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Identification of organic material in Los Buitres 1 rock art shelter, Badajoz, Spain

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Abstract. This research aimed to characterize the chemical and mineralogical nature of prehistoric painted figures from the Los Buitres 1 rock shelter and to identify organic material from the pigment samples. Micro-Raman spectroscopy and ATR-FTIR analysis were made. Four pigment samples were selected: three red and one dark-red granules of pigment. Micro-Raman spectroscopy was applied to determine the mineralogical composition of selected samples while ATR-FTIR was applied in order to identify organic material present in each. Samples 1 and 2 are almost identical and registered montmorillonite being present. Analyses by ATR-FTIR points to organic components in sample 3 while sample 4 was identified as burnt umber. A comparison with a nearby shelter with the same organic compounds in the same type of figure causes some alarms to sound due to the possibility that a real pigment recipe has been in use in the same region for the same time spectrum.
Keywords: Schematic Rock Art; Iberian Peninsula; ATR-FTIR; Micro-Raman; Organics; Burnt Umber.

[es] Identificación de material orgánico en el yacimiento de arte rupestre Los Buitres 1, Badajoz, España

Resumen. El objetivo de esta investigación ha sido caracterizar la naturaleza química y mineralógica del pigmento empleado en los motivos esquemáticos prehistóricos de la cueva de Los Buitres 1 (Capilla, Badajoz), y tratar de identificar la presencia de materia orgánica en su composición. Para ello se han realizado análisis de espectroscopia Micro-Raman y ATR-FTIR sobre cuatro muestras de pigmento, tres de pigmento rojo y una más también roja, aunque de tonalidad más oscura. Se aplicó la espectroscopia Micro-Raman para determinar la composición mineralógica de las muestras seleccionadas, mientras que el ATR-FTIR se aplicó para determinar la presencia de materia orgánica presente en cada una de ellas. Destacar que las muestras 1 y 2 son casi idénticas y registraron la presencia de montmorillonite. Por su parte, los análisis por ATR-FTIR señalaron la presencia de componentes orgánicos en la muestra 3, mientras que la muestra 4 se caracterizó como ocre oscuro quemado. La comparación con los pigmentos empleados en el arte rupestre esquemático de un abrigo cercano, en donde han sido identificados los mismos componentes orgánicos en similares tipologías figurativas, invita a considerar la posibilidad de que nos encontremos con una suerte de "receta" para preparar el pigmento que debió estar en uso en este territorio durante un periodo cronológico concreto.
Palabras clave: Arte rupestre esquemático; Península Ibérica; ATR-FTIR; Micro-Raman; Orgánicos; Umber quemado.

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1. Definition

The Los Buitres 1 rock shelter is located in the municipality of Capilla, the north-eastern area of Badajoz province in Spain (Fig. 1). The site was extensively studied by Henri Breuil in the early part of the 20th century (Breuil 1933) and, more recently, some critical reviews of shelters in the same area have also been undertaken (Bécares Pérez, 2009). The quartzite walls of this open-air rock-shelter are decorated with painted images that belong to the schematic rock art style: a tradition that is relatively common across the Iberian Peninsula.

The wall of the Los Buitres 1 rock shelter measures c. 11.20m deep from its access area and has a ceiling that exceeds 15m in height in places. The site opens towards the southeast, revealing a wide panoramic aspect over the Zújar River which would have once been an important communication route that connects the plains of La Serena with the Guadalquivir Valley.

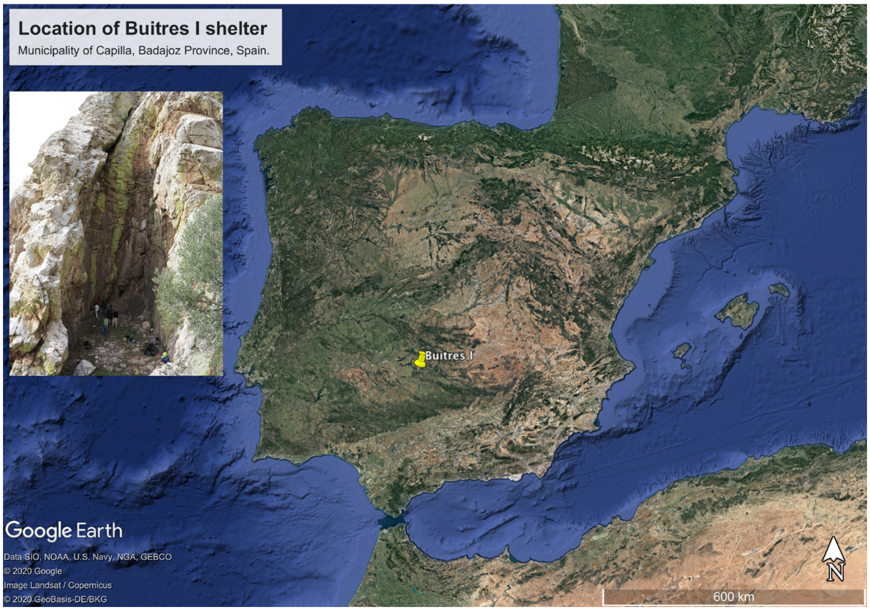

Figure 1. Location map of Buitres 1 Shelter, Capilla, Badajoz, Spain

Unfortunately, Buitres 1 shelter has many natural and probably human-induced conservation issues such as potentially harmful biological activity, natural coatings and limited damage caused by nesting vultures within the upper sections of the shelter.

The primary aim of this work was to characterize the chemical and mineralogical nature of the prehistoric painted figures of the Los Buitres 1 shelter and to identify where possible the organic material within the samples. The research focused particularly on results from the micro-Fourier transform interferometer analysis (ATR-FTIR). Our sampling strategy would hopefully identify the presence of possible binders within each sample.

As part of our research, fifteen panels were documented in the Los Buitres 1 rock shelter (Fig. 2). The panels contained schematic imagery including anthropomorphic figures, schematic animal figures, sun-shape figures and a large variety of circular and geometric motifs. Scrutiny of the panels indicated that the panel assemblage was constructed of figures ranging over several different chronological phases. The observation was based upon figurative style, typology and superimpositions. The schematic figures were painted mainly in dark and light red hues, but occasionally in black. As far as the authors are concerned, the site has never been investigated for archaeometric analysis.

In addition to recording the rock art, an archaeological test pit programme was undertaken inside the shelter. This programme was initiated to fully understand the contextual record of potential human occupation and the association between human activity and the painted imagery (Collado *et al.* 2017). Unfortunately, the test pit programme revealed negative results.

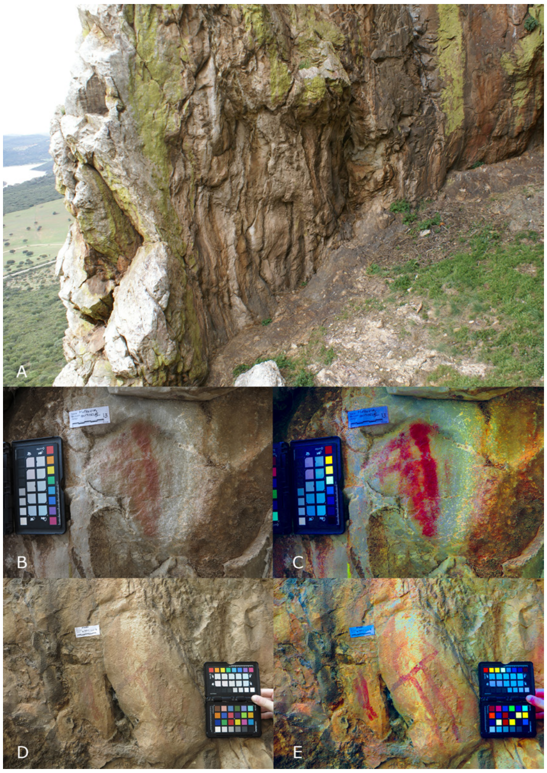

Figure 2. Photographic documentation on the Buitres 1 Shelter: A) The Buitres 1 Shelter; B) Panel 13; C) DStretchÒ LDS filter of Panel 13; D) Panel 3; E) DStretchÒ LDS filter of Panel 3.

a. Characterisation and chrono-cultural framework of Schematic Art

Schematic art, especially in the Iberian Peninsula, constitutes one of the varied modes of graphic expression and multiple cultural expressions of the human groups that lived during Recent Prehistory. It is defined as a cultural phenomenon with wide dissemination in the Iberian Peninsula and other areas in its immediate surroundings, which is characterised by the representation on natural rocky surfaces of a series of typified figures "understood as representations of a thing attending only to its most significant lines" (Hernández Pérez, 2006).

These are figures that morphologically simplify a human figure, an object, an animal or other natural or artificial elements, or that even reach total abstraction with the representation of geometric symbols. These representations respond to certain formal, technical and thematic rules (Collado Giraldo & García Arranz, 2007). It is thus a system of representation that breaks away from previous iconographic models, giving rise to a new type of motif with specific typologies that can also be found in ceramics and even in stratigraphically defined painted pebbles, for example (Collado Giraldo & García Arranz, 2013). Some of the classic and best-known works on the subject include the "Rock paintings of southern Andalusia" (Breuil and Burkitt, 1929), the famous work by Abbé Breuil himself on schematic painting "Les Peintures Rupestres Schématiques de la Péninsule Ibérique" (Breuil 1933-1935) or the synthesis of peninsular rock 'art' in the "Prehistoria del solar hispano" by Hernández Pacheco (Hernández Pacheco, 1959). However, for Schematic Art, the study carried out by Pilar Acosta in her work "La Pintura Rupestre Esquemática en España" (Acosta, 1968), is a work that marked the threshold of a new stage in the study of schematic painting, which is fundamental. For the first time, a typological systematisation was made which has served as a classificatory basis for numerous studies. This was followed by the works of Ripoll (1968, 1983), Beltrán (1983), Jordá (1983), etc. In many parts of Spain, works regarding the study of schematic art were made (Hernández, 2009; 2016). Some regional works were very important such as in Villuercas (García Arranz 1990), Extremadura (Martínez Perelló 1999, Collado 1997), Sierra Morena (Caballero 1983, Cuenca del Ebro (Utrilla, 2013), López and Soria 1988, Fernández Rodríguez 2003), the Subbetic (Carrasco et al. 1985), the Laguna de la Janda (Más 2000) the Southeast (Soria and López, 1989; Martínez, 1984 and 1988, Mateo 1999, 2003; Carrasco, Martínez, Pachón and Gámiz, 2015) and in the ARAMPI (El Arte Rupestre del Arco Mediterráneo de la península Ibérica) (Rock Art of the Mediterranean Arc of the Iberian Peninsula) territory (Ruiz López, et al., 2009; Fernández Ruiz, 2020).

The contextualisation of schematic art, as an understanding of its spatial and temporal phenomenon as well as its origins and interrelationships, has been one of the main objectives of current research. Sites of schematic rock art that can be studied in association with a material culture context are rare. On the contrary, usually the sites with schematic paintings and/or engravings are located outside the residential or funerary context of the communities concerned. In the case of Extremadura, for a long time the two most classical and recurrent ways of framing schematic rock art have been to identify motifs with which parallels can be drawn and to understand a possible stylistic evolution of the motifs (González Cordero, 1999). In recent years, a new line of research has focused on the archaeometric investigation of the pigments used in several schematic art sites in Extremadura, an area rich in painted shelters and whose results help us to better contextualise the symbolic behaviour of the first farmers and herders of the central-western Iberian Peninsula. It should be noted that this ongoing archaeometry survey which has been active for the past ten years covered, so far, only a fraction of the immense rock art heritage in Extremadura, central western Spain (Rosina *et al.* 2018; Gomes *et al.* 2015; García Arranz, *et al.* 2015; Collado *et al.* 2014; Gomes *et al*. 2014). It is within this project that the Los Buitres 1 rock shelter is included fits.

Schematic rock art is considered a form of graphic expression that extends into a broad temporal period, from the Early Neolithic to the final stages of the Bronze Age (Collado 2006; Ruiz *et al*. 2012). Arguably, the first synthesis of this artistic tradition was made during the middle of the 20th century by Pilar Acosta (Acosta 1968) and since then many researchers have developed a lot of research on this prehistoric art style in different parts of the Iberian Peninsula. Since it is not possible to mention the entire bibliography, the following bibliographical references are only examples of some of the work carried out: Collado 1995; 2009; Collado *et al.* 1997; Torregrosa and Galiana, 2001; Utrilla and Baldellou, 2001/2002; Utrilla, 2013; Carrasco, Navarrete and Pachón, 2005; 2006; Carrasco et al., 2015; Hernandez Pérez, 2006, 2009, 2016; Martí Oliver et al., 2018; Oms, Petit and López, 2016.

b. State of the art

Organic binders are thought to be contemporaneous with ancient pigment production even though their trace elements are considered to be less significant than that of inorganic materials (Brook *et al.* 2018). Known organic binding agents in rock art paintings include various animal fats, blood, bone marrow fat, egg yolk and/or albumen, human saliva, plant residues and urine (Watchman, 1993; Watchman and Cole, 1993; Dobrez 2014; Oliveira *et al,* 2017, 2019; Brook *et al*. 2018).

Normally, organic compounds are hard to find in prehistoric pigments research. However, some attempts have been applied recently with new techniques such as protein digestion and LC-MS analysis (Roldán *et al.* 2018; Vinciguerra *et al.* 2016; Villa *et al.* 2015), DNA isolation and quantification, PCR amplification, library construction, DNA sequencing, bioinformatic analysis of metagenomic data (Roldán *et al.* 2018) and portable spectrometer ASD (Analytical Spectral Device) (Horn *et al.* 2020).

The presence of binders in prehistoric paintings is hard to identify and some authors even have described processes in which gypsum and calcite exudations from walls could have acted as binders in paints without it (Montes and Cabrera, 1992), Smith, Bouchard and Lorblanchet (1999).

Ethnographic studies give us many references to organic binders being used in rock art (Rudner, 1983) and also many experimental works have been done (Garcês *et al.* 2019), however, the easy characterization of organic compounds for modern paintings works, for prehistoric art, not so much. The problem seems to be the hypothetical use of volatile mediums, sampling randomness, and the technical limits of equipment and analysis procedures (Hernanz *et al.* 2012b) and not the lack of organic use in prehistoric art. The recognition of pigments that are made only of organic matter (black pigments made of charcoal and whites made of beeswax) are easily identified (Gomes *et al.* 2013; López-Montalvo *et al.* 2017).

This work formed part of a much larger project entitled "The Context of Schematic Rock Art in Badajoz Province". The project aimed to create a baseline study that also considered a post-site interpretation and the long-term conservation and management (Collado *et al.* 2017).

2. Materials and Methods

From Los Buitres 1 shelter, four samples of pigments were selected (individual masses not exceeding several milligrams). Because of the poor state of conservation of the painted panels, sampling was hard, resulting in a short sampling list. This list took into consideration the necessity to avoid a major impact on the panel. Therefore, sample 1 was taken from a red circular thick figure; sample 2 was taken from a red line figure near figure 1; sample 3 was taken from dark-red fingerprints and sample 4 was taken from a red figure that could be interpreted as a schematic animal (Fig. 3 and table 1). The choice of specific sites for sampling is related to pictographic interest (different types of figures, superimposed figures, different types of colour), pigment availability and minor risk of damage. Samples were analysed using micro-Raman spectroscopy and ATR-FT-IR. Samples included three red pigments and one dark-red sample, and they were collected from strategic figurative motifs in order to encompass several typological spectra of motives and taking into account the variation of pigment colouration (i.e., different hues of red). This authorized sampling strategy was made in compliance with national and international guidance on sampling, to assure that the integrity of the imagery was not compromised. Where possible, sample collection was undertaken using non-contact ethical extraction techniques (using guidelines set within the American Institute for Conservation) (A.I.C. 2015). Each sample, weighing between 10 and 100 mg, was extracted in areas of the panel where the pigment was observed or in areas where minute fractures and niches were present. Normally fractures and niches are considered from an ethical point of view the most preferred places to extract pigment because it is a way to reduce the impact of the sampling from a rock art surface. Each sample was obtained using a sterilized tungsten scalpel, samples were inserted into 0,5ml microcentrifuge tubes.

Figure 3: Sampling location in rock art paintings panels in Buitres 1 shelter with details using DStretchÒ to better understand the different variation of pigment colouration.

A sample from the undecorated wall blank (bedrock) was also taken to discriminate which mineral elements belong to the decorated part of the wall and what minerals formed the bedrock (Fig. 7 – supplementary material).

Micro-Raman spectroscopy was employed to determine the mineralogical composition of pigment samples. Micro-Raman measurements were obtained using a LabRam HR800 spectrometer (Horiba Jobin Yvon, France), coupled with an Olympus BXFM optical microscope. The spectrometer was equipped with an air-cooled CCD detector (1024 × 256 pixels) at –70º C. A 600 grooves/mm grating hole of 200 mm allowed the sample collection of Raman spectra with a spectral resolution of 2 cm^{-1}. The He Ne laser line at 632.82 nm was used as an excitation source and was filtered to keep the laser power varying from 0.2 to 10mW. Exposure time, beam power and accumulations were optimized for each sample in order to obtain sufficient spectra but at the same time ensuring avoidance alteration of each sample. Several measurements were ob-

Table 1. Results of Los Buitres 1 she

Sample Code	**Figures**	**Color**	**ATR-FTIR PEAKS**														
Buitres 1_sample 1	Circular figure with inner cross of thick stroke	Red					3034			1617	1460			1434			1382
Buitres 1_sample 2	Figure with thick cross overlapped by the figure in sample 1	Red				3048			1616			1461	1433			1380	
Buitres 1_sample 3	Digits above solar figure	Dark Red		2924	2853					1617							
Buitres 1_sample 4	Zoomorphic figure	Red	3383					1622							1424		
INTERPRETATION			Water	Organics		Water									Calcium		

tained initially using a reduced power source and increasing it gradually (where possible).

Raman spectra were recorded within the range of 200–2000 cm^{-1} with an exposure time of 5–16 seconds and 5-11 accumulations. The 10 x and 50 x microscope objectives were employed to focus the laser beam onto the samples. Each sample was placed on the X-Y motorized sample holder; the spot size diameter was about 2–3µm. The wavelength scale was calibrated using a Silicon standard (520.5 cm^{-1}) and the acquired spectra were compared with scientifically published data and reference databases, such as Horiba LabSpec 5 (Horiba) and RRUFF (RRUFF, University of Arizona, AZ, USA).

ATR-FTIR spectra samples were collected using a Bruker Alpha FT-IR, Opus 7.5 software. The spectrometer employed an ATR (Attenuated Total Reflection) sampling device. The ATR-FTIR spectrometer was equipped with a global source – a KBr beam splitter, and a Deuterated Lanthanum α Alanine doped TriGlycine Sulphate detector (at room temperature). The ATR sampling device worked with a diamond internal reflection element (IRE) in a single-reflection configuration. Spectra were recorded over the spectral range of 400–4000 cm^{-1} at a 4 cm^{-1} resolution, 24 scans. Microstratigraphic studies were not possible due to the minute size of each sample.

Similar materials and methods have already been applied in other studies within the same area (Rosina *et al.* 2018; 2019). Other complementary analysis are not possible to carry on the same samples due to their small size.

3. Results

The red figures at the Los Buitres 1 open-air rock-shelter are mainly composed of hematite (see table 1 for results). The part of the undecorated wall black (the bedrock) that was analysed presents similar results as other rock shelters in the area, that of quartzite, (Fig. 7 – supplementary material). The interpretation of each ATR-FTIR peak is presented in figure 5.

From our analysis, the Raman spectra produced positive results for Sample 1 and a partial result for Sample 2 (Fig. 4), identifying hematite and possibly iron oxide as a significant constituent. These results are consistent with those provided by Fourier-transform infrared spectroscopy (ATR-FTIR) analysis, performed on the samples, which shows the presence of hematite on both samples 1 and 2.

Moreover, Fourier-transform infrared spectroscopy (ATR-FTIR) has been used to distinguish different types of clay minerals and to extract information concerning their geochemical structure, composition and changes following chemical modification. Unfortunately, the exact identification of clay minerals employing this method is complex and often inaccurate. The main analytical difficulties relate to variable chemical composition and common structural disorders within the clay matrix.

ATR-FTIR spectroscopy allows the analysis to be made of individual minerals, non-crystalline admixtures and, simultaneously, to detect the presence of organic matter. There was an ochre composed of montmorillonite $(Na,Ca)_{0.33}(AI,Mg)_2(Si_4O_{10})$ identified from our analysis of two red pigment samples from the two painted figures sampled (red circular thick figure and a red line) (see Fig. 5). One of the samples (sample 1) peaked at 3034, 1617, 1460, 1434, 1382, 1315, 1011, 777, 536, 457 cm^{1} while sample 2 peaked at 3038, 1616, 1461, 1433, 1315, 1091, 906, 777, 532, 463 cm^{-1} (similar to the first one). Based on the results of our study and elsewhere, the presence of montmorillonite is common in red ochre rock shelter paintings (Más *et al.* 2013).

elter ATR-FTIR and Raman analysis

																				RAMAN	**PIGMENTS**
	1315						1011				777		536					457		Hematite	Montmorillonite
	1315			1091		1009			908		777			532			463			Hematite	Montmorillonite
		1314			1007			911				778			518				451	-	Ochre + Fatty Acids
			1030							795						466				-	Burn Umber
	Calcium		Clay							Quartz			Hematite				Silicates				

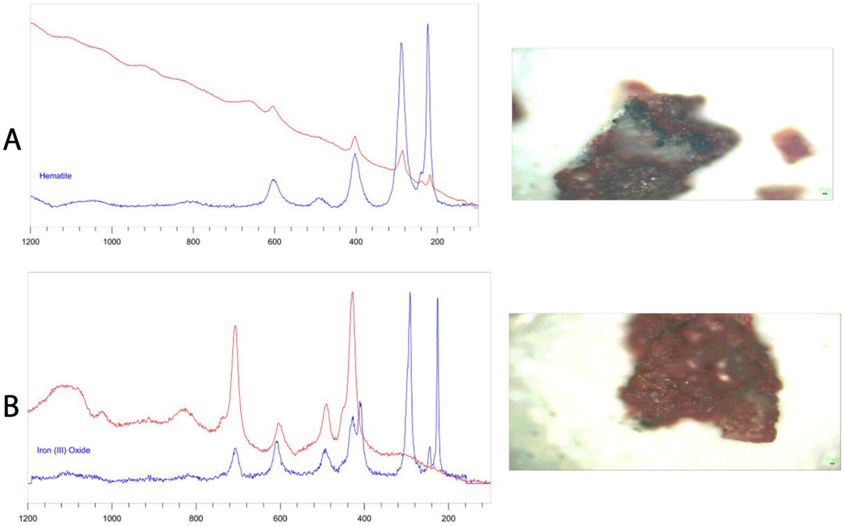

Figure 4. Raman spectra of Buitres 1 samples. A) Raman spectra from sample 1; B) Raman spectra from sample 2

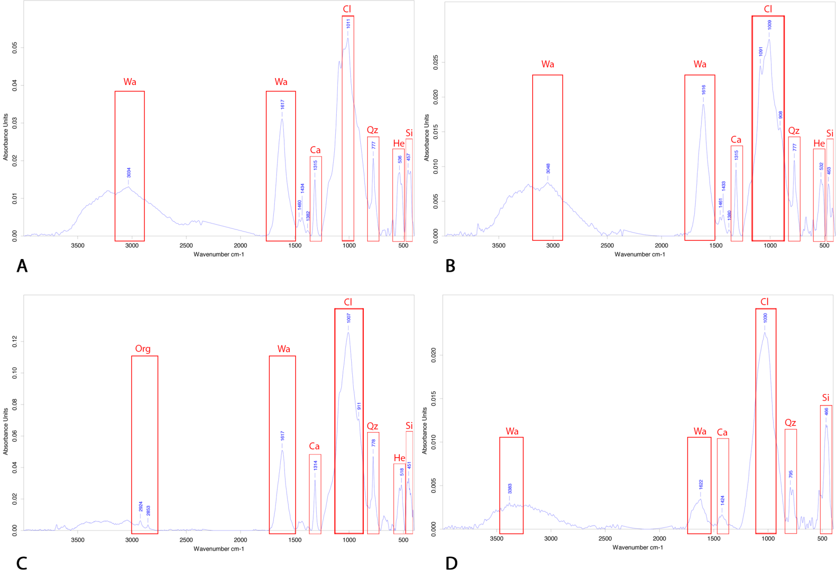

Figure 5. ATR-FTIR spectra of Buitres 1 samples. A) ATR_FTIR sample 1; B) ATR_FTIR sample 2; C) ATR_FTIR sample 3; D) ATR_FTIR sample 4. Captions of spectra: Wa: Water; QZ: Quartz; Si: Silicates; H: hematite; Cl: Clay; Org: Organics; Ca: Calcium.

Through ATR-FTIR analyses, red ochre and fatty acids were registered within the dark-red fingerprints figures. The corresponding sample (sample 3) exhibited trace elements of red ochre (peaks in 1007, 911, 778, 518 and 451 cm^{-1}) and organic compounds molecules peaking at 2924 cm^{-1} (C-H stretching of CH^3) and 2853 cm^{-1} (C-H stretching of CH^2).

In the darker red sample (sample 4), hematite is the dominant constituent. According to ATR-FTIR analyses, it probably derives from the processing of burnt umber (regolith). Two zones with intense bandwidths are visible; the first of these is at 1026 – 1043 cm^{-1} and is related to the Orthosilicic acid (Si–O–Si) group. The second, with a bandwidth at 470 cm^{-1} and the other, between 535 cm^{-1} and 555 cm^{-1}, derives from peaks related to iron oxides. The characteristic absorption band belongs to MnO2 (1030 cm^{-1}). The presence of goethite may identify the sample as raw umber. The presence of iron oxide as haematite allows us to identify the sample as being burnt umber. Raw umber is usually light brown but when heated moisture is removed, yielding a warmer, darker brown hue.

The term *burnt umber* came into use during the 17th century and the term *raw umber* sometime before the 19th century. Raw umber is a yellowish-brown earth pigment similar to yellow ochre (a natural clay earth pigment. Burnt umber is produced by roasting the raw umber until the desired shade is obtained. When applied to a panel wall, the burnt umber is visible as a dark reddish-brown calcinated pigment. The heating of the umber dehydrates the hydrated ferric oxide, therefore, turning pigment into a deeper red, more so than an applied raw umber. No significant differences are found between umbers in their ATR-FTIR spectra. When goethite is present, the sample may be identified as raw umber. In this case, the presence of iron oxide as hematite and taking into account all the characteristics above mentioned, it allows us to identify the sample as burnt umber (e.g., Genestar and Pons 2005). The spectra of the standard material identified as umber can be checked here: http://lisa.chem.ut.ee/IR_spectra/paint/pigments/burnt-umber-winsornewton/

4. Discussion

While this study has benefitted from the use of advanced analytical techniques, observations on the field regarding the superimposition of figures and state of conservation of the figures have also aided in raising questions related to pigment production and application, figure superimposition and site conservation (Marshal and Pirrie 2013).

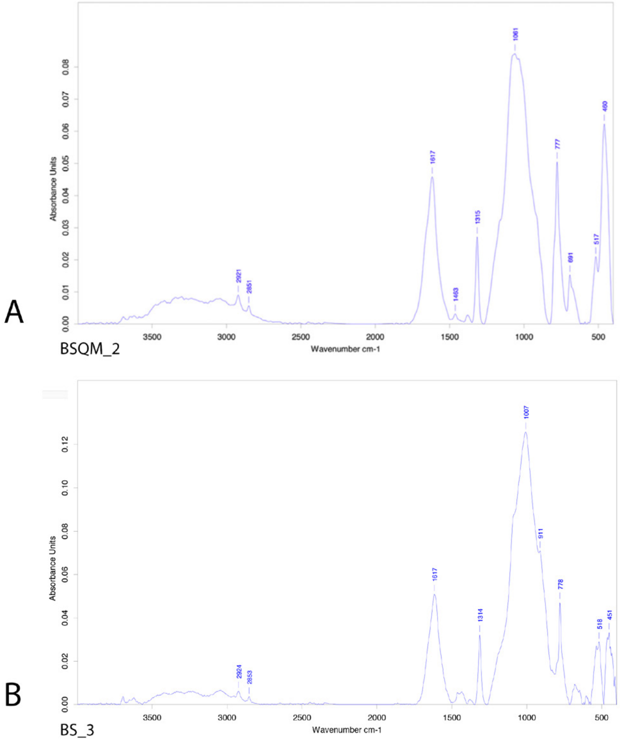

Figure 6: Comparison between spectra from Benquerencia La Serena fingerprints and Buitres 1 shelter fingerprints. A) sample 2 from Cueva Media of Benquerencia La Serena Shelter (Rosina et al., 2019); B) Sample 3 from Buitres 1 shelter.

Within the schematic rock-art paintings of the Iberian Peninsula, painted figures are usually constructed using red pigmentation, produced from mineral pigments that are rich in iron oxides, such as hematite (Fe_2O_3) or goethite (FeO(OH) (Gomes, 2015).

The red colour is produced in various shades, ranging from orange to dark brown hues.

The different shades could be due to several factors such as the state of preservation of the panel and its paintings, environmental and biological degradation, chemical interaction with rock surface, the condition of the rock art surface or the relative thicknesses of pigments; or a combination of some or all of the above (Rosina *et al.* 2018).

Hematite, as a pigment, was commonly used in the Iberian Peninsula, especially during the Late Upper Palaeolithic and Mesolithic periods (Hernanz *et al.* 2012a; García Arranz *et al.* 2012). It was also applied during the first stages of the Neolithic together with goethite and/or cinnabar (Domingo *et al.* 2012; Oliveira *et al*. 2019). Hematite was also used in combination with goethite in Schematic rock paintings from the late prehistoric rock shelters of western Iberia (Gomes 2015) and also used as the main constituent when creating red pictographs within megalithic burial-ritual monuments of Atlantic Europe (Hernanz *et al.* 2016; Oliveira *et al.* 2017).

In Buitres 1, there are different types of hues in different figures suggesting several possible scenarios. Firstly, the artist was probably aware of the technical intricacies of manufacturing-specific hues from hematite to create desired shading effects on certain figures. In several cases, the shading of these figures would have created a 3-dimensional effect. Secondly, the production of certain colour hues may have had a ritual purpose when engaged with the production of a shading colour; one cannot ignore the importance of colour symbolism of artistic endeavour. There are of course other potential scenarios that extend beyond this paper. However, the frequency of shaded hues is not uncommon and is considered a widely used technique within the schematic rock art style (Gomes *et al.* 2015) (as with earlier rock art traditions); therefore, the Los Buitres 1 rock shelter figures cannot be looked at in isolation.

The organic compounds that were registered in ATR-FTIR analyses in sample 3 could be assigned to carbonate impurity (Mastandrea *et al.* 2011), bacteria or fungi activity (Kooli *et al.* 2018), or linked to the preparation of the pigment itself. The presence of specific fatty acids should be considered with caution but may lead to new and interesting interpretive perspectives, which may be corroborated by future analyses (Mas *et al.* 2013). Even considering the hypothesis that the organic compounds are from a biological origin (fungi, lichens or bacteria), supported by the presence of carbonaceous particles and product of the metabolism of these microorganisms, the absence of phosphorus and nitrogen in the sample limits the chance of being considered a bacterium or fungus. The weak C-H stretching bands in the infrared spectrum, despite being the most interesting, are hard to be attributed. However, in this case it is considered that this compound is effectively an organic material mixed with hematite, and some data refer us to the possibility of this being of animal origin. Recent results from animal structural characterization of meats such as camel, buffalo, sheep and pork were studied using Fourier transform infrared spectroscopy (FTIR) in the range (4000 cm^{-1} – 400 cm^{-1}) (Lamyaa, 2013). The ATR-FTIR analyses has revealed that spectra show absorption peaks at 2924 cm^{-1} (2928 cm^{-1} for camel spectra), 1654, 1540 (1546 cm^{-1} for sheep) 1456, 1395, 1306 (1308 cm^{-1} for camel) 1240, 1170 (1165 cm^{-1} for pig), 1117 (1113 cm^{-1} for camel) (Lamyaa 2013). The spectra of buffalo, pig and sheep, for example, exhibit absorption bands at 2853 cm-^{1} (C-H stretching of CH^3) and 1745 cm-^{1} (C=O of ester). These two absorption bands were diagnostic for lipids and are the most intense for the pig spectrum, more so than buffalo and sheep. Therefore, the two absorption bands of 2924 and 2853 cm^{-1} are assigned to the asymmetric and symmetric CH^3 and CH^2, thus stretching vibration of lipids, respectively (Lamyaa 2013). Also, we should take into consideration that according to Maniatis and Tsirtsoni (2002), organic compounds (if present) should produce sharp lines in the spectral region that are close to 3000 cm-^{1}.

Fatty acids have been previously recorded, even though with different methods. Degraded animal fats can serve as binders has seen in other sites (Boschín *et al.* 2002; Fiore *et al*. 2008; Vázquez *et al*. 2008; Rivas and Carreras 2010) and are sometimes mixed with pigments while processing, applying, or placed into storage (Mas, *et al*. 2013). Rivas and Carrera (2010) describe the use of animal fats as *binders*.

ATR-FTIR organic bands (2853, and 2924 cm^{1}) of the reddish could also correspond to herbs (Ch'ng *et al.* 2016; Omotoso and Ajagum 2016). Spectrum displayed the presence of quartz and possibly clay (characteristic band at 1007and 778 cm^{1}). The peak at 1314 should be attributed to calcium oxalate. The absence of OH bands over 3000 cm^{1} could be an indication of heating (Schuttlefield *et al.* 2007).

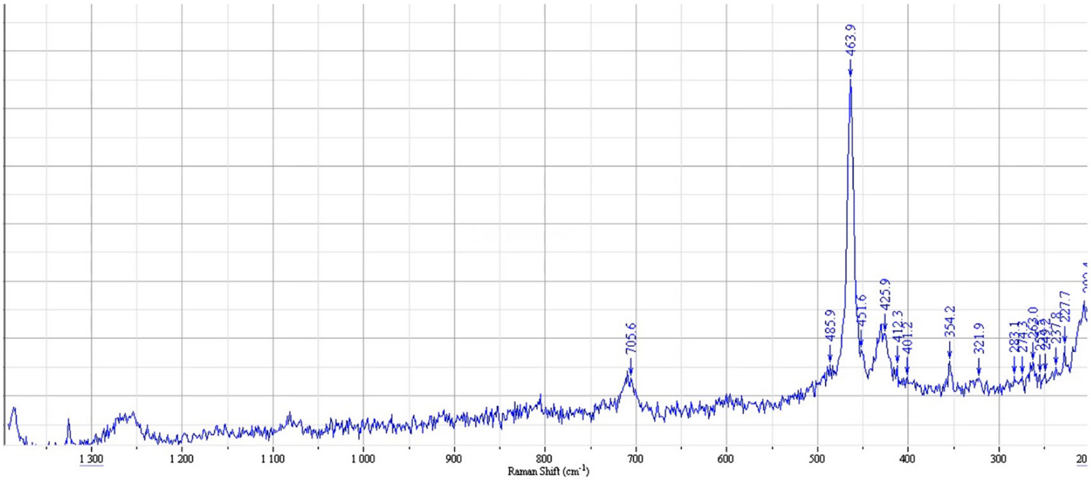

Figure 7: Raman spectra of Buitres bedrock sample.

The possibility of the organic matter found in sample 3 being considered as a binder made from plants/herbs gains importance when we compare with the data already published from other shelters of schematic art of the region (Rosina *et al.* 2019). Not too far from the Los Buitres 1 shelter, the Cueva Media in Benquerencia La Serena shelter also presents fingerprints figures that show similarities both in the composition of their materials (comparable in ATR-FTIR spectra) and in colouring. What makes these data even more interesting is the fact that similar spectra correspond in both shelters to samples from fingerprints figures. Within the Benquerencia La Serena shelter, fingerprints from Sample BSQM-2 should correspond to any herbs (Ch'ng *et al.* 2016; Omotoso and Ajagum 2016). Spectrum displayed the presence of quartz and possibly clay (characteristic band at 1060vs cm^{1}). The fluorescence observed at micro-Raman and the impossibility of detecting spectra for this sample is compatible with the presence of organic matter and oxalates, detected by ATR-FTIR (Rosina *et al.* 2019) (see Fig. 6).

Concluding remarks

The geochemical elements of the first two samples (samples 1 and 2) were identified as being identical. Both samples were taken from figures that do not possess filler pigments within their respective recipes, which would be unnecessary if abundant high-quality raw pigmenting materials were readily available.

Analyses using Fourier-Transform Infrared Spectroscopy (ATR-FTIR) for one pigment sample from Los Buitres 1 (sample 3) provided preliminary data on the presence of organic constituents within the pigment sample. While ATR-FTIR spectra of the first two samples were dominated by inorganic components, Sample 3 showed the presence of lipids together with ochre as the inorganic constituent. The constituents of the residual organic phase in the sample suggest mainly fatty acids. The absence of phosphorus in the sample limits the chance of being considered a bacterium or fungus.

Analysis of Sample 4 revealed traces of burnt umber. The presence of such residues suggests that this painting was executed applying a more complex preparation painting process.

It would be interesting to find the specific point of sources of raw materials in the area but that was not possible yet.

The recognition of organics in samples of prehistoric pigments has always been difficult. Of the few existing examples, it should be noted that a lot depends on the instruments available. Despite the difficulty to recognize organic material in pigments in the Iberian Peninsula (Gomes 2015), the literature points to greater success when using Gas Chromatography (GC) (Oliveira *et al.* 2017, 2019; Gomes *et al.* 2019) or when the pigment composition is entirely made with organic components (Gomes *et al.* 2013; López-Montalvo *et al.* 2017; Rosina *et al.* 2018).

The similarity with the published sample from the Benquerencia shelter (Rosina *et al.* 2019) is quite suggestive. Bearing in mind that both the Los Buitres 1 and Benquerencia La Serena shelters are in the same region, they contain figures from the same chronological spectrum and the fact that the same mixture of ingredients was used in the same type of figures (fingerprints figures) causes some alarms to sound due to the possibility that a real pigment recipe has been in use in the same region for the same time spectrum. This possibility is still remote and needs more data, however, it opens the way for future interpretations on the use of prehistoric pigments in a wide landscape setting.

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