Palaeoart and Materiality

The Scientific Study of Rock Art

edited by

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Cover image: Part of the Huashan site in Guangxi Province, southern China, the largest rock painting site in the world. Photograph by R. G. Bednarik.

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Relevant Issues for the Design of a Protocol for the Interdisciplinary Study of Rock Art

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In recent years, an increasing number of interdisciplinary teams of researchers from the human and natural sciences have addressed the study and characterisation of materials in order to account for the manufacturing processes of objects and visual manifestations developed by social groups in the past. Our work is aimed to study the production of rock paintings in north-west Argentina as well as their processes of alteration or deterioration. Here, we discuss the most relevant issues to be considered for the design of a protocol for the interdisciplinary study of rock paintings in order to assure an accurate interpretation of the analytical results.

Aspectos relevantes para el diseño de un protocolo para el studio interdisciplinario del arte rupestre

En los últimos años cada vez más equipos interdisciplinarios integrados por investigadores de las ciencias humanas y experimentales se dedican al estudio y caracterización de materiales que dan cuenta de los procesos de manufactura de objetos y de las manifestaciones visuales desarrolladas por los grupos sociales en el pasado. Nuestro trabajo tiene como objetivo el estudio de la producción de las pinturas rupestres en el Noroeste de Argentina así como sus procesos de alteración o deterioro. En este capítulo se discuten los aspectos más importantes a considerar al diseñar un protocolo para el estudio interdisciplinario de pinturas rupestres a los efectos de garantizar una correcta interpretación de los resultados analíticos.

Introduction

In their exhaustive review on the state of rock art research in Argentina, Fiore and Hernández Llosas (2007) and Fiore (2012) have indicated that, among numerous challenges to be faced, the techniques of field survey have not been properly discussed. In our opinion this warning also includes the sampling of paintings without any standardised procedures. Therefore, the aim of our work was to discuss the most relevant issues to be considered for the design of a protocol for the interdisciplinary study of rock paintings. In particular, aspects related to sampling procedures, preservation of samples and registration of site characteristics, were addressed. The importance of these topics has already been noticed by researchers of other latitudes, who agree that criteria for sampling must be discussed and established in the frame of an integral research (Wainwright 1995; Bednarik 1992, 2007).

We consider that the design of a protocol is an unavoidable task to strengthen the interdisciplinary work between researchers from the human and natural sciences carrying out the study and characterisation of materials in objects and visual manifestations produced by social groups in the past. Chemists and archaeologists have questions and procedures of their own, which must be articulated according to the objectives in common and/or their specific problems. Therefore, we believe that reaching a consensus for a protocol for sample extraction and storage contributes to the intra as well as the interdisciplinary work. Our work aims to study the production of rock art and the processes involved in its deterioration.

We are conscious that the extraction of a sample alters the intervened pictorial manifestation. This could be avoided by performing analytical determinations with portable equipment in the site where the paintings are set. Portable equipment allows a preliminary survey of materials in situ with no extraction of samples from the paintings. Nevertheless, these equipments present some limitations. For example, they are more adequate for inorganic material identification because organic components are generally complex mixtures of natural compounds and their degradation products that require a chromatographic separation prior to their analysis by mass spectrometric techniques. On the other hand, these instruments do not discriminate between materials that are on the surface from those detected underneath it, and in some cases, materials are not detectable due to the limit in penetration depth of the instruments. Nowadays, the high sensitivity of modern benchtop instruments allows the analysis of microsamples avoiding the alteration of rock art due to extensive sampling (Miliani et al. 2010). Moreover, inclusion of a microsample in a synthetic resin is the only way to have access to the stratigraphy that may reflect the processes the paintings have gone through. This stratigraphy accounts for the life history of the paintings, since not all the chemical processes that occur on rock art materials are superficial.

In order to minimise sampling and perform a reliable interpretation of the analytical data, a protocol for the interdisciplinary study of rock art must be conveniently designed taking into account the following issues:

(i) the record and documentation of the environmental variables of the intervened site (humidity, wind, exposure to sunlight);

(ii) the site location (geographic coordinates, altitude, topography, geology);

(iii) the presence of agents of deterioration (biological, chemical and physicochemical);

(iv) the collection of the samples for analysis (tools used for the extraction, areas of extraction, storage and conservation until laboratory entry); and

(v) the photographic record of each step during sampling.

We believe that the design of a protocol that includes the issues mentioned above will help to systematise the most important aspects involved in the extraction and preservation of the samples, as well as the information regarding rock art and site characteristics, which might be helpful for the interpretation of the results of the chemical analysis on which the cultural interpretations will be built.

A short review on pigment analyses in South America

In Argentina, the procedures for rock art survey have been conducted with an emphasis on visual documentation, preservation and management of sites for public use. In this respect, systematic approach achieved by the Argentinean Rock Art Documentation and Preservation program (Rolandi et al. 1998) and the contributions by Sánchez Proaño (1991) highlighted the emphasis placed on visual documentation and visitor management in Argentinean rock art research. But in these mentioned programs, the way of taking and storing samples for pigment analysis was not systematised, even though such studies have long been dealt with in archaeological studies in different regions of our country, mainly in the northwest and Patagonia. Two exhaustive synthesis based on works of specialists in the field have been recently published, pointing out the theoretical-methodological tendencies of rock art research in Argentina (Fiore and Hernandez Llosas 2007; Fiore 2012). Fiore and Hernández Llosas's (2007) review spans the period from the beginning of the archaeological practice to the moment the work was edited; while Fiore's (2012) concentrates in the period 2005–2009.

Fiore and Hernández Llosas (2007) identify three moments in the historical development of the discipline, starting in the nineteenth century and finishing in the present. These moments were named: *pioneer, founding* and *contemporary*. In this work, it is clearly shown that a wider range of analytic techniques have been applied in the last thirteen years. In this respect, in the works belonging to the founding period (from the year 1936 to 2000), there is an effort in providing details about the diversity of the analytic methods employed to characterise the pigments composition and their absolute dating. The most recurrent technique at this stage was x-ray diffraction (XRD) in northwestern Argentina as well as in Patagonia (Gradin 1966–1968; Gradin et al. 1976; Iñiguez and Gradin 1978; Aschero 1983–1985; Rial and Barbosa 1983–1985; Barbosa and Gradin 1986–1987; Hernández Llosas et al. 1988–1989; Wainwright et al. 2000, 2002, among others). It is only in the contemporary stage (year 2000 to the present) when a greater spectrum of analytic techniques is applied. Among the most commonly applied are scanning electron microscopy with energy-dispersed x-ray spectroscopy (SEM-EDS), liquid and gas chromatography, infrared spectroscopy and mass spectrometry to determine the composition of wall painting materials and painting remains recovered from the excavations (Boschín et al. 2002; Wainright et al. 2002; Aschero et al. 2005; Maier et al. 2007, among others), with an explicit mention of the scopes and limitations of each of these techniques in some cases (Sepúlveda and Laval 2010). Unfortunately, these investigations are uncommon in South America but the few interdisciplinary works published recently are establishing a new trend to be followed in the future.

A critical look on the valuable contributions made by different researchers in the founding stage, as well as in the contemporary one, accounts for the fact that although more sophisticated analytic techniques have been applied, there is a lack of information regarding the procedures followed for sampling and conservation of the samples, except in some cases. Yacobaccio et al. (2008) report on scraping the samples from the most deteriorated areas of the paintings with the use of a tungsten carbide scalpel and further storage of the samples in plastic bags. Sampling procedures have also been proposed in Chile, especially by the contributions of Sepúlveda (2009, 2011) and Sepúlveda and Laval (2010), who explicitly mention the need of using field-sealed receptacles for sample storage in order to avoid contamination after sampling. Whereas these authors mention the use of a sampling protocol in the frame of various projects, they do not delve deeper into the subject or refer to any bibliography.

In our country, the explicitness of the importance of sampling protocols for archaeological studies was reflected in the last national archaeological congress held in La Rioja in April 2013. The discussions of this topic at a round table remarked that the responsibility of sampling must be taken by both, the archaeologist and the chemist, since the correct extraction of the samples is as important as their appropriate storage and analysis. Particularly, the storage of samples is a very important issue, since the results of the analysis performed in the future with new analytical technologies will depend on the adequate preservation of the samples. It is interesting to remark that in such round tables there was no presentation related to rock art sampling. A bibliographical survey of presentations given at Argentinean and Latin American archaeometry congresses shows a constant interest on pigment analyses since the first conference in 2005 up to the present (López et al. 2012). In spite of the fact that most of the presentations did not focus on sampling procedures, symposium moderators have emphasised the need of interdisciplinary work from the very first steps of the research process, including sampling strategies (ibid.).

This short review based on Fiore and Hernández Llosas (2007) and Fiore's (2012) works together with the examination of the local rock art research publications reporting archaeometric analysis of the period 2005–2009, allows us to define the state of the art with respect to sampling and sample storage as follows:

a) Interdisciplinary works between archaeologists and chemists or geologists dealing with the analysis of rock art do not make explicit the way samples are taken. In general, we find that researchers describe in detail the samples and techniques employed in their analysis but there is a lack of information related to the procedures and tools used in the extraction of the samples and the receptacles used for their storage.

b) The importance of recording information on the site context and the rock panel is often mentioned, but no reference is made regarding the importance of these variables in sampling and in the further analysis and interpretation of the analytical results.

Finally, we agree with Bednarik (2007) when he states that the diversity in the rock art record is the result of the historic development of the discipline, differences in the regional practices and individual preferences. To this statement we add that it is notable the irrelevant place given today, in the literature of our country, to the sampling procedure and sample storage since the analytical results are part of the construction of the data on which the interpretations are made.

Analytical techniques for the characterisation of rock art materials

Chemistry has been applied to the field of archaeology since the 18th century (Polland and Heron 1996). The main goals are the identification of materials, their provenance and techniques of production, and the causes and mechanisms of their degradation. Spectroscopic studies have contributed to the knowledge of the materials and execution techniques used in rock art (Scott and Hyder 1993; Guineau et al. 2001; Chalmin et al. 2003; Garate et al. 2004; Vignaud et al. 2006). Different analytical techniques, such as XRD, SEM-EDS, Fourier-transform infrared (FT-IR) and Raman spectroscopies, and gas chromatography coupled to mass spectrometry (GC-MS) have been applied to the study of pigments and the technologies used for their preparation and application in Patagonia and northern Argentina (Aschero 1983–85; Rial and Barbosa 1983–85; Aschero and Podestá 1986; Edwards et al. 2000; Wainwright et al. 2000, 2002, 2004; Boschín et al. 2002; Boschín et al. 2011; Maier et al. 2007; Vázquez et al. 2008; Fiore et al. 2008; Galván Josa et al. 2010; Darchuk et al. 2010).

Recently, new methodologies based on noninvasive (x-ray fluorescence (XRF), reflectance fiber optic mid-IR and Raman spectroscopies) or microdestructive mass spectrometry techniques have been developed, including the use of portable instruments (Miliani et al. 2010; Mazzeo et al. 2011; Colombini et al. 2010). Optical microscopy with UV and polarised light and electronic microscopy allow the visual characterisation and the study of the morphology of the materials of an archaeological object, giving additional information on the composition and heterogeneity of the materials. Nowadays, vibrational spectroscopies like Raman and infrared in combination with optical microscopy as well as x-ray diffraction and techniques using synchrotron radiation are used for the characterisation of compounds in artworks and archaeology at structural and molecular levels (van der Weerd et al. 2004; Derrick et al. 1999; Vandenabeele et al. 2007; Cavalheri et al. 2010; Bikiaris et al. 1999; Smith et al. 1999; Smith and Clarck 2004; Edwards et al. 2005; Clark 2007). XRF and SEM-EDS give information on the elemental composition of a sample and are complementary to structural and molecular characterisation techniques such as XRD and spectroscopic techniques, allowing the identification of crystalline and amorphous materials. Recently, portable instruments (XRF, IR and Raman) have been developed and, although they lack the high sensitivity of a benchtop instrument, they provide in situ preliminary information on the materials of an object in a non invasive way. They are also helpful in evaluating the need of sampling and in selecting the places where it is convenient to extract samples (Hernanz et al. 2006). Nevertheless, more information on structure and materials composition can be gained when a sample is extracted and analysed. Moreover, when a cross-section of the sample is prepared, information on the materials and their degradation products as well as the manufacturing technique can be obtained. On the other hand, cromatographic techniques like liquid and gas chromatography coupled to mass spectrometry give precise information on the composition of organic compounds and their degradation products (Colombini et al. 2010; Maier et al. 2007). These materials are natural products composed of mixtures of structurally related compounds that are prone to suffer oxidation and hydrolysis reactions, whose products sum up to the complexity of the mixtures.

Rock art painting samples are complex in composition since they generally comprise a mixture of materials vulnerable to a variety of deterioration factors largely dependent on environmental conditions. The analysis of rock art samples generally requires the application of a combination of analytical techniques to characterise mixtures of organic and inorganic materials, as well as a careful design of the analytical procedure. Each analytical technique has a different sensitivity and in some cases this depends on the material under study. The sequence of the analyses must be carefully designed, particularly if inorganic and organic materials are to be characterised in the same sample. As stated before, the analysis of organic compounds generally requires the application of microdestructive techniques while inorganic materials can be characterised by nondestructive techniques such as SEM-EDS and IR and Raman spectroscopies. Therefore, a specific protocol must be designed and followed in order to maximise the information to be obtained from these unique samples.

The necessity for an interdisciplinary protocol for the study of rock art

The study of rock art by an interdisciplinary team requires that the team previously establishes the main goals of the research project. If the aims comprise the identification of pigments and binders or the determination of the degree of deterioration of the paintings, a sampling plan and a protocol must be designed by archaeologists and chemists, especially if the chemists are not going to be involved in the selection and extraction of the samples. The design of the analyses to be performed will determine the size and type of the samples to be extracted, the places and ways of extraction and the characteristics of the preservation and storage of the samples. This will ensure that the samples meet the requirements for their subsequent analyses and that contamination is minimised. On the other hand, a comprehensive record of the characteristics of the site location and its surroundings will provide essential information for the interpretation of the results of the analysis of the materials.

In this section we discuss some relevant issues to be taken into account for the design of an interdisciplinary protocol for the extraction of rock art samples that integrates environmental and geographic variables characteristic of the archaeological site together with those related to the sampling process and preservation of the samples. Any intervention on cultural heritage is invasive. Therefore, we consider that following an interdisciplinary protocol minimises sample contamination as well as misinterpretations. In addition, we are aware that portable instruments have their limitations since they provide information on the surface of the sample and not on its stratigraphy, which accounts for the history of the chemical and physical processes the sample went through.

Record of site characteristics

The rock art site environment can influence the state of preservation of the paintings. Anthropogenic or natural factors cause alterations of the materials and can lead, in some cases, to severe deterioration (Bednarik 2001; Podestá et al. 2004; Tomasini et al. 2013). Natural aspects comprise climatic factors, presence of atmospheric gases, the composition of the rock base, and the environmental conditions of the site, such as humidity, exposure to sunlight, temperature and winds. Natural factors also include biological ones, i.e. presence of animals, plants, lichens and microorganisms. Anthropogenic factors comprise acts of vandalism, such as graffiti, and those not intentional such as tourism, which generates moisture, fire and changes in the concentration of atmospheric gases (Bednarik 1995, 2003; Wainwright 1995).

Moreover, the environment is also modified by human activities that introduce gaseous pollutants or cause the change of watercourses. The evidence of some of these alterations may be macroscopic and, therefore, easily observable on the site. It is important to register at the site if there are water filtrations, moisture, exposure to the sun or winds, growth of plants or lichens on the rock next to the images, and if there is evidence of the presence of animals (nests, depositions, etc.). Microscopically, the alterations may be evidenced by chemical processes that lead to discoloration in specific areas, formation of crystals on surfaces, flakes etc., which are often closely related to the macroscopic evidences (Smith et al. 1999; Pérez Alonso et al. 2004; Doménech-Carbó et al. 2009). It is important to take photographs of the site and the sample location for further interpretation of the results of the scientific analyses of the materials. The correlation of all the recorded data with the results of the analytical studies may explain alterations or degradation of the materials, which in other cases would be matter of speculation. In the appendix at the end of this chapter we include two tables which can be used during fieldwork as survey guidelines for the description of the site and for recording the sample characteristics.

Sample extraction and preservation

Particular care must be taken during the collection of the samples. We stress that these must be small enough to minimise any damage to the paintings. When rock art exhibits the effects of a flaking process due to an alteration of the materials, collection of samples can be facilitated. According to Wainwright (1995) there are two types of samples that can be extracted from pigmented areas, i.e. particles and cross-sections. Particles are very small and shallow samples, which often include flakes of paint detached from the bedrock due to some alteration process. This type of samples allows identification of the components of the paintings as well as the study of alterations that may occur on their surface, like the formation of crystals by reaction with the environment (sulphates, carbonates, nitrates etc.) or the deposit of salts such as calcium oxalates, which are secreted by some lichens (Edwards et al. 2000; Frost 2004; Smith and Clark 2004). Cross-sections comprise the paint layer and part of the base rock. In some cases, extraction of these stratigraphies may pose some difficulty but this kind of samples offers valuable information about the rock panel composition that can interact with the paintings.

During the sampling process, it is important to collect samples that are representative of the art of the site, together with those that show macroscopic evidences of the alterations observed in situ. It is also advisable to collect samples from the unpainted base rock for its chemical characterisation and identification of natural organic compounds that may interfere with the identification of organic binders used in the preparation of the paints (Fiore et al. 2008).

The instruments used for extraction of the samples and the containers in which they are stored should be composed of materials that avoid contamination. The use of scalpels of tungsten carbide prevents the contamination with oxides, while handling the samples with latex gloves avoids contamination with skin lipids. Powder-free gloves are preferred because they do not contain starch. For the determination of organic compounds, such as binders, samples should be stored in glass jars or wrapped with aluminium foil and then kept in zip-lock plastic bags. It is not recommended to store the samples directly in plastic bags because these contain plasticisers, as esters of phtalic acid, which can contaminate the samples and mask lipids present in low concentrations. For inorganic materials, such as pigments, additives, crystalline formations etc., glass jars are recommended, as well as wrapping the samples in cellophane sheets or keeping them in zip-lock plastic bags. If organic and inorganic components are intended to be determined on the same sample, this must be split into two and each part stored in accordance with the type of analysis to be performed since techniques for characterisation of inorganic and organic materials require different preparations and set-ups.

Samples must be labelled immediately after their extraction, assuring that the label does not fall off during handling and transport of the samples. The code on each label must correspond to the one on the spreadsheet that records each sample. It is suitable to include a brief description of the sample, avoiding the use of chemical names, such as gypsum, carbonates or haematite, as well as names of geochemical or physico-chemical processes, such as accretions, efflorescence, etc., which can lead to misunderstandings. Samples should be stored in appropriate conditions that reduce the risks of alterations prior to their analysis, avoiding exposure to air, light, extreme temperatures and unnecessary manipulation.

Finally, we report a case study of rock art from the cave La Salamanca (Catamarca province, Argentina) that shows the importance of physico-chemical analysis of the stratigraphy of painting samples and further correlation of these data with the environmental characteristics of the site.

Case study: La Salamanca cave

We present here a case study to illustrate the results obtained from the spectroscopic studies performed on painting samples from La Salamanca cave (Tomasini et al. 2012) taking into account the relevant issues proposed for the design of an interdisciplinary protocol. The aim of our study was to determine the composition of the red pigment and to characterise crystalline formations on the surface of the paintings.

La Salamanca is a cave located in a precordilleran environment (3385 masl), on the eastern slope of Las Planchadas and Narváez sierras (Tinogasta department, Catamarca) (Figure 1). The cave is placed in a narrow ravine of restricted access and elevated 20 m above the level of Pie de la Cuesta river-bed, where its entrance is located. The cave does not have direct sunlight, resulting in a cold, wet and inhospitable place. This is supported by the lack of artefacts and biofacts in the excavated cave deposits, as well as of soot adhered to the rock walls (Basile and Ratto 2011). The roof and upper sides of the cave show 60 images painted in red, distributed on 11 panels. The recorded images are exclusively nonfigurative, where the linear strokes, circular figures, zigzag figures, and dots and crosses of curvilinear outline stand out (Basile and Ratto 2011). These designs could refer to the late Archaic period or the beginning of the first agropastoral societies of northwestern Catamarca (c. 1000 BCE), based on the stylistic similarities with extra-regional sequences chronologically calibrated (Aschero 2006). During the survey, pigment samples were taken from different images (Basile and Ratto 2009, 2011)

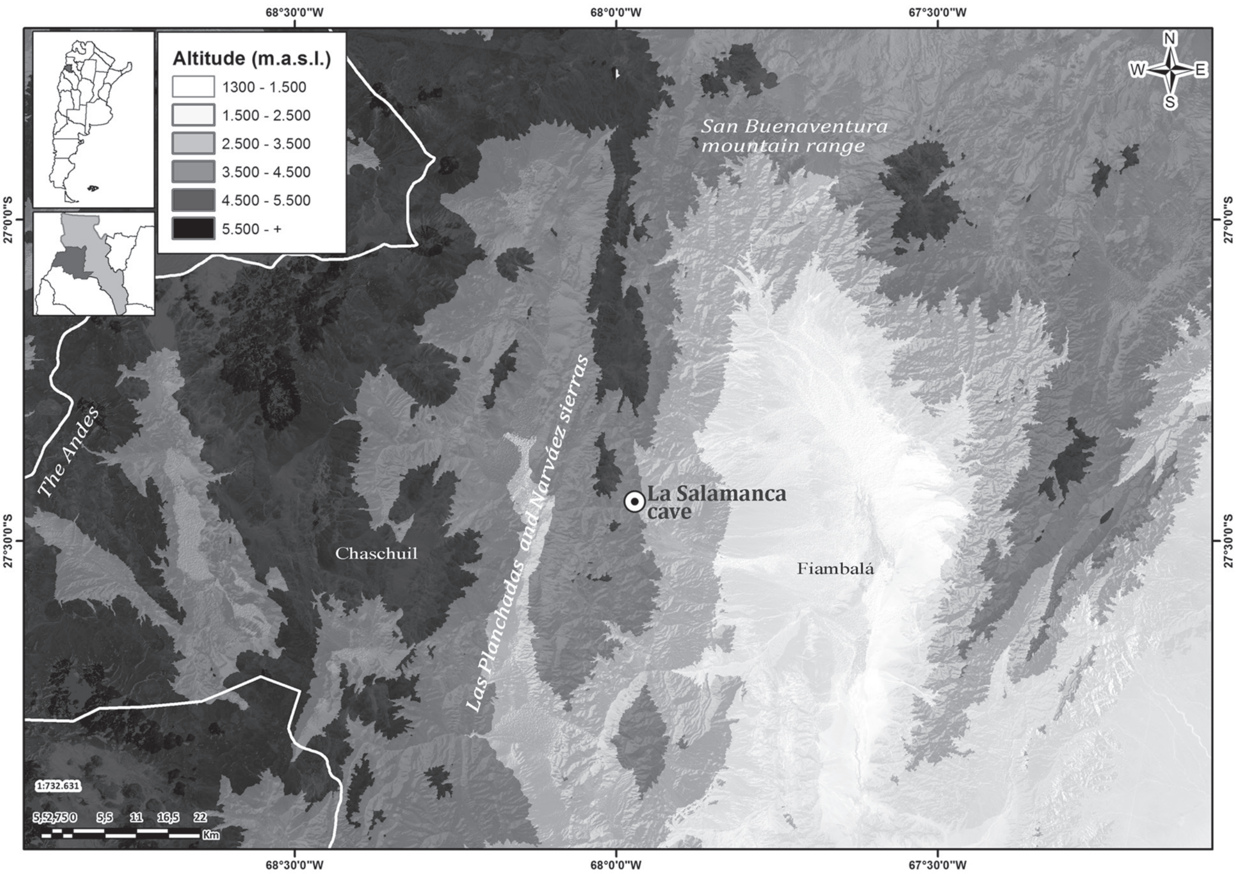

Figure 1. Map including the location of La Salamanca cave and principal references of the study area in northwestern Catamarca.

and a description of the characteristics of the site and its surroundings was recorded.

Pigment samples were taken from the images trying to avoid a negative impact on the paintings. Therefore, those places presenting detachment processes or natural scaling were preferentially selected as sampling locations. Salt deposits macroscopically visible on the surface as well as other crystalline formations were recorded.

Samples and results of the physicochemical analysis

For the physicochemical analysis, samples were extracted from five of the 11 panels displaying paintings using a tungsten carbide scalpel. Samples were wrapped in cellophane sheets and placed in plastic bags. It is interesting to compare samples taken from areas with red pigment from panels number 5 and 6 (Figures 2 and 3), as they represent two different types of samples. The sample from panel number 5 was analysed without previous treatment; whereas that of number 6 was included in an acrylic resin and polished to obtain its stratigraphic sequence. Both samples were recorded as corresponding to Munsell scale (2000) #10R 4/4 under the same lighting conditions in the field.

An analysis of a petrographical cut of a sample of the rock base of the cave indicated the record of plagioclase, orthose, quartz, biotite, amphibole, hornblend, ilmenite, chlorite and scmectite (Tomasini et al. 2012).

The sample from panel number 5 was a flake of a heteregenous pigmented surface (Figure 4). Analysis by SEM-EDS revealed the presence of calcium and sulphur in a one to one relation, characteristic of gypsum ($CaSO_4.2H_2O$). The Raman spectrum from the surface of the sample confirmed the presence of gypsum and revealed the existence of weddellite (calcium oxalate) and minor amounts of calcium carbonate ($CaCO_3$), as confirmed by infrared spectroscopy. The presence of weddellite on the surface of the paintings suggests that these had been in contact with lichens, whose growth is favoured by the presence of gypsum (Ortega et al. 1994). This is a clear evidence of deterioration of the paintings due to mechanical and chemical damage as a result of a biological factor. Nevertheless, the origin of the red colour could not be determined in this sample. On the other hand, the petrographic analysis of the supporting rock showed the presence of granitic compounds as the major components and the absence of gypsum in its composition.

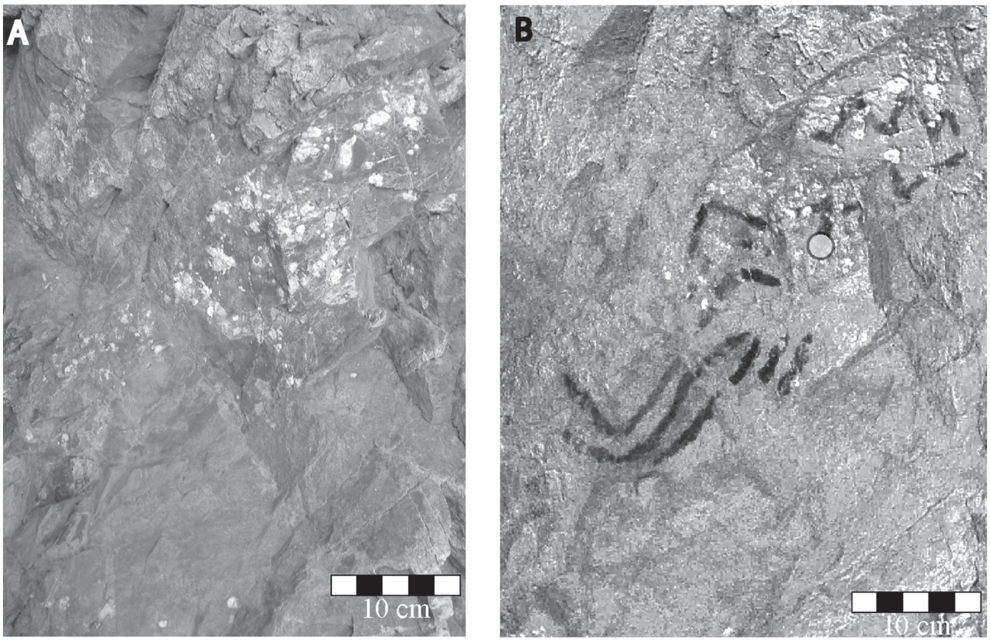

Figure 2. Detail of panel 5 where the place of sample extraction is pointed out. The (B) image was enhanced by decorrelation stretch using filter YRE, 15 points of scale (Harman 2008 [2005]).

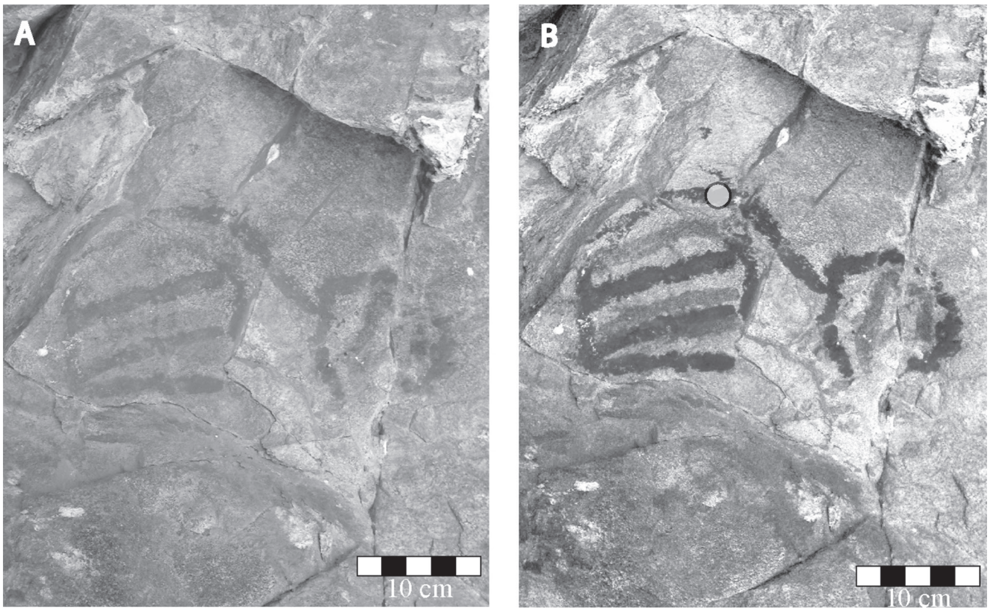

Figure 3. Detail of panel 6 where the place of sample extraction is pointed out. The (B) image was enhanced by decorrelation stretch using filter LXX, 15 points of scale (Harman 2008 [2005]).

The sample from panel number 6 was also a flake, which included part of the supporting rock. Its stratigraphy showed three layers by optical microscopy (Figure 5), which revealed different morphologies by SEM analysis. The elemental analysis by means of EDS revealed the presence of iron in the red layer, while the white areas showed the presence of calcium and sulphur. Analysis of each layer by Raman spectroscopy confirmed haematite as the red pigment and gypsum in the white layers.

Discussion and conclusions

Both samples contain gypsum, while weddellite was identified only on the surface of the sample from panel

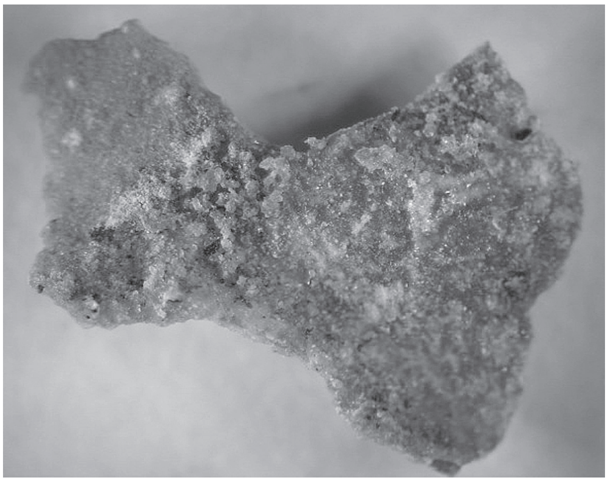

Figure 4. Image of the panel 5 sample with stereoscopic microscope. The length of the sample is about 4 mm.

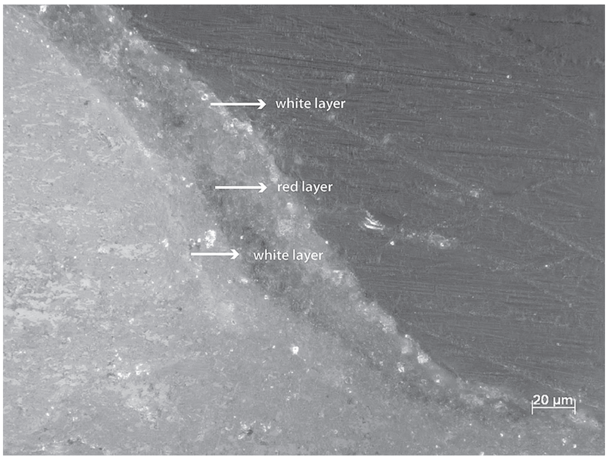

Figure 5. Image of the cross-section of the panel 6 sample, observed through optical microscope (50×)

number 5. The presence of calcium oxalate is a clear evidence of biodeterioration by lichens. The presence of calcite may be related to its use as an extender in the pigment preparation (Chalmin et al. 2003; Garate et al. 2004). Given that calcite is a minor component of the sample, its concentration might have decreased over time due to environmental factors. Carbonates are basic substances that can react with acid gases from the atmosphere, as sulfur dioxide (SO_2), to produce gypsum and release carbon dioxide (CO_2) in the presence of moisture (Charola 2000; Charola and Centeno 2002; Pérez Alonso et al. 2004), as shown in the following reaction scheme:

$$SO_2 + O_2 + H_2O \leftrightarrow H_2SO_4$$

$$H_2SO_4 + CaCO_3 \leftrightarrow CaSO_4 + CO_2 + H_2O$$

In this way, our hypothesis is that gypsum replaced gradually the calcium carbonate from the painting layer and migrated from the surface into the rock, leaving the pigment confined between two layers of gypsum (Charola 2000). This could have been the result of a high sulphur dioxide concentration in the environment of the cave, in accordance with an intense volcanic activity that occurred in the region after 5500 BP (Montero et al. 2009, 2010) and was recently dated in 4200 BP (Fernández Turriel et al. 2013, 2014). Finally, the deterioration process of flaking of the paintings can be related to the formation of gypsum (Mol and Viles 2010; Bednarik 2003).

Our findings reinforce the idea that chemical processes that alter the composition of the materials of an image depend on the climatic, geological, atmospheric and environmental conditions of the place where the paintings are located. These results mark the importance of recording site characteristics and sample description as well as the extraction of a microsample in order to gain information on the composition and degradation process of rock art. Only by careful observation of the stratigraphy of the sample it is possible to understand the chemical processes that occur beneath its surface and which are the result of the interaction with the environment.

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