

Article

Penedo Do Gato Rock Art Shelter (Monterrei, NW Iberian Peninsula): In Situ and Laboratory Characterisation

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Abstract: This paper focuses on the study of the prehistoric art site at Penedo do Gato Rock Art Shelter (NW Spain) through an interdisciplinary collaboration. A key objective was to develop and implement a multi-analytical protocol for characterising prehistoric rock paintings with portable analytical techniques such as colour spectrophotometry and Raman spectroscopy. Additionally, three possible colouring materials collected during the archaeological survey of the site were investigated by means of X-ray diffraction, stereomicroscopy, and scanning electron microscopy (surface and cross-section modes) with the aim of determining their mineralogical composition and texture. The results indicate that hematite (α -Fe₂O₃) is the main component of the red motifs. Amorphous carbon has been found in several motifs. The presence of amorphous carbon on the rock suggests it may have been deposited onto the paintings by nearby bonfires; however, the potential use of charcoal as an additive in the red pigments to modify their colour should not be overlooked. Regarding the mineralogical composition of potential colouring materials, only one of the samples can be considered as a viable source. This was the only sample with a compact and homogeneous composition, rich in hematite, making it likely that, after grinding, it was used for painting. In contrast, the other collected samples either lacked hematite or contained only a thin layer of it. In these cases, it is unlikely that the hematite layer was extracted using tools to obtain the pigment.



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1. Introduction

This paper addresses a set of rock paintings within the framework of the so-called Iberian Schematic Rock Art. These rock art paintings are applied on all kinds of open-air natural rock surfaces, which are generally exposed to a variety of natural and anthropogenic alteration processes that can severely impact their preservation and readability. Over millennia, physico-chemical processes derived from environmental agents such as water, temperature fluctuations, insolation, wind, and biological colonisation have gradually degraded the paintings and the rock surfaces on which they were applied [1–4]. Chemical interactions between the paintings and the underlying rock, as well as with external

agents such as moisture and salts, can lead to material losses, chromatic changes, or the formation of patinas or crusts that obscure the original painting [5]. Additionally, the likely presence of microorganisms (e.g., lichens, cyanobacteria, algae, and fungi) or plants not only affects the visual appearance of the pictorial motifs but also accelerates their degradation, as some of these organisms penetrate the rock surface, causing physical damage and contributing to chemical weathering [5–7]. Human interaction also plays a significant role in the degradation of rock art, whether intentional defacement or unintentional damage from tourism [8–10].

Traditionally, the study of rock art paintings has relied on laboratory-based techniques that require the extraction of microsamples. While these methods—such as petrographic microscopy, scanning electron microscopy, and X-ray diffraction—provide detailed insights into the paintings' composition and their degradation processes, they are invasive and result in the loss of valuable material. This is particularly concerning when dealing with fragile and irreplaceable prehistoric artworks. In response to this challenge, there is a growing interest in the use of portable, non-invasive, and non-destructive analytical techniques that can be applied directly on the surface without causing any damage (e.g., [11–13]). These techniques not only reduce the need for sampling but also allow a continuous monitoring of the alterations over time. Portable Raman spectroscopy, for instance, can identify the mineralogical composition of pigments *in situ*, offering precise chemical characterisation without the need for sampling [14,15]. However, the application of Raman spectroscopy *in situ* in this kind of artwork is not widespread since it has been reported in a few studies [14–17]. Thus, further studies applying portable systems are required. In addition to chemical characterisation, other portable analytical techniques, such as colour spectrophotometry, are invaluable for monitoring aesthetic changes [18]. By measuring colour, researchers can associate different colouration with different mineralogical compositions [14]. They can also track the chromatic change of a painting, which could give indications of ongoing chemical reactions or biological colonisation [19,20]. These colourimetric measures are essential for early detection of deterioration, enabling conservator-restorers to implement preventive measures before significant damage occurs.

The integration of these portable analytical techniques for the characterisation of these prehistoric paintings allows full respect for their integrity, as they are few in number and often present in a very delicate state of preservation. Also, the use of non-invasive techniques in a holistic and multi-disciplinary approach allows a more complete understanding of the complex interactions between the painting, the rock substrate, and the surrounding environment. Despite the clear advantages of portable and non-invasive analytical techniques, they remain underutilised in the field of prehistoric rock art research. A wider adoption of these technologies would enable more comprehensive and large-scale studies of rock art sites, without compromising their integrity. In this article, four prehistoric reddish rock art painting panels from the Penedo do Gato site (NW Spain) were studied. A methodological approach based on portable and non-destructive analytical techniques was carried out, including digital photographic enhancement, morphological characterisation of the painted motifs using DStretch, evaluation of colour parameters by spectrophotometry, and molecular characterisation by portable Raman spectrometry. Furthermore, it was also possible to analyse three different reddish stone samples that were collected during the archaeological survey (June–August 2019) conducted in the site's surroundings, allowing for the evaluation of their potential as the original pigment source. For this purpose, these three samples were evaluated in the laboratory by X-ray diffraction (XRD), stereomicroscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS).

2. The Rock Art Shelter at the Penedo Do Gato Site (Monterrei, NW Iberian Peninsula)

2.1. Historical Precedents

Studies related to post-Palaeolithic rock art in the NW Iberian Peninsula have mainly focused on coastline open-air engravings, while those related to inland areas have received less attention, overlooking other possible potential rock painting manifestations hidden under rock shelters. The study of rock art paintings in the southeastern area of Galicia has been approached from a cross-border perspective, given the previously known evidence of schematic paintings in northern Portugal [21]. To date, six rock art sites with paintings of schematic tradition have been found in Galicia: Cova dos Mouros (Baleira, Lugo) [22], Pala de Cabras [23,24], and more recently, Colobredos (Casaio, Carballeda de Valdeorras, and Ourense), along with three other sites located in the Támega basin. Some of these, along with additional examples, are discussed collectively in Alves and Comendador (2018) [21]. One of the sites in the Támega basin is Penedo Gordo (Vilardevós, Ourense), where stratified archaeological deposits have been documented in direct connection with the painted walls, dating from the Middle Neolithic (3500–2800 BC) to the Chalcolithic periods (3000–1700 BC) [25]. In this paper, we present another site, the Penedo do Gato in Vilaza (Monterrei, Ourense), which features paintings on granite surfaces. Although painted manifestations are also found inside megalithic chambers, this is the only case known to date in Galician territory where the paintings appear on the natural walls of a granite rock shelter, applied directly onto the rock surface. The Penedo Gordo and Penedo do Gato sites, together with another unpublished site in the Monterrei region, expand the known area of schematic rock art manifestations, filling a previously unknown gap in northwestern Iberia [26].

The identification of these Holocene schematic paintings represents a milestone in the historiography of Galician rock art and emphasises the importance of the Galicia/Trás-Os-Montes cross-border for a better understanding of Iberian rock art. The western cross-border region breaks the geographical limitations previously attributed to Galicia [26]. Some authors argue for the permeability between schematic painted art and megalithic art [27,28], a point that has been nuanced by researchers such as Alves [29].

The discovery of the rock art paintings inside the Penedo do Gato cave system took place during the archaeological survey carried out in 2019. The site is characterised by evidence that shows a sequence of occupations from prehistoric to medieval times [29,30]. Archaeological works led to the recovery of abundant archaeological artefacts, distributed over an area of 18 ha. The pottery fragments found, along with their decorative patterns, suggest the site's occupation at the end of the Neolithic/Chalcolithic periods, hypothesising an occupation prior to the 3rd millennium BC [30,31].

2.2. Localisation and Context

The prehistoric rock art paintings at the Penedo do Gato site are part of a system of block cavities within the archaeological and natural site of A Ceada das Chás/Castelo de Lobarzán, located in the region of Monterrei, in the province of Ourense (Galicia, Spain) (Figure 1a). The site is located inland, close to the Támega River, within the hydrographic basin of the Duero River, near the administrative border between Spain and Portugal. Penedo do Gato is placed on an orographic spur with a wide visual domain over the lowlands of the valleys of the Támega and its Búbal tributary, surrounded by O Mazairo (653 m above sea level), A Ceada (651 m above sea level), and O Castelo (649 m above sea level) hills. The paintings are located on the northern slope of the O Castelo hill, in a place that is difficult to access due to the steep slope and rocky morphology (Figure 1b,c).

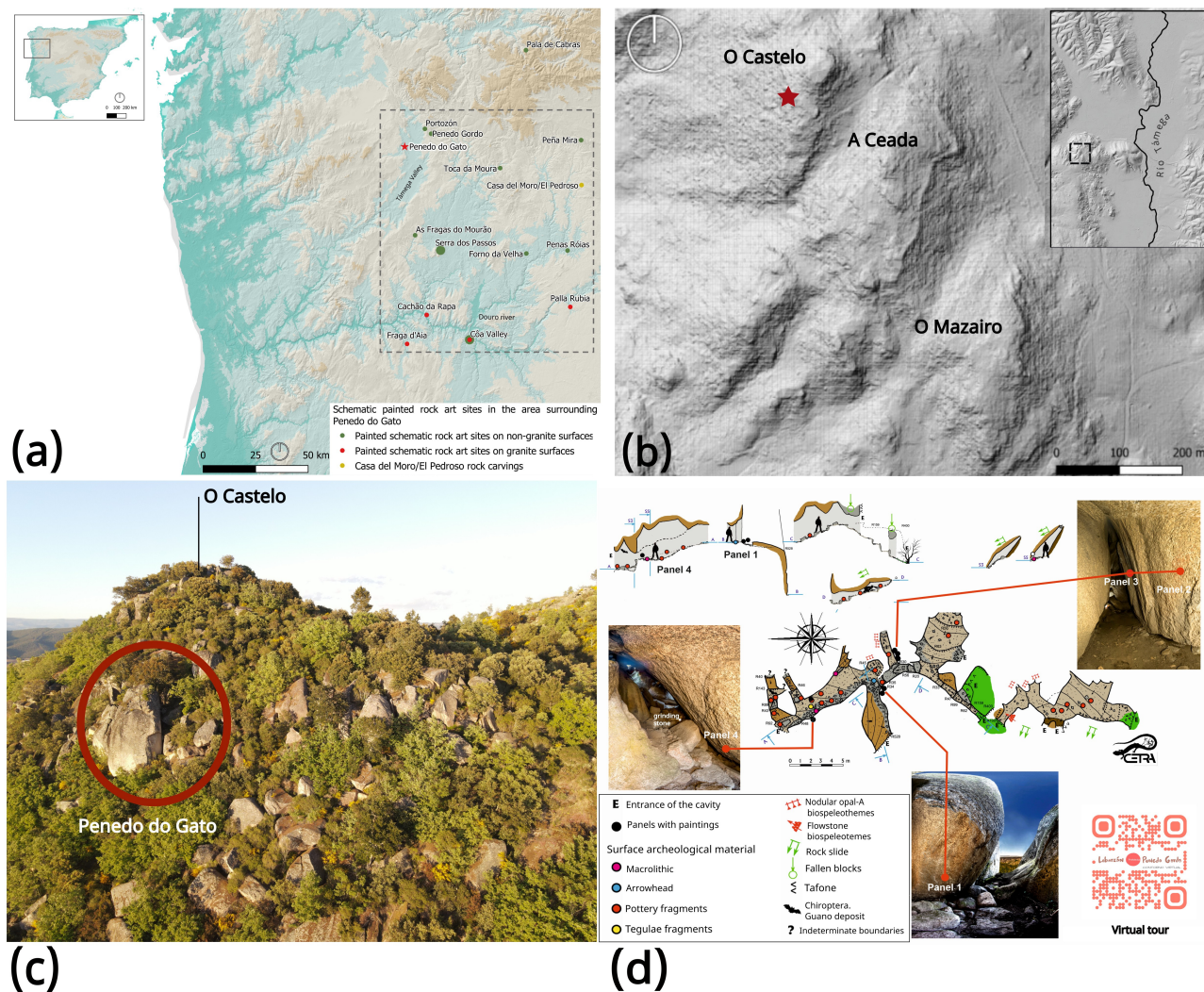


Figure 1. (a,b): Location of Penedo do Gato site in NW Spain, marked with a red star in (b). (a) Location of schematic painted rock art sites in the area surrounding Penedo do Gato. (c) A view of the outcrop. (d) Details of the four panels in the different shelters and cavities.

The site is in an area of medium to coarse-grained post-cinematic granites [32]. Fractured blocks form the different shelters and cavities inside which the rock art paintings were discovered. These blocks present little movement, apparently related to a slide in favour of the slab structure that forms the dome. Tafoni formations are present at both levels, though they are minor in size and development, generally appearing as superficial alveolisation. In total, 67 m of galleries and passages were mapped, forming two distinct levels of shelters and cavities (Figure 1d) [33]. The upper level, where the painted panels are located, is made up of large blocks that show relatively recent fractures. The spatial arrangement of certain anthropogenic elements suggests that some rotations and tilting of these large blocks occurred after this horizon of use/occupation. The painted panels identified so far are located in the upper level of this gallery system and are distributed across three sites and four panels (Figures 1d and 2).

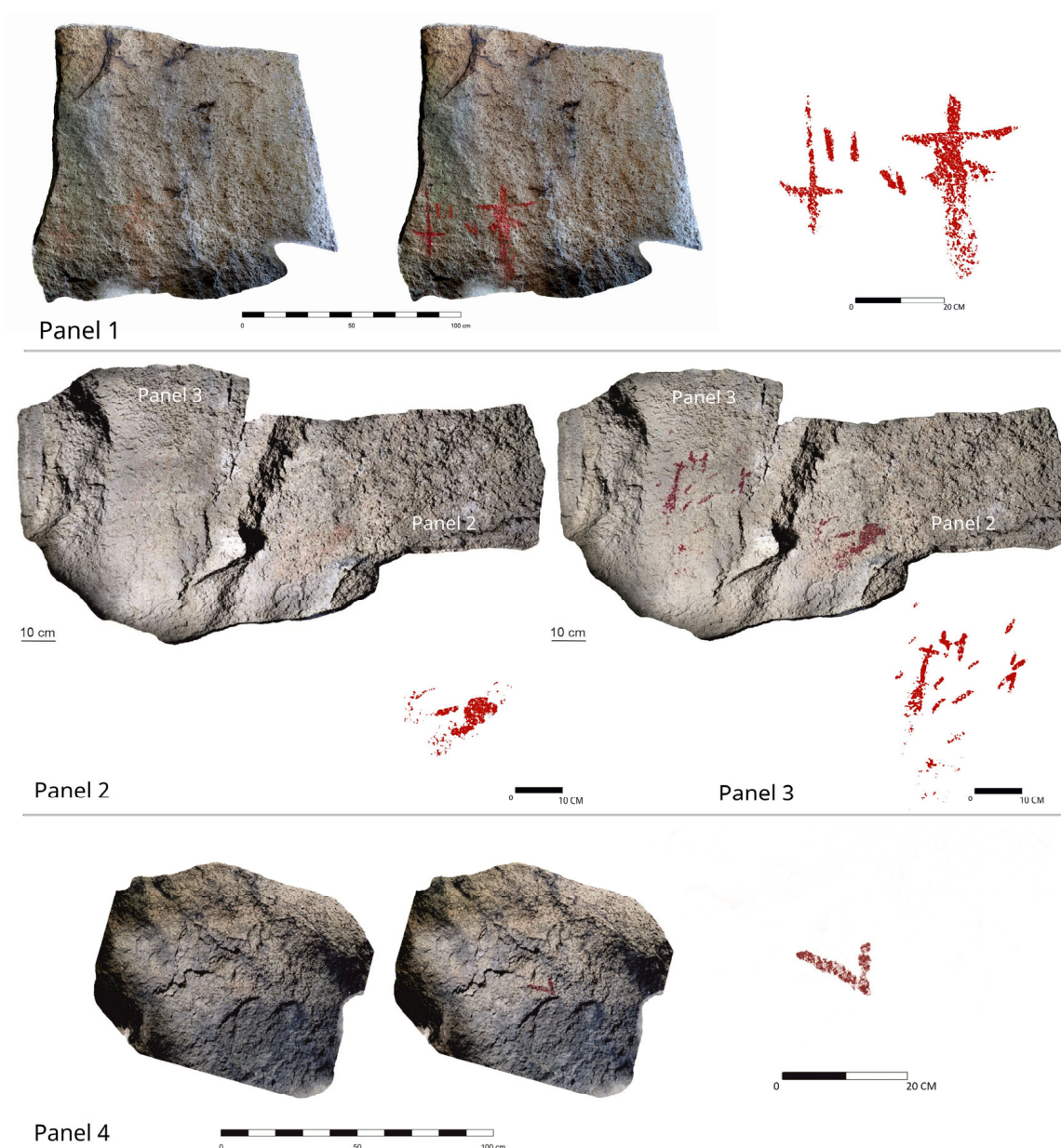


Figure 2. Photorealistic tracing of the panels (P) present at Penedo do Gato, with the representation of the different motifs.

Inside the cavity, heterogeneous deposits can be observed, generally consisting of mixtures of terrigenous material and alteration detritus, including sands and gravels, as well as clastic deposits formed by angular fragments of local materials of varying sizes, ranging from decimetric to even metric scales. Among these deposits, allochthonous materials, particularly quartz and schist, are found alongside abundant archaeological remains. Some surface finds, especially fragments of tegula and wheel-thrown pottery, appear to have been naturally transported into the cavity by erosive processes. This is expected considering the presence of remains on the nearby hill of O Castelo and the steep slope of the hillside (Figure 1c). However, in other instances, certain materials seem to have been deliberately deposited before the more recent displacement of the cavity walls, which subsequently trapped them between large blocks.

3. Analytical Protocol

3.1. In Situ Characterisation

The first stage of the analytical protocol involved recording the rock art using a combination of direct and vector tracing of digitally enhanced images. The CETRA speleological team conducted the planimetric mapping of the cavity system, while the University of Vigo was responsible for documenting the painted motifs. Digital photographs were captured with a Canon 5D Mark II, and the plugin DStretch was used to identify the number and morphological features of the paintings.

As part of the virtual tour project (Figure 1d, <https://premedia.webs.uvigo.es/>, accessed on 15 January 2025), 360° photographs, partial photogrammetry, and photographic recordings for digital tracings were conducted. The processing relied on uncompressed digital photographs, providing a broad dataset for analysis, though without the capacity to differentiate wavelengths or spectra such as UV or IR. However, since the paintings are visible to the naked eye, the morphology of the motif could be distinguished, enhancing its colour and facilitating a better differentiation of the pictorial motifs [34]. These techniques provided a detailed representation of the painted panels, enabling an exhaustive analysis of the pictorial motifs. Subsequently, as part of the PreMedia Project, a virtual tour of the Penedo do Gato site was developed. This virtual tour, available online, serves as a valuable tool for the conservation, dissemination, and study of the rock art present at the site [34].

Once the motifs were catalogued, both their colour and the colour of the stones (without motifs) in the outcrop of all four panels were measured using spectrophotometry. The measurements were obtained with a portable spectrophotometer (Konica Minolta CM-700d, Tokyo, Japan) equipped with CM-S100w 1895-244 ver. 1.6 (SpectraMagic™ NX, Tokyo, Japan) software. The working conditions of the device were as follows: area view (MAV) of 8 mm, CIE standard daylight illuminant D65 and observer 10°, with Specular Component Excluded (SCE) mode. The colour was measured in the CIELAB and CIELCH spaces [35]. Therefore, the colour parameters measured were as follows: 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, chroma C^*_{ab} and hue h were also measured. For each motif, 15 measurements were randomly made on the motif. The changes in colour were evaluated by calculating the ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} , and ΔH^* colour differences and the difference colour (ΔE^*_{ab}). The original colour of the unpainted stone next to the motifs was used as the reference value for each motif.

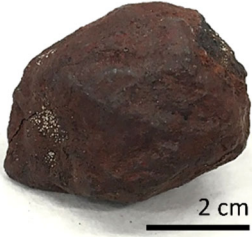
As a spectroscopic technique, Raman spectroscopy was used to detect the molecular composition of the motifs and the stones. Raman spectroscopy was applied in the same motifs where colour measurements were performed. Excitation at 785 nm was provided by a continuous wave diode laser, coupled to an optical 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, the 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 motif.

3.2. Sampling

During the archaeological survey, three red-coloured stone samples were collected (Table 1) as possible sources of the pigments used in the Penedo do Gato rock art paintings:

- A dark reddish stone (ID 300).
- A grey stone with bright yellow-orange-coloured deposits (ID 698).
- A grey stone with a light reddish coloured deposit (ID 705).

Table 1. Samples collected from the surface during the archaeological survey at the A Ceada das Chás/Castelo de Lobarzán site, where Penedo do Gato is located, with digital photographs of each sample. The sector and specific location details are indicated.

ID 300	ID 698	ID 705
		
C-LOB19 PSS 0300 SECTOR 2. South. Surface	C-LOB19 PSN 0698 SECTOR 1. Surface	C-LOB19 PSN 0705 SECTOR 1 Surface

3.3. Laboratory Characterisation

The samples collected were investigated in the laboratory using the following protocol:

- The mineralogical composition of all three samples was determined by X-ray diffraction (XRD, Siemens D5000, München, Germany), applying the random powder method. Powder was scraped off the surface using a punch. Samples were ground in a mechanical ball mill. Analyses were performed using Cu-K α radiation, Ni filter, 45 kV voltage, and 40 mA intensity. The exploration range was 3° to 60° 2 θ , and the goniometer speed was 0.05° 2 θ s^{−1}.
- Samples were then embedded in an epoxy resin (EpoThin 2 Epoxy Resin and EpoThin 2 Epoxy Hardener, Lake Bluff, IL, USA). Once hard, a transversal cut was made to obtain specimens measuring 2 cm × 2 cm × 1 cm. These cross-sections were visualised by stereomicroscopy (SMZ800 NIKON®, Tokyo, Japan).
- Lastly, the cross-sections were coated using carbon, and they were visualised using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) in backscattered (BSE) and secondary (SE) electrons modes using a FEI Quanta 200 (Hillsboro, OR, USA). Optimum conditions of observation were obtained for an accelerating potential of 20 kV, a working distance of 9–11 mm, and a specimen current of ca. 60 mA.

4. Results and Discussion

4.1. Penedo Do Gato Paintings

The rock paintings at *Penedo do Gato* are distributed across four panels (Figure 2), each featuring motifs of varying size and complexity (Table 2). These panels are located within a cavity system, in narrow passages where some areas are exposed to sunlight.

Table 2. Description of the different motifs (M) identified in panels 1 to 4 at Penedo do Gato.

Panel	Description	Motif
Panel 1	P1-M1: Semi-schematic anthropomorphic figure with broad strokes. Cruciform shape with extended arms and legs in an inverted “V”. The lower half is less distinct, showing a phallic symbol and an oblique stroke that may represent a weapon. 25 × 25 cm. P1-M2: Highly schematic anthropomorphic figure, resembling the cruciform type. 30 × 20 cm. P1-M3 to P1-M6: Four smaller vertical motifs.	
Panel 2	P2-M1 to P2-M3: Three horizontal elements, possibly part of a larger figure. P2-M1 is an oval red stain, followed by two horizontal bars (P2-M2, P2-M3) aligned with a thicker stroke. P2-M4: Four lighter-coloured dots. P2-M5 to P2-M8: Finer strokes, oblique lines, and small dots made with a finer instrument and lighter pigment.	
Panel 3	P3-M1: Oblique bar inclined to the right. P3-M2: Oblique bar inclined to the right. P3-M3: Two vertical bars connected by a horizontal stroke. It could form part of a single figure with P3-M4. P3-M4: Cruciform motif. It could form part of a single figure with P3-M3. P3-M5: Oblique bar inclined to the right. P3-M6: Set of three digitations. P3-M7: Oblique bar inclined to the right. P3-M8: Cruciform motif, representing a very simple human figure. P3-M9: Oblique bar inclined to the right. P3-M10: Oblique bar inclined to the right. P3-M11: Oblique bar inclined to the right. P3-M12: Cruciform motif. P3-M13: Oblique bar inclined to the right. P3-M14: Oblique bar inclined to the right. P3-M15: Vertical bar, slightly oblique and inclined to the right, with a pigment lighter in colour than the previous ones. P3-M16: Oblique bar inclined to the right. P3-M17: Cruciform motif, with a pigment lighter than the previous ones.	Detail of P3-M3 and P3-M4, with a possible zoomorphic motif.
Panel 4	P4-M1. Angular stroke 12 × 8 cm.	

Panel 1 is situated in a narrow south–southwest-oriented corridor that opens to a steep drop of nearly five meters, offering a panoramic view of the deeply incised Búbal River valley and Mount Larouco in the distance (Figures 1d and 2). Forming a small shelter with a 50° slope, the panel contains several motifs, the most prominent being P1-M1, a semi-schematic human figure created with broad strokes (Table 2). It has a cruciform shape

with extended arms and legs arranged in an inverted “V” formation. The lower half is less distinct but includes a visible phallic symbol and an oblique stroke that may represent a weapon. To its left, P1-M2 is another highly schematic human figure of the cruciform type (see Table 2 for detailed descriptions). Additionally, P1-M3 to P1-M6 consist of four smaller vertical motifs that could correspond to bars or other motifs of a similar tone (Table 2). The motifs in this panel are currently located close to ground level, surrounded by an accumulation of stone blocks of varying sizes. Among these, fragments of pottery with incised decoration have been found. A flint barbed and tanged arrowhead with convex sides was recovered from the surface [31]. This typology is consistent with others associated with Late Prehistoric occupations in the Tâmega Valley [36].

Panels 2 and 3, separated by a change in plane, are located on the eastern wall of a narrow branch of the main cavity, with a maximum length of 3 m (Figures 1d and 2). The limited space barely allows a person to enter while standing. The rock surface in this section is remarkably smooth, in contrast to the opposite wall, which is much rougher. The paintings were applied directly onto this smooth surface, where several red motifs can be observed. However, the presence and development of encrustations (speleothems) make it difficult to distinguish the motifs with the naked eye, as does the narrowness of the space, which is barely 45 cm wide. Capturing images for documentation was challenging, as it was not possible to obtain a full-frontal view of all the motifs. Initially, several mosaic composition studies were conducted to create a preliminary visualisation of the motifs present on the walls. Ultimately, the processing was carried out using the photographic composition obtained for photogrammetric recording, with additional work on detailed images of specific motifs. This process led to the identification of new motifs and a clearer definition of previously known ones, highlighting the high value of the applied methodology [34]. Panel 2 is located near the entrance of a corridor, where the notably smooth rock surface provides an ideal background for finer motifs. It includes several horizontal elements, dots, and delicate strokes, some of which were only identifiable after cleaning, suggesting the use of a finer instrument and lighter pigment (see Table 2 for details). Panel 3 is located deeper within the corridor and contains a combination of human motifs of the cruciform type and numerous oblique bars. Although this section is covered with abundant speleothems that obscure the visibility of the motifs, post-cleaning documentation efforts led to the identification of a total of 17 elements (Table 2).

Panel 4 is positioned in a narrow space along the south wall of a wider and darker section, partially concealed by accumulated debris (Figures 1d and 2). This makes it difficult to fully appreciate the motif, which consists of a single, isolated angular stroke measuring 12 cm × 8 cm (Table 2). Despite its simplicity, this type of motif, with angular or bent strokes, is also common in Iberian schematic art. Although in our case the motif appears isolated, there are documented examples where similar angular figures appear in groups, such as in the Cova dos Mouros rock shelter in Galicia [22], as well examples of grouped angular figures, such as in Panel 4 from the “Castillo de Monfragüe” shelter (Torrejón el Rubio, Cáceres, Spain) and Panel 3 from “La Calderita” (La Zarza, Badajoz, Spain) [37].

In the absence of a more comprehensive archaeological intervention, the preliminary review of the panels reveals a concise and synthetic imagery, featuring anthropomorphic figures alongside simple geometric motifs. Regarding size, both the motifs and the thickness of the strokes can be described as medium. No superimpositions have been observed, and all the documented figures across the four panels are executed in red pigment.

Given the instability of the cavity system, it is possible that some of the current rock formations shifted after the paintings were created. This may explain why several motifs are located in such a marginal and difficult-to-access position. The discovery of two displaced

fragments of prehistoric grinding stones—one near Panel 4 and the other in the narrow corridor between Panels 2 and 3—further supports this hypothesis.

The current positioning of these panels in tight or marginal spaces—potentially the result of granite block displacement over time—suggests that the original configuration of the rock shelter may have been slightly different. Even so, the motifs remain in confined areas with limited mobility, requiring specific bodily positions and precluding the presence of large audiences, a context that Collado describes as an “intimate shelter” [38]. This setting raises questions about possible access restrictions based on community roles or other factors. Additionally, the location of motifs in narrow galleries and low or marginal positions, along with the presence of sediment filling parts of the floor, suggests that further, currently inaccessible paintings may remain hidden.

The analysis of various factors—including the geographical location of the site, the specific placement of the motifs, the characteristics of the rock surface, as well as the arrangement, definition, and shape of the red-painted motifs—alongside the archaeological background of the surrounding territory, leads us to classify this site within the so-called schematic tradition. Based on the current state of research, considering both the iconography of the motifs and the associated materials found nearby, a chronological framework between the 4th and 3rd millennium BC is suggested, though the possibility of diachronic phases among different representations cannot be ruled out. In terms of location, placement, granite substrate, motif arrangement, and iconographic features, Penedo do Gato shares the greatest affinities with rock shelters found in the granite landscapes of Zamora, Salamanca, and Cáceres, or North Portugal. Until recently, painted manifestations on natural rock shelters or open-air granite surfaces had been scarcely studied. Although the current research does not delve deeply into this aspect, numerous sites have been discovered in recent years, some of which have undergone archaeological work. Examples include “Los Barruecos” (Cáceres) in the Salor Valley [39], and rock shelters in the Amblés Valley such as “La Atalaya” and “Canto del Cuervo” (Muñopepe, Ávila) [40,41], associated with occupation levels ranging from the Early Neolithic to the Chalcolithic. These granite outcrops are often visually dominant within the landscape and linked to livestock routes. Guerra Doce et al. [38] highlight the parallels between this settlement model, emerging in the Early Neolithic in the Salamanca and Ávila regions, and sites from the 6th millennium BC in northern Cáceres and the Portuguese Atlantic façade, characterised by settlements atop granite promontories with wide visual control. Some other painted sites have barely been described, yet they show a coexistence of occupation traces, simple engravings, and open-air rock paintings on prominent rock formations or shallow shelters. One remarkable example is Campo Arañuelo (Cáceres), where a gradual increase in site density from the periphery to the inhabited core has been suggested [42]. These and other comparable sites provide significant references when contextualising Penedo do Gato within the broader framework of Iberian schematic art and the Neolithic transition of inland territories, closely linked to pastoralism, an idea previously proposed by Gómez [43]. Other examples of granite cavities containing anthropomorphic motifs include cruciform figures that also align with known schematic representations. A close parallel is also found at “Casa del Moro”, located on one of the slopes of the Chalcolithic settlement of “El Pedroso” (Aliste, Zamora), where a large figure with outstretched arms, open legs, and a phallic representation is engraved inside a granite block cavity [44].

Comparable cases have been documented in small granite-block shelters in the province of Cáceres, such as “Cueva Larga del Pradillo” and “Los Canchalejos de Belén” (Trujillo) [45], as well as “Cueva de Moro” (Aldea del Cano) [46]. In this study, we propose several hypotheses regarding the potential function of the Penedo do Gato cavity. One possibility is that the cavity had a funerary function. The system’s configuration—with

multiple interconnected branches and galleries—bears a strong resemblance to a “natural megalithic chamber”. This parallel is reinforced by the presence of painted motifs similar to those found within megalithic chambers, although, in such structures, the orthostat surfaces were usually prepared in advance, as documented, for example, in the case of the megalithic chamber of Dombate, where Carrera (2013) [47] and Carrera and Vilaseco (2014) [48] identified the application of a preparatory layer of plaster. In this regard, the paintings at Penedo do Gato diverge from the technical procedures typical of megalithic parietal art and instead align more closely with those of open-air shelters on other types of rock surfaces, where the pigment is applied directly onto the natural rock. Moreover, the iconography in these tombs is often more geometric, with some exceptions documented in Portugal [29]. Furthermore, the surface discovery of an arrowhead and incised Penha-style ceramics near Panel 1 supports this hypothesis. A similar arrowhead and ceramic fragment were found at the end of a narrow corridor in a nearby cavity at A Ceada [30].

As noted in previous studies, the archaeological evidence around this site suggests repeated, cyclic, and temporary occupations, leading to the accumulation of a significant number of surface materials, which are consistent with a 4th–3rd millennium BC chronology, though an earlier occupation cannot be ruled out [29,30]. Some of these materials are directly linked to rock shelters and formations, which appear to have played a structuring and referential role in the lives of these communities. The peripheral location of Penedo do Gato in relation to the primary concentrations of archaeological materials, combined with the intimate nature of the panels and the potential necrolatric function, suggests a ritual and symbolic use of the site. However, the presence of grinding equipment also indicates domestic activities. Similar grinding tools have been found in rock shelters with cyclic occupations from the Late Neolithic to the Early Bronze Age [49]. Penedo do Gato presents an exceptional case, where portable grinding equipment coexists with painted motifs inside the cavity, highlighting the potential interplay between rock art and daily activities.

Finally, the coexistence of painted motifs inside the cavity and cup-mark engravings in the open-air section invites reflection on the dialogue between different techniques and styles. Whether contemporaneous or successive, they share the same occupied space, emphasising the complexity and longevity of human interaction with this site.

4.2. In Situ Characterisation

Based on digital photography, enhanced photographic images and vector drawings, the four panels with rock art paintings were reproduced, as shown in Figure 2.

Colour measurements were carried out by spectrophotometry on the painting support (the rock without motifs, R hereinafter) and on some of the identified motifs (Table 3). This characterisation allowed the recognition of colour parameters in the motifs that were clearly different to those of the rock. Therefore, the total colour variation (ΔE^*_{ab}) between the motifs and the rock was above 3.5 CIELAB units, value from which two different colours can be observed [48]. On the one hand, all the motifs present in P1, P2, and P4 presented ΔE^*_{ab} above 3.5 CIELAB units. On the other hand, motifs M7, M12, and M14 in P3 showed a ΔE^*_{ab} below 3.5 CIELAB units, and were therefore not visible to the naked eye.

Within the CIELAB space parameters, the L^* parameter was most affected in P1–M2, P2–M1, and in all the motifs from P3 (except P3–M12). In the first two motifs, a reduction in L^* was observed, indicating a clear blackening compared to the rock substrate (Figure 3a). However, the motifs present in P3 experienced an increase in the L^* parameter. This difference was statistically significant in most cases (Figure 3a). Regarding the a^* (red–green) coordinate, it was the most affected parameter in P1–M1, P2–M2, and P4–M1, showing an increase which translates as a higher presence of the red parameter ($+a^*$). These differences were statistically significant (Figure 3b). As for the P3–M12 motif, the b^*

(yellow-blue) coordinate was the most affected, presenting a statistically significant increase in the yellow hue with respect to the rock value (Figure 3c). As a result of the variations in the a^* and b^* coordinates, the C^*_{ab} and h parameters increased and decreased, respectively, except for P3-M7, though these variations were below 1 CIELAB unit (Table 3). Overall, spectrophotometry made it possible to detect that the motifs identified in situ had a much more intense reddish hue than the rock substrate on which they were found, as is reflected by the greater modification of the a^* parameter, compared to the variations in L^* and b^* .

Table 3. Colourimetric differences (ΔL^* , Δa^* , Δb^* , ΔC^*_{ab} and ΔH^*) and the colour difference (ΔE^*_{ab}) of the motifs measured in each panel with respect to the colour of the rock without motifs. ΔE^*_{ab} cells marked in grey indicate that this parameter is greater than 3.5 CIELAB units, the threshold at which an untrained human eye can distinguish between two different colours [50].

Motif	ΔL^*	Δa^*	Δb^*	ΔC^*_{ab}	ΔH^*	ΔE^*_{ab}
P1-M1	−1.07	8.14	2.79	5.68	−6.44	8.67
P1-M2	−6.84	6.73	1.18	3.59	−5.79	9.67
P2-M1	−3.59	5.51	0.31	2.60	−4.88	6.58
P2-M2	−4.46	2.70	−0.87	0.22	−2.83	5.29
P2-M3	−4.22	3.09	−1.27	0.04	−3.37	5.38
P3-M3	6.36	1.65	1.08	1.64	−1.11	6.65
P3-M4	5.51	2.34	3.64	4.26	−0.77	7.01
P3-M7	1.79	−0.38	−0.52	−0.63	0.13	1.90
P3-M8	4.66	0.89	−0.29	0.08	−0.96	4.75
P3-M10	5.44	0.98	1.33	1.60	−0.42	5.68
P3-M12	0.75	1.18	2.81	3.04	−0.11	3.14
P3-M13	5.07	0.67	0.43	1.95	0.00	5.13
P3-M14	1.67	0.89	1.43	1.66	−0.32	2.37
P4-M1	−0.82	5.81	1.09	3.55	−4.67	5.97

Figure 4 shows the Raman spectra from the rock substrate and the pictorial motifs from each of the panels. The spectra of the rock (R) analysed in each of the panels showed strong peaks at 205 cm^{-1} and 465 cm^{-1} assigned to Si–O–Si related to the presence of quartz (SiO_2) [51–54], the main compound of the Galician granites [55]. The presence of lower-intensity Raman peaks at 1225 and 1257 cm^{-1} in the same stone substrates was also detected. The assignment of these peaks will be discussed below, along with the reporting of peaks in this region for the pictorial motifs.

Regarding the coloured pictograph motifs, Raman characteristic peaks assigned to hematite ($\alpha\text{-Fe}_2\text{O}_3$) were identified in most of them. This pigment has been widely reported in the literature as a common mineral used by prehistoric artists in the manufacture of red paints in the Iberian Peninsula [15,56–58]. Based on the literature, seven vibrational modes of hematite are expected to be active in Raman spectroscopy around 225 , 250 , 293 , 298 , 412 , 500 , and 610 cm^{-1} [56,59]. Two of them, with A_{1g} symmetry, give rise to the fundamental Raman bands observed at 225 and 500 cm^{-1} . The remaining five modes, with E_g symmetry, generate the Raman fundamentals at 250 , 293 , 298 , 412 , and 610 cm^{-1} . An additional strong and broad Raman band observed at about 1320 cm^{-1} is assigned to a two-phonon interaction [60]. The other band at 660 cm^{-1} is assigned to a Raman forbidden longitudinal optical E_u mode, explained by disordered hematite structures that reduce its original D^6_{3d} symmetry, consequently modifying the properties for scattering the longitudinal optical phonon [61,62]. This band is associated with hematite lattice disorder in natural red ochre [60,62]. In this study, based on the Raman spectra obtained, the peaks used as key features were 250 , 500 and 660 cm^{-1} (marked with black arrows in Figure 4). Therefore, the motifs in which hematite was identified were the two motifs in P1 (Figure 4a),

M1 and M2 in P2 (Figure 4b), M4, M10, M12, M13, and M14 in P3 (Figure 4c), and M1 in P4 (Figure 4d). It is important to note that no other iron oxides or oxy-hydroxides commonly found in rock art paintings, such as goethite (α -FeOOH) [14], were detected.

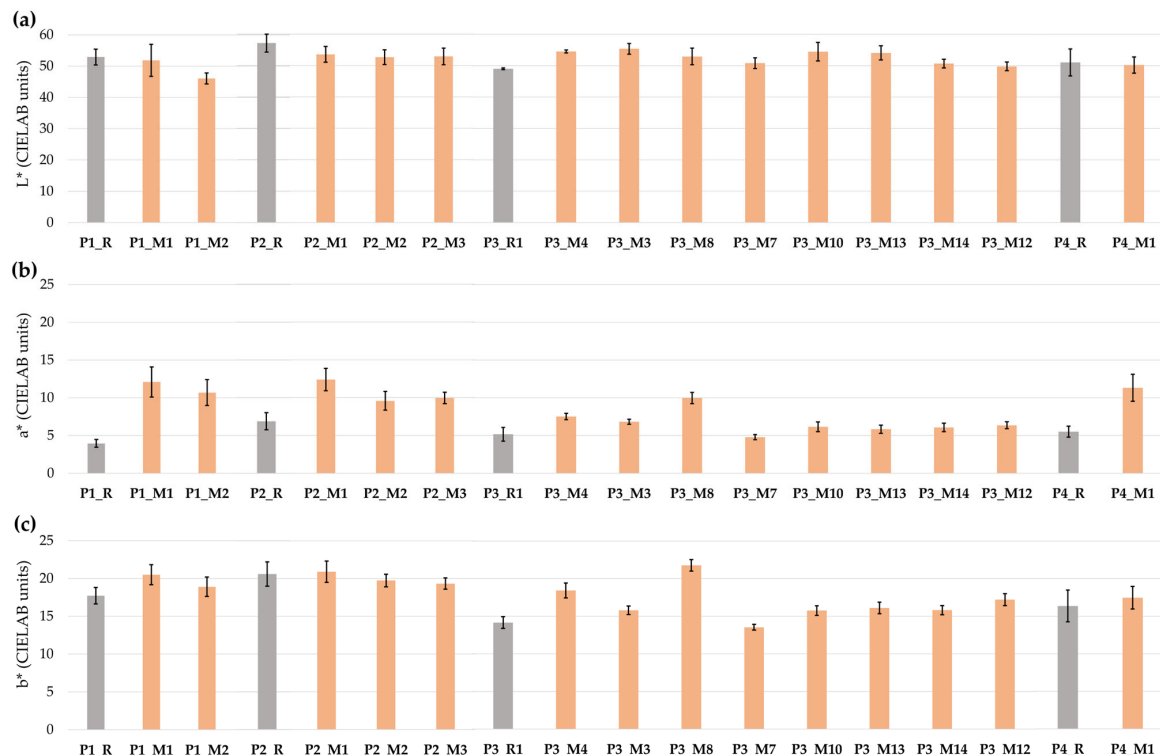


Figure 3. Colourimetric parameters L* (a), a* (b) and b* (c) of the motifs (M) and the rock substrate without paintings (R) measured in each panel (P).

In some of the red motifs, peaks between 1000 and 1600 cm^{-1} , assigned to amorphous carbon, with different intensity levels (all of them marked with black rectangles in Figure 4), were detected. In P1, M1 and M2 motifs showed low-intensity peaks at 1445 cm^{-1} (Figure 4a). In P2-M3, a broad band within the aforementioned region was detected (Figure 4b), as well as in P3-M4 and P3-M12 (Figure 4c). In the case of P4-M1, intense peaks were detected at 1110, 1220, 1250, and 1420 cm^{-1} (Figure 4d). Peaks between 1000 and 1600 cm^{-1} can be attributed to amorphous carbon, which may originate from either (i) charcoal (Raman peaks at 1590 and 1360 cm^{-1} [63]), used as an additive or deposited on the decorated surfaces from bonfires; or (ii) bone black (Raman peaks at 1590, 1370, 1070, 964, and 670 cm^{-1} [63]), also used as an additive. However, as Raman spectroscopy makes it possible to distinguish between charcoal and bone black by the phosphatic stretching mode near 960 cm^{-1} in the latter, it is most likely that the peaks registered in the Raman spectra are related to charcoal, since this 960 cm^{-1} peak is not present in the spectra obtained [64]. Additionally, Rosina et al. [58] assigned the presence of peaks at 1176, 1232, 1359, 1371, 1484, and 1590 cm^{-1} to organic matter, suggesting it may or may not be part of the original painting. On the one hand, organic dyes and organic binders, as components of the paintings, are very difficult to preserve. Dyes can come from different parts of the plants: leaves, flowers, roots, fruits, trunks, or seeds [65]. Binders can be plant resins (e.g., sandarac, copal, dammar, etc.) or casein [66]. However, considering the difficulty in identifying organic substances in rock art paintings, the presence of organic dyes or binders should be ruled out. On the other hand, organic matter may be associated with the presence of microorganisms such as lichens or fungi. However, no evidence of calcium oxalates like whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) or weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$),

which are products of the metabolic activity of microorganisms like lichens or fungi, were detected [67]; these calcium oxalates are generally detectable through the presence of a doublet around 1470 and 1490 cm^{-1} [63]. Therefore, we could hypothesise that the peaks between 1000 and 1600 cm^{-1} could be related to carbon from charcoal (either as an additive or as a result of bonfires). Considering the spectra of the rock substrate already showed the peaks at 1225 and 1257 cm^{-1} , charcoal from bonfires deposited on the rock surfaces seems to be the most appropriate provenance of this. However, the greater intensity of some of these peaks from the motifs compared to those detected in the rock leads us to consider the possibility of a greater accumulation of charcoal on the surface of the motifs, or even the possibility that the charcoal has been mixed with the red pigments to modify the colour.

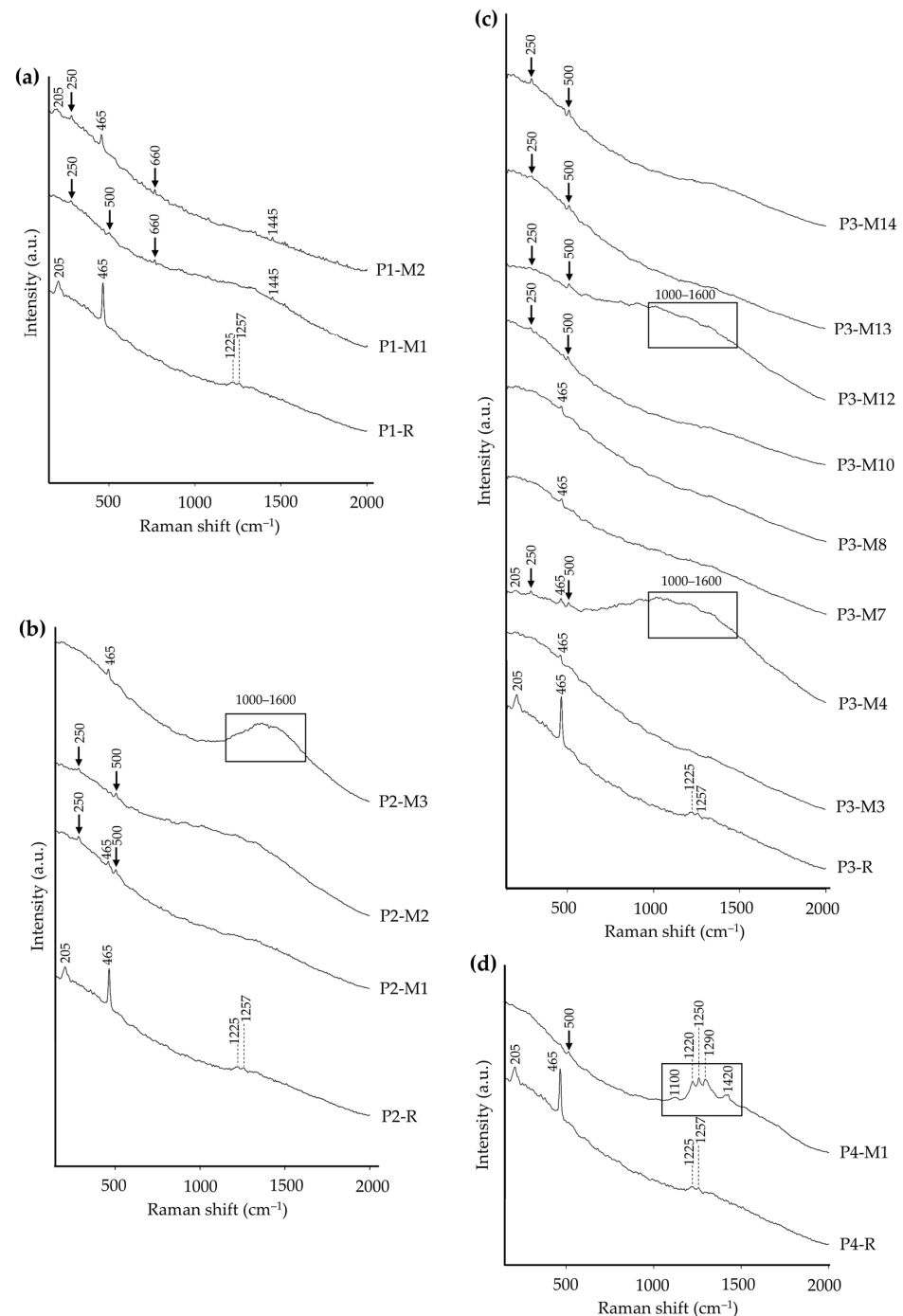


Figure 4. Raman spectra of the motifs (M) and the rock substrate (R) detected on each panel (P): (a) P1; (b) P2; (c) P3; and (d) P4.

4.3. Laboratory Characterisation

The study of the cross-sections by stereomicroscopy allowed a preliminary observation of physical features such as texture and colour. Sample 300 showed a homogeneous purplish hue, with a more compact appearance compared to the other two samples (Figure 5a). As for samples 698 and 705, they manifested a more reddish colour, and were slightly powdery, especially the latter (Figure 5b,c, respectively). Sample 698 (Figure 5b) showed a reddish external layer with mineral grains.

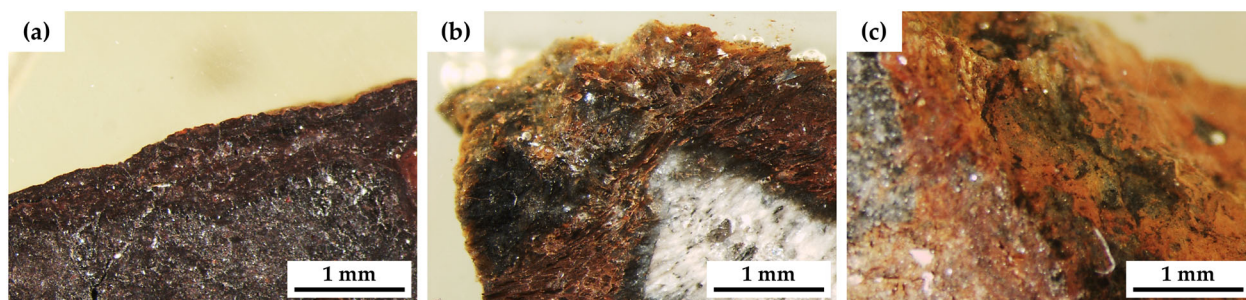


Figure 5. Micrographs of the cross-sections by stereomicroscopy of the red-coloured samples collected in the excavation: (a) 300, (b) 698, and (c) 705 samples.

Table 4 shows the mineralogical characterisation carried out by XRD. The results show that all three samples presented quartz (SiO_2) and muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) in their composition. Samples 698 and 705 were additionally composed of other silicate minerals: andalusite (Al_2SiO_5) and microcline (KAlSi_3O_8). Moreover, in sample 698, ephesite ($\text{NaLiAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) and illite ($(\text{K},\text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}$) were detected. In sample 705, kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and albite ($\text{NaAlSi}_3\text{O}_8$) were identified. Rutile (TiO_2) was found only in sample 705. Regarding hematite, which was the mineral phase identified by Raman spectroscopy as the red pigment used in the reddish motifs, only samples 300 and 705 presented this mineral within their mineralogical composition.

Table 4. Mineralogical composition by XRD: (*) detected; (-) not detected.

Mineral	Mineralogical Formula	Samples		
		300	698	705
Quartz	SiO_2	*	*	*
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	*	*	*
Andalusite	Al_2SiO_5	-	*	*
Ephesite	$\text{NaLiAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$	-	*	-
Rutile	TiO_2	-	-	*
Illite	$(\text{K},\text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}$	-	*	-
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-	-	*
Microcline	KAlSi_3O_8	-	*	*
Albite	$\text{NaAlSi}_3\text{O}_8$	-	-	*
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	*	-	*

The study by SEM-EDS of sample 300 allowed us to observe a compact matrix mainly composed of iron-Fe- together with other trace elements (aluminium-Al-, silica-Si-, phosphor-P-, and potassium-K-) as shown in Figure 6a,b (EDS spectra 1). This could be related to the mineral hematite, previously identified by XRD. Regarding trace elements, they could be related either to impurities in hematite, as reported in other rock art paintings studies from the Iberian Peninsula [59], or to the other mineral phases identified by XRD (Table 4). Other laminar particles were detected, composed of Al and Si in a 1:1 intensity

ratio, together with K (Figure 6b, EDS-2). The habit and chemical composition detected could be related to the mineral muscovite. In addition, Si-rich particles were also detected (Figure 6b, EDS-3), likely related to quartz. Titanium (Ti) and Fe-rich micrometric particles, with high contrast, were sporadically observed (marked with a black square in Figure 6b, EDS-4), which could be related to the TiO_2 -based minerals such as rutile. Even though XRD analysis did not identify any Ti-oxides in this sample, their presence cannot be discarded as they could be present in low concentrations, below the detection limit of the technique (3–5% wt.). Lastly, punctual fissures and holes (marked with black arrows in Figure 6c) were observed within the Fe-rich matrix of the sample.

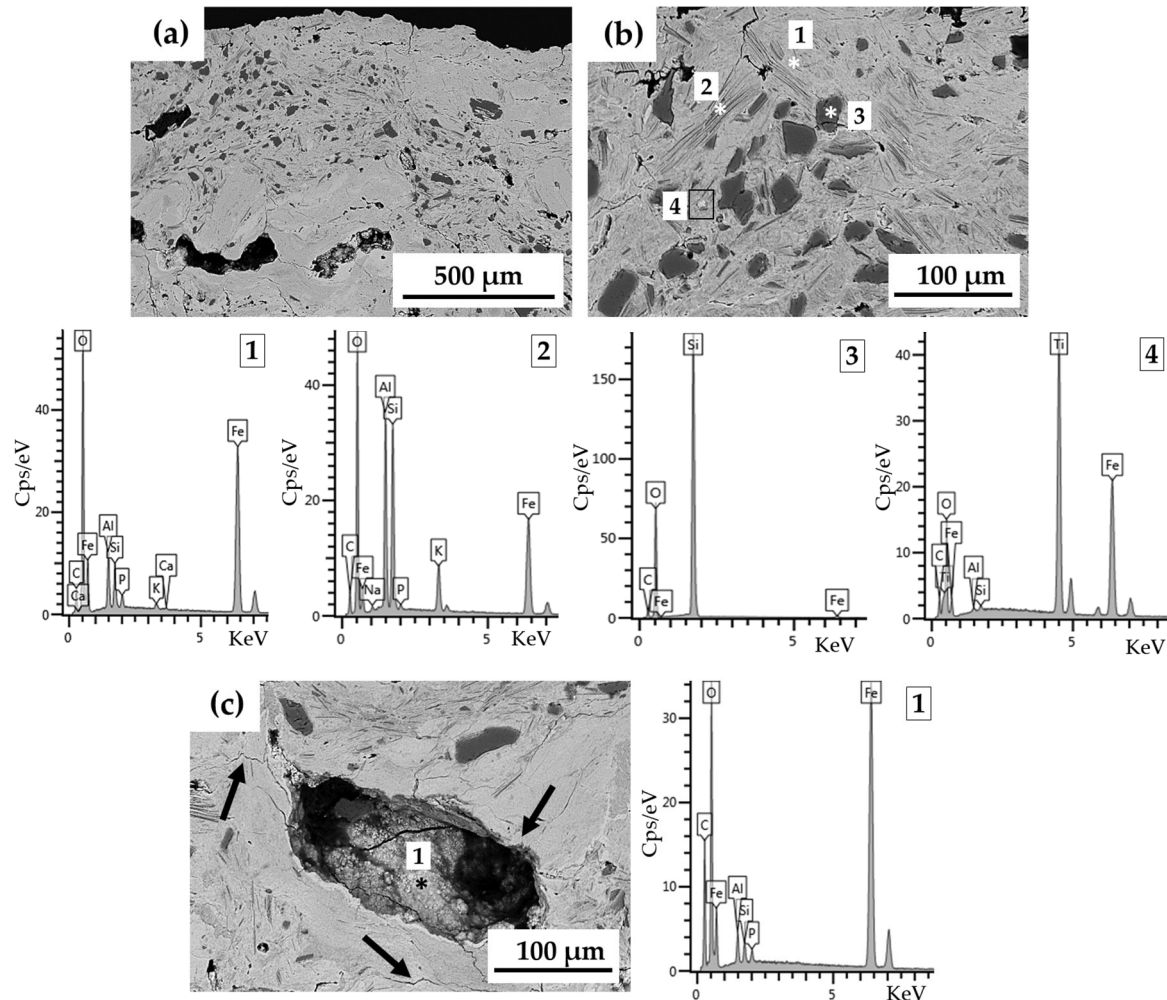


Figure 6. Cross-section micrographs observed by SEM of sample 300 and EDS spectra analysis. *: location where the EDS analyses were performed. Arrows: location of punctual fissures and holes.

Sample 698 was mainly composed of two types of crystals, both with laminar habit by SEM analysis (Figure 7a–c). On the one hand, those that showed less contrast were rich in Si, Al, and K. Other elements were also present in low percentages, such as Fe, magnesium-Mg-, sodium-Na-, and Ti (Figure 7b, EDS-1). The laminar habit (marked with a white arrow in Figure 7c) and the elemental composition could be related to the presence of muscovite, as identified by XRD. On the other hand, the crystals with higher contrast were composed of Al, Si, Fe, and Mg, together with K, P, and calcium-Ca- as trace elements (Figure 7b, EDS-2). This chemical composition could be related to that of clays such as illite $((\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10})$, previously detected by XRD, which present a typical laminar habit (marked with a white rectangle in Figure 7c). Finally, in the upper part of

the sample, Ti-rich deposits were observed (Figure 7b, EDS-3). As reported for sample 300, even though XRD analysis did not identify any Ti-oxides in this sample, their presence cannot be discarded as they could be present in low concentrations, below the detection limit of the technique (3–5% wt.). Overall, none of the minerals identified in this sample could be related to hematite, and therefore, it was discarded as a possible source of the red pigment.

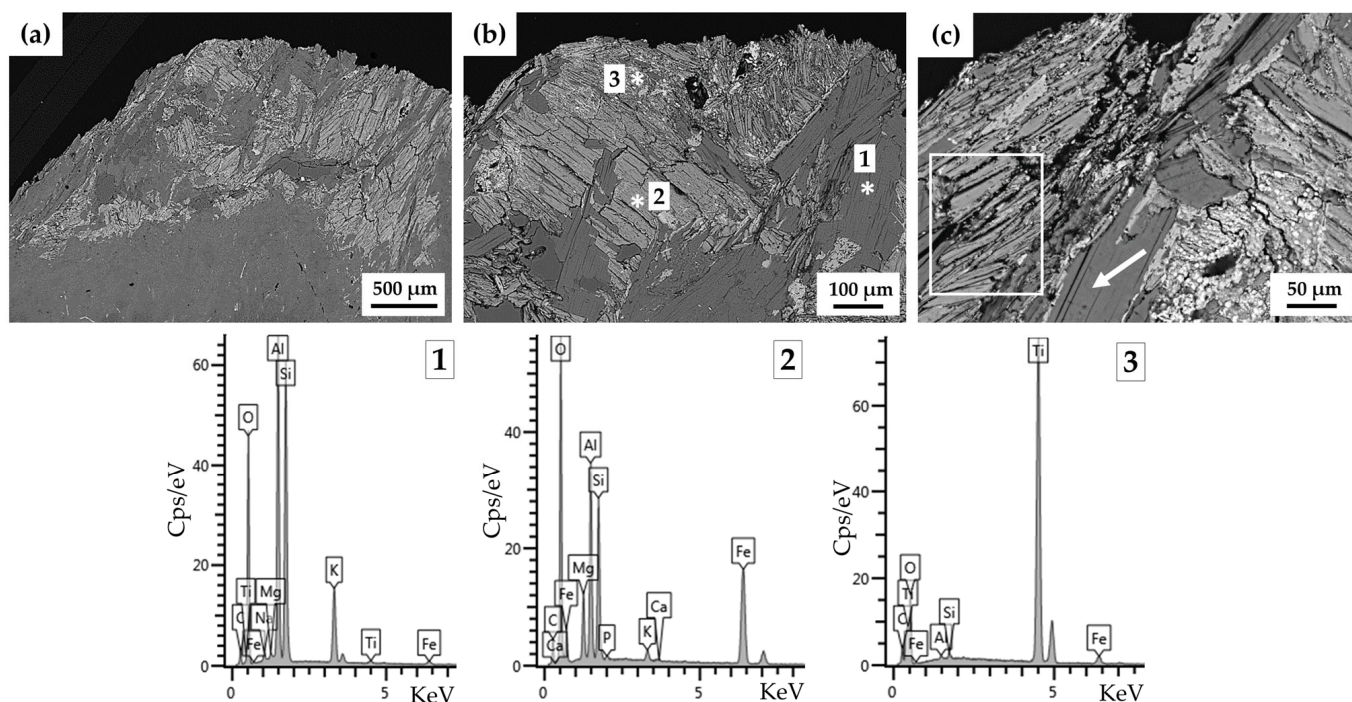


Figure 7. Cross-section micrographs observed by SEM of sample 698 and EDS spectra analysis. *: location where the EDS analyses were performed. Arrows: showing the laminar habit of the muscovite. Rectangle: showing the laminar habit of the clays.

Sample 705 showed a homogeneous surface mainly composed of Al- and Si-rich minerals (Figure 8a,b, EDS-1). This could be related to the mineral andalusite (Al_2SiO_5), previously identified by XRD. High-contrast particles were sporadically observed, forming accumulations of Fe-rich granular crystals, with Al, Si, and P in low proportions (Figure 8c, EDS-1). This could also be related to hematite particles, as in sample 300. Its presence was also found forming a thin layer (less than $5 \pm 2 \mu\text{m}$ thick) surrounding the sample, as marked with a white arrow in Figure 8d (EDS spectra 1 and 2). In the outermost part of the sample, above this Fe-rich layer, another thin layer (less than $5 \pm 2 \mu\text{m}$ thick) was observed, composed of Al and Si, and to a lesser extent Fe, P, K, and Ti. This could be related to the presence of illite. Lastly, within the interior of the sample, between voids and fissures, an accumulation of Ti- and Fe-rich crystals was observed (Figure 8e, EDS-1). This filler mineral could be assigned to the Ti-oxide mineral rutile, identified by XRD.

Overall, after XRD and SEM-EDS characterisation, we could state that sample 698 was not the pigmenting material used in the motifs, as it did not present hematite in its composition. On the contrary, the other two samples (300 and 705) could be. However, SEM-EDS analysis suggested that sample 300 was more likely the source of the pigment, mainly because it presented a compact Fe-rich matrix, whilst sample 705 only presented an external layer of around $5 \pm 2 \mu\text{m}$ thick. Therefore, obtaining the red pigment from sample 705 would have presented greater difficulty.

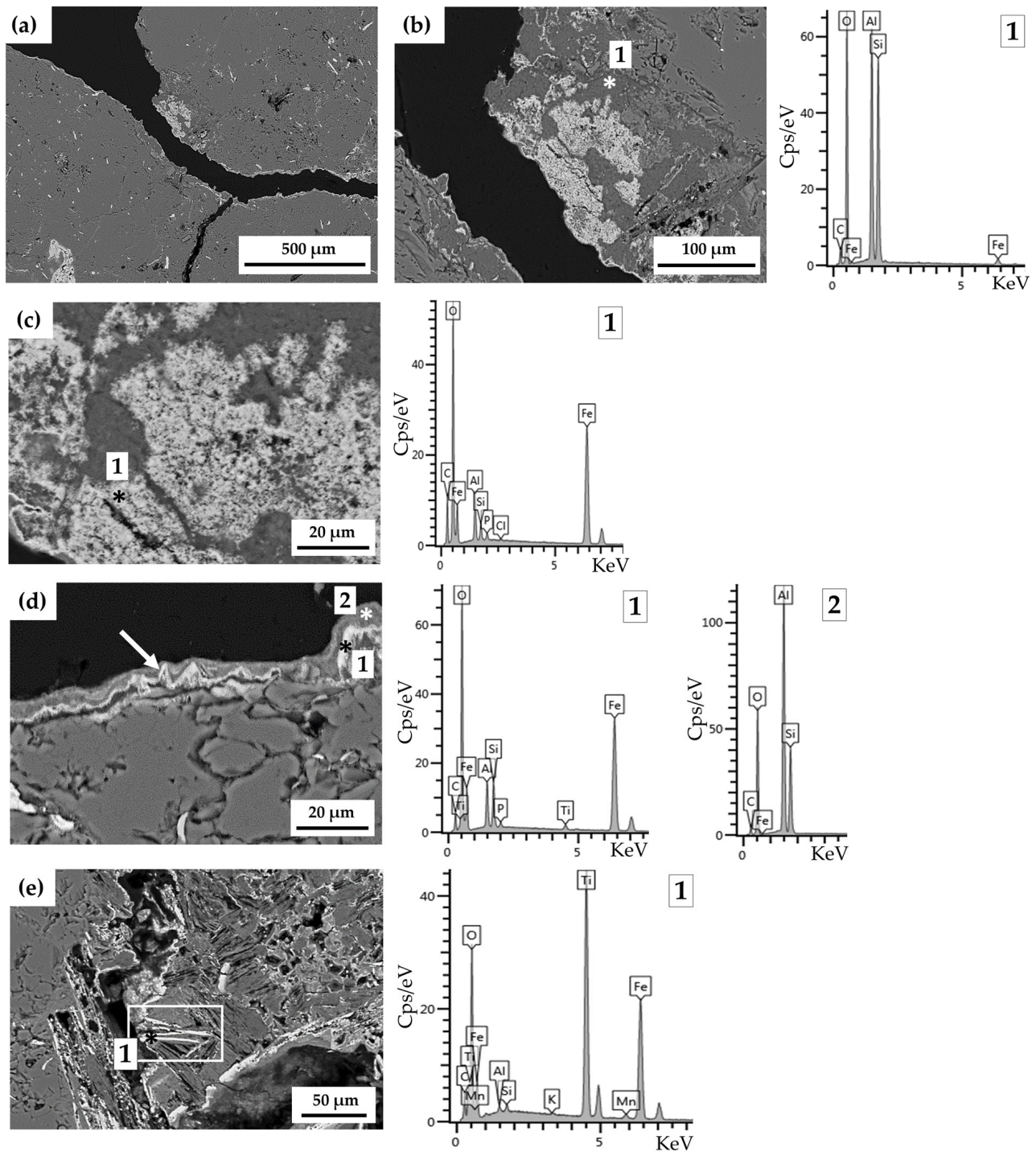


Figure 8. Cross-section micrographs observed by SEM of the sample 705 and EDS spectra analysis. *: location where the EDS analyses were performed. Arrows: showing the thin layer (less than $5 \pm 2 \mu\text{m}$ thick) surrounding the sample. Rectangle: location where the EDS 1 from Figure 8e, was performed.

5. Conclusions

Archaeometric analysis carried out by the use of non-destructive and non-invasive analytical techniques has made possible the characterisation of these newly discovered rock art shelter paintings found in the Penedo do Gato site in Spain. The use of basic techniques such as digital photography, enhanced photographic images, and vector drawings has allowed the identification of prehistoric schematic motifs that were not visible to the naked

eye. Spectrophotometry made it possible to identify the motifs since they presented a more intense reddish hue than the rock substrate, as reflected by the higher presence of the a^* parameter. Through the application of Raman spectroscopy, hematite ($\alpha\text{-Fe}_2\text{O}_3$) was mainly identified as the red pigment used in the pictorial motifs. The detection of amorphous carbon on the motifs and the unpainted rocks may indicate the deposition of charcoal from bonfires; however, the possibility that it was intentionally added to the red pigments to alter their colour cannot be ruled out. Furthermore, the additional study of samples taken from the archaeological survey that was carried out at the site allowed the identification of a local potential source for the red pigment used in prehistory.

Overall, this study contributes to expanding the use of portable techniques into the field of rock art research, thus moving towards more sustainable and ethical practices that prioritise scientific discovery and the in situ preservation of prehistoric cultural heritage.

From an archaeological standpoint, the discoveries at Penedo do Gato significantly enhance our understanding of schematic art in the northwestern Iberian Peninsula. The motifs—executed in confined, difficult-to-access granite shelters—suggest the intentional selection of intimate and restricted spaces for symbolic expression. This spatial context, along with parallels in iconography and technique with nearby granite landscapes in northwestern Iberia, points to a broader cultural pattern in the use of granite shelters for prehistoric graphic expression. Furthermore, this study emphasises the uniqueness of the Penedo do Gato paintings, currently the only known example in Galicia featuring painting on granite support within a rock shelter. Interestingly, in the Monterrei Valley, at a short distance from each other, schematic paintings have been found on both quartzite and granite outcrops located in proximity. This confers a unique character to the site, combining geological substrate, landscape, and support. Finally, although the context of the panels evokes the symbolic and enclosed nature of megalithic chambers, it differs in a technical aspect, as the granite support shows no evidence of prior surface preparation. The pigment was applied directly onto the natural rock, as seen in open-air shelters. In this regard, Penedo do Gato provides valuable data for future comparative studies on the application and handling of pigments in Neolithic and Chalcolithic contexts.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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