, present a different hue (orange-reddish tone). Likewise, m2 and m7 motifs are, of all, the ones with the lightest colour.

In sector 2 (S2) of Colmeal, the PCA reduces the 5 variables to 2 factors that together explain 86.96% of the variance of the data population. Factor F1 is defined by h with positive weight and the coordinates a* and b* and the parameter C^*_{ab} with negative weights (Fig. 2c). Factor F2 is defined by h and b* with negative weights and a* with positive weights. The projection of the motifs, crusts and backdrop stones onto the factors space (Fig. 2d) confirms a grouping around the field defined by L* and h of the stone colour (S2P1-B) and one crust (S2P2-Cd). In contrast, the 2 motifs in the panel 1 (S2P1-m1 and S2P1-m2) are located in the factor F2 defined by the coordinate a*. This coordinate defines the colour between green and red tones; the position of the motifs reflects the reddish colour with respect to the backdrop stones and crusts.

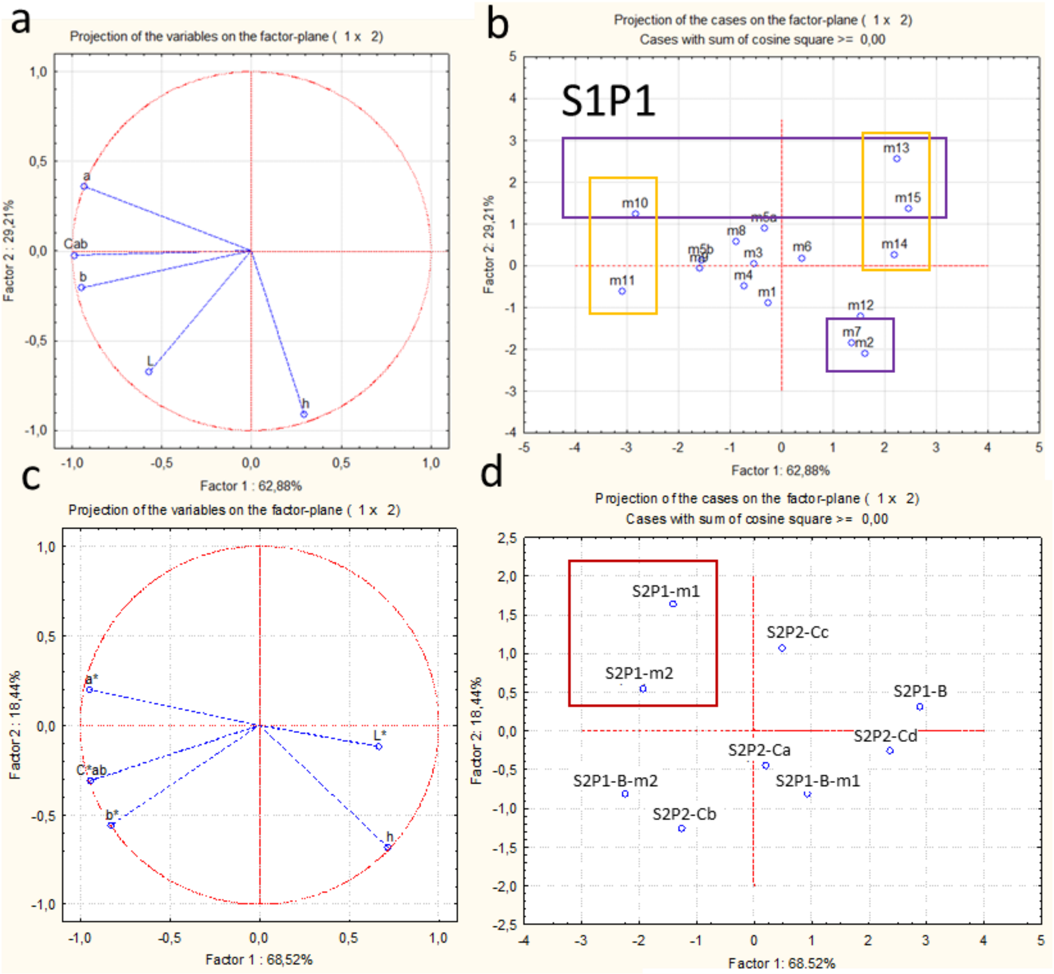

Fig. 2. a-b: result of the PCA carried out with the motif data from P1 of Lapas Cabreiras. a: projection of the colorimetric variables in the space defined by the two main factors F1 and F2. b: projection of the motifs in the space defined by these two factors. c-d: result of the PCA performed with the data of motifs, crusts and backdrop stones from S1 of Colmeal. a: projection of the colorimetric variables in the space defined by the two main factors F1 and F2. b: projection of the motifs, crusts and backdrop stones in the space defined by both factors.

C. Raman spectroscopy

Raman spectra allowed the identification of the chemical composition of the forming minerals from the backdrop stones in the different areas of the Côa Valley: granite, schist and quartzite. In the Raman spectra of the crusts from Colmeal and Lapas Cabreiras, Si-O band assigned to quartz (130, 206, 262 and 466 cm^{-1}[16]), Fe-O band assigned to goethite (Raman peaks at 244, 299, 385, 480, 548 and 681 cm^{-1} [17]) and/or hematite (225, 245, 291, 411, 500, 611 and 1321 cm^{-1} [17]) were identified (Fig. 3a).

In Lapas Cabreiras, most of the motifs show Raman spectra with peaks corresponding to hematite except for P1M1, P1M2, P2M1 and P5M2. For example, in Fig. 3b, the peaks of the Raman spectra from the P1-m4 motif in Lapas Cabreiras are assigned to hematite while those corresponding to the backdrop granite, are assigned to quartz. In addition, some spectra, besides showing peaks assigned to hematite and/or goethite, also show peaks assigned to the forming minerals of the stones, such as quartz, feldspar, etc. In Fig. 3c, in the motif P1-m15 from Lapas Cabreiras, peaks assigned to hematite mixed with those assigned to feldspar were detected. Potassium feldspar is identified through the peaks at 295cm, 483 and 510 cm^{-1} [18]. Therefore, it is important to address further studies to find the provenance of these minerals in order to ensure the use of ochres as pigments in these sites.

In Colmeal, hematite was also detected in most of the motifs. In addition to hematite, in the S1P1-M3, S1P1-M20 and S1P1-M22, S1P2-M2, S2-P1-M1, S3P1-M1, S3P2-M1, S3P3-M1 and S3P3-M2, peaks assigned to goethite were also detected.

In Ribeirinha, the presence of a clear pigment in the motifs through the spectra obtained cannot be established.

In Poço Torto, hematite was clearly detected in the motif P1-m10 with this Raman spectrometer.

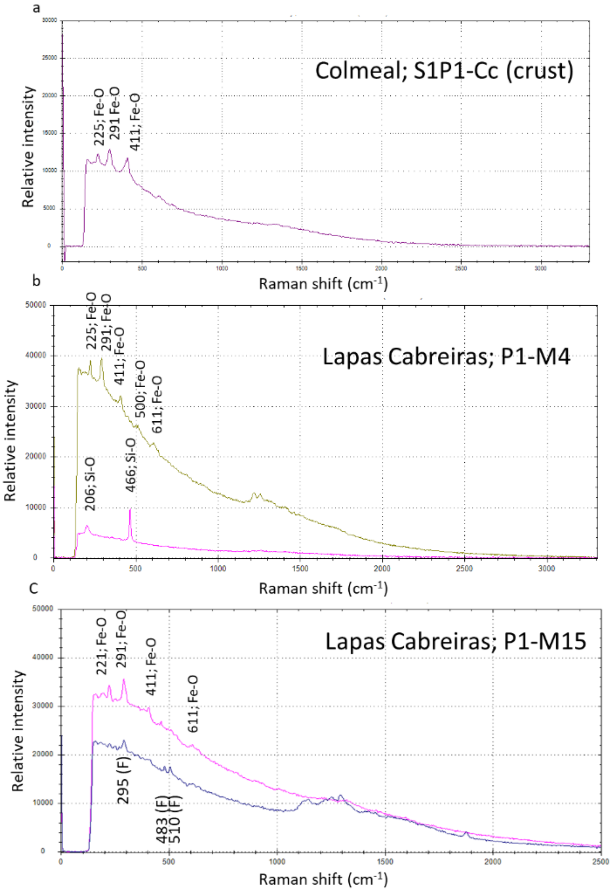

Fig. 3. Raman spectra. a) one crust measured in Colmeal. b and c) two motifs (upper spectra in each graph) and their backdrop stones (lower spectra) from Lapas Cabreiras. Molecular effects are depicted for each Raman peak. F: feldspar.

IV. CONCLUSIONS

An *in situ* characterization of the motifs from the decorated panels in four different sites in the Côa Valley was performed through enhanced photographic images, colour spectrophotometry and Raman spectroscopy. This research allows us to group the motifs considering their CIELAB and CIELCH parameters L*, a*, b*, C^*_{ab} and h. These groups corresponded to the different reddish hues. It was found that hematite is the predominant pigment in the motifs. The presence of goethite and silicates such as quartz and feldspars in some motifs could show that ochres were used beyond pure hematite. However, these minerals could come from the backdrop stone since the presence of goethite was detected in some of the crusts developed on the surfaces. Therefore, the application of other portable analytical techniques, such as XRF would be necessary to confirm the composition of the pigments.

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