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Analysis and State of Conservation of Prehistoric Pigments in Juanita Rock Art-Shelter, (Oliva De Mérida, Badajoz, Spain)

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Abstract

This paper investigates Prehistoric rock art painted figures attributed to the post-palaeolithic schematic style. Through SEM-EDS, Raman spectroscopy and X-microfluorescence analysis, a chemical-mineralogical characterisation is made, and natural alteration products (biological, by lichen and chemical, through the formation of patina) are investigated to assess the impact of lichen colonization on the open-air rock-art sites. The eventual aim is to develop a control strategy for the Juanita rock-shelter in Extremadura, Spain.

The main mineral component in the red pigment (hematite) was identified using micro-Raman spectroscopy. Energy-Dispersive X-ray micro-fluorescence (ED-µXRF) registered iron, aluminium, and potassium as main elements in the pigments, indicating red ochre or earth ochre were used to produce them. The presence of calcium and phosphorus is linked to alteration, as both elements can be attributed to the substrate or to mineral accretion over the pigment itself. SEM observations have revealed the presence of early lichen colonization on the painted surface. Furthermore, amorphous carbon particles were identified on this surface. From these observations it is hypothesized that the state of conservation of the rock art is related to external factors (organic materials, patina, fire) more than to alteration of the substrate.

Keywords: Geosciences; Pigments; Prehistoric rock art; SEM-EDS; Micro-raman spectroscopy

Introduction

Extremadura, one of the largest regions in Spain, is situated in the southwestern part of the Iberian Peninsula. It shares borders with Castilla y León to the north, Andalusia to the south, Castilla la Mancha to the east, and the Portuguese border to the west. The region is divided into two provinces, namely Cáceres in the north and Badajoz in the south. The Tagus and Guadiana rivers flow through both provinces, serving as vital communication links between the east and west.

During the early decades of the previous century, numerous open-air sites featuring post-Palaeolithic rock art were identified in this region [1,2]. However, it is the research undertaken by some of the authors of this paper over the last twenty years that has uncovered one of the most significant collections of rock art in Europe, comprising over a thousand enclaves with prehistoric painted or engraved rock art [3-9].

Over half of these enclaves have been recorded in the province of Badajoz, making it a crucial site for the study of schematic rock art,

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the primary symbolic expression of human groups during recent prehistory in the Iberian Peninsula. The province's significance is further emphasized by the abundance of well-preserved prehistoric settlements situated in diverse and stunning natural landscapes, making it an essential reference point for researchers.

Schematic rock art is characterized by the depiction of typified figures on natural rocky surfaces, which are considered as representations of a "thing" based only on its most significant lines as defined by Hernández Pérez [10]. This cultural phenomenon is widely spread in the Iberian Peninsula and other neighbouring areas. Representations in schematic art departs from previous iconographic models and introduces new motifs with specific typologies that can be observed in ceramics and even in stratigraphically defined painted pebbles [11]. Some well-known works on the subject include "Rock paintings of southern Andalusia" [12], Abbé Breuil's famous study on schematic painting "Les Peintures Rupestres Schématiques de la Péninsule Ibérique" [2], and the synthesis of peninsular rock art in "Prehistoria del solar hispano" by Hernández Pacheco [13]. However, Pilar Acosta's book "La Pintura Rupestre Esquemática en España" [14] is fundamental for the study of schematic painting, as it marks the beginning of a new stage in its analysis. A typological systematisation was carried out for the first time, which served as a basis for classification in numerous studies. This was followed by works by Ripoll [15,16], Beltrán [17], Jordá [18], among others. Many studies on schematic art were conducted in different parts of Spain [19,10]. Regional studies were particularly important, such as those in Villuercas [20], Extremadura [21,6], Sierra Morena [22] Cuenca del Ebro [23-25], the Subbetic [26], Laguna de la Janda [27], the Southeast [28-33], and in the ARAMPI territory (El Arte Rupestre del Arco Mediterráneo de la península Ibérica) [34,35].

Archaeological and geographical context of Juanita rock art shelter

The Juanita shelter is situated in Oliva de Mérida, a small town in the central region of the Badajoz province, approximately 30km southeast of Mérida, the regional capital. The open-air shelter is specifically located on the northern slope of Sierra del Conde, a gentle quartzite hill southeast of Oliva de Mérida. This hill, along with La Oliva and Sierra de la Garza Mountain ranges, forms an impressive alignment of mountains approximately 9km in length, with a mainly Hercynian orientation (NW-SE) and peaks reaching up to 650 meters above sea level.

The natural environment surrounding the shelter has been heavily modified by human activity, with vast areas of olive groves occupying much of the landscape. However, in the steeper areas of the slopes, there remain remnants of the Mediterranean landscape, with an open forest of oaks and cork oaks coexisting with a rich undergrowth of rockrose, heathland, and strawberry trees, providing refuge for a wide variety of wildlife and game species, including deer and wild boar, which are particularly notable (Figure 1).

Figure 1: Juanita rock art shelter (Oliva de Mérida, Badajoz) and its surroundings.

Due to its abundance, quality, and excellent state of preservation, the "Juanita" shelter is arguably one of the most significant locations with schematic art in the Extremadura region. It serves as a key reference point for over 35 painted shelters in the surrounding mountains, as documented in various sources [3,5-7,36]. Additionally, the nearby Cueva de la Charneca, a funerary site containing a substantial collection of archaeological and ritual objects linked to the early phases of the peninsular Neolithic, is of considerable interest from an archaeological contextualization standpoint [37,6] (see Figure 2).

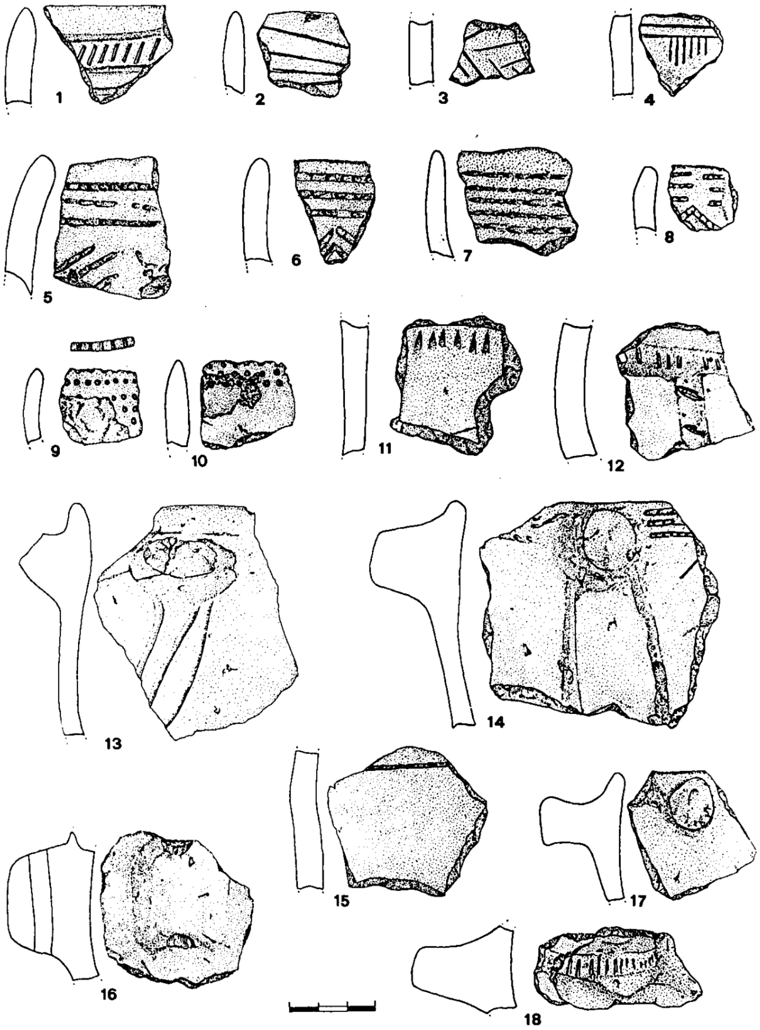

Figure 2: Neolithic ceramics from the Charneca Cave (Oliva de Mérida, Badajoz) [Source: 37].

The "Juanita" shelter is situated on a high rocky wall that measures over eight meters tall and is positioned before a spacious platform that extends more than 4.5 meters wide. Access to the platform can be obtained by climbing on its eastern end. The shelter faces north, providing a panoramic view of the vast and productive plain of the Guadiana River. The significant wall, where the schematic rock art depictions are found, spans over 23 meters in length and has a maximum height of 5.35 meters. It features a gentle overhang, which shields the entire collection of rock art from the effects of weathering.

We have documented 25 panels in this shelter, which contain more than 300 individualized figures. These figures encompass almost all the classic typologies that have been defined for schematic rock art, including anthropomorphs, zoomorphs, series of bars, astral figures, groupings of points, digitations, sun-shape figures, and infantile hands in positive. Most of the figures were created using red pigments, applied to the rocky surface through various means, ranging from finger-painting to the probable use of rustic brushes made of hair or vegetable fibers. This has resulted in a wide diversity of sizes and thicknesses, both in the figures themselves and in the strokes used to create them.

Despite the extensive collection of rock art (with over three hundred figures represented), there are few and insignificant superimpositions. Instead, the shelter's scenic design revolves around two large central anthropomorphic motifs that are over 30 centimeters tall. These motifs serve as the axis for the composition and conceptual discourse in a space that likely played a vital role in the symbolic appropriation of the territory (see Figure 3).

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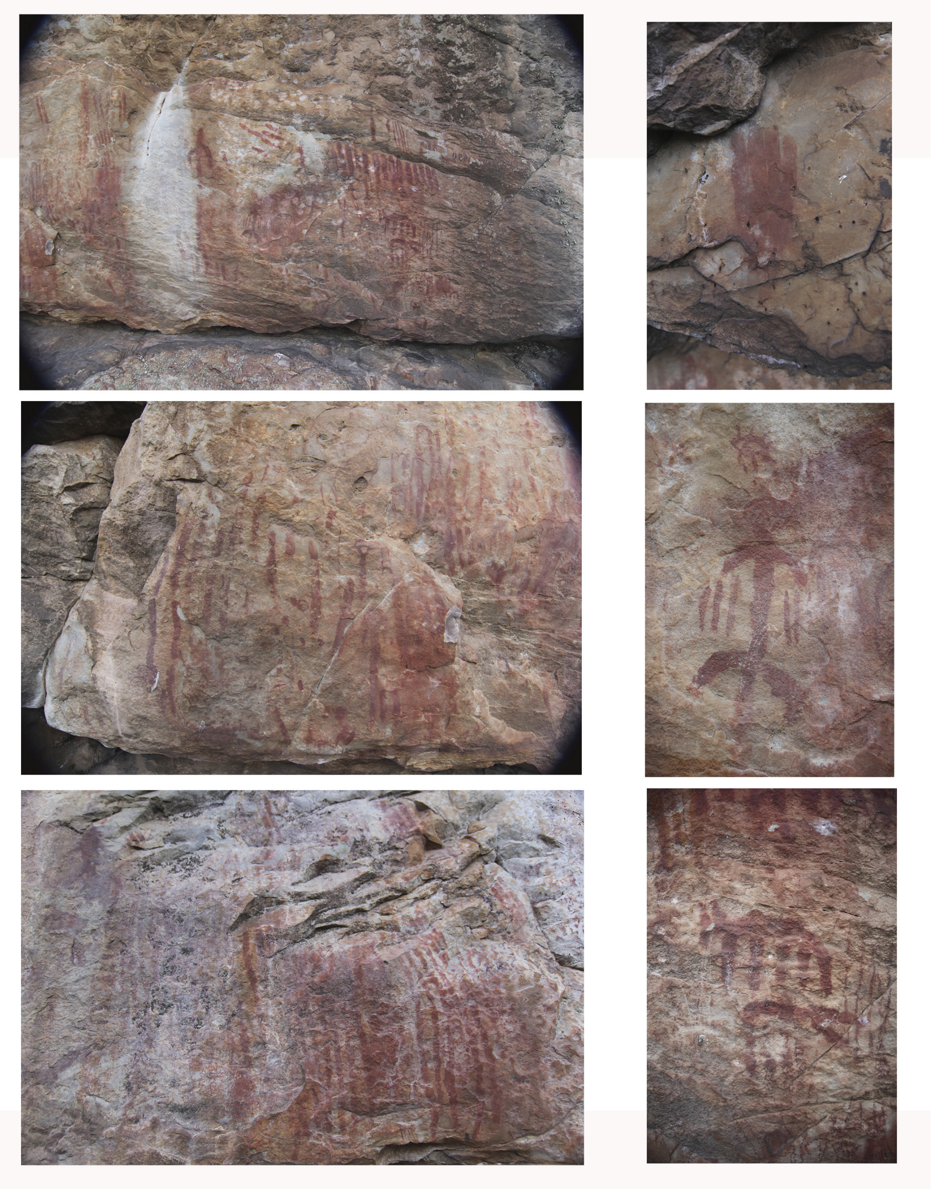

Figure 3: Schematic depictions in Juanita rock art shelter (Oliva de Mérida, Badajoz). Photos: [38].

Main objectives

The purpose of the study was to investigate the impact of lichen colonization on the open-air rock-art site and to develop a control strategy. The site consists of quartzites that lack feldspars and micas, and thus do not undergo mineral neogenesis associated with lichen activity. As a result, it exhibits limited biodegradation and high resistance to weathering.

Lichens are commonly known to be agents of biodegradation of open-air rock-art. They are categorized by their growth form into several types, including crustose (flat and paint-like, such as Caloplaca), filamentous (hair-like), foliose (leafy), fruticose (branched), leprose (powdery), squamulose (lacking a lower cortex), and gelatinous lichens (which produce a polysaccharide that absorbs and retains water). While their metabolic activities can induce chromatic variations, they can also cause structural modifications to the rock that may result in irretrievable losses. Over time, these processes can contribute to the erosion of the rock and have a negative impact on the substrata.

Lichens are among the most common agents of biodegradation of open-air rock-art. According to Dandridge and Meen [39] lichens are informally classified by growth form into crustose (paint-like, flat), (e.g., Caloplaca); filamentous (hair-like); foliose (leafy); fruticose (branched); leprose (powdery); squamulose (lacking a lower cortex), gelatinous lichens, (the cyanobacteria produce a polysaccharide that absorbs and retains water). Their metabolic activities can induce chromatic variations but also structural modifications of the rock which can lead to irretrievable losses. These procedures can share in erosion of rock and can have, through time, a negative impact on the substrata.

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Materials and Methods

In the context of Juanita's shelter, a set of archaeometry methods widely used in conservation or pigment characterization work in other contexts around the world [40-47] was applied. Nine samples were selected for analysis from Juanita rock-shelter, including four pigment samples (P1, P2, P3, P4), three concretion samples (C1, C2, C3), and two bedrock samples (AJ2, AJ3). Figure 4 displays the location of the sampling points.

Figure 4: Location of the sampling points.

Table 01 provides a summary of the samples used in this study, along with the analytical techniques employed. Sampling locations were chosen based on their pictographic significance, pigment availability, and minimal risk of damage. Four pigment samples were collected, with P1 and P4 identified as orange pigments, and P2 and P3 as red. The selected samples were taken from strategic locations featuring different types of figurative motifs.

The sampling procedure was conducted with full authorization and adherence to national and international guidelines for preserving the integrity of the rock-art. Ethical extraction techniques were utilized wherever possible, in compliance with the European standard for sampling in cultural heritage research [48]. The samples, weighing between 10 and 100mg, were collected from areas of the panel displaying small fractures and niches, which are considered the most appropriate extraction points from an ethical standpoint, as they minimize the impact on the rock-art surface. All samples were obtained using a sterilized tungsten scalpel and stored in 0.5-mL microcentrifuge tubes for analysis. Table 01 lists the samples and the analytic methods employed in this study. Selected samples were taken from specific locations of pictorial interest, ensuring availability of pigments, and minimizing the risk of damage to the rock-art.

Table 1 : List of the samples and the analytic methods employed in this study : Pigment (P) concretions (C) and substrate (J).

Stereomicroscope	EDxrf	Raman	SEM-EDS	Optical microscope	Photo
P1	P1	P1	P1	--	--
P2	P2	P2	P2	--	--
--	P3	P3	--	--	--
--	P4	P4	--	--	--
--	C1	C1	C1	--	--
--	C2	C2	C2	--	--
--	C3	--	--	--	--
AJ2	--	--	AJ2	--	AJ2
AJ3	--	--	AJ3	AJ3	AJ3

citation: Pierluigi Rosina*, Hipólito Collado, Sara Garcês, Hugo Gomes, Virginia Lattao, Negar Eftekhari, Marilena Leis, Maria Nicoli and Carmela Vaccaro. Analysis and State of Conservation of Prehistoric Pigments in Juanita Rock Art-Shelter, (Oliva De Mérida, Badajoz, Spain). Open Access J Arch & Anthropol. 5(1): 2023. OAJAA.MS.ID.000603. DOI: 10.33552/OAJAA.2023.05.000603

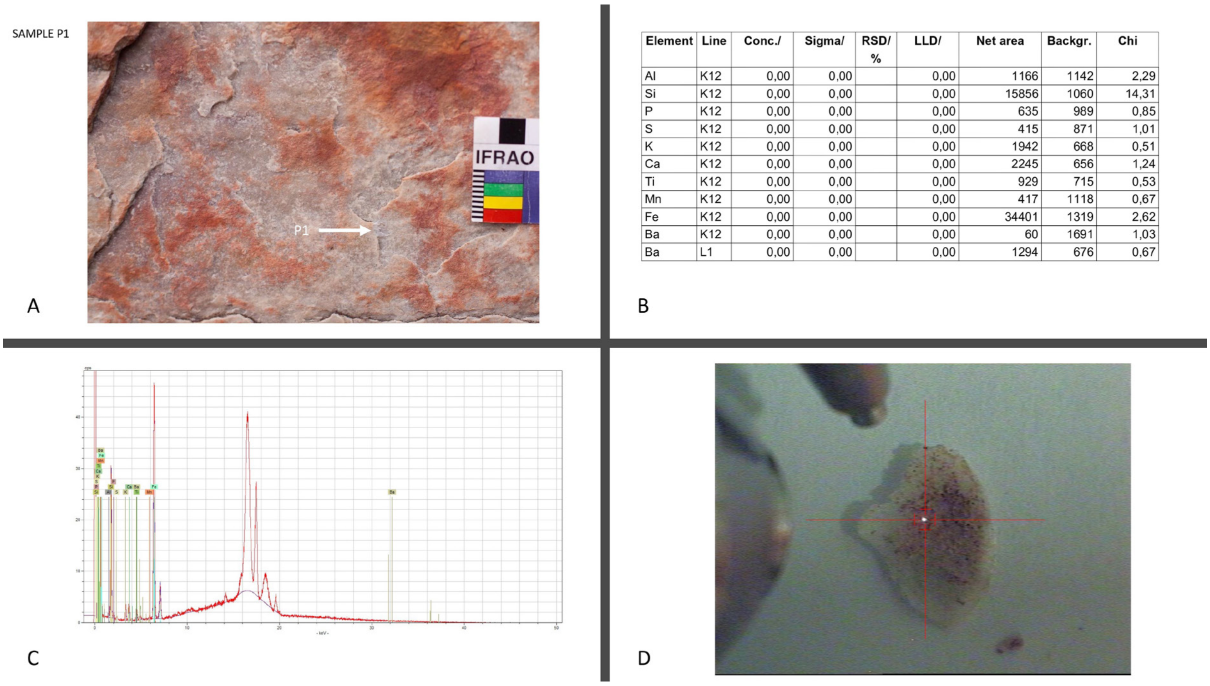
The characteristics of the instruments' technical features that were used are the following: an Optical microscope and stereomicroscope: using SZ6745TR equipped with a MOTICAM 2500 5.0 M pixel webcam and Motic Images Plus 2.0ML software; an Energy-Dispersive x-ray micro-fluorescence (EDxrf): Bruker ARTAX 200 μEDxrf spectrometer, with a Mo X-ray tube and a collimator with 200 μm of diameter A 15 to 50 kV voltage with a current range between 1500 μA and 700 μA. To detect the light elements, a helium flow was applied. The μEDxrf spectra were acquired by an ARTAX Control 7.2 software; for Micro-Raman was used the LabRam HR800 from Horiba Scientific with an air-cooled CCD detector at −70 °C, an Olympus BXFM microscope, 600 groove/mm grating, objective 10X and 50X; the excitation source was a He-Ne laser (632.8 nm line) with a maximum laser power of 17 mW. The Scanning electron microscope (SEM) used was coupled with an energy-dispersive X-ray spectroscopy (EDS) using a ZEISS EVO MA 15, system (Aztec Oxford), equipped with a (SDD) silicon drift detector, a LaB6 filament as an electron source, and cobalt as a calibration standard.

The team's previous research [42-44,49,50] has shown that using microscopic observation to study the surface of samples yields better diagnostics and allows for identification of sample surfaces with better characteristics for further analysis. For the petrographic characterization of substrates, both the Optical Microscope and SEM-EDS were employed. The pigment samples from Juanita rock-shelter were analysed using the SEM-EDS technique to characterize their microstructure and semi-quantitative elemental composition. Micro-Raman spectroscopy was used to identify the main mineral components of the paintings by referring to the BIO-RAD database and published literature for mineral phase and peak attribution. In addition, Energy-Dispersive x-ray micro-fluorescence (EDxrf) analysis was conducted to measure elemental concentration in the selected samples.

Results and Discussion

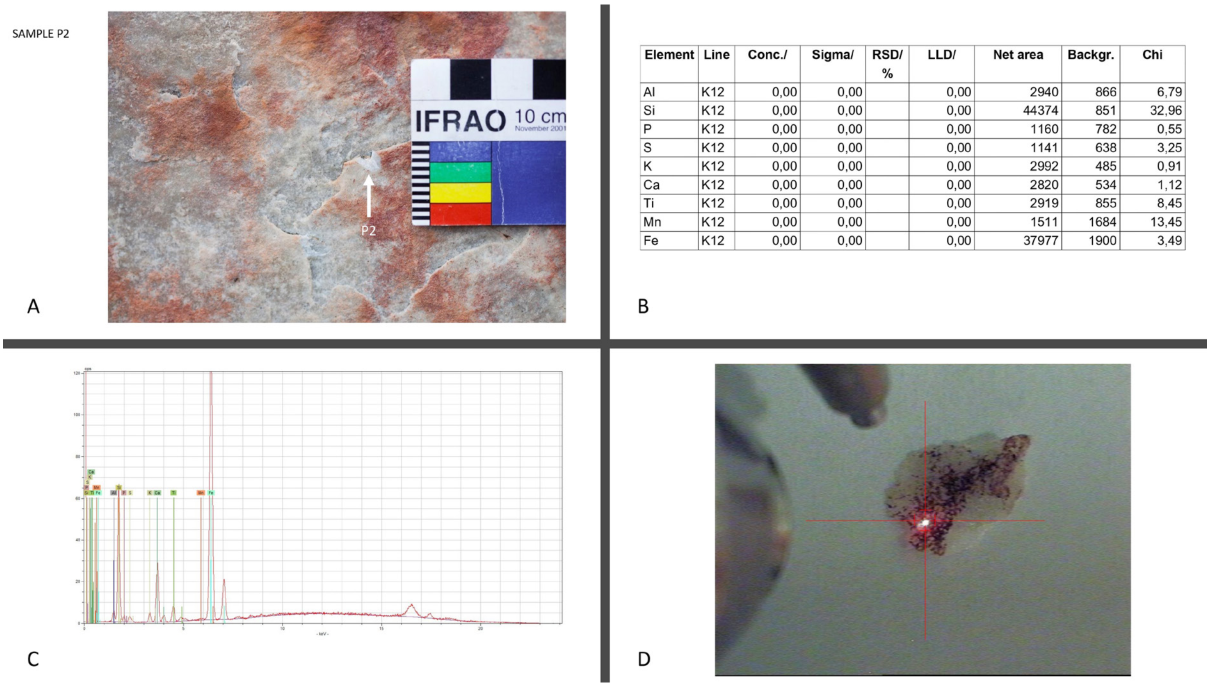
Insights into the chemical composition and state of conservation of the pictorial layer were obtained through microscopic and analytical investigation of the samples collected from Juanita rock-shelter (refer to Tab 01). Microscopic observations of the substrate (samples AJ2 and AJ3) confirmed that it is made of quartzite rock. Small black particles of amorphous carbon, which may correspond to burnt lichens, were also observed under the optical microscope and SEM.

The chemical analysis results obtained through x-ray fluorescence showed the presence of iron, potassium, and aluminium as the primary elements (Figures 4, 5, 6, and 7). Notably, calcium and phosphorus were found to be present in significant amounts in samples P2, P3, and P4 (with calcium only in P4).



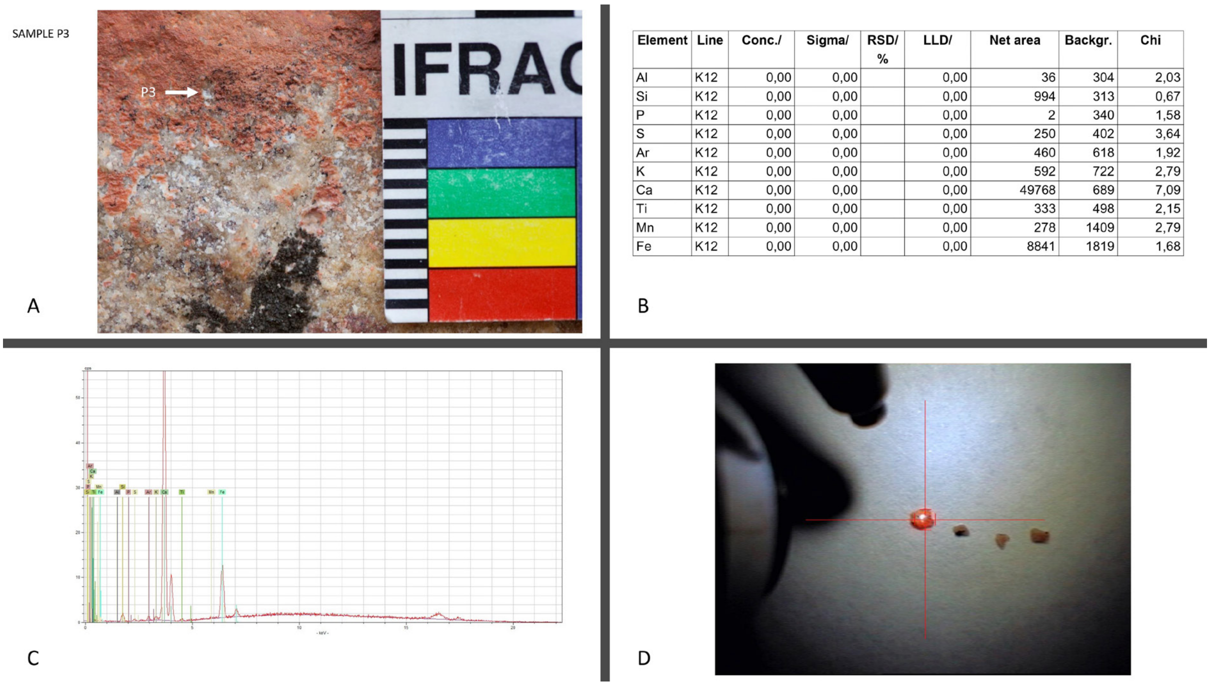
Element	Line	Conc./	Sigma/	RSD/ %	LLD/	Net area	Backgr.	Chi
Al	K12	0,00	0,00		0,00	1166	1142	2,29
Si	K12	0,00	0,00		0,00	15856	1060	14,31
P	K12	0,00	0,00		0,00	635	989	0,85
S	K12	0,00	0,00		0,00	415	871	1,01
K	K12	0,00	0,00		0,00	1942	668	0,51
Ca	K12	0,00	0,00		0,00	2245	656	1,24
Ti	K12	0,00	0,00		0,00	929	715	0,53
Mn	K12	0,00	0,00		0,00	417	1118	0,67
Fe	K12	0,00	0,00		0,00	34401	1319	2,62
Ba	K12	0,00	0,00		0,00	60	1691	1,03
Ba	L1	0,00	0,00		0,00	1294	676	0,67

Figure 5: X-ray fluorescence results of sample P1: A) sample detail; B) table of results; C) X-ray fluorescence spectrum; D) micro photo of the sample.



Element	Line	Conc./	Sigma/	RSD/ %	LLD/	Net area	Backgr.	Chi
Al	K12	0,00	0,00		0,00	2940	866	6,79
Si	K12	0,00	0,00		0,00	44374	851	32,96
P	K12	0,00	0,00		0,00	1160	782	0,55
S	K12	0,00	0,00		0,00	1141	638	3,25
K	K12	0,00	0,00		0,00	2992	485	0,91
Ca	K12	0,00	0,00		0,00	2820	534	1,12
Ti	K12	0,00	0,00		0,00	2919	855	8,45
Mn	K12	0,00	0,00		0,00	1511	1684	13,45
Fe	K12	0,00	0,00		0,00	37977	1900	3,49

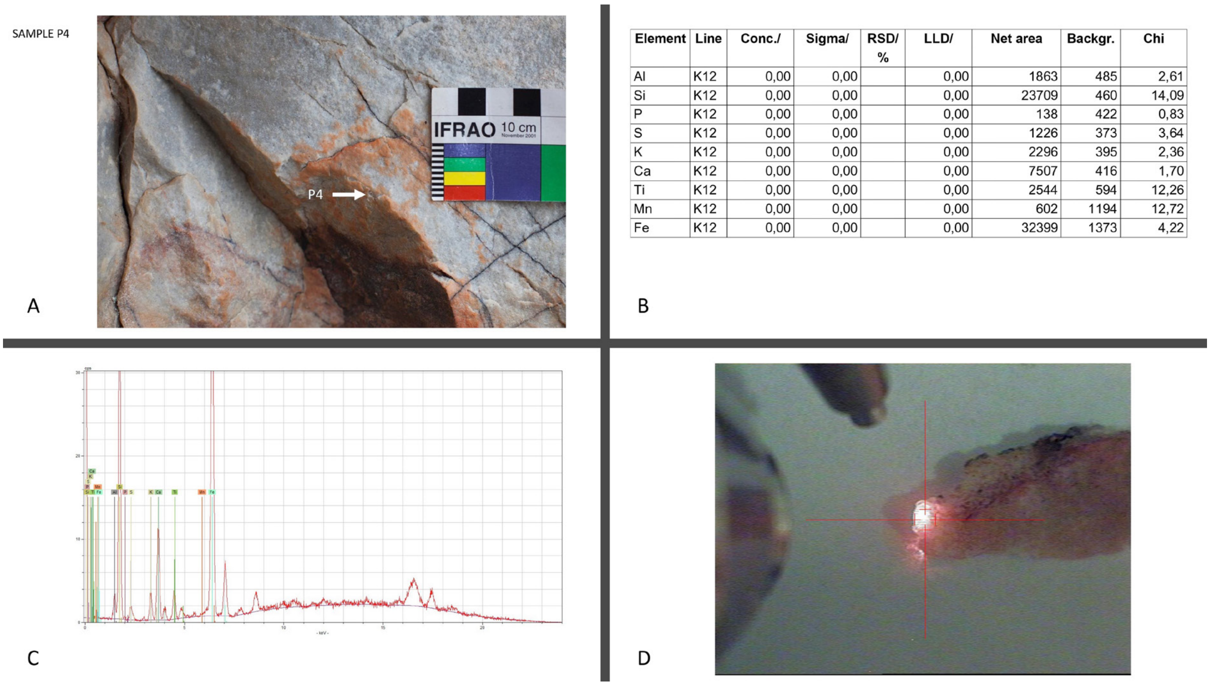
Figure 6: X-ray fluorescence results of sample P2: A) sample detail; B) table of results; C) X-ray fluorescence spectrum; D) micro photo of the sample.



Element	Line	Conc./	Sigma/	RSD/ %	LLD/	Net area	Backgr.	Chi
Al	K12	0,00	0,00		0,00	36	304	2,03
Si	K12	0,00	0,00		0,00	994	313	0,67
P	K12	0,00	0,00		0,00	2	340	1,58
S	K12	0,00	0,00		0,00	250	402	3,64
Ar	K12	0,00	0,00		0,00	460	618	1,92
K	K12	0,00	0,00		0,00	592	722	2,79
Ca	K12	0,00	0,00		0,00	49768	689	7,09
Ti	K12	0,00	0,00		0,00	333	498	2,15
Mn	K12	0,00	0,00		0,00	278	1409	2,79
Fe	K12	0,00	0,00		0,00	8841	1819	1,68

Figure 7: X-ray fluorescence results of sample P3: A) sample detail; B) table of results; C) X-ray fluorescence spectrum; D) micro photo of the sample

citation: Pierluigi Rosina*, Hipólito Collado, Sara Garcês, Hugo Gomes, Virginia Lattao, Negar Eftekhari, Marilena Leis, Maria Nicoli and Carmela Vaccaro. Analysis and State of Conservation of Prehistoric Pigments in Juanita Rock Art-Shelter, (Oliva De Mérida, Badajoz, Spain). Open Access J Arch & Anthropol. 5(1): 2023. OAJAA.MS.ID.000603. DOI: 10.33552/OAJAA.2023.05.000603



Element	Line	Conc./	Sigma/	RSD/ %	LLD/	Net area	Backgr.	Chi
Al	K12	0,00	0,00		0,00	1863	485	2,61
Si	K12	0,00	0,00		0,00	23709	460	14,09
P	K12	0,00	0,00		0,00	138	422	0,83
S	K12	0,00	0,00		0,00	1226	373	3,64
K	K12	0,00	0,00		0,00	2296	395	2,36
Ca	K12	0,00	0,00		0,00	7507	416	1,70
Ti	K12	0,00	0,00		0,00	2544	594	12,26
Mn	K12	0,00	0,00		0,00	602	1194	12,72
Fe	K12	0,00	0,00		0,00	32399	1373	4,22

Figure 8: X-ray fluorescence results of sample P4: A) sample detail; B) table of results; C) X-ray fluorescence spectrum; D) micro photo of the sample.

According to the results of μ-Raman spectroscopy conducted on pigment samples, the main component of the pigments is hematite (Fe_2O_3), although peaks of maghemite (γ-Fe2O3) are also present in both samples, likely due to environmental factors causing mineral alteration. These results suggest that the pigments are made using red ochre or earth ochre, indicated by the presence of iron (hematite), aluminium, and potassium. Furthermore, SEM observations showed that an initial lichen colonization was present on the painted surface, which was not visible to the naked eye. Bio-colonies were observed on sample P1, P2, and P4. Additionally, SEM-EDS provided a chemical image of the pigment distribution over the sample and a better understanding of its morphology.

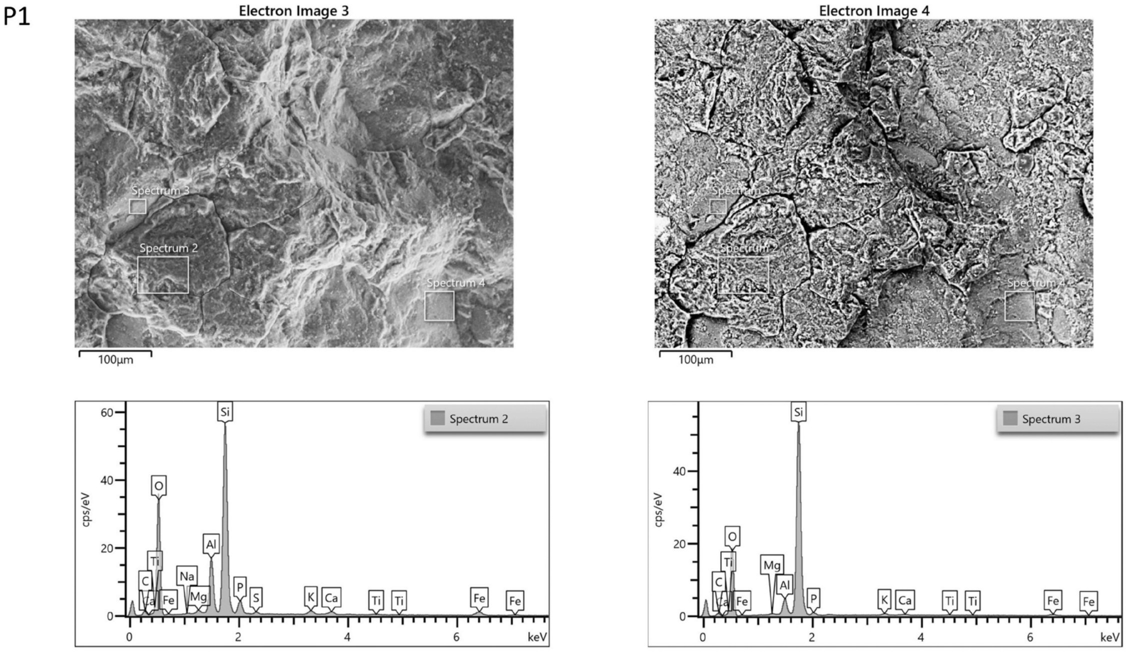


Figure 9: SEM-EDS results of Sample P1.

citation: Pierluigi Rosina*, Hipólito Collado, Sara Garcês, Hugo Gomes, Virginia Lattao, Negar Eftekhari, Marilena Leis, Maria Nicoli and Carmela Vaccaro. Analysis and State of Conservation of Prehistoric Pigments in Juanita Rock Art-Shelter, (Oliva De Mérida, Badajoz, Spain). Open Access J Arch & Anthropol. 5(1): 2023. OAJAA.MS.ID.000603. DOI: 10.33552/OAJAA.2023.05.000603

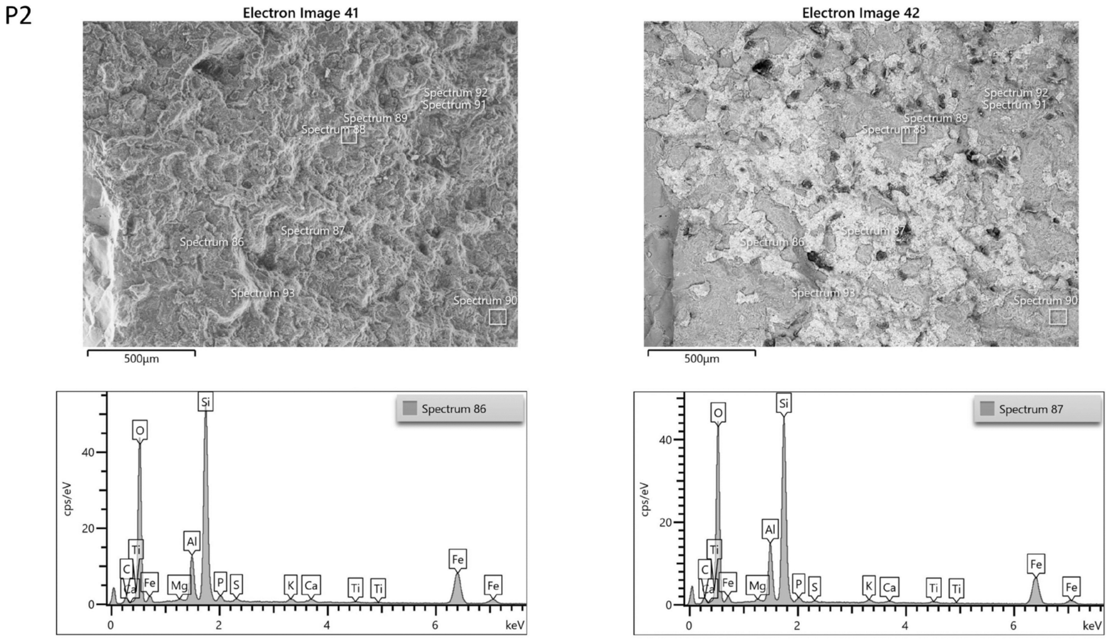


Figure 10: SEM-EDS results of Sample P2.

Despite P1 and P2 having different shades of colour, the analytical findings indicate a uniform composition, at least with respect to the main chemical and mineralogical elements. Unfortunately, analysis of P3 did not yield any results, likely due to the sample's small size. A rock wall sample was collected to examine the lichen growth of leafy and fruticose type. The initial analysis of the substrate biodegradation was carried out using stereomicroscope and SEM observations, which revealed a significant presence of fungal hyphae, bacteria, and insects, in line with the findings of Pozo-Antonio et al. [51,52].

The author highlighted the way in which lichens attach to the substrate, with a preference for pits in the rock, and suggested that the lichens may even be responsible for creating these pits. This supports the findings of Caneva et al. [53], who noted that the pits created in the rock provide a highly favourable microhabitat for microorganisms including bacteria, algae, fungi, and lichens. Other authors [54] have also observed that the depth to which epilithic lichens penetrate is dependent not only on the species but also on the porosity and texture of the stone, as well as its physical-chemical degradation and, to a lesser extent, the mineralogical composition. In the case of quartzite, which is a very hard rock, the surface underneath the lichens is fractured and altered.

When a thin section of this rock is viewed under a polarizing microscope, it reveals a semi-metamorphic structure that resulted from lithostatic pressure causing a recrystallization of grains in bands. The observation shows that in certain areas, the grains have lost definition to a greater extent, whereas in other areas, the grains have well-defined edges (idioblasts) with jagged shapes, due to the impact of pressure. The size of the granules in the bands varies depending on the degree of recrystallization.

In areas where recrystallization is more prominent, the quartz grains have less defined edges (known as xenoblasts) and contain fluid inclusions that often appear in a distinctive "train" form. These fluid inclusions contain CO2 and H2O, which make the rock susceptible to biological attack over time. Microorganisms like lichens, which feed on rocks, can lead to surface biodeterioration. The fluid inclusions indicate that the original rock underwent hydrothermalism. The inclusion trains, formed during this process, run through the grains, and create planes of cryptic weakness, which become areas of degradation. Surprisingly, degradation occurs along these planes and not along the edges of the crystals as one would expect. The quartzite rock also contains oxides that are responsible for the distinctive red veins often seen in this type of quartzite. The oxides can be of two types [55]:

a) The intergranular oxide, situated between individual granules, is composed primarily of hematite and limonite, and displays the characteristic colours of red and yellow.

b) Conversely, the intragranular oxide, on the other hand, is white, very bright and consist mainly of magnetite and ilmenite.

Besides iron oxides, the intergranular veins also contain micas that form due to the transformation of clay minerals caused by lithostatic pressure. Unlike the intergranular oxides that develop in the spaces between granules and have an undefined shape, the intragranular oxides are idioblastic metamorphic minerals with a distinct square or rectangular shape (in the case of ilmenite). As magnetite and ilmenite form, they can trap other minerals inside them, and in some cases, sulphides and spinels were found within certain intragranular oxides.

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By conducting a chemical analysis using an EDS microscope, the composition of the rock substrate was determined, and the results, as seen in Figure 11, highlighted the existence of both copper and manganese.

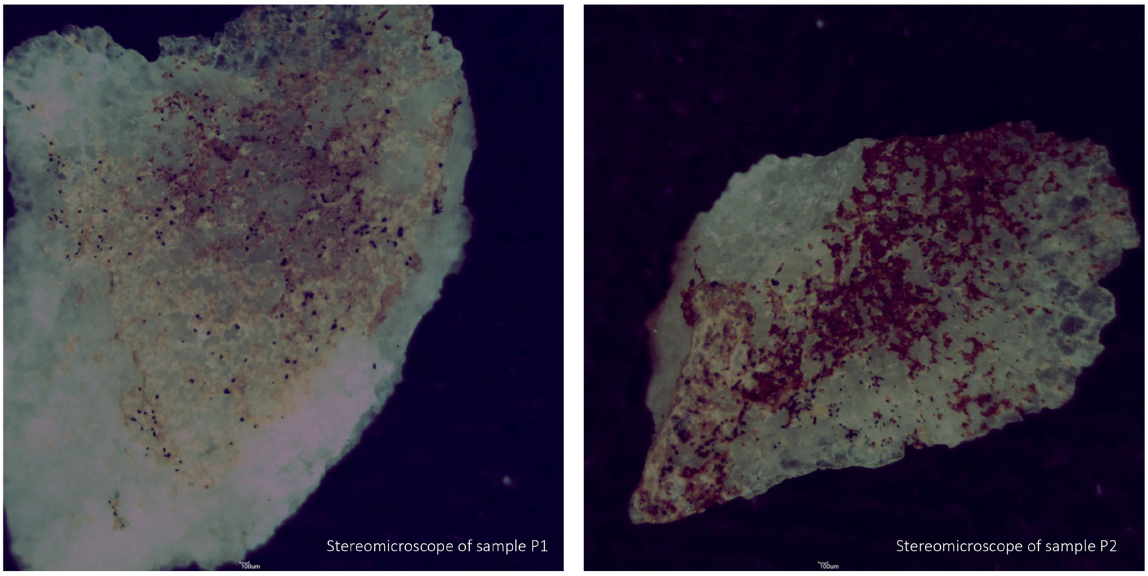

Figure 11: Stereomicroscope of sample P1 and P2.

It is possible that these elements are present in oxalates, which are secondary alteration products formed due to the action of lichens on the rock. This finding further supports the results of previous research studies [56-58] Purvis & Halls [56] and Chisholm et al. [58] have conducted studies suggesting that the presence of copper could indicate the existence of moolootite Cu2 + (C2O4) 0.44 (H2O), a copper oxalate that is formed as a secondary alteration product due to the interaction of oxalic acid produced by lichens with the rock substrate. Purvis & Halls [56] documented the presence of copper oxalate on rock substrates containing copper and colonized by lichens. From this observation, he hypothesized that the precipitation of moolootite could be due to:

a) when the lichen thallus is in direct contact with a rock rich in copper ores, it is possible for a direct reaction to occur between the oxalic acid produced by the mycobiont and the minerals of the substrate, leading to the formation of moolootite.

b) The reaction between the lichen and copper-enriched runoff waters occurs after they pass over the rock. This possibility is supported by the presence of Lecidea lactea, a copper accumulator lichen, on quartzite veins that are copper-free.

c) A process that involves the accumulation and isolation of toxic elements by the lichen, which occurs when the levels of these elements exceed certain levels of danger for the survival of the lichen.

Chisholm et al.'s study [58] provided further evidence supporting the notion that moolootite, an oxalate copper compound, could be produced as a secondary alteration product resulting from lichen activity on rocks. This may occur when oxalic acid, produced by the mycobiont, reacts with guano, particularly when the oxalate is linked with phosphates or with copper-enriched seepage water. The "Chisholm hypothesis" appears to be the most plausible explanation in our case, based on this study. However, another hypothesis could be proposed. As Juanita shelter is an open-air rock-art site, it is possible that the copper traces found are a result of using an inorganic pigment comprised of malachite (Cu2(CO3)(OH)2). This carbonate-based pigment is soluble and could have been dissolved by rainwater. However, the copper within it may have been fixed as copper oxalate via a reaction between water containing Cu2+ ions and oxalic acid produced by lichens.

The substrate's characterization served as a reference point for assessing and interpreting the data obtained during sample analysis, particularly in evaluating factors like calcium content. The presence of phosphatic structures observed in rock samples was likely connected to biological activities and/or the existence of organic matter, as documented in field observations by Gallinaro and Zerboni (2021) and Prinsloo (2007). The existence of copper could offer indirect evidence of a long-lost blue-green pigment that was presumably once present on the wall but is no longer visible today due to taphonomic reasons. In a study on prehistoric art conservation, Bednarik [59] emphasizes that only a small portion of the original artistic expressions have survived. This is because, like the engravings, the pigments used have undergone various selection processes.

All these selection processes are deliberate and not accidental. They favour specific techniques, pigment types, locations, supports, climates, and so on. For instance, the fact that the earliest paintings are almost always dark red is likely a result of taphonomic processes. It is not a coincidence that hematite, the most stable iron oxide, is of this colour and is the mineral most identified in pigment studies of open-air rock art [42,43,49]. Bednarik [60] discusses the formation of iron-manganese crusts on panels with open-air rock art, caused by runoff waters containing high levels of these solutes.

These crusts typically have a dendritic structure, which is not visible in our case study. This could be because the crust is still in the early stages of formation, or it may not be an iron-manganesiferous crust at all. Instead, it could be a manganese oxalate ($MnC2O4·2H2O$) formed by the reaction between oxalic acid and minerals in the substrate. Wilson & Jones [57] observed the appearance of manganese oxalates dihydrate in Petrusaria corallina on manganese outcrops. In this case, manganese may be present within the rock as a residual element due to its low solubility.

Regarding the amorphous carbon in the form of tiny black particles that has been identified on the surface of the panel could relate to fires occurrence. The presence of small black particles of amorphous carbon on the surface of an open-air rock art shelter could be due to a variety of factors and attributing it solely to recent fires would be premature. While it’s possible that the fires contributed to the accumulation of these particles, there are other sources of amorphous carbon that could be responsible. For example, industrial pollution could also produce these particles and deposit them on the object’s surface [61,62]. However, considering the location of this open-air rock art shelter, which experiences absence of industrial interference, it is logical to conclude that the most probable source of amorphous carbon is related to fires.

Conclusion

In conclusion, this paper describes a study that investigates the chemical composition and state of conservation of the pictorial layer in the Juanita rock-shelter, the results of which show the impact of lichen colonization on the open-air rock-art panels and permit to develop a control strategy of the site. The research was carried out by microscopic and chemical analytical investigation of rock samples, including substrate and pigment samples, and SEM observations of lichen growth. The results indicated that the substrate is made of quartzite rock, mostly siliceous with iron, potassium, and aluminium as the secondary elements. Calcium and phosphorus were found to be present in significant amounts in some samples.

The pigments were identified as hematite and maghemite, likely made using red ochre or earth ochre, indicated by the presence of iron, aluminium, and potassium. The analysis also showed the presence of bio-colonies on some pigment samples, and lichen growth on the rock substrate. The study found that lichen prefer to attach to pits in the rock, which they may have created themselves, and that the degree of penetration is dependent on several factors, including species, porosity, texture, and degradation of the stone. The study also examined the composition of the quartzite rock substrate, revealing the presence of copper and manganese, which may be present in oxalates formed due to the action of lichen on the rock. The study also relates the presence of amorphous carbon on the shelter wall to fire events.

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Conflict of interest

No conflict of interest.

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