h4 PIGMENTS: FROM SCIENCE TO ART

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Evidence indicates that pigments have been used since the beginning of mankind. Therefore, the study of these materials can reveal the continuous relationship of societies with the environment or the technological skills of different groups. Their conservation is especially challenging.

In rock art, the origin of the material used is very diverse, including organic preparations, plant extracts and minerals. But while trying to characterize the pigment itself, we cannot forget the binding agents, the possible diluents and the contaminants resulting from the production, the application processes and/or decomposition.

In this section a non-limitative list of topics will be discussed, including:

Application of different techniques (e.g., FTIR, RAMAN, chromatography, SEM-EDS, XRF, XRD) in the material characterization:

- Study of degradation processes;
- Recent advances in in-situ analysis;
- Forensic applications in art and archaeology (e.g. forensic archaeology, authentications procedures);
- Studies about production, use, trade and provenance of the material;
- Other topics

The binders and the Paleolithic rock art

The use of organic binders in Paleolithic rock painting is a debated topic since its discovery. All paint requires a vehicle that binds pigment particles and facilitates their application. The binders conditionate the transformation of the color of the pigments and their conservation. However, various theories maintain that the use of organic materials as binders would have meant the almost total disappearance of the paintings due to the biological agents. Although the fat-based binders do not offer a good performance on wet surfaces, some researches on Paleolithic paintings have revealed the presence of traces of organic matter. These results led us to explore the possible use of these organic materials as binders for the pigments used, despite water probably being the most used binder due to its abundance. Consequently, we have designed a research plan based on the execution of empirical tests using the most common pigments used in Paleolithic rock art (iron oxide, charcoal, manganese, etc.) and their possible binders (animal fat, mainly marrow , beeswax or vegetable resins). Accordingly, we have been able to study their different combinations and responses when applying them on different supports.

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Keyword: rock art, Paleolithic paintings, painting techniques, binder, pigments

Integrating Science and Rock Art in the University Curriculum

This paper describes a course for university students in their third year of studying chemistry. A series of experiments and projects explores the science of pigments, rock art, and art conservation. Analytical techniques include powder X-ray diffraction (XRD), polarized light microscopy (crystal shape, pleochroism, Becke line, and isotropy), infrared spectroscopy (FT-IR), and liquid chromatography (LC-MS). For example, we heat natural goethite both in the laboratory and in an open wood fire. The conversion of goethite to hematite and other minerals is studied with XRD. In another experiment, natural dyes are extracted from plant materials and characterized by LC-MS. Student-initiated projects include the study of desert varnish, identification of fibers, degradation of pigments by light, and many others. Throughout the course, science is applied to understanding methods and technologies of past artists and conservation of their works. Primary literature is emphasized.

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Keyword: pigment, analysis, rock art, conservation, pedagogy

Fig. 1 - Polychrome Rock Art in Sedona, AZ, USA. (copyright Walter Bowyer)
Fig. 2 - Pigments and XRD. (copyright Walter Bowyer)

Pigment studies at shulgan-tash (Kapova) Cave with upper palaeolithic parietal art at the borderlands of the Russian plain

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Keyword: Shulgan-Tash (Kapova) Cave, camel, cave art, restoration, pigment analyses.

Since 2014, the Republic of Bashkortostan has been consistently implementing a program aimed at improving the state of preservation of the Shulgan-Tash (Kapova) Cave and providing better access to accurate information on the cave art. After two years of work, the restoration team, headed by Eudald Guillamet, removed more than 800 items of graffiti on an area of about 120 square meters enabling a new recording of the images in the cave. In the fall of 2017, the image of a camel was revealed from under calcite sediments. According to the preliminary data, one may assume that the camel image was made in one color, and the visual difference between the dark and light paint within that image is due to the state of preservation on the edges of the figure – the charcoal was washed down with water back in prehistoric times. The paint of the better-preserved central part of the image, as well as that of the geometric sign to the right, does contain the charcoal, which was recorded using infrared photography and microanalytic techniques.

Fig.1 - View through the entrance to the Kapova Cave. (photo A. Pakhunov, © Centre for Paleoart Studies, Institute of Archaeology Russian Academy of Sciences, 2017)

Pigment use in the early modern human records of Australasia

The Australasian region features prominently in recent research concerning when we evolved the artistic practices that unequivocally signal human behavioural modernity. Ground ochres are consistently among the earliest evidence for colonisation, including the initial peopling of the Australian mainland, the earliest end-point for human migration out of Africa. While in Indonesia some of the earliest rock art in the world is preserved. Here I will present the results of a variety of recent physiochemical characterisations that I have undertaken on some of the earliest circumstantial, and uncontested, evidence for the production of art in Australasia, including the sites of Madjedbebe and Nawarla Gabarnmung in Arnhem Land, northern Australia and Leang Bulu Bettue on the Indonesian Island of Sulawesi. I will showcase the value of a myriad of techniques including Scanning Electron Microscopy, portable X-Ray Fluorescence Spectrometry, and Synchrotron Powder Diffraction/X-Ray Florescence Microscopy.

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Keyword: Australasia, behavioural modernity, SEM, pXRF, Synchrotron PD, Shychrotron XFM

Reconstructing Pigment Technologies: Evidence for Harvesting and Thermal Alteration of Iron Oxide Producing Bacteria to Produce Pigment for Rock Art

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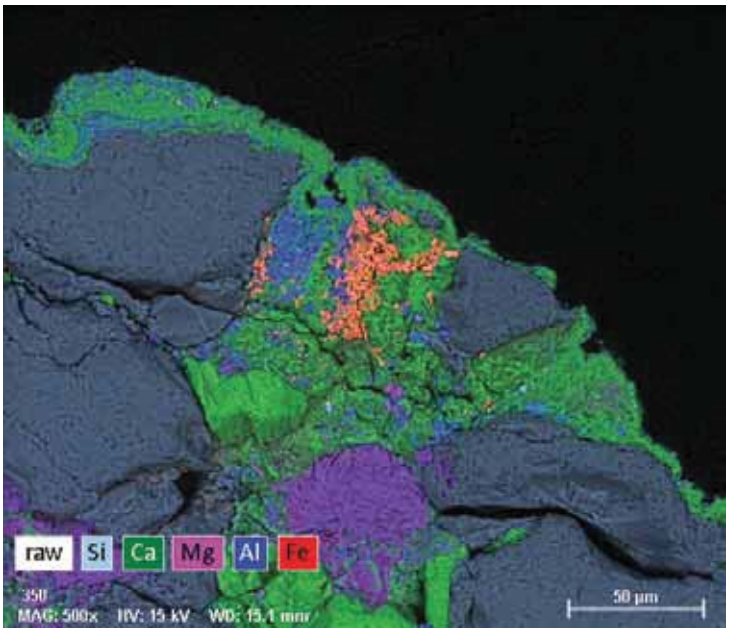
Keyword: ochre, pigment technology, rock art, microanalysis, pyrotechnology, human-mineral interaction

Pictographs are important archaeological locales that can provide insight into histories of mineral use and pigment preparation technologies. We present the results of a multi-method investigation of pigments used to produce rock art at Babine Lake, British Columbia (Canada). Examination by microanalytical techniques (SEM-EDS, TEM, FIB-SEM, FTIR, high-sensitivity magnetometry) revealed information pertaining to Fe-oxide source selection, the mineral depositional environment of the panels, and evidence for pigment enhancement by pyrotechnology. The pictographs at Babine Lake were painted on an outcrop of argillaceous limestone covered in a kaolinitic weathering deposit. This natural canvas, and subsequent accretionary deposition, has aided in the long-term preservation of the rock art panel. The red pigment is composed of a homogenized mixture of ferrihydrite and hematite that was biogenically produced ex situ by aquatic Fe-oxide producing bacteria, including Leptothrix ochracea. Results from high-sensitivity magnetometry and comparative analysis of fired Fe-oxide bacteria control samples also suggest that the pigments were thermally altered to induce Fe-oxide phase change to enhance colour properties. Our results demonstrate the potential of microanalytical applications in rock art studies, and have archaeological implications for pigment harvesting and source selection, preparation practices, and decision-making in the placement of rock art in British Columbia.



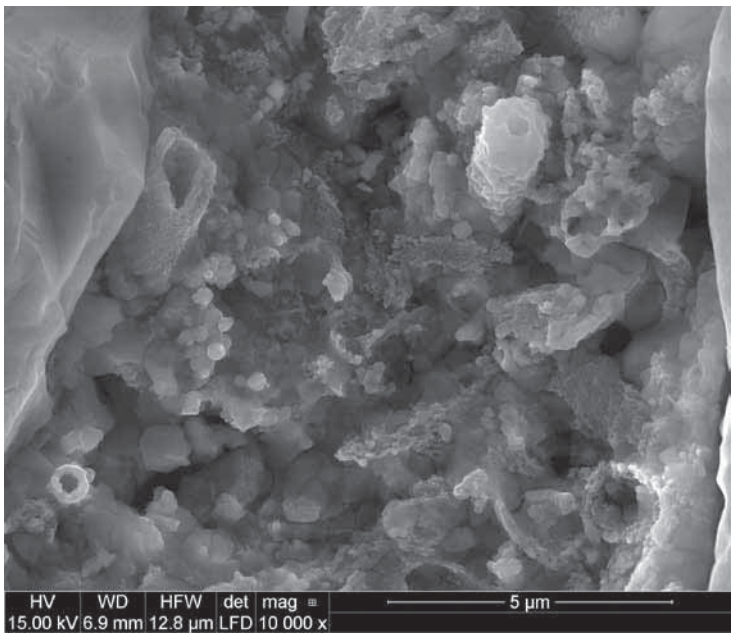


Fig.1 - SEM-EDS hyperspectral map showing distribution of paint particles, accretionary deposits, rock substrate, and associated elements.
Fig.2 - Secondary electron micrograph illustrating pulverized and thermally altered Leptothrix ochracea microfossils.

From pigments to histories: archaeometric analyses on late-Holocene rock paintings from North-Central Chile

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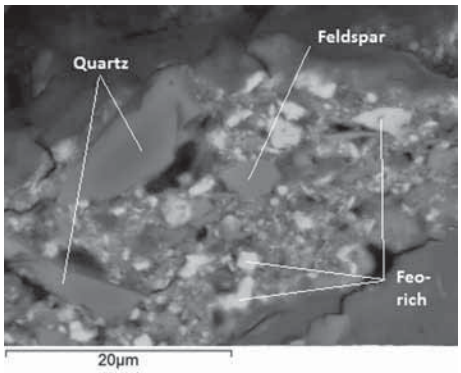
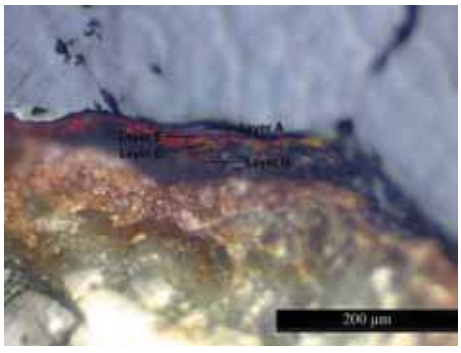
Keyword: pigments, archaeometry, rock art, practices, histories

Rock art is the result of historically situated social practices unfolded through its production and use. Taking this into account, we argue that an understanding of the components and manufacture processes of rock paintings allow us to discuss how rock art production was enmeshed in a historical field of social practices, places, and substances. In this regard, our work discusses the potentiality of archaeometric analyses of paintings to understand the historical and social dynamics of the practices. Our research, funded by the FONDECYT project 1150776, focuses on rock paintings made by Late Holocene hunter-gatherers in North-Central of Chile (30° S). We analyzed micro-samples of red, black, yellow, and green paintings using Optical microscopy, Raman Spectroscopy, and Scanning Electron Microscopy equipped with an Energy Dispersive X-ray Spectroscopy system (SEM-EDS). The results revealed the different pigments used, as well as some binders and possible extenders. We argue that the identified components are related to diverse practices, with different spatial, material, and chronological expressions, and briefly discuss how they are participated in broader relational fields that gave rock art its social and cultural relevance. Our research reveals the potential of archaeometric analysis for understanding rock art production and consumption, and its material reality, as fundamentally historical and relational.





Riparo Cassataro in Centuripe (Sicily): noninvasive investigation of rock paintings

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Keyword: Riparo Cassataro, rock art in Sicily, Simeto Valley, MA-XRF scanning

Riparo Cassataro, Centuripe (Sicily), is about 400 meters from the Simeto River and close to one of the rocky peaks in the area. Riparo Cassataro is mainly known for its rock paintings, the only site known in Eastern Sicily.

The paintings are on the western side of a boulder that, together with two others, form part of a cavity open on three sides (Figure 1). The cavity is accessed from an opening on the western side, where the prehistoric figures are drawn. Inside the shelter, spread on top of a smooth horizontal surface, around twenty cup marks are also found.

The pictorial complex (Figure 2) is in a good state of conservation and is characterized by figures drawn in red, realized with a rudimentary brush. The pigment was probably derived from nodules of iron oxide common in the area. In order to characterize the pigments, the combined use of different analytical techniques was carried out in situ. Portable PIXE and XRD devices were used to determining the elemental and mineralogical composition of the paintings.

Fig.1 - Riparo Cassataro, Centuripe, Enna, rock paintings. (photo Giacomo Biondi)
Fig.2 - Riparo Cassataro, Centuripe, Enna. (relief Giacomo Biondi)

Unfolding the Prehistoric World: Portable and Benchtop Raman Spectroscopy for the Analysis of Rock Art

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Keyword: Raman Spectroscopy, pigments, weathering products, rock art, mobile and benchtop instrumentation

Raman spectroscopy is considered one of the most powerful techniques in the field of non-destructive analysis of artworks. One of its numerous advantages is that its application is non-invasive, yielding exceptional results without jeopardizing the artefacts. In prehistoric rock painting analysis, Raman spectroscopy can be used in the laboratory or in the field for characterizing pigments (mostly different haematitic compositions, natural green and yellow pigments, gypsum, manganese oxides, carbon or bone black, etc.) as well as causes of deterioration and the substrata. Its contribution for rock art documentation is twofold: identification of the "palette" used by indigenous people and investigating weathering processes that affect these magnificent works of art. The latter being quite significant as most rock art is at risk from both natural processes and human activity.

The use of Raman spectroscopy on the investigation of prehistoric rock art paintings will be illustrated through several examples of rock art found internationally. Its use as a guide technique will be discussed as the results can be utilized in a decision-making process regarding the employment of other techniques (e.g. radiocarbon dating).

Acknowledgements: this work has been financially supported by FWO (project K204416N-Travel Grant for a short stay abroad) and a Concerted Research Action (GOA) of Ghent University.

From rock art to science: elemental and molecular analysis of paintings from Taltal locality, Atacama Desert Coast (northern Chile)

The rock art from Taltal, on the Atacama Desert coast in northern Chile, stands out for its references to a coastal imaginary, where hunting scenes of different marine animals and fishes prevails, accompanied in a lower degree by camelids, anthropomorphs, and others terrestrial mammals. These scenes have been studied mainly from a motif and stylistic approaches. Therefore, in this communication we present an elemental and molecular physiochemical study (Microscopy, SEM-EDX, RAMAN) of multiples samples from El Médano site, located in the upper part of the coastal mountain (600-1300 masl), in addition to several small rock shelters located along the coastline. Between the different sites we have identified a high mixture variability. Nevertheless, the paintings location, beside the sea and in unceasing contact with the coastal fog, facilitated the formation of dense salt layers, damaging their preservation. These conservation aspects should be considered with caution, and have become a methodological challenge for the analytical process and interpretations. Our research finally allows us to ponder and discuss the management of specific knowledge and possible pigments recipes in the rock art technologies developed by the coastal people of the Atacama Desert before European contact (XVI c.).

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Keyword: rock art painting technology, pigments, microscopy, SEM-EDX, RAMAN

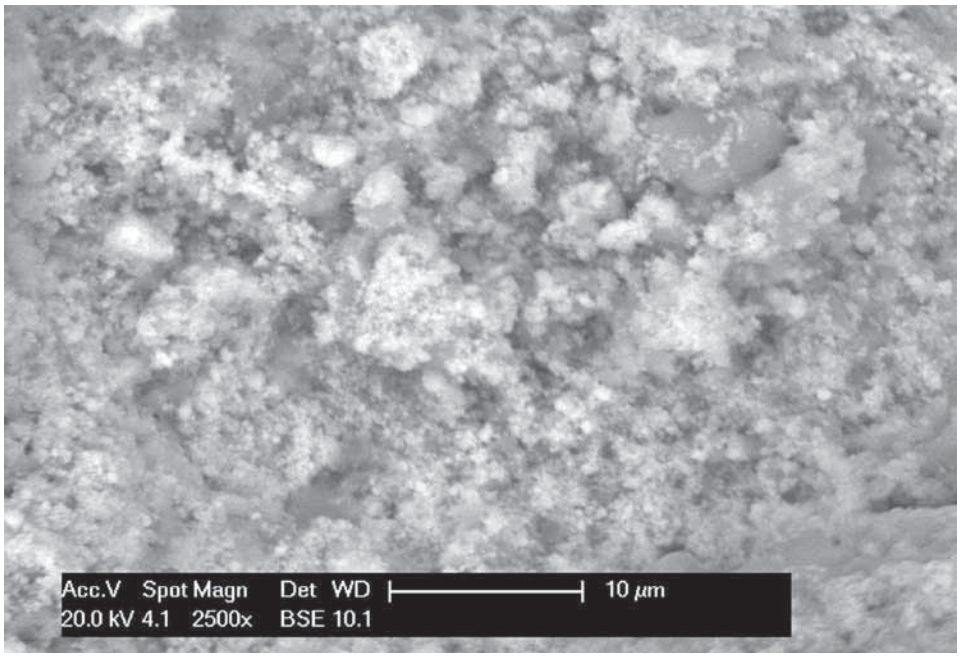

Fig.1 - One of the motifs from El Médano site, Taltal, Northern Chile. (photo Francisco Gallardo)
Fig.2 - Elemental images by SEM-EDX. (photo Marcela Sepúlveda at C2RMF laboratory)

The pigments of rock paintings in Colombia

Since 2008, different studies have been carried out on the pigments of Colombian rock art. For this purpose, different analytical techniques have been used in the identification and characterization of the possible raw materials, their treatments, recipes and visual manifestations after they have been applied. In this presentation, the analysis protocols used in three different zones of rock paintings will be shown to compare their results, advantages and disadvantages. Evidence of the heating of clay minerals was found in Soacha through the use of Infrared Spectroscopy, in Facatativa some experimental practices were performed to try to reproduce the heating processes of the pigments and were analyzed with the help of Raman spectroscopy. In the case of Guaviare, the geochemical analysis of XRF and electron microprobe revealed that the pigments are composed of iron oxides (red pigments) and oxides and hydroxides of titanium, phosphorus and other siliceous aggregates (white pigments). Raman analysis confirmed that red pigments are composed predominantly of hematite and white anatase pigments.

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Keyword: pigments, Colombia, infrared spectroscopy, Raman spectroscopy, X-ray fluorescence, electron microprobe

Fig.1 - The analysis of elemental composition of pigments with X Ray Fluorescence Portable, Serrania La Lindosa Colombia. (photo Gipri)
Fig.2 - Possible row material of rock painting pigments in Serrania La Lindosa Colombia. (photo Gegema)

A diachronic analysis of ochre-related behaviour throughout the Upper Palaeolithic at Hohle Fels Cave, Germany

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Keyword: red ochre, pigments, symbolic behaviour, Upper Palaeolithic, archaeometry

In this paper, we explore the use of red ochre at Hohle Fels cave in southwestern Germany. Here, the ca. 3-metre-deep stratigraphic sequence spans several millennia from the earliest onset of the Aurignacian (32-40ka BP) to the Holocene (ca. 11ka). Nodules of red and yellow ochre materials, some with evidence of anthropogenic modification, were recovered from most archaeological layers and present a unique opportunity to observe diachronic changes in ochre-related behaviors at the site. The ochre pieces were classified by various qualitative criteria, including color, size, and streak, and visual assessment indicates clear changes through time in patterns of source exploitation and utilization, especially between the Aurignacian and Gravettian (27-32ka BP) time periods. Numerous other artefacts with ochre residues, such as bones, shells, teeth, and limestone fragments provide evidence for continued interactions with ochre at the site. In order to address questions of source selection, 193 ochre pieces were elementally characterised by neutron activation analysis (NAA). The use of compositional analyses allows us to explore continuity and change in mineral acquisition strategies. Furthermore, the combined use of qualitative and quantitative methodologies provides an overview of the range of ochre behaviours and how these changed over time.