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Micro-spectroscopic analysis of pigments and carbonization layers on prehispanic rock art at the Oyola's caves, Argentina, using a stratigraphic approach

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ABSTRACT

Samples of prehispanic rock art from Oyola's archaeological site, near the city of Catamarca, Argentina have been analyzed using micro-Raman spectroscopy, SEM-EDS and BSD, and optical microscopy. These samples are representative of diverse figures and non-painted surface of one of the caves at the site: Oyola 7. The pigments employed in the rock art were fully characterized. The red colors are confirmed to be red ochre (hematite) and clay. White areas of the painting have been identified as gypsum whereas black pigment is attributed to graphite. In addition, it was demonstrated that all the samples analyzed, including underlying strata, contain large amounts of calcium oxalate as the mineral whewellite. Because of the distribution along the sample, it was conclude that the presence of this compound is due to biodeterioration produced by microorganisms, fungi, algae or lichens.

Moreover, a methodology to differentiate black painting layers from carbon deposition layers from bonfires and to characterize them is presented. These results have a great impact in both chemical and archaeological sciences because allow an interdisciplinary approach bringing relevant information about relative and absolute dating. Finally, the information collected with this methodology establish a sound basis to develop complementary studies between the wall and painting stratigraphies with archaeological excavations resulting in a new and fundamental tool henceforth.

1. Introduction

The archeaological site of Oyola, on the east hillside of *Sierra de Ancasti* at the province of Catamarca, Argentina, is investigated. This site is located 80–90 km from San Fernando Del Valle de Catamarca, capital of Catamarca province, 500–900 m above sea level, corresponding to the biosystem known as *Bosque Subtropical Chaqueño* (Fig. 1).

The earlier reports from Oyola were published by Gramajo A. et al. in 1978 and 1982 [1,2]. They documented, at that time, eight shelters containing rock art into a circular batholith of 2.5 km of diameter. Moreover, all the caves and shelters are located on the base of huge granitic rocks and surrounded of dense semiarid forests. From 2009 until nowadays, new archaeological research investigations have been performed, documenting more than thirty seven shelters and caves with rock art including the previously reported ones. In the caves of Oyola exists a great diversity of anthropomorphic, zoomorphic and geometrical motives painted in white, red and black colors. The rock art of this region was attributed to the Aguada culture (500–1100 CE) [1,3]. However, in Oyola, different studies had demonstrated not only the presence of a single culture into a specific period of time but also the existence of different styles and relative chronologies, corresponding to times before and after the well-known Aguada culture [4].

The chemical analysis of the pigment composition has a relevant importance in archaeology. It can give information about the technology of the culture and the resources they had. Also, it may be noticed the influence of other cultures or the existence of trades between villages. Several authors had been studied the pigments employed in rock paintings, addressing to a certain and limited list of minerals such as hematite (or other iron oxide mineral) for red and ochre, calcite or gypsum for white colors and carbon-based pigments, magnetite or manganese oxides/hydroxides for black colors [5–9]. To this purpose, the most employed analytical techniques, due mainly to its micro-invasive or noninvasive character, were scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) [9,10], infrared

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spectroscopy [11–13], Raman spectroscopy [6,8,9,14–17] and X-ray diffraction (XRD) [18,19]. However, the pigment characterization of ancient rock art provides a challenge since the specimens have been subjected to environmental aging for thousands of years [5]. Moreover, most of the materials involved in the color can be also found as a product of deterioration in these samples. Changes in crystalline integrity of the materials, degradation of organic pigments and bindings, and the biodeterioration produced by microorganisms, fungi, algae or lichens difficult the procurance or reliable results. The appearance of great amounts of calcium oxalate, as whewellite or weddellite minerals, in rock art samples is a discussed issue in several works [13,20–23]. It was attributed not only to the presence of biodeterioration [23] but also to human activities such as the addition of oxalates from certain plants as painting binders [7,24]. Furthermore, it is a very useful source of carbon for C^{14} dating analysis [25,26]. Another important source of C^{14}, and hence, of archaeological information, are the bonfire carbon deposition on walls. The correct and reliable identification of these strata not only on the surface but also in underlying layers can permit a relative dating of different events occurred in the cave. Also, the collected information from the walls might be complemented with results from archaeological excavations in order to elucidate the sequence of events along the social history of the cave. It must be highlighted that, if such correlation between date exists, the dating may become absolute because C^{14} dating information is obtained from excavation or wall sources.

The aim of this work consists on the study of sub-millimeter rock art samples using optical microscopy, Raman micro-spectroscopy, SEM-EDS and back-scattered electron detection (BSD). It must be highlighted the importance of studying the underlying strata. For such purpose, the cross section of the samples is studied along this work. A complete characterization, chemically and morphologically, of the pigments employed in this work is showed. Besides the development of a methodology to localize and characterize, in a reliable and robust way, bonfire events in surface and underlying strata from the wall, differences between black painting layers and natural carbon depositions are indicated. All the collected information is carefully discussed taking into account all the results achieved in parallel by the archaeological excavations on the floor of the cave.

2. Materials and methods

2.1. Instrumental

Optical microscopy was performed on a polarizing microscope Leica DM EP until a 500× magnification. The microscope is capable to work on both transmitted and incident light modes. The incident illumination was made with a visible 100 W Tungsten lamp also from Leica. Photographs were recorded using the inbuilt camera system Leica DFC280. Size measurements were carried out by LAS (Leica Application Suite) software, Version 3.8.0 (Build:878) from Leica Microsystems.

Raman spectra were recorded on a Lab RAM HR Raman system (Horiba Jobin Yvon), equipped with two monochromator gratings and a charge coupled device detector. A grating of 1800 g/mm and hole of 100 mm resulted in a spectral resolution of 1.5 cm^{-1}. The spectrograph was coupled to an imaging microscope with a 10×, 50×, and 100× magnifications. The He—Ne laser line at 632.82 nm was used as excitation source and was filtered to give a laser fluence or density power at the exit of the objective lens varying from 0.1 to 2 W/mm^2. Several measurements were performed at low powers to ensure that the heating produced by the laser was minimized to avoid the alteration of the sample. Typically, for a 50× magnification, the spot size diameter was about 2–3 μm. Each spectrum was averaged over six scans corresponding to a collection time of 30 s.

Micrographs and elemental composition was carried out using a SEM-EDS FEI QUANTA 200 (FEI, Oregon, USA). For elemental Imaging a BSD detector was employed. An accelerating voltage of 20 kV and a current of 1.1 nA at a working distance of 10 mm were used. The samples were mounted on carbon stubs and metallized with gold.

2.2. Sample collection

Painted rock samples were collected from Oyola 7 cave (Fig. 1). This step is a fundamental part from the micro-stratigraphy procedure thus several considerations must be taken into account. From the conservation point of view, the samples must be as small as possible (area < 1 mm^2) and cannot be collected from zones where the aesthetical and physical integrity of the motif may result injured. On the other side, from the chemical point of view, the samples should be taken as deep as possible in order to penetrate the maximum number of paint layers. In addition, several samples should be collected to ensure the representativeness of the analytical results. These two points of view are confronted resulting in a compromise between the quality of the final micro stratigraphy and the painting invasiveness.

For all paintings, sampling sites were selected after discussion with archaeologists, conservators, and a meticulous observation with a magnifier (Opti VISOR, Donegan Optical Company, U.S.A.) aimed to detect the most appropriated areas of the paintings. More than forty samples were taken with a scalpel blade from the rock art and stored in individual polyethylene tubes. These include painting samples, areas of the wall where soot depositions were presumed and clean rock samples of the cave's walls. The sampling maps of each painting are show in Fig. 2-a) and -b). Once the micro-samples were collected, they were included in an acrylic resin Subiton® (Buenos Aires, Argentina) and polished with a decreasing sandpaper particle size (until 12,000 mesh) for cross-section analysis. The stratigraphy is observed under the optical microscope allowing us to raise information from all the subjacent layers under the more external strata. Examples of stratigraphies can be found in Fig. 2.

3. Results and discussion

3.1. Cross section analysis

The collected samples came from two different panels from cave Oyola 7. In Fig. 2-a) five different stratigraphies were selected from this panel in order to elucidate the painting composition and relative dating. Sample 1 shows the superposition of three strata. The more external layer is white follows by one black and another white layer again. It must be pointed out, that this sample was taken from a superposition of motives (denominated as a rectangular guard over a zoomorphic motif, perhaps a bird) so the black layer between the white strata, presumably soot deposition, indicates a lag of time between both paintings. This black stratum cannot be related to a preparation of the rock for painting because the underlying motive is not cover. As will be explained later deeply, the most probably hypothesis in this particular case is the presence of bonfires into the cave. Sample 2, in concordance, evidences the presence of the guard (white layer) on a black stratum. In addition, the ochre final layer at the bottom is rock and not a pictorial layer. Moreover, in samples 3 and 4, we can compare clearly the difference between pictorial layers from the black motive (Fig. 2-a-3) in contrast with the thin black layer (Fig. 2-a-4) product of soot deposition [27,28]. Finally, the sample 5 collected from the geometrical motive demonstrates that the soot layer is over the white layer. Therefore, panel A results on two motives under the white guard motive. We can describe stratigraphically the morphological composition of the paintings, indicating, in this way, that the bird and the geometrical figures were painted earlier than the guard. As an indicative, we may observe the black layer, attributed to soot, between motives. In this way, we can estimate, using optical microscopy and stratigraphies from paintings, the relative dating of the motives. The chemical characterization of the strata will be discussed in detail on the following section.