Microchemical Journal 129 (2016) 297–304

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

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

Marcos Tascon [a,*], Noemi Mastrangelo [a], Lucas Gheco [b], Marcos Gastaldi [c], Marcos Quesada [b], Fernando Marte [a,*]

[a] IIPC-Tarea, Universidad Nacional de San Martin, Quinquela Martin 1784, CABA, Argentina
[b] Centro de Investigaciones y Transferencia de Catamarca (CITCA, CONICET-UNCa) y Escuela de Arqueología, UNCa, Argentina
[c] Instituto de Antropología de Córdoba (IDACOR), CONICET-UNC, Museo de Antropología, FFyH-UNC, Argentina

ARTICLE INFO

Article history:
Received 29 March 2016
Received in revised form 29 June 2016
Accepted 1 July 2016
Available online 02 July 2016

Keywords:
Carbonization layers
Micro-Raman spectroscopy
Pigment
Rock art
Scanning electron microscopy

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 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

http://dx.doi.org/10.1016/j.microc.2016.07.003

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.

On the other side, Fig. 2-b) shows the other panel from Oyola 7, which corresponds to the motives of a jaguar, in red and white colors, and of a geometrical figure in white. Sample 1 (Fig. 2-b-1) was taken from an area of rock without painting, sample 2 from the jaguar and

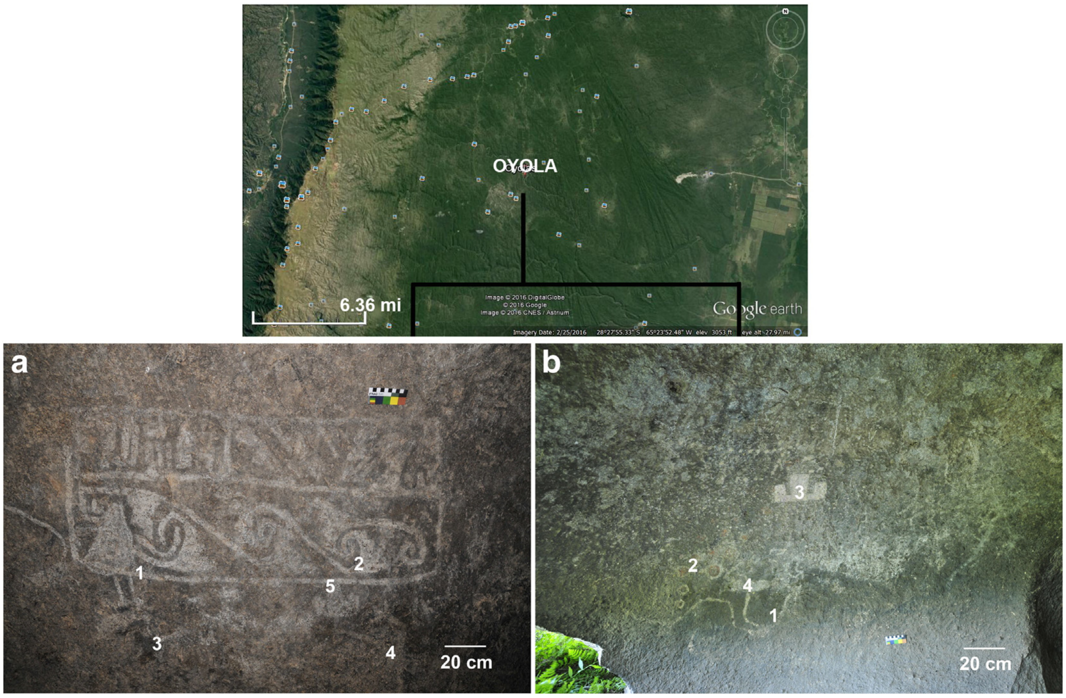

Fig. 1. Map of the slope of El Alto-Ancasti in the province of Catamarca. Pointed the region of Oyola. Picture a) is a superposition of various motives of different styles in Oyola 7 denominated panel A and, b) is the other superposition of rock art motives found in Oyola 7 called panel B.

sample 4 from a unknown motif under de jaguar (Fig. 2-b-2 and 4). Sample 1 was chosen considering the results from the archaeological excavation on the cave which revealed that in this area some bonfires were made. It must be pointed out that all the sampling surrounding areas were carefully excavated, finding out several horizontal strata which higher contents of carbon, ash and burned sediments. After the chemical analysis of this samples and the confirmation of this hypothesis, we were allow to state that in this area several bonfire events were made. Consequently, it could be expected to find one or more carbonization layers in the wall painting. In perfect agreement with these results, it can be noticed the existence of two different black layers on the samples that possibly fits with the idea of soot depositions on the wall. On the other hand, sample 2 shows that the red stains of the jaguar were painted as a red layer over a white one whereas the information addressed from sample 4 indicates that the jaguar and the unknown motif were painted over a black layer possibly attributed to a soot layer. Finally, sample 3 (Fig. 2-b-3) from the other motive, does not give relevant information more than the identification of a white layer without the presence of any other particles or pigments. To conclude, the stratigraphy *per se* is a powerful methodology to illustrate in deepness the structure of a painting but it results fundamental methodology if is complemented with micro-spectroscopic techniques such as micro-Raman, micro-FTIR, *etc*. One of the main challenges is related to the possibility to identify and differentiate black paint layers from the soot depositions made by bonfires.

3.2. Pigment determination

The Raman microscope spectra of the prehistoric rock art samples show several features of interest regarding the pigments and their substrata. The colors collected correspond to red, white and black pigments. Respect to the red pigment, the cross section on Fig. 3-a illustrates the area where the Raman spectra was taken. It seems to be a homogenous layer without the presence of particles. The spectrum shows the characteristic bands associated to hematite (224, 244, 293, 299, 409 and 610 cm^{-1}) [6,29]. The bands at 293 cm^{-1} and 299 cm^{-1} are overlapped, however, a small shoulder from de main peak can be observed. It must be highlighted that the additional band at 660 cm^{-1} is attributed to an impurity phase and is denoted a 'disorder band' [30]. The presence of another structure modifies the unit cell parameters and affects the Raman-active vibrations of this mineral [9,31]. The lack of disorder band indicates the absence of any impurity or elemental substitution in the Fe_2O_3 structure. Despite the hematite is an antiferromagnetic material and the collective spin movement can be excited in what is called magnon. The intense feature 1320 cm^{-1} is assigned to a two-magnon scattering which arises from the interaction of two magnons created on antiparallel close spin sites [29]. In addition, the remaining unassigned bands are attributed to whewellite (1496, 1464, 906 and 506 cm^{-1}). This Calcium Oxalate did not took part of the materials employed on the painting but also was produced by biodeterioration of lichens and fungus [23]. In order to complement the Raman studies, SEM-EDS analyses were made. Fig. 3-b shows a micrograph took by SEM, using the backscatter electron's detector, and the corresponding area where the spectra were measured. The results show the presence of high amounts of silicon, aluminum, sulfur and in less proportions calcium, potassium, iron, magnesium and sodium. The presence of Fe in the pictorial layer is indicative of an iron oxide. It must be highlighted that is not necessary a great concentration of iron oxide to achieve an acceptable color [10]. This fact explains the low relative amounts found in the results (5%). In addition, this pigment also contains Al and Si in ratios that indicate the presence of a clay. The presence of smaller quantities of K, Mg and S in concentrations of the order of 4–5% of each element in the red pigment implies the presence of small quantities of other minerals [9].

Regarding the black pigment, Raman spectra from several samples were collected. Fig. 4-a shows the spectrum of the black layer, it can be easily observed the characteristics broad bands of a carbon-based pigment (1350 cm^{-1} and 1601 cm^{-1}) [13,32,33]. These correspond to overlapping bands known as graphitic band (1601 cm^{-1}) and disorder band (1350 cm^{-1}), assigned to crystalline graphite and to structural disorder in the graphitic structure, respectively. According to the classification proposed by Tomasini et al. [33], the Raman shifts correspond to graphite pigment, however, the full width at half maximum (FWHM) of D (180 cm^{-1}) and G (90 cm^{-1}) bands do not are in fully agreement

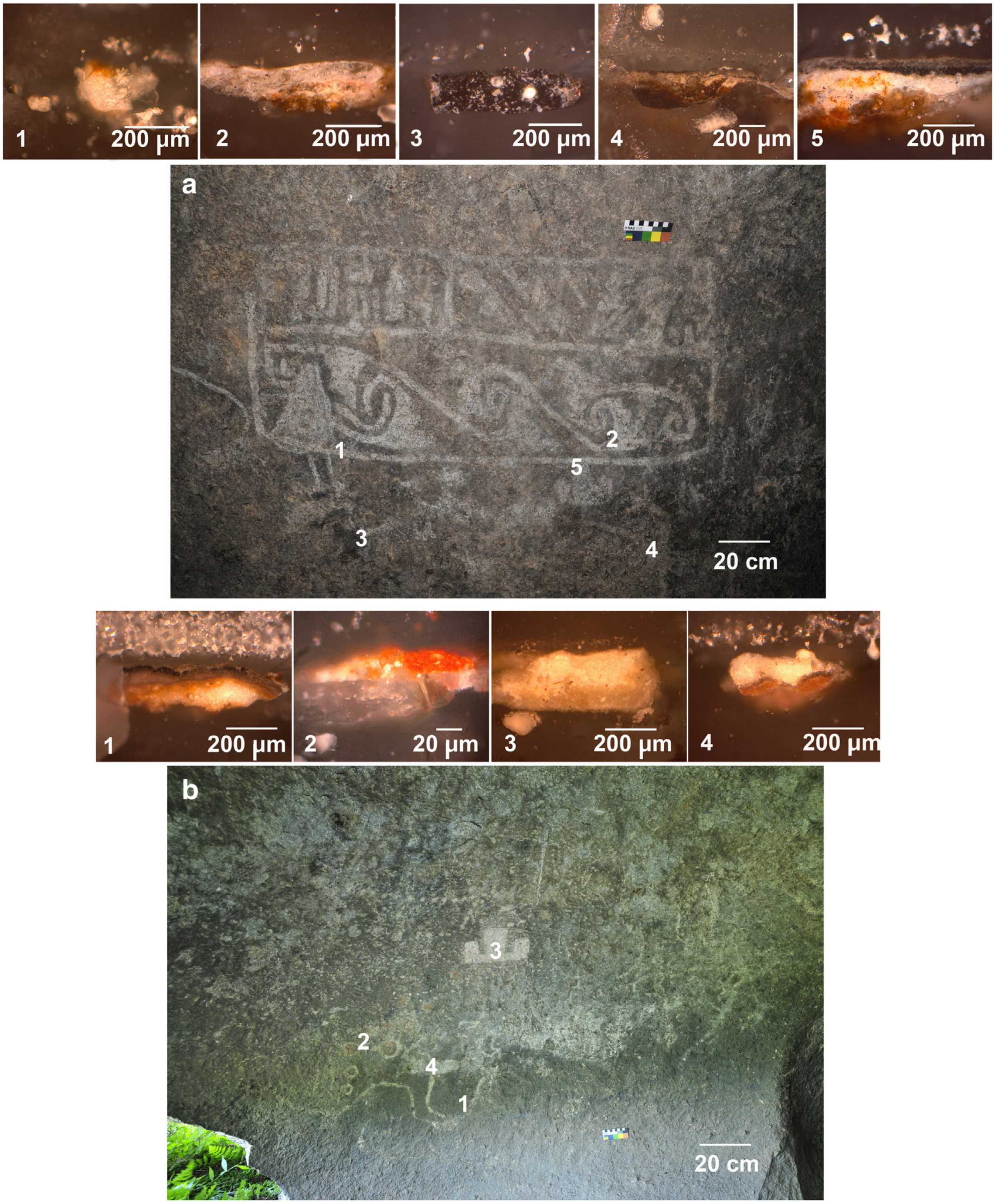

Fig. 2. Scheme of the samples took from a) panel A and b) panel B with its respective cross sections. All the micrographs were taken with a magnification of 200×.

with those referenced (188 ± 18 cm^{-1} and 67 ± 2). This indicates that the right term to describe the nature of the black pigment is amorphous carbon. The source of this substance can be from charcoal, soot or other poorly organized carbon based crystalline structure [34,35]. Finally, Fig. 4-b shows the Raman spectrum of the white-painted area. The stratigraphy reveals, apart from the white pigment, a great concentration of black particles. Those were analyzed by Raman spectroscopy confirming the presence of graphite. Besides the particles, the analysis of the white paint evidenced the presence of gypsum with the characteristics Raman bands at 140, 181, 679, 1007 and 1132 cm^{-1} [6]. Moreover, the whewellite also appears in the white pigmented areas with the aforementioned characteristic Raman shifts. This particular mineral is confirmed not only in the painted strata but also in the rock as a calcium oxalate crust in underlying or superficial layers. Some authors have proposed that whewellite could be deliberately collected to manufacture the paint, as a consequence of the highly different amounts found in pigmented areas respect to unpainted areas [13,25]. However, the signal distribution of whewellite across the different strata was completely uniform, in other words, the concentration of this compound is similar in the whole sample. Therefore, the possibility to assign the presence of these crusts of calcium oxalate to biological attacks of algae, fungi or lichens results the most natural option [13,16,17,25,26].

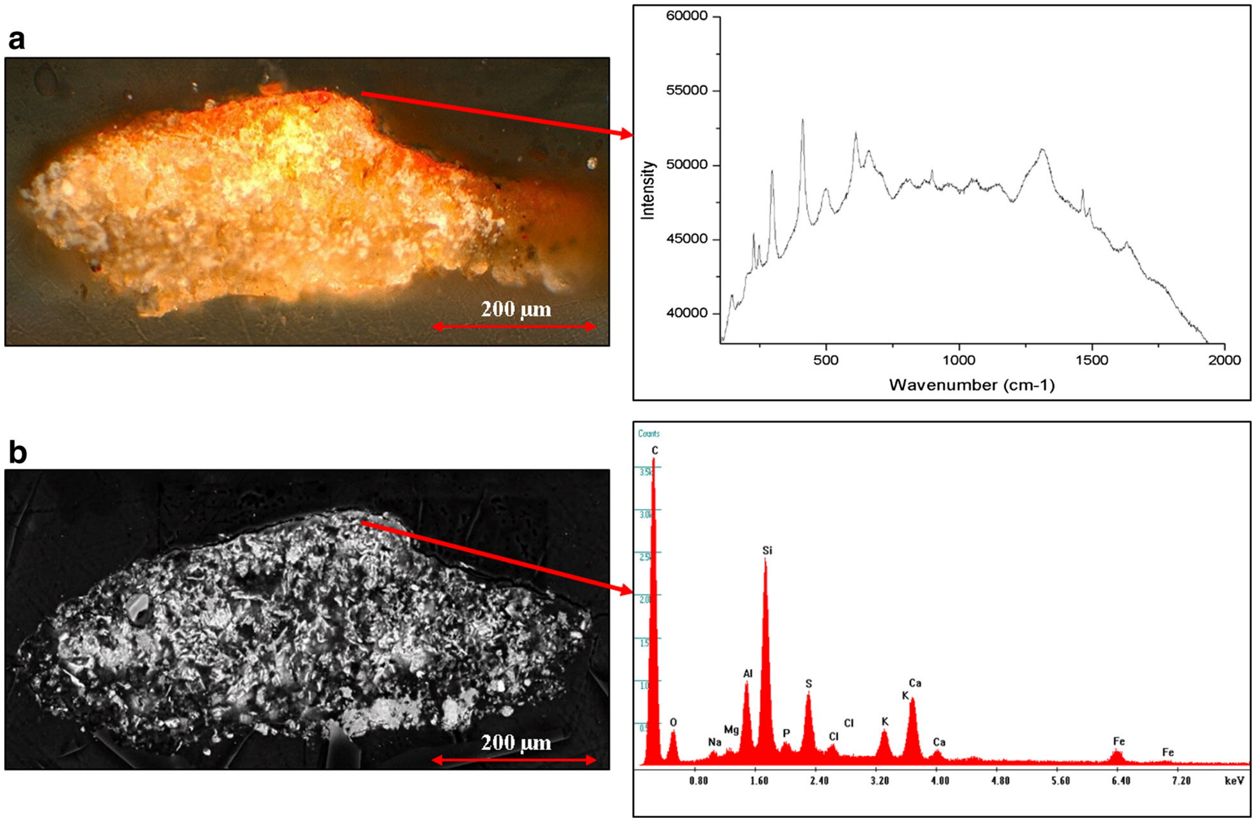

Fig. 3. Analysis of the red sample cross section with a) micro-Raman spectroscopy and b) SEM-EDS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Carbon and oxalate layers

The identification of carbon and oxalate layers in stratigraphy samples of rock art is important not only to the analytical characterization of the materials involved on painting and the study of deterioration mechanisms but also to study the relative history and chronology of the different events recorded on the walls and complement the dating data available from the archaeological excavations. On one hand, the carbon layers founded do not represent black pigmented strata but events of bonfires into the cave. It could be used as an absolute indicative of time in case it can be directly dated by some C^{14} technique or precisely correlated with C^{14} dating results obtained from carbon material found in the archaeological excavation. On the other hand, the oxalate strata result useful as an indirect indicator of the pass of time. Therefore, layers composed by only great amounts of whewellite might point out the course of a long period of time between the subjacent layer (or event) and the layer (or event) located over the oxalate stratum. Therefore, results to a great analytical challenge, the characterization of carbonaceous layers. More specifically the differentiation of carbon-based painting layers from the bonfire events performed on the cave.

The first attempt to overcome this issue emerges from the morphological differences between both layers. While the black painting layer stratum was applied by humans with its available technology, the bonfire event should made a thin and homogeneous deposition on the rock. Assuming that, it must expected more heterogeneous (presence of pigment and binding media) and thick strata from pictorial layers than the ones produced by the carbonization depositions. In Fig. 5 are compared two samples, while Fig. 5-a was taken from a black paint motif, the Fig. 5-b belonged to a surface over a bonfire zone. It can be clearly appreciated the great differences between them. On the one side, the painting layer is much thicker than the bonfire. Measurements using the optical microscope give an average dimension of 26.7 μm and 8.1 μm for painting layers and carbonization depositions, respectively. In addition, the strata that correspond to a carbon-based pigment are quite heterogeneous, with the presence of some particles of SiO_2 while, in the case of carbon deposits, the layers are not only very homogeneous but have a deeper black color, also, it seems like the layer was adhered directly to the rock surface. These analyses under the microscope are important because give proofs that the strata can be morphologically differentiated without the use of chemical analysis, only considering the way how was applied.

Once the step to determine the nature of the layer was performed, the next one consisted on the properly chemical identification. To precisely delimit the number of carbon deposition or other useful organic layer, the first chemical approach consisted on taking micrographs with SEM but using the backscatter electron detector. This allowed us to obtain chemical contrast images where the brightest colors indicate high atomic weight while, the darkest ones, low atomic weight. In Fig. 6-a is appreciated a micrograph analyzed with SEM-BSD. The sample was taken from a zone of the cave where the archaeological excavation indicated the presence of more than one bonfire event. It can be seen there are two clearly low molecular weight strata (point out with red arrows). On the other side, in Fig. 6-b is shown a micrograph of the same sample took with an optical microscope in order to compare both images. As a result, the black strata in the Fig. 6-b corresponds exactly with the dark ones present in Fig. 6-a. Therefore, it gives important but not conclusive information to characterize them, being necessary an alternative to complement unequivocally the results obtained. At this point naturally emerge as a complementary technique the Raman micro-spectroscopy. In Fig. 7 can be seen the Raman spectra of four different layers of the sample studied by SEM-BSD in Fig. 6. The most superficial layer corresponds to a calcium oxalate (whewellite) layer follows by a carbon layer (Fig. 7). The subsequent pair of layers repeat the sequence of whewellite and carbon, respectively. The Raman shifts of the graphitic band was 1595 cm^{-1} while for the crystalline band

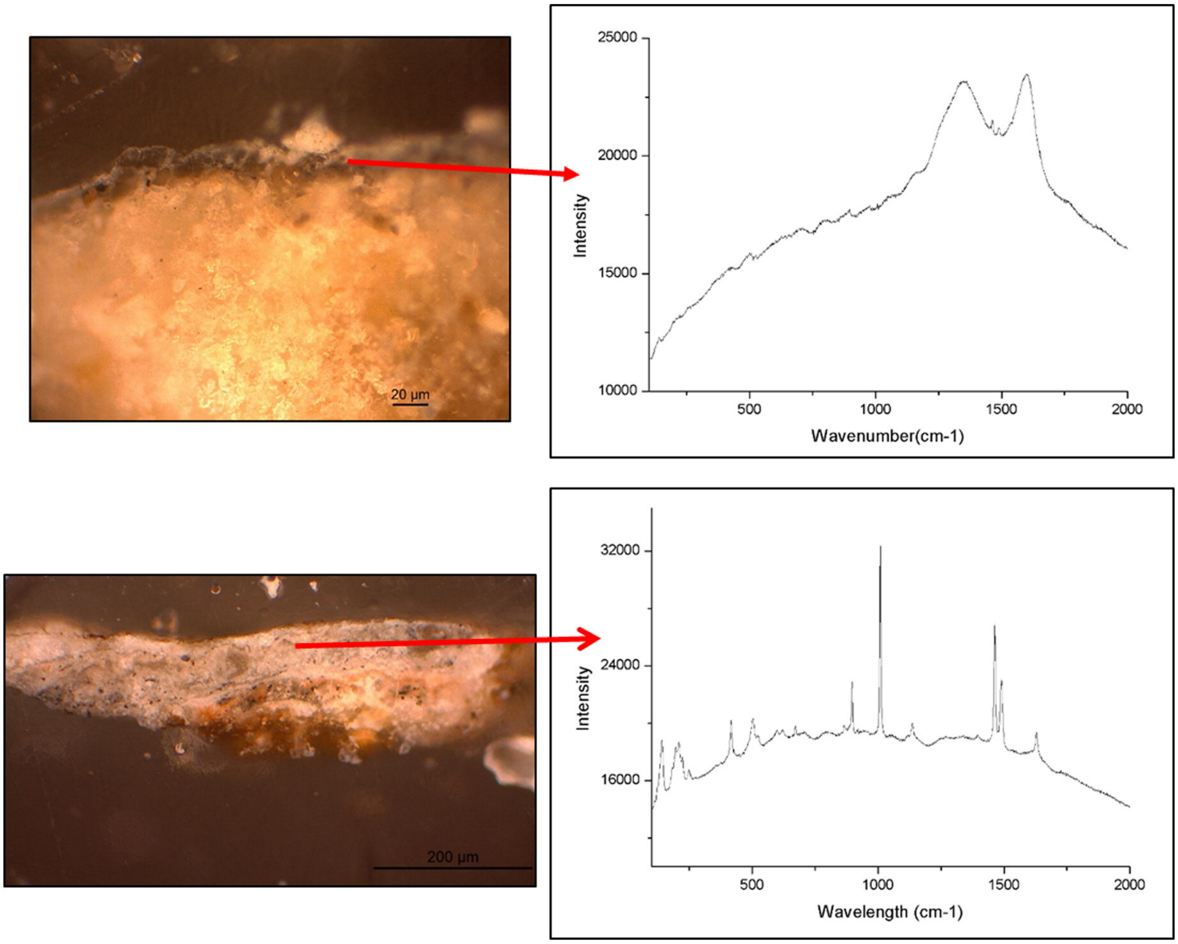

Fig. 4. Analysis of the a) black sample and b) white sample using micro-Raman spectroscopy. Magnification 200×.

was 1340 cm^{-1}. The corresponding FWHM were 92.5 cm^{-1} and 175 cm^{-1} for the graphitic and crystalline bands, respectively. The Raman shifts are also in agreement with the presence of graphite considering the aforementioned classification but the FWHM also fails at least for the crystalline band. Therefore, we also characterize the main component in the black layers as an amorphous carbon [34]. This points out the presence of two bonfire events with the presence of a quite thick oxalate layer between them which can be related to a great lag of time between the events.

Additionally, these results were contrasted with the information of the archaeological excavations where the zone showed two horizontal strata with carbonization rests strongly related to bonfire events. It clearly shows not only a novel methodology to find and qualify carbonization strata in painting samples but also to collect complementary information for archaeological purposes.

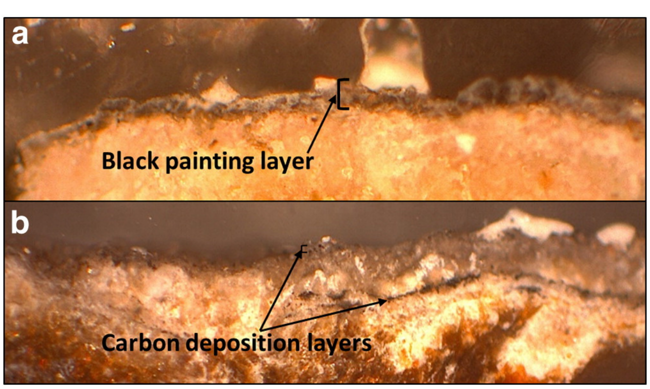

Fig. 5. Comparison between two cross sections. a) Black painting layer and b) carbon deposition layer. Pictures took with a magnification of 200×.

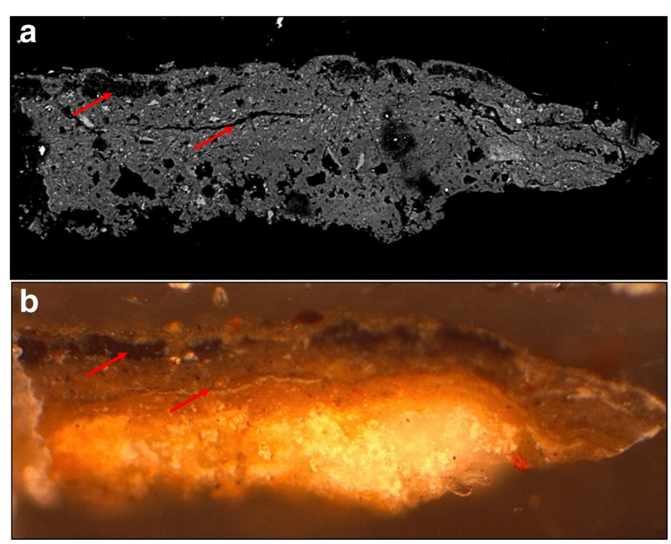

Fig. 6. Pictures of a sample taken from a zone where bonfires were documented by archaeological excavations. a) Picture taken with a SEM-BSD and b) optical microscope.

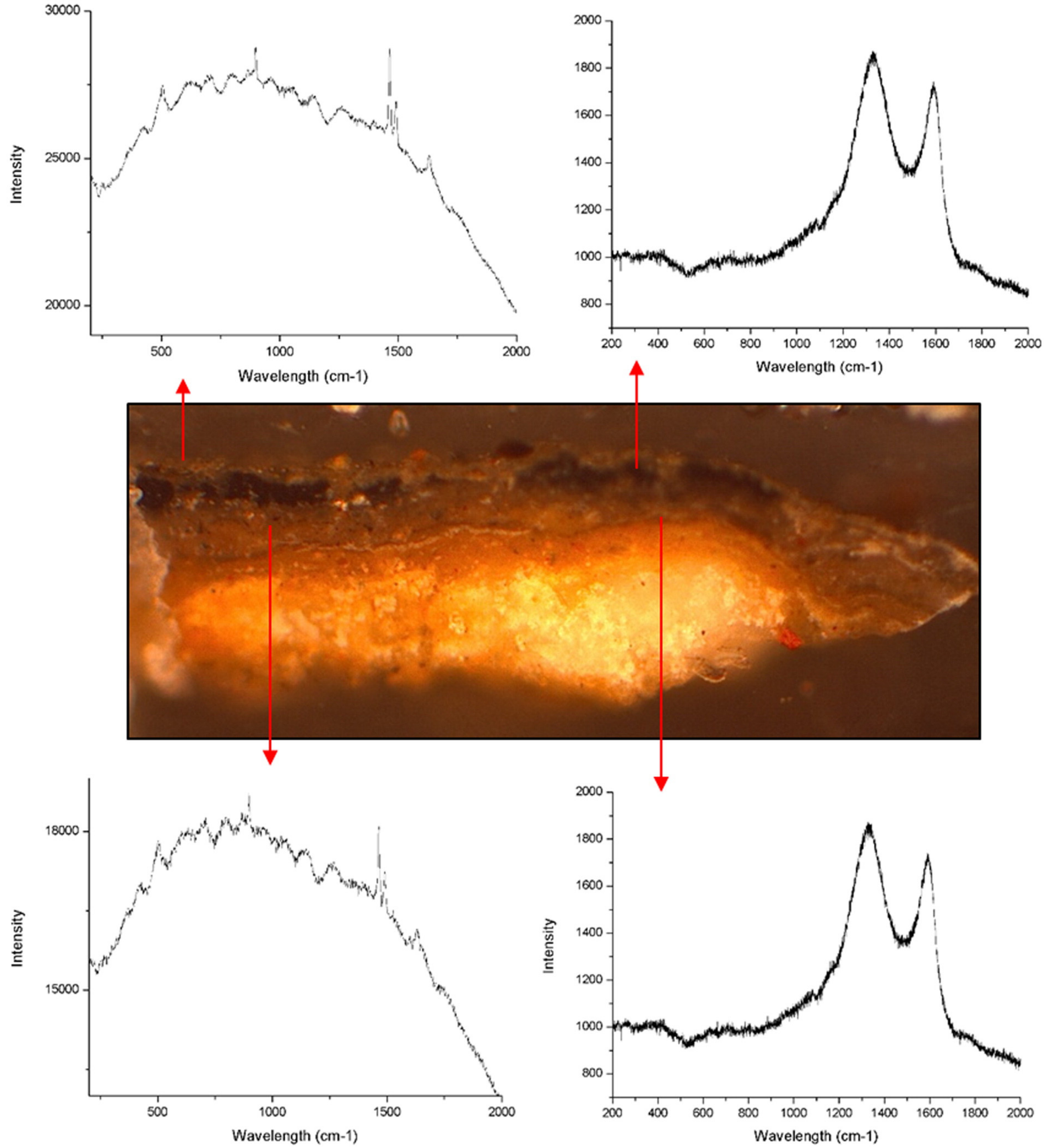

Fig. 7. Scheme where can be observed the chemical composition using micro-Raman spectroscopy for the different strata. Picture taken with a magnification of 200×.

4. Conclusions

By using complementary analytical techniques this study has helped to determine the three color types used in Oyola's cave paintings. Gypsum was identified as the main component of the white pigment. Hematite has been shown to be responsible for the red colorations. It also was elucidated from SEM-EDS that hematite was applied together with clay and small quantities of other minerals. Despite the presence of carbon based painting layers and carbon deposition, the nature of the layers were differentiated based on morphological studies. Raman results show the presence of graphite as a main pigment.

Additionally, a methodology to identify carbon depositions was developed. It includes the morphological analysis by optical microcopy, follows by a precise localization by means of SEM-BSD to finally characterize the nature of the stratum by micro-Raman spectroscopy. It must be highlighted the important implications of this methodology in archaeology because it allows, not only perform relative dating, but also valuable absolute dating information-in case of C^{14} dating measurements are obtained in order to supplement the results. More important is that this approach can be easily complemented with archaeological excavations in order to obtain a holistic view of the history of practices done at the cave.

Acknowledgements

Research was funded by Fondo Nacional de las Artes 2014, CONICET, ANPCyT (PICT-2012-0886), Ministry of Culture of Argentina, the Universidad Nacional de San Martin and the Universidad Nacional de Catamarca grants EA 27957535 and EA 23243440.

References

[1] A. Gramajo, H.M. Moreno, Otros Aportes al Arte Rupestre del Este Catamarqueño, Antiquitas (1978) 26–27.
[2] A. Gramajo, H.M. Moreno, Posibles influencias incaicas en Santiago del Estero, Ser. Estud. 3 (1982) 35–59.
[3] I. Gordillo, M. Baldini, M.F. Kusch, Entre objetos, rocas y cuevas: significados y relaciones entre la iconografía rupestre y mobiliar de Aguada, in: M. Podesta, M. de Hoyos (Eds.),Arte En Las Rocas Arte Rupestre, Menhires Y Piedras Color. En Argentina 2000, pp. 101–111.
[4] M. Quesada, L. Gheco, Tiempos, cuevas y pinturas. reflexiones sobre la policronía del arte rupestre de oyola (provincia de catamarca, argentina), Relac. La Soc. Argentina Antropol. (2015) 455–476.
[5] H.G.M. Edwards, L. Drummond, J. Russ, Fourier-transform Raman spectroscopic study of pigments in native American Indian rock art: Seminole canyon, Spectrochim. Acta Part A. 54 (1998) 1849–1856.
[6] H.G.M. Edwards, E.M. Newton, J. Russ, Raman spectroscopic analysis of pigments and substrata in prehistoric rock art, J. Mol. Struct. 550-551 (2000) 245–256.
[7] L.C. Prinsloo, B. Werner, I. Maikklejohn, K. Hall, The first Raman spectroscopic study of San rock art in the Ukhahlamba Drakensberg Park, South Africa, J. Raman Spectrosc. 38 (2007) 1538–1553, http://dx.doi.org/10.1002/jrs.
[8] M. Iriarte, A. Hernanz, J.F. Ruiz-Lopez, S. Martin, Raman spectroscopy of prehistoric paintings from the Abrigo Remacha rock shelter (Villaseca, Segovia, Spain), J. Raman Spectrosc. 44 (2013) 1557–1562, http://dx.doi.org/10.1002/jrs.4367.
[9] A. Hunt, P. Thomas, D. James, B. David, J. Geneste, J. Delannoy, B. Stuart, The characterisation of pigments used in X-ray rock art at Dalakngalarr 1, central-western Arnhem Land, Microchem. J. 126 (2016) 524–529.
[10] A. Bonneau, D.G. Pearce, A.M. Pollard, A multi-technique characterization and provenance study of the pigments used in San rock art, South Africa, 39 (2012). doi: http://dx.doi.org/10.1016/j.jas.2011.09.011.
[11] D. Bikiaris, S. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies : application on wall paintings at Meteora and Mount Athos, Greece, Spectrochim. Acta Part A. 56 (1999) 3–18.
[12] L.C. Prinsloo, A. Tournié, P. Colomban, C. Paris, S.T. Bassett, In Search of the Optimum Raman/IR Signatures of Potential Ingredients Used in San/Bushman Rock Art Paint, 402013.
[13] C. Lofrumento, M. Ricci, L. Bachechi, D. Feo, E. Mario, The first spectroscopic analysis of Ethiopian prehistoric rock painting, J. Raman Spectrosc. (2011), http://dx.doi.org/10.1002/jrs.3096.
[14] B. Prieto, M.R.D. Seaward, H.G.M. Edwards, T. Rivas, B. Silva, An Fourier transform-Raman spectroscopic study of gypsum neoformation by lichens growing on granitic rocks, Spectrochim. Acta Part A. 55 (1999) 211–217.
[15] A. Zoppi, C. Lofrumento, E.M. Castellucci, M.G. Migliorini, The Raman spectrum of hematite: possible indicator for a compositional or firing distinction among terra sigillata wares, Ann. Chim. 95 (2005).
[16] A. Hernanz, M. Mas, B. Gavilán, B. Hernández, Raman microscopy and IR spectroscopy of prehistoric paintings from Los Murciélagos cave (Zuheros, Córdoba, Spain), J. Raman Spectrosc. 37 (2006) 492–497, http://dx.doi.org/10.1002/jrs.1422.
[17] A. Hernanz, J.M. Gavira-Vallejo, J.F. Ruiz-López, Introduction to Raman microscopy of prehistoric rock paintings from the Sierra de las Cuerdas, Cuenca, Spain, J. Raman Spectrosc. 37 (2006) 1054–1062, http://dx.doi.org/10.1002/jrs.1588.
[18] M. Hyman, S.A. Turpin, M.E. Zolensky, Pigment analyses from Panther Cave, Texas, Rock Art Res. 13 (1996) 93–103, http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=169091 (accessed March 16, 2016).
[19] D.A. Scott, W.D. Hyder, A study of some Californian Indian rock art pigments, Stud. Conserv. (2013), http://dx.doi.org/10.1179/sic.1993.38.3.155.
[20] A.L. Watchman, Age and composition of oxalate-rich crusts in the Northern Territory, Australia, Stud. Conserv. 36 (1991) 24–32, http://dx.doi.org/10.1179/sic.1991.36.1.24.
[21] A. Watchman, Evidence of a 25,000-year-old pictograph in Northern Australia, Geoarchaeology 8 (1993) 465–473, http://dx.doi.org/10.1002/gea.3340080603.
[22] N.C. Rusself, Calcium oxalate in lichen biodeterioration FT-Raman spectroscopy 53 (1997) 99–105.
[23] J. Russ, W.D. Kaluarachchi, L. Drummond, H.G.M. Edwards, The nature of a whewellite-rich rock crust associated with pictographs in Southwestern Texas, Stud. Conserv. 44 (2015) 91–103, http://dx.doi.org/10.2307/1506721.
[24] L.C. Prinsloo, Rock hyraces: a cause of San rock art deterioration? J. Raman Spectrosc. 38 (2007) 496–503, http://dx.doi.org/10.1002/jrs.1671.
[25] R.E.M. Hedges, C.B. Ramsey, G.J.V.A.N. Klinken, C. Nielsen, A. Etchegoyen, J.D.F. Niello, M.T. Boschin, A.M. Llamazares, C. Rock, A. Sites, Methodological issues in the 14C dating of rock paintings, Proc. 16th Int. 14C Conf. 1998, pp. 35–44.
[26] J.F. Ruiz, A. Hernanz, R. Ann, M.W. Rowe, R. Viñas, J.M. Gavira-vallejo, A. Rubio, Calcium oxalate AMS 14C dating and chronology of post-Palaeolithic rock paintings in the Iberian Peninsula. Two dates from Abrigo de los Oculados, J. Archaeol. Sci. 39 (2012) 2655–2667, http://dx.doi.org/10.1016/j.jas.2012.02.038.
[27] F. Marte, N. Mastrangelo, M. Tascon, The art of measuring: optical microscopy applied to the measurement of transversal sections, EADEM UTRAQUE Eur. 13 (2011) 257–268.
[28] F. Marte, M. Tascón, N. Mastrangelo, The art of measuring II: challenges in measuring particles in cross-sections, EADEM UTRAQUE Eur. 14 (2013) 245–254.
[29] D.L.A. de Faria, S. Silva Venancio, M.T. de Oliveira, Raman microspectroscopy of some iron oxides and oxyhydroxides, J. Raman Spectrosc. 28 (1997) 873–878.
[30] D. Bersani, P.P. Lottici, A. Montenero, Micro-Raman investigation of iron oxide films and powders produced by sol–gel syntheses, J. Raman Spectrosc. 30 (1999) 355–360.
[31] A. Zoppi, C. Lofrumento, E.M. Castellucci, P. Sciau, Al-for-Fe substitution in hematite: the effect of low Al concentrations in the Raman spectrum of Fe_2O_3, J. Raman Spectrosc. 39 (2008) 40–46, http://dx.doi.org/10.1002/jrs.
[32] H.G.M. Edwards, E.M. Newton, S. O'Connor, D. Evans, FT-Raman spectroscopic analysis of pigments from an Augustinian friary, Anal. Bioanal. Chem. 397 (2010) 2685–2691, http://dx.doi.org/10.1007/s00216-010-3568-0.
[33] E.P. Tomasini, E.B. Halac, M. Reinoso, E.J. Di Liscia, M.S. Maier, Micro-Raman spectroscopy of carbon-based black pigments, J. Raman Spectrosc. 43 (2012) 1671–1675, http://dx.doi.org/10.1002/jrs.4159.
[34] O. Beyssac, B. Goffé, J.P. Petitet, E. Froigneux, M. Moreau, J.N. Rouzaud, On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 59 (2003) 2267–2276, http://dx.doi.org/10.1016/S1386-1425(03)00070-2.
[35] S. Potgieter-Vermaak, N. Maledi, N. Wagner, J.H.P. Van Heerden, R. Van Grieken, J.H. Potgieter, Raman spectroscopy for the analysis of coal: a review, J. Raman Spectrosc. 42 (2011) 123–129, http://dx.doi.org/10.1002/jrs.2636.