



KEYWORDS: *Organic – Binder – Rock painting – Serra da Capivara National Park – Brazil*

IDENTIFICATION OF ORGANIC BINDERS IN PRE-HISTORIC PIGMENTS THROUGH MULTIPROXY ARCHAEOMETRIC ANALYSES FROM THE TOCA DO PARAGUAIO AND BOQUEIRÃO DA PEDRA FURADA SHELTERS (SERRA DA CAPIVARA NATIONAL PARK, PIAUÍ, BRAZIL)

Hugo Gomes, Pierluigi Rosina, Niéde Guidon, Cristiane Bucu, Thalison dos Santos, Lisa Volpe, Carmela Vaccaro, George H. Nash and Sara Garcês

Abstract. Pigments from several pre-Historic rock art painting samples were analysed through a multiproxy archaeometric approach. Sampling occurred in two rockshelters within the National Park of Serra da Capivara National Park area (a UNESCO World Heritage Site): Toca do Paraguaio and Toca do Boqueirão da Pedra Furada. Five complementary techniques x-ray micro-fluorescence, Raman spectroscopy, scanning electron microscopy, stereomicroscope observation and high temperature-gas chromatography (HT-GC) were combined to identify and characterise the inorganic and organic material. In particular, gas-chromatography analyses revealed the presence of binders, hardly recognised in rock art pre-Historic pigments. These binder substances (plant fatty acids) could be included in the pigment process ‘chain-opératoire’.

Introduction

The Piauí state (north-eastern Brazil) hosts an extraordinary number of pre-Historic rock art sites. Two of its national parks, Serra da Capivara and Serra das Confusões, draw the interest of scientists for their archaeological and palaeontological remains, which are found in rockshelters, caves and external walls of cliffs. The Serra da Capivara National Park became a UNESCO World Heritage site in 1991 and covers 129 140 hectares. The rockshelters contain more than 1300 highly diverse archaeological sites and many of them contain pre-Historic rock paintings and petroglyphs (Guidon 1984, 2003, 2004, 2007, 2008).

Sites chosen for analysis are located within the Serra da Capivara National Park (Fig. 1). The Toca do Paraguaio site and the Toca do Boqueirão da Pedra Furada site are two rockshelters located in the archaeological area of São Raimundo Nonato closer to the municipality of Coronel José Dias, inside the area of Serra da Capivara National Park. Toca do Paraguaio is placed in a deep and narrow valley (Arnaud et al. 1984) on the top of the plateau, which can reach between 400 m to 600 m height above sea level. The Boqueirão da Pedra Furada shelter is located at an altitude of 437 m above sea level in a well-dissected concavity in a dissymmetrical cuesta relief feature, with a concave profile, in the contact zone between the plateau formed by the sedimentary basin of Parnaíba and the pre-Cambrian plain.

Research within this part of Brazil is relatively recent with initial interest extending back to 1973. At this time there was a research agenda that considered possible anthropogenic activity dating to the Late Pleistocene (Lahaye et al. 2013). The concept of human movement into the Serra da Capivara at such an early date was based on the discovery of human remains that were found at several sites including Garrincho, Coqueiros and Antônio sites. Chronometric dating techniques indicated that human occupation in this area dated between 10 and 12 ka cal. BP (Boeda et al. 2014).

Regarding chemical analysis on pigments, several studies have been undertaken in Serra da Capivara since the 1990s (Lage 1990, 1997, 1998). It was noticed that sampled red pigments were made of haematite (iron oxide), along with a quantity of calcium. In addition, analysis of yellow pigments showed the presence of goethite (hydrated iron oxide), whilst white pigments comprised kaolinite or gypsum. Similarly, grey pigments showed a fusion of kaolinite and haematite (Lage 1998; Lage et al. 2007). The values obtained revealed that the chemical-mineralogical data from selected sampled pigments and from natural deposits provided important information for understanding the process of pigment utilisation, in particular, the process of mixing and binding certain elements to produce a usable pigment paste (Lage 1996), or what we term recipe (Solomon 2000).

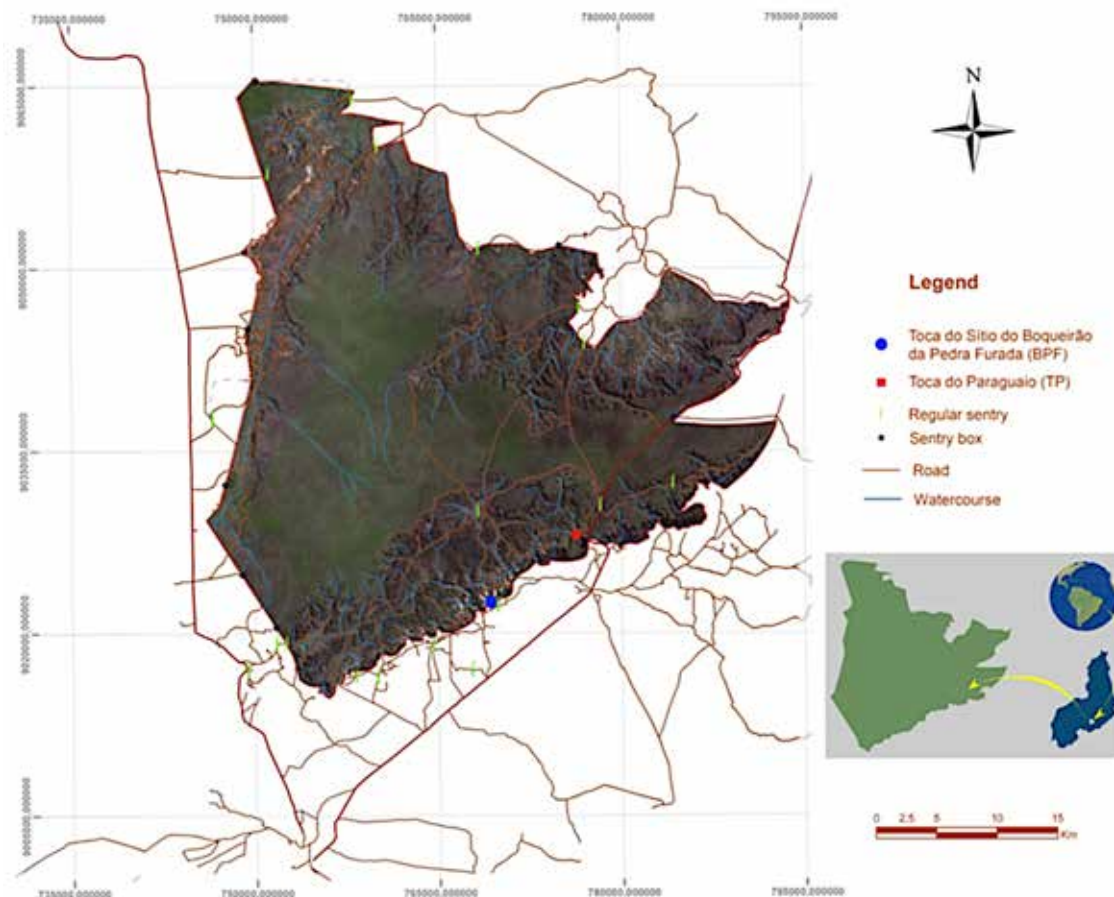


Figure 1. Location of the sites in the National Park of Serra da Capivara, south-eastern Piauí, Brazil.

Despite recent analysis on pigments still being undertaken in Serra da Capivara (Lage et al. 2016), results concerning the nature of the binders of the pigments have not yet been provided. Therefore, the main objective of this research was to identify the elementary chemical and mineralogical organic and inorganic composition of the pre-Historic rock art pigments used during the process of painting at two sites within the Serra da Capivara: Toca do Paraguaio and Toca do Boqueirão da Pedra Furada rockshelters. Although the Toca do Paraguaio site has been the focus of limited study (Santos 2013), the Toca do Boqueirão da Pedra Furada is being intensively researched over 40 years, including systematic excavation (Guidon 1984, 1985, 2008).

1. Regional settings

The two sites are located on the plateau of Bom Jesus do Gurguéia, a sandstone massif containing metasilts and conglomerates. The massif stands between 400 and 600 m above sea level and forms part of the south-eastern edge of the sedimentary basin of the Parnaíba river, being oriented longitudinally southwest-northeast (Arnaud 1984). Within the cuestas massif sequence, the boundaries of the peripheral depressions of the São Francisco River are established where the surface limestone is exposed.

The largest concentrations of rock paintings are

located in rockshelters along the river valleys on the top of the plateau or in rockshelters at the base of the cuesta (Pessis et al. 2010). Toca do Paraguaio and Toca do Boqueirão da Pedra Furada are typical examples. The choice of sites for this particular study was largely associated with the quality, quantity and varying colouration of the pigments used to create the images that were found at both sites. Furthermore, the sampling strategy was also focused on what we considered a 'typical' rock art assemblage for the Capivara region.

1.1. Toca do Boqueirão da Pedra Furada

Toca do Boqueirão da Pedra Furada (or simply known as Pedra Furada) is probably the most well-known tourist site in the region. The site presents more than 1200 figurative pictorial representations in yellow, grey, white and predominantly red. The figures are accepted to belong to the 'northeast tradition' and in it are represented the characteristics of the various evolutionary moments of this tradition (Lage and Borges 2003) (Fig. 2). The Pedra Furada rockshelter is located at the foot of a sandstone cliff and on the top of a steep bank composed of naturally-eroded debris that has fallen from the top of the plateau via escarpments and gullies.

The frequency of superposition between the figures of the same style is common. Many are hidden away on panels within small natural niches; this trait



Figure 2. (A) Toca do Boqueirão da Pedra Furada; (B) Toca do Paraguaio archaeological rock art site (photos TdS, 2013).

appears to be an intentional decision that was made by the artist (Guidon 1985). Pigment colours including shades of grey, red, white and yellow were utilised by artists who frequented the site over many years. Despite the colour range, red pigments were the most frequently used, as well as bi-chrome figures (red and white). Polychrome figures (red, white, grey) though are considered to be a rare occurrence (Guidon 1985).

1.2. Toca do Paraguaio

The Toca do Paraguaio (Fig. 3) is a rockshelter located within a deep and narrow valley on the top of the plateau of Bom Jesus do Gurguéia (Arnaud et al. 1984), adjacent to the municipality of Coronel José

Dias, inside the Serra de Capivara. This site is around 70 m in length, oriented north-south and opens out towards the east and stands around 420 m above sea level (Guidon 1975). Based on the local geology, the site is divided into two sections, viewed as upper and lower floor levels. The upper sector is sheltered inside a conglomerate deposit which overlays a sandstone layer; the latter forming the lower section (Guidon 1975). In terms of artistic representation, zoomorphic figures are few in number with anthropomorphs dominating the assemblage.

2. Materials and methods

Analysis of the pigments required the acquisition of micro-samples from both sites. Our sampling techniques followed established protocols (Wainwright et al. 2002; Hernanz et al. 2006; Mas et al. 2013; Gomes et al. 2013, 2015) and the process has been undertaken acknowledging the universal recognised conservation principles that included minimal intervention and the use of appropriate materials and methods.

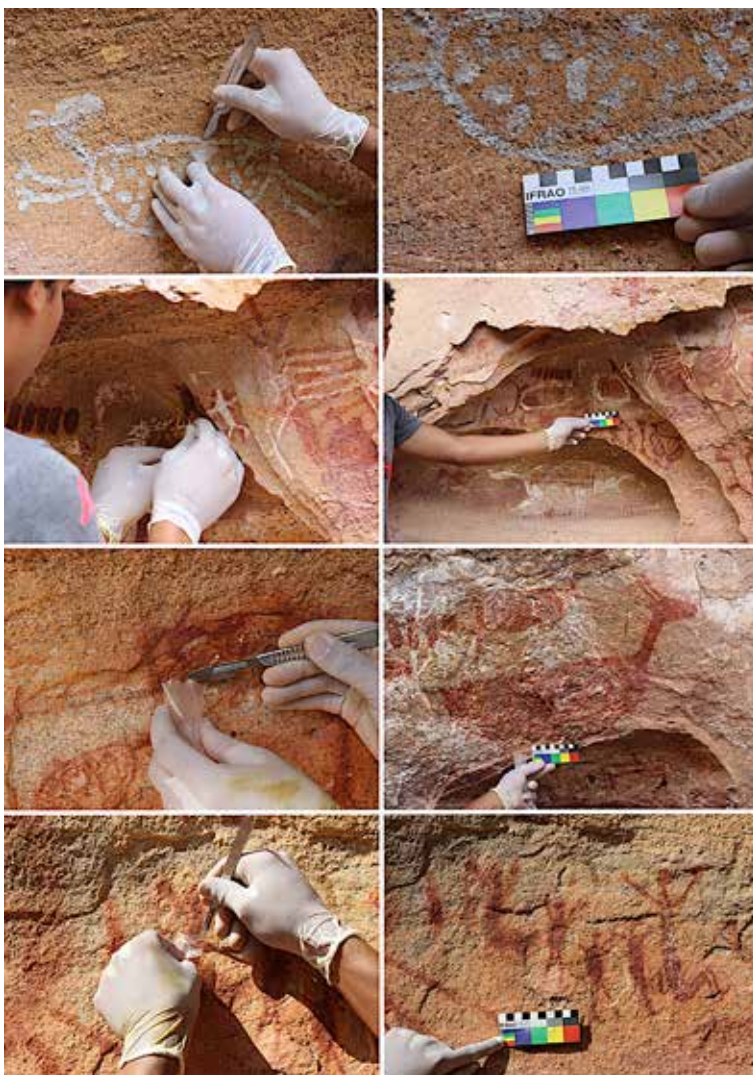


Figure 3. Sampling procedures of the data collection procedures. (A, B) Toca do Boqueirão da Pedra Furada; BPF1 (grey) (C, D) Toca do Boqueirão da Pedra Furada; BPF2 (white) (E, F) Toca do Boqueirão da Pedra Furada; BPF3 (red); (G, H) Toca do Paraguaio. TP01 (red) (photos TdS, 2013).

2.1. Sampling techniques and location

The samples were obtained using sterile tungsten scalpels, latex gloves and masks to avoid any possible contamination and then stored in Eppendorf tubes (Wainwright et al. 2002). All sample sizes were kept to a minimum, according to standards of recent advances in analytic techniques (Gomes et al. 2013, 2015). To minimise deterioration and facilitate the sampling process, special attention was focused on sites containing tiny cracks, flakes, or scales. The characteristics of the rock surface were considered to establish the sampling point. To conduct the characterisation analysis, pigments, substrate, concretions and natural oxides (as micro-samples) were collected. All the sampling area was recorded photographically before, during and after the sampling collection.

At Pedra Furada, three samples were extracted from figures that are made from grey, red and white pigments; these were recorded as samples BPF1 (grey) BPF2 (white) and BPF3 (red). Not surprisingly, each sample had unique characteristics (Fig. 3). Sample BPF1 was taken from a grey pigment that formed a cervid. Sample BPF2 was extracted from a white motif, interpreted as a circular abstract form. Parts of this composition were superimposed over a red figure. As a result, this pigment was not hardened or fused onto the wall and was considered to be friable. Sample BPF3 was taken from a red figure which was interpreted as a cervid. This painted figure was located within a weathering zone. The pigment was considered to be very hard and completely fused with the substrate.

At the Toca do Paraguaio site the predominant pigment material used for paintings is painted in varying shades of red. The four samples were carefully extracted from figures within the lower and upper sectors of the site. Samples collected showed considerable variation in red pigment characteristics such as tonalities and texture. Sample TP01 was extracted from an anthropomorph, whilst sample TP02 was from a zoomorph. Within the upper section of the site, sample TP03 was taken from a coloured smear that represented a geometric form, and sample TP04 was from a clear infilled geometric motif.

2.2. X-ray micro-fluorescence

The energy-dispersive x-ray micro-fluorescence (EDxrf) analysis was undertaken using a portable Bruker ARTAX 200 μ EDxrf spectrometer (held at TekneHub, Ferrara University, Italy). The instrument was equipped with a Mo x-ray tube and a collimator with a diameter of 200 μ m. This allowed the precise focusing of a laser beam into a target area for each sample. The analysis was conducted with voltage from 15 to 50 kV and with a current range between 700 μ A and 1500 μ A; the acquisition time was 60 seconds and was assigned by a helium flow to better detect the light elements of each sample (i.e. Na etc.). XRF spectra were acquired by ARTAXControl 7.2 software, thus obtaining desirable results.

2.3. Raman spectroscopy

Raman spectroscopy measurements were performed using a HORIBA Jobin Yvon LabRam HR800 spectrometer (held within the Department of Physics and Earth Science, Ferrara University, Italy), matched with an Olympus BXM optical microscope and equipped with an air-cooled CCD detector (1024 \times 256 pixels), set at -70 centigrade. This instrumentation works alongside a He-Ne laser source with an excitation wavelength set at 632.81 nm. The spectrometer had a focal length of 80 mm and was calibrated with two settings: 600 and 1800 groove/mm. The laser beam diameter was c. 1 mm and the spectral resolution was 2 cm^{-1} . The laser power was calibrated to between 0.2 and 4 mW and the exposure time varied between 3 and 5 seconds with 5–10 accumulations. The Raman signals were collated using 50 \times microscope objective, calibrating and checking the spectrometer with silicon at 520 cm^{-1} , whilst the Raman spectra were recorded by the LabSpec5 software. For the identification of materials used to create the pigment paste, these were compared using online databases.

2.4. Scanning electron microscopy

Concerning SEM/EDS analysis, this was undertaken using a scanning electron microscope ZEISS EVO MA15-HR equipped with OXFORD Smatmap EDS INCA for EDS chemical microanalysis (held within the Department of Physics and Earth Science, University of Ferrara, Italy). Several experiments were undertaken using electron source LaB6 cathode, with accelerating voltage 20 kV and variable working distance.

2.5. Stereomicroscope observation

An Optika SZ6745TR stereomicroscope was used for the observation of specimens at high magnification (total magnification 90 \times) combined with webcam MOTICAM 2005 5.0 Mp. The images were acquired using a Moticam Image Plus 2.0 desk-based program.

2.6. High temperature-gas chromatography (HT-GC).

Lipid residue analyses and interpretations were based on established protocols (Charters et al. 1993), in the School of Chemistry of the University of Bristol in the UK. Samples were extracted using a mixture of chloroform/methanol (2:1, v/v) to obtain the total lipid extract (TLE). Aliquots of the TLE (generally one-quarter aliquots) were trimethylsilylated using N,O is (trimethylsilyl)trifluoroacetamide containing 1% trimethylsilyl chloride (20 μ L, 70°C, 1 h) and re-dissolved into hexane for analysis by high-temperature gas chromatography (HT-GC). All the trimethylsilylated aliquots of the lipid extracts were run on an HT-GC-mass spectrometer (HT-GC-MS) enabling the elucidation of structures of components.

3. Results

Raman, SEM and EDxrf results for samples taken

Sample	Hue	Figure	Raman	EDXRF	Interpretation
TP_1	Red	Anthropomorphic	Haematite	Fe, Si, (K, Al, Ti, Ca, S)	Ochre + Substrate?+Clay
TP_2	Red	Hunting	Haematite	Fe, (K, Si, Sr, Ca, Ti, P, Al, Mn, S)	Ochre+?
TP_3	Dark Red	Abstract	Haematite	Fe, Ca, (Zn, Sr, Mn, Ti, K)	Ca?=/concretions
TP_4	Dark Red	Geometric	Haematite	Ca, Fe, (Sr, Si, Zn, K, Ti, Al)	Ca?=/concretions

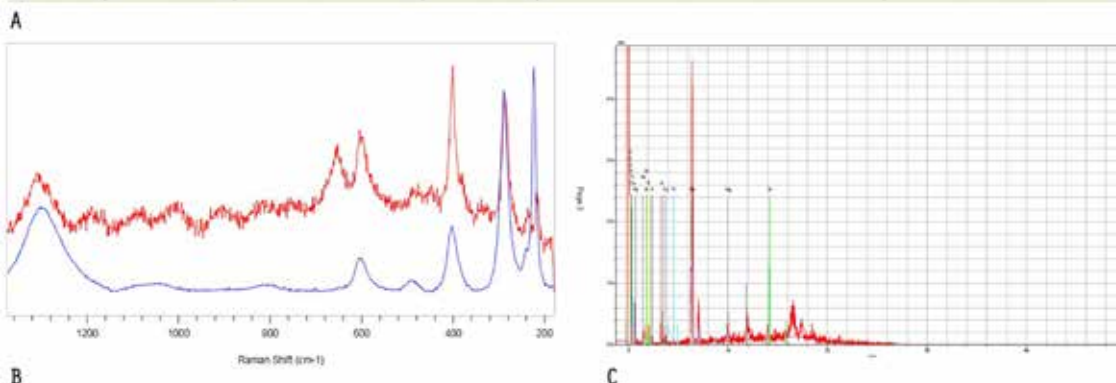


Figure 4. (A) Raman, SEM and EDXrf results for samples taken from red paintings at the Toca do Paraguaio rock-art site; (B) Raman and (C) EDXrf spectra of red pigment samples of Toca do Paraguaio.

from red paintings at the Toca do Paraguaio rock art site (Fig. 4A) indicate that all analysed sampling using micro-Raman spectroscopy presents a similar spectrum, and all reveal the presence of haematite ($\alpha\text{-Fe}_2\text{O}_3$). This was the only mineral which gave a clear recognisable Raman signal (Fig. 4B). Results from the EDXrf analyses show several chemical elements besides iron oxide were identified. In sample TP1 silicon (Si) and potassium (K) were identified which could be associated with the substrate and/or clay deposition/secretion (Fig. 4C).

For sample TP2, there was difficulty in explaining traces of many of the chemical elements present that could be associated with the substrate, such as the presence of some alumina-silicate minerals and concretions recorded. In samples TP3 and TP4, the main characteristic was the significant presence of calcium (Ca), particularly in TP4, in which calcium is the most abundant chemical element detected. The presence of calcium and haematite was also detected within the samples from Toca da Pinga da Escada (Cavalcante et al. 2008) and in other previous studies in the Serra de Capivara pigments (Lage 1998; Lage et al. 2007). Previously, no clear explanation has been made. However, considering the preservation condition of each panel, we suggest that the presence of calcium (Ca) within our samples could be associated with concretion formation. We claim this despite the negative results for oxalate in Raman spectra. An alternative but weaker hypothesis is that the calcite has been deliberately used within the pigment preparation process (for some unknown reason).

At the Boqueirão da Pedra Furada site, pigment samples revealed several pigment variants (greys, whites and reds). These variant hues originate from different chromophore minerals (see Fig. 5A). For the

grey sample (sample BPF1) the Raman spectrum did not give any clear indication of a substance. Results obtained from EDXrf and SEM analyses (Fig. 5B), however, did record the presence of iron oxide, potassium and silica and traces of aluminium, suggesting that this pigment could have been made from varying quantities of haematite and clay, as postulated by Lage et al. (2007). The white pigment sample (BPF2) reveals a specific complexity in its composition (Fig. 5C and 5D). Taking into account the analysis undertaken by our team, we suggest the use of a pigment recipe comprising varying quantities of gypsum and kaolin. Raman analyses made it possible to observe clear peaks of gypsum and kaolin (clay). This composition was also noticed within the SEM / EDS analysis. This mineral association correlates with some results from other researchers (Lage 1998; Lage et al. 2007) and suggests that a tested and applied recipe was universally used by pre-Historic rock artists.

Raman analyses for the red pigment (sample BPF3) show that the principal mineral is haematite (Fig. 4E), recorded as a strong-peak at 1002 cm^{-1} . Analysis indicates a possible association with the presence of phosphorus (P-O stretching mode; Rudolph 2010).

In EDXrf and in EDS spectra the presence of aluminium, calcium and phosphorus was also recognised, supporting the previous hypothesis of contamination by traces of concretion (a result of possible careless quarrying by the artist). Natural ochre collected near to the rock art sites are composed exclusively by haematite and EDXrf analysis has shown only iron oxide in the spectra (Fig. 5A).

Detectable total lipid extract (TLE) were only detected in samples BPF1 and BPF2. The TLE from BPF1 is dominated by even-carbon numbered alcohols (12–18), $\text{C}_{12:0}$, $\text{C}_{14:0}$, $\text{C}_{16:0}$ and $\text{C}_{18:0}$ saturated fatty

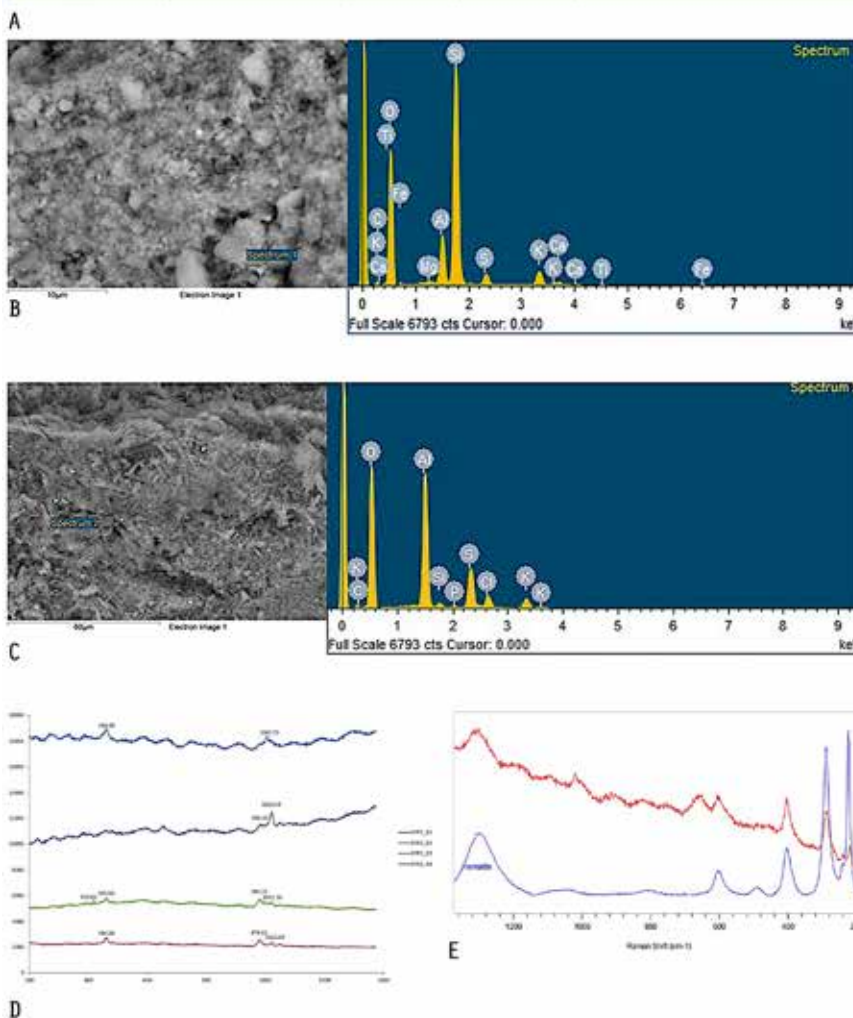
Figure 5. (A) Raman, SEM and EDXrf results for samples taken from red paintings at the Toca do Boqueirão da Pedra Furada rock art site; (B) Results obtained from EDXrf and SEM analyses; (C and D) the white pigment sample (BPF2); (E) Raman analyses for the red pigment.

acids and C_{16:1} and C_{18:1} fatty acid (Fig. 5B). The TLE from BPF2 is dominated by C_{14:0}, C_{15:0}, C_{16:0} and C_{18:0} saturated fatty acid and C_{16:1} and C_{18:1} unsaturated fatty acid. Even-carbon numbered alcohols (16–18) were also detected (Fig. 5C). Moderate concentrations of phthalates were detected in both samples. Lipids in samples BPF1 and BPF2 are tentatively identified as coming from plants, although the concentration of lipids is very low and the presence of plasticisers suggest that the samples could have been contaminated by modern compounds.

4. Conclusion

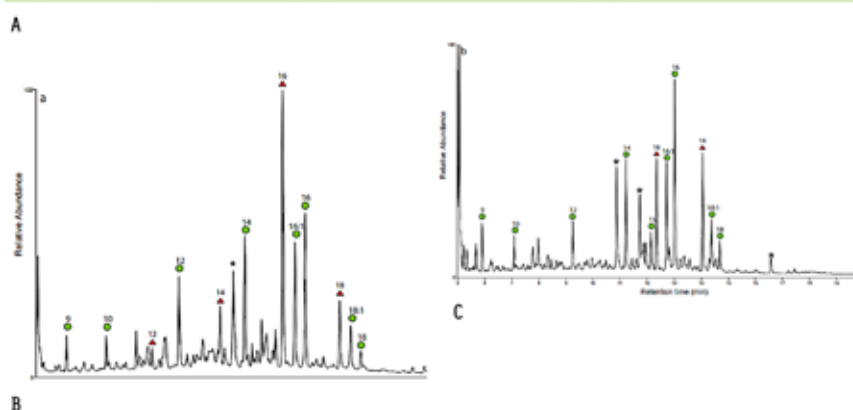
The multiproxy approach establishes the complete pigment and raw material chemical-mineralogical composition at a granular level. From our sampling, the principal identified mineral in red pigments is haematite; however, using EDXrf and SEM analyses, other chemical elements besides iron were identified. The presence of other chemical elements could be a result of ochre manipulation during the production process or a consequence of natural alterations. Raman spectra indicated that applied haematite could well have been used from natural ochre. Our sampling analysis also identified

Sample	Raman	EDXRF	SEM	Hue	Interpretation
BPF-1	---	Fe, K, Si	O, Si, C, Al	Grey	Haematite? +Clay?
BPF-2	Gypsum +Kaolin	S, K, Al, Cl + Fe, Ca	O, C, Al, S	White	Gypsum +kaolin+?
BPF-3	Haematite	Fe, Ca	O, C, Al, P	Red	Haematite (+Clay) +Ca ?+ concretions



	Raman	EDXRF	Hue	Microscopy
Ochre - 1	Haematite	Fe (Ti, Si)	Red	
Ochre - 2	Haematite	Fe (Ti, K)	Red	Quartz crystals

Figure 6. (A) Raman analyses on natural ochre. Gas chromatograms obtained from lipid extracts identified from a BPF1 (B) and BPF2 (C). Peak identities are green circles: fatty acids containing n carbon atoms and double bonds; red triangles: n-alcohols containing n carbon atoms; * = contamination.



the consistency of different pigments. This difference could be related to the pre-application treatment of ochre (e.g. the grinding or mixing of the raw material) or related to the composition of [foreign] accretions.

Our analysis on white pigments and grey pigment established that they were made from clays (in particular kaolin) and gypsum, and revealed the presence of organic components probably coming from plants. These lipid analyses indicate the presence of binders, hardly recognised in rock art pre-Historic pigments. These binder substances (fatty acids) could be included in the pigment process 'chain-opérateur'.

Studies on the use of plants in pre-Historic pigments are still scarce. A few known examples deal with plants fibres being identified in paint from seven sites sampled throughout the Laura region in Deighton and Little Laura Rivers, north Queensland, Australia (Cole and Watchman 1992), with the detection of plants cells on black pigments in Spanish Levantine rock art (Lopez-Montalvo et al. 2017), and on a combination of aquatic plants with eggs as binders from two megalithic barrows in north Portugal (Oliveira et al. 2017).

The high presence of calcium in several samples is probably linked to [foreign] concretions, as there was a slight presence of phosphorus in sample BPF3, even though no oxalates were recognised in the Raman analysis.

The fieldwork and analysis reported in this paper have indicated that the processes of extracting the raw material and creation of a pliable pigmented paste to a rockshelter wall are complex.

These results open a quite new research objective: to quantify and recognise the organic substances included and hardly recognised so far in pre-Historic rock art pigments. This multiproxy methodology is an asset that can be replicated in other rock art contexts, both open-air and inside caves. Also, in the future, it is necessary to identify the organic materials originally used in the preparation of the pigments using ethnographic studies and to develop approaches to absolute dating.

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Hugo Gomes,¹ Pierluigi Rosina^{1,2}, Niéde Guidon,³ Cristiane Buco,⁴ Thalison dos Santos,⁴ Lisa Volpe⁵, Carmela Vaccaro⁵ George H. Nash^{1,2} and Sara Garcês^{1,2}

¹ Quaternary and Prehistory Group of Geosciences Centre, Coimbra University (u. ID73 – FCT), Portugal

² Polytechnic Institute of Tomar (IPT)

³ Fundação Museu do Homem Americano (FUMDHAM) – Brazil

⁴ IPHAN, Instituto do Patrimônio Histórico e Artístico Nacional, Fortaleza, Ceará, Brazil

⁵ Physics and Earth Sciences Department of Ferrara University, Italy

Dr Hugo Gomes (corresponding author): hugo.hugomes@gmail.com

Dr Pierluigi Rosina: prosina@ipt.pt

Dr Niéde Guidon: guidon@fumdham.org.br

Dr Cristiane Buco: archeart.cons@gmail.com

Dr Thalison dos Santos: sthalison@yahoo.com

Dr Lisa Volpe: vlpsi@unife.it

Dr Carmela Vaccaro: vcr@unife.it

Dr George H. Nash: george.h.nash@hotmail.com

Dr Sara Garcês: saragarc.es.rockart@gmail.com

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