Article

Study of micro-samples from the open-air rock art site of Cueva de la Vieja (Alpera, Albacete, Spain) for assessing the performance of a desalination treatment

Ilaria Costantini , Julene Aramendia , Nagore Prieto-Taboada , Gorka Arana , Juan Manuel Madariaga * ,
Juan Francisco Ruiz

Posted Date: 4 July 2023

doi: 10.20944/preprints202307.0126.v1

Keywords: Levantine rock art, μ-Raman spectroscopy, μ-EDXRF, XRD, sulfates, biodeterioration

Article

Study of Micro-Samples from the Open-Air Rock Art Site of Cueva de la Vieja (Alpera, Albacete, Spain) for Assessing the Performance of a Desalination Treatment

Ilaria Costantini [1], Julene Aramendia [1], Nagore Prieto-Taboada [1], Gorka Arana [1], Juan Manuel Madariaga [1] and Juan Francisco Ruiz [2]

[1] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Spain.
[2] Department of History, Area of Prehistory, Faculty of Education Sciences and Humanities, University of Castilla-La Mancha (UCLM), Avda. de los Alfares 42, 16002 Cuenca, Spain
* Correspondence: e-mail@e-mail.com; Tel.: (optional; include country code; if there are multiple corresponding authors, add author initials) +xx-xxxx-xxx-xxxx (F.L.)

Abstract: In this work, some micro-samples belonging to the open-air rock art site of *Cueva de la Vieja* (Alpera, Albacete, Spain) were analysed. These samples were collected after and before a desalination treatment carried out with the aim of removing a whitish layer of concretion that affected the painted panel. The diagnostic study was performed to study the conservation state of the panel and then to confirm the effectiveness of treatment. Micro energy dispersive X-ray fluorescence spectrometry, Raman spectroscopy and X-ray diffraction were employed for the characterization of the degradation product as well as that of mineral substrate and pigments. The micro-samples analysis demonstrated that the painted layer was settled on a dolomitic limestone with silicon aggregates and aluminosilicates as well as iron oxides. The whitish crust was composed by sulfate compounds like gypsum ($CaSO_4{\cdot}2H_2O$) with minor amount of epsomite ($MgSO_4.7H_2O$). An extensive phenomenon of biological activity was demonstrated since, in almost all the samples analysed, the presence of calcium oxalates monohydrate ($CaC_2O_4H_2O$) and dehydrate ($CaC_2O_42H_2O$) were found. Probably the presence of both calcium oxalates had favoured the conservation of pictographs. In addition, some carotenoids pigments, scytonemin ($C_{36}H_{20}N_2O_4$) and astaxanthin ($C_{40}H_{52}O_4$) were characterized both by Raman spectroscopy and by X-ray diffraction. Hematite was found as a pigment voluntarily used for the painting of the panels used in mix with hydroxyapatite and amorphous carbon. The results of the analyses of the samples taken after the cleaning treatment confirmed a substantial decrease in sulphate patina on the panel surface

Keywords: Levantine rock art; μ-Raman spectroscopy; μ-EDXRF; XRD; sulfates; biodeterioration

1. Introduction

Several examples of rupestrian art that include paintings and engraving are surprisingly preserved at present from their production. The first evidence of rock art known to this day have been recently dated with a minimum age of 45.500 ka, from Leang Tedongnge (Sulawesi Island, Indonesia), based on Uranium-series isotope analysis, conducted on two small coralloid speleothems overlying the red painting. Prior to this discovery the first representation created was at least 43,900 years ago from image from Leang Bulu' Sipong 4 in the limestone karsts of Maros-Pangkep, (South Sulawesi, Indonesia) [1].

Thus, the main discoveries in terms of cave paintings occurred in South Africa [2], Argentina [3], Peru [4], Southeast Asia [5,6], Australia [7] etc. while in Europe the most important findings were found in France and Spain, belonging to the transition period between the Paleolithic and the Neolithic.

Normally, this kind of art expressions were carried out in closed spaces, caves, or rock shelters, cavities dug by atmospheric agents where the populations could find shelter. These spaces suffer a constant environmental impact, making prehistoric artwork particularly fragile. This is why they need constant monitoring to preserve them for many years to come. In this way, our research group developed a long-term monitoring methodology to better understand the conservation dynamics of rock art and their evolution over time based on the use of both non-destructive elementary and molecular spectroscopies [8].

The multi-analytical approach has been widely employed, in the last twenty years for the diagnostic study of the conservation state of caves and rock shelters where prehistoric art were realized [9]. They have proven to be fundamental for the study of the composition of raw materials as well as the study of painting technologies [10,11]. The palette of pigments employed was quite reduced being essentially composed of mineral based-pigment obtained from the natural resources of the surrounding areas [12]. Although in most cases the pigments could be used pure, bi-colour pictograph could be obtained like in the case of the mixture of hematite and paracoquimbite ($Fe_2(SO_4)_3.9H_2O$), this last discovered for the first time in the Abrigo Remacha rock shelter (Villaseca, Segovia, Spain) [13].

In addition, since these materials are exposed to the open-air, several forms of alteration, in form of discolorations, crusts and patinas, mainly due to the impact of weathering, were characterized thank to the use of portable and laboratory analysis. As reported by Hernanz et al. a crust composed of whewellite, gypsum, calcite, clay, dolomite, α-quartz, anatase, and hematite was detected in several rock art sites in Iberian Peninsula. Wind-blown dust and surface water runoff may also have contributed to the formation of these layers [14]. In this sense, gypsum and clayish minerals were characterized as the main components of an ochre-coloured accretion covering several parts of the third painted panel of the Hoz de Vicente rock shelter (Minglanilla, Cuenca, Spain) and the responsible of a flaking process observed in some areas of the painting panel [15].

In the open-air site of the engraved rock art of the Burrup Peninsula (Western Australia) high concentrations of acidic and nitrate-rich pollution, from nearby industrial complexes, provoked the colour change of the pictographs. The degradation phenomenon was due to the dissolution of manganese oxide (MnO_2) and iron compounds such us magnetite minerals triggered by acidic rain. This alteration induced the peeling of the rock varnish layer and produced hematite minerals, illite $(K, H_3O)(Al, Mg, Fe)_2 (Si, Al)_4O_{10}[(OH)_2,(H_2O)]$ and kaolinite $[Al_2Si_2O_5(OH)_4]$ [7].

The study of Pozo-Antonio et al. [16] also reported the process of colour change of rock art on a granitic outcrop at the Mougas site of Galicia (Spain). Here the colour change phenomenon occurs on yellow and red nodes on the surface of the rock art. High temperatures provoked by wildfires cause mineral transformations increased the susceptibility of the rock to weathering which lead to mineral transformation (of goethite into hematite) and fracturing. Although most of the degradation phenomena are caused by atmospheric agents, degradation processes caused by anthropic factors were discussed by Hernanz et al. [17] detecting the presence of electric welding splashes from the erection of protective iron fances around the rock art panels.

In addition gypsum and other salts such as jarosite, and bassanite as well as biofilms were identified in tafoni, generated by the weathering of sandstones (Cerro Colorado, Argentina). These secondary products were the result of impact weathering revealing hydroclastic and haloclastic processes. These activities formed active granular disintegration, flaking and chipping affected the preservation of some painted panels [18]. Another extensive no invasive study of Argentinean rock shelter paintings was carried out by Rousaki et al. [19]. In this study, gypsum and calcite were commonly found to be responsible of severe degradation in form of crusts on pigmented and as well as non-pigmented areas together with calcium oxalate patina. Most recently the work of Moh. M. [20] demonstrated that the discoloration of Leang Tedongnge (Sulawesi. Island, Indonesia) rock painting was caused by the presence of grey/yellowish crust composed mainly by gypsum. It was caused by the reaction between the calcium ions dissolved in karst water infiltrations with the sulphate ions of minerals deposited on the rock surface.

The presence of biological patinas in the form of calcium oxalate monohydrate (whewellite, $CaC_2O_4 \cdot H_2O$)) and dihydrate (weddellite [CaC_2O_4 (2+x) H_2O, $x \leq 0.5$]) have been frequently identified in rock shelters. They are generated by the interaction of oxalic acid, a metabolic products of microorganisms, with carbonaceous materials of the substrate [17]. Besides, oxalate layers have been used for attempting an indirect dating of post-Palaeolithic open-air paintings [21,22]. Although the presence of these compounds was mainly linked to microorganisms' activity, previous studies on Ethiopian prehistoric rock painting, showed that they can be the result of the degradation of organic matter, such as binder, employed to spread the pigments on the substrate [23]. On the other hand, the investigation of Hedges et al. [24] demonstrated the use pigmentation contain calcium oxalate derived from local cacti, and calcium carbonate derived probably from local plant ash. However, these hypotheses have not been entirely refuted and the origin of oxalate compounds on rock paintings is a current topic that is still being investigated.

In the investigation of Lower Pecos Region, in south-western Texas (USA), the colour change of the rock art was caused by the formation whewellite-rich rock crust with gypsum and clay [25]. In addition, the study demonstrated a palaeoclimate change, from dry to wet condition, of this area since the biopatina revealed similarities between whewellite microstructures and the desert lichen Aspicilia calcarea [26].

Therefore, due to the many factors that can degrade these extraordinary works of art, the study of original and secondary is essential in order to plan an appropriate restoration and conservation strategy. This work was focused on the study of the conservation state of the *Cueva de la Vieja* located near Alpera (Albacete, Spain). Indeed, the main evidences of rock art in the Iberian Peninsula come from the eastern part of the peninsula and they extend along the entire Mediterranean coast. They have been a UNESCO World Heritage Site since 1998 because the *Levantine* style represents a unique artistic expression in the European context. Levantine art is mainly composed of paintings realized in semi-open spaces like rocky shelters. It is characterized by a figurative art dominated by scenes of daily life and social activities such as individual or group hunting, dance, rituals etc. Levantine art is composed mainly of paintings and it was realized with red pigments, ochre and oxides of manganese and iron. However, it has also documented the use of charcoal from the organic origin (wood charcoal and burnt bone) as black pigments and white earths (α-quartz, anatase, muscovite and illite) and calcined bones (apatite) as white colours [17,27–29]. Numerous scientific studies have been carried out in the last 20 years with the aim of studying original compounds and degradation and to indicate the best conservation strategy [27,30–32].

This study is contextualised in an intervention aimed at recovering the visibility of the pictographs, realized in the rock shelter, which includes a diagnostic phase, subsequent followed by cleaning and consolidation interventions by specialized restorers. Finally, and a final phase that will produce a new digital tracing. Some samples were taken with the aim of studying the composition of support and the white patina that covered the paintings and which did not allow to appreciate their original appearance from a chromatic point of view. This first approach permitted to indicate the most adequate cleaning intervention that consisted of desalination of the panel. At the conclusion of the previous works, other samples were taken after the treatment to verify its effectiveness. In this work, the elemental and molecular analyses of all micro-samples were performed by means micro Raman spectroscopy, micro X-ray fluorescence and X-ray diffraction in laboratory.

2. Result and discussion

2.1. Sample Analysis Prior to Cleaning Treatment

Micro X-ray fluorescence analyses were performed to define the elemental composition of the samples. For this purpose, several elemental images were acquired (Figure 1) on the both sides of the sample CV01. Although the whitish patina was not appreciable at the naked eye on this sample, according to the restorers, the sulphur was homogeneously distributed throughout the sample exposed surface if compared to the inner face where only some areas showed the presence of the element. On the other hand, calcium maps showed the presence of this element distributed throughout the piece. The presence of magnesium stood out in the CV01 sample and was more evident on the inner face.

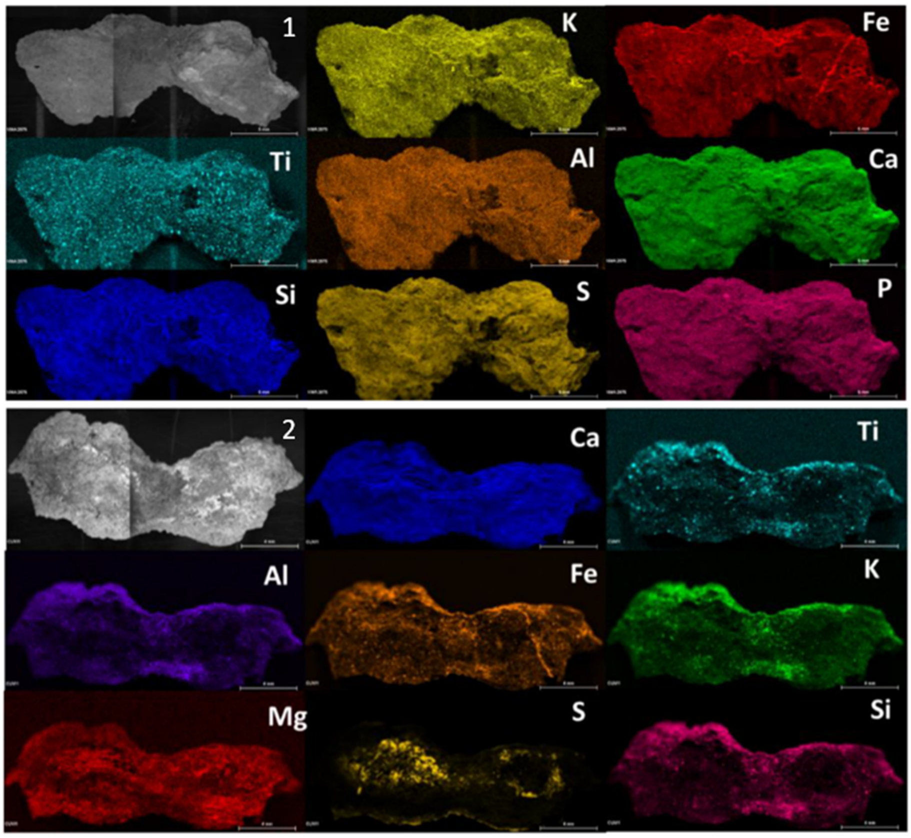

Figure 1. Micro-EDXRF maps of the exterior (1) and inner (2) layer of the sample CuVi01 respectively.

In all the micro-samples analysed, the presence of sulfur was less perceptible at the elemental level on the inner face, while calcium and silicon in less extent, were the major elements. The main composition of the samples coming from the rocky support was based on calcium, silicon, magnesium, aluminium, iron, potassium, titanium varying slightly in its relative presence. On the other hand, in some samples aggregates of titanium, zinc, chrome, manganese, copper and chlorine were evident corresponding to the composition of the support. In some samples, sulfur was observed also on the internal face mainly in the cracking zone of the samples (Figure S1 in supporting information) This suggested that the formation of sulfur compounds from the exterior part could be responsible for the phenomenon of exfoliation of the support described by restorers.

Regarding the only micro-sample that showed traces of visible red pigmentation (Figure 2) the elemental map of iron coincided with the red area suggesting the use of iron oxide for the painting. On the other hand, the elemental maps of this sample did not show a homogeneous layer of sulphur in the surface as indicated by the rock-bearing analysis and only some S hotspots were visible.

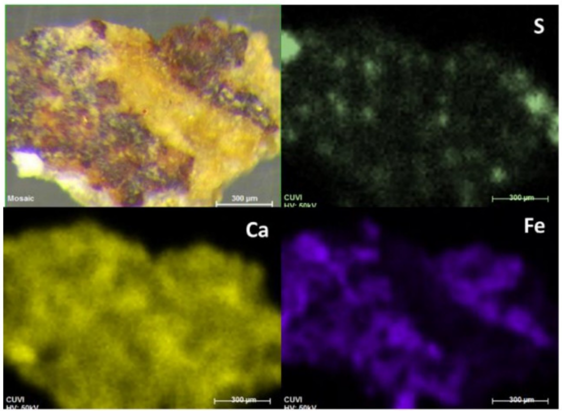

Figure 2. Micro-EDXRF maps of the sample whit trace of red pigment.

By means of Raman spectroscopy in the majority of the points analysed, on the external face of all samples, the presence of gypsum ($CaSO_4{\cdot}2H_2O$, Raman bands: 180, 414, 492,620, 670, 1008 and 1135 cm^{-1}) and calcium carbonate ($CaCO_3$, Raman bands: 154, 282, 712 y 1986 cm^{-1}) was largely detected. Even calcium magnesium carbonate dolomite ($CaMg(CO_3)_2$, Raman bands: 178, 300, 724 and 1098 cm^{-1}) was identified in many analysis points, recognized like one of the main compounds of the support. Between the original compounds of the rock, Raman spectra of anatase (TiO_2, Raman bands 142, 395, 514, 638 cm^{-1}), rutile (TiO_2, Raman bands: 142, 242, 446, 612 cm^{-1}) and quartz (SiO_2, Raman bands 204, 264, 354, 465, 807 cm^{-1}) were also recorded. In red and orange grains, Raman analysis showed the presence of hematite iron oxides (Fe_2O_3, Raman bands: 224, 245, 294, 402, 500, 612 and 1315 cm^{-1}) and goethite (α-FeOOH, Raman bands: 204, 246, 302, 389, 480 550 cm^{-1}) which could be responsible for the orange colour of the stone. These oxides were found as loose grains on the surface of the sample and, therefore, their presence does not seem to be due to the presence of pigmentation in these samples.

In addition, a band at 985 cm^{-1} was detected in several spectra together with other compounds, mainly gypsum and calcite. This signal could belong to the magnesium sulfate heptahydrate so-called epsomite ($MgSO_4{\cdot}7H_2O$) present on the surface of the sample as a degradation product of dolomite. Moreover, on the internal face, in most of the analysed points, the Raman spectrum of dolomite and calcium sulfate dihydrate or gypsum were observed. In several cases, the same Raman spectrum shows the coexistence of more than one compound at the same point of analysis. In fact, several spectra have evidenced the presence of a mixture of dolomite, gypsum and epsomite, which could clearly indicate sulfation of the original material.

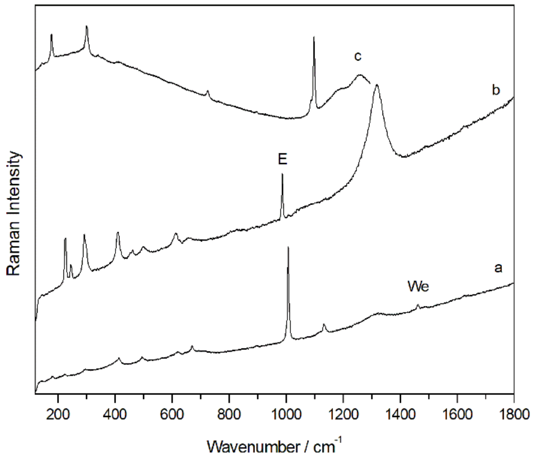

Figure 3. Raman spectra of gypsum with trace of weddellite (**a**), hematite with epsomite (E) (**b**) and dolomite (c).

This process could be favoured by the infiltration of sulfate-rich water coming from the back of the painted panel which carries sulphates from the stone and accumulates them on the surface after evaporating in the open-air. The formation of sulphates, especially with various hydration molecules, like epsomite, create an increases of the porous pressure within the rocky substrate during the hydration phase. Thus, sulfur was dissolved from rainwater, mobilised and precipitated during the crystallisation process due to rising temperatures.

In addition, according to the archaeologists, the repeated humidification of the panel has been proven. This practice was common to all open-air rock art sites since their discovery until a couple of decades ago in order to improve the visualization of the pictographs to visitors. Considering that the white patina was located in the middle of the panel, where the pictographs were made, the anthropic factor could be possibly the reason of the formation of the sulphate patina. However, we cannot know exactly where the water used for this practice comes from (probably from the spring adjacent to rock shelter). It is not possible to know the composition of the water used when this practice was carried out. However, the water in the province of Albacete is characterised by a high hardness and presence of sulphates, so much so that just this year an osmosis plant for the treatment of drinking water to reduce the presence of salts and improve its quality.

The possibility of S being mobilised from the top of the rock shelter, as shown in other studies [8], up to the painted wall, by a runoff process, seems to be ruled out, as a percolation process from the top of the panel was not evident. On the other hand, the sulfation of the support does not appear to be due to the presence of atmospheric contaminants, as the area where the *Cueva de la Vieja* is located is not highly affected by urban traffic or industrial contamination.

With regard to the degradation by microorganisms, it was detected in both the outer and inner parts of many samples. For example, in the inner face of the CuVi02 sample, in addition to hematite, calcite and dolomite, the presence of very well defined spectra of carotenoid pigments standed out. Specifically, Raman spectra of the carotenoid pigment astaxanthin ($C_{40}H_{52}O_4$, Figure 4a), the most oxidized species among the carotenoid pigments and synthesized by species such as lichens, were recorded at several points. Its identification has been possible thanks to the main Raman bands at 1001, 1154, 1508 cm^{-1} and its overtones (2150, 2298, 2509, 2654 cm^{-1}) that allowed distinguishing it from other carotenoid pigments such as carotene and zeaxanthin. In addition to astaxanthin, Raman spectra of scytonemin ($C_{36}H_{20}N_2O_4$), a pigment generally synthesized by cyanobacteria, were recorded (Figure 4b). The highest intensity Raman bands that allowed its identification are at 1170, 1382, 1554, 1600, 1632, 1715 cm^{-1}.

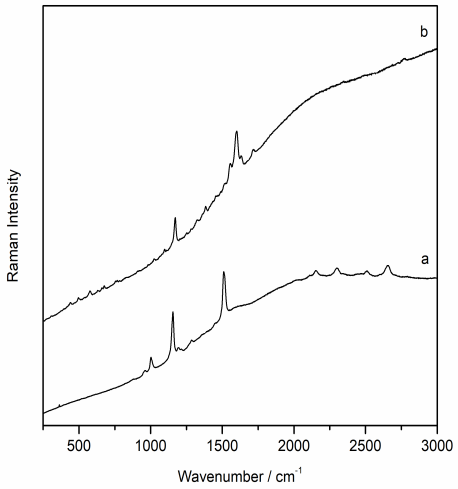

Figure 4. Raman spectra of astaxantin (**a**) and scytonemin (**b**).

As observed under the microscope, the outer face of the sample CuVi 03 was characterized by a homogeneous white colour. In this layer, mainly gypsum and dolomite spectra were recorded. Moreover, as observed in the image obtained with the microscope (Figure), the traces of hematite were clearly visible with Raman analyses. This could suggest the presence of pigmentation as it did not appear as loose grains as in the previous samples, suggesting an original composition. Therefore, this would indicate the loss of polychrome. Besides, Raman bands belonging to the calcium oxalates whewellite (192, 204, 220, 248, 895, 1461, 1488 cm^{-1}) and weddelite (138, 1475 cm^{-1}) were also detected in the same area. The presence of calcium oxalates could have favoured the preservation of pigmentation in that area.

Even in the unique sample taken from a painted area the presence of hematite was recognized by means Raman spectroscopy as pigment voluntary used. In all recorded spectra, the presence of calcium oxalate was also identified along with the broad bands between 1120 and 1650 cm^{-1} that belong to the aluminosilicate compounds of the substrate. Calcium oxalates were even detected in the internal face of the sample. According to previous investigations of painted rock shelter the pictorial layer, composed mainly of hematite, was located between layers of calcium oxalate [33] both caused by microorganism activity. The presence of this layer and one superior to the pictographs would be one of the factors that have allowed the conservation of prehistoric paintings to this day. Although the presence of calcium oxalate in the internal part of the sample with red pigmentation was also identified in our samples, its small size did not allow a more in-depth study by means of a cross-section study of the sample.

In addition, in mixture with the iron oxide even a single weak band located at 962 cm^{-1}, typical of the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) (Figure 5a), was visible in the spectra that suggested that the red pigment hematite was probably mixed with amounts of calcined bones. In the same spectra, also the broad bands belonging to amorphous carbon were evident (Figure 5b). Thus, was plausible that a black pigment was voluntary added to hematite to obtain a darker colour.

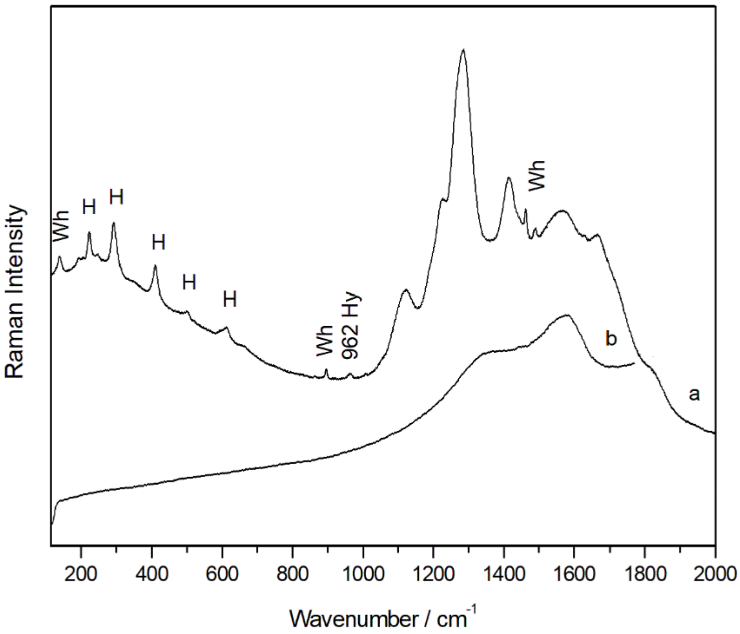

Figure 5. Raman spectra of hematite (H) with the signal of aluminosilicates, whewellite (Wh) and hydroxyapatite (Hy) (**a**) and black carbon (**b**).

Finally, molecular analysis of the crystalline part of the samples was performed with X-ray diffraction analysis. As with the other techniques, the analysis was performed on both the external and internal sides. In all samples sample quartz, dolomite and calcite high in magnesium were identified as original compounds, in agreement with the Raman spectroscopy analysis. Gypsum and compounds related to microbiological activity such as hydrated and dihydrated calcium oxalate (whewellite and weddelite) were identified as degradation compounds (Figure S3). Significant differences were observed between the internal and external part. Indeed, gypsum and oxalates were detected only on the outside of the samples.

Finally, in the case of the sample containing with red pigment, this technique could only identify dolomite, hydrated calcium oxalate and gypsum as impurities. Without being able to identify the pigment. Although Raman spectroscopy identified hematite, as this technique is only sensitive to crystalline compounds, it could indicate a low crystallization of this compound in this sample. In addition, in this sample, a small amount of sulphates was also identified by all analytical techniques. It is therefore plausible that the whitish sulphate patina is affecting the integrity of the substrate more than the areas where the pictographs are present. Undoubtedly, the presence of oxalates has guaranteed the conservation of the paintings over the years and it is for this reason that they seem better preserved than the support itself. In any case, the sulfation of the panel had to be treated with the aim of bringing the pictographs back to light. In addition, the exfoliation of the support could cause the loss of the painted areas in the long term.

From this diagnostic study, it was decided to carry out a desalination treatment by restorers on the surface of the panel with the aim of removing the whitish patina that covered the pictographs. According to the restorers report, paper dressings impregnated with low mineralization water was used, applied directly to the sulfate crust. After a few minutes, they were removed and then, the surface was cleaned with brushes, removing the remains. The operation was repeated a couple of times and was completed using only distilled water. The stability of the paint was monitored continuously during the treatment.

2.2. Samples Analysis after the Cleaning Treatment

After completing the cleaning treatment, it was considered crucial to check its effectiveness and to verify the reduction of salts. Archaeologists attention was also drawn to a series of points on the panel where an insoluble greyish crust remained after cleaning. These were areas arranged around natural holes in the support, through which, perhaps, there was a certain periodic emanation of water in the passage. In collaboration with the restorer in charge of the cleaning of the panel, samples were collected so that the nature of these grey crusts could be identified.

At first view, there was a considerable reduction in the surface sulphates at naked eye. (Figure 9) Thus, the objective of the analysis of these samples was the characterization of the rock surface after cleaning, verifying the removalof the sulfates and identifying other substances remaining in the rock, in order to raise hypotheses about their link to the conservation processes in *Cueva de la Vieja*.

Although micro-EDXRF analyses still identified the presence of sulfur in the samples taken after treatment, it was heterogeneously present in the surface of the samples. As this is a microanalysis technique, we were not surprised to still detect the presence of sulphur remain after the cleaning treatment. However, the semi-quantitative data from this technique, based on the intensity of the emission lines, indicated a decrease in the percentage of sulphur in the samples collected after desalination. As can be seen from the micro XRF map (Figure 6), the sulfur was still present on the surface of the micro-sample due to the irregular surface while the distribution of calcium was homogeneous. Therefore, the treatment did not act in hard-to-reach areas.

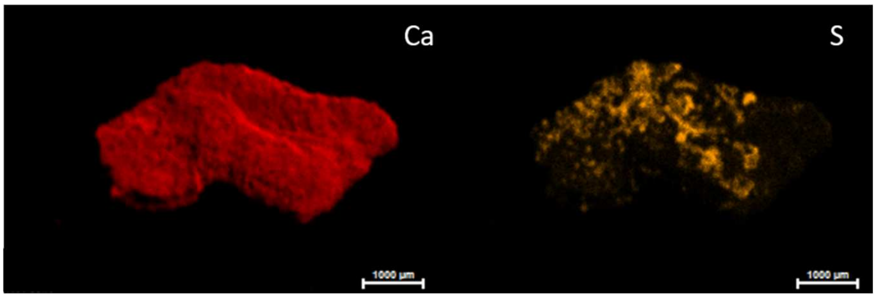

Figure 6. Micro-EDXRF maps where calcium and sulfur distribution after desalination treatment are showed.

However, from an elemental point of view, the analyzes carried out on the samples after the cleaning treatment highlighted the presence of other elements whose emission bands were weak or absent in the samples previously analysed. The presence of strontium associated with calcium was noticed in the samples after cleaning as well as the bands of iron, zinc, copper, phosphorus and manganese appeared much more evident. The emission lines of these elements belonging to the rocky support were partially hidden by the high presence of sulfur in the white patina in some samples.

In the three samples that were collected in grey crusts, which had not been solubilised during the cleaning treatment, high percentages of calcium were identified together with silicon in less extent. Raman spectroscopy detected the presence of very sharp Raman bands of calcium carbonate always together with calcium oxalate peaks (Figure S4c). The samples looked under the light of the microscope as flat, grey coloured flakes. No Raman spectra of gypsum were recorded in these samples. On the other hand, in one sample a strong band at 1067 cm^{-1} was visible. (Figure S4b) According to the literature this band together with the other of low intensity at 722 cm^{-1} belonged to the sodium nitrate nitratine ($NaNO_3$). This compound was not identified by XRD analysis probably its presence was less than the detection limit of this technique. On the other hand, XRD analyses clearly identified the presence of calcium carbonate, silicon dioxide and hydrated calcium oxalate in all three samples. Despite being a soluble compound, some traces of nitrate remained even after cleaning. This compound was only identified in one sample. Considering that these samples were taken from an area where water runs off, the formation of nitrates must be related to traces of organic matter carried away by rainwater. In all samples the most abundant compounds identified were calcite and calcium oxalate hydrate demonstrating that the treatment significantly removed the presence of sulphates without affecting the oxalate patina that could contribute to the preservation of pictographs.

On the other hand, both Raman and XRD analyses demonstrated a very low presence of gypsum in the remaining samples taken from the rock substrate. In these samples in addition to calcium carbonate, the compounds belonging to the rocky support, dolomite, quartz and hematite were recognized.

In order to obtain further confirmation of the effectiveness of the cleaning treatment a statistical analysis of the data obtained by micro EDXRF was carried out. By performing Principal Component Analysis (PCA) using EDXRF spectra, allowed separating considerably the samples considering the treatment they underwent (Figure 7). Concretely, the PC2 vs PC3 plot resulted the more explicative to see which differences appeared after applying the treatment on the samples. In Figure 7A, it can be observed how samples before treatment are grouped mostly on the positive part of PC2 whereas samples analysed after the treatment are mostly grouped on the negative part of the PC2. It is clear that PC2 (Figure 7B) is the component that better explains the differences induced by the application of the conservation treatment in the samples. By analysing this PC, it can be concluded that sulfur is the main element removed during the treatment (from the elements detected by means of micro EDXRF). Actually, the samples located on the positive side of the PC2 are characterized by a high presence of sulfur and those located on the negative side are characterized by almost absence of sulfur and high presence of iron. This fact helps understanding the clustering of the samples in the PC2 vs PC3 plot as the samples collected before the treatment are located in the more sulfur rich area and the samples collected after applying the conservation treatment appear in the region of the plot dominated by high Fe presence and low sulfur. Positive Al, Si and Fe K bands instead, characterize PC3 (Figure 7C). These elements are the main components of the rocky support and the dispersion of the samples along this PC, especially after the treatment, is explained by the heterogeneity of a natural rock. Samples before the treatment seemed to have a sulfur coating that masked rocky composition, preventing EDXRF to detect this natural heterogeneity.

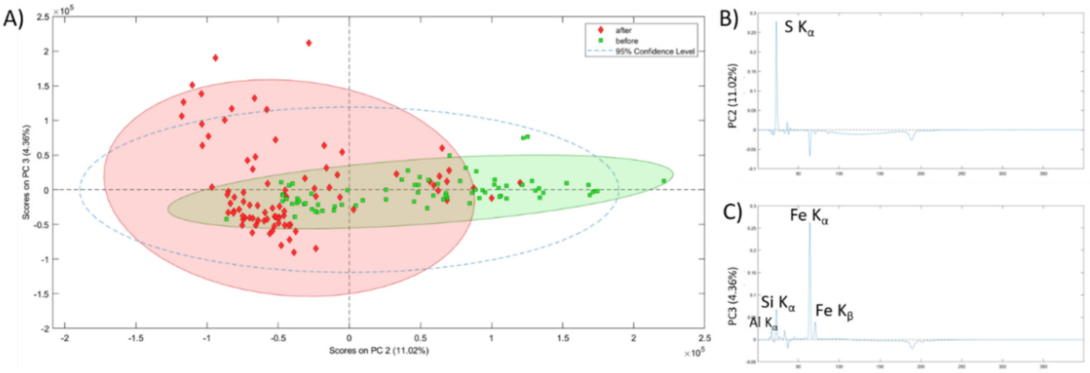

Figure 7. (**A**) PCA score plot of XRF spectra obtained from the sample analysis before and after the conservation treatment. (**B**) PC2 loading plot. (**C**) PC3 loading plot.

To understand better the element variations and their relationship with the studied samples, semi-quantitative XRF analyses were performed on the samples´ surface. Then, these data were studied by chemometric methods by performing scores and loading bi-plots. First of all an outlier study was performed through Hotelling T2 vs Q residuals study. After removing outliers, scores and loading PCA bi-plot (Figure 8) showed, once again, the previously mentioned separation between non-treated and treated samples. Actually, it is worthy to mention that both PCA look very similar regarding the distribution of the samples.

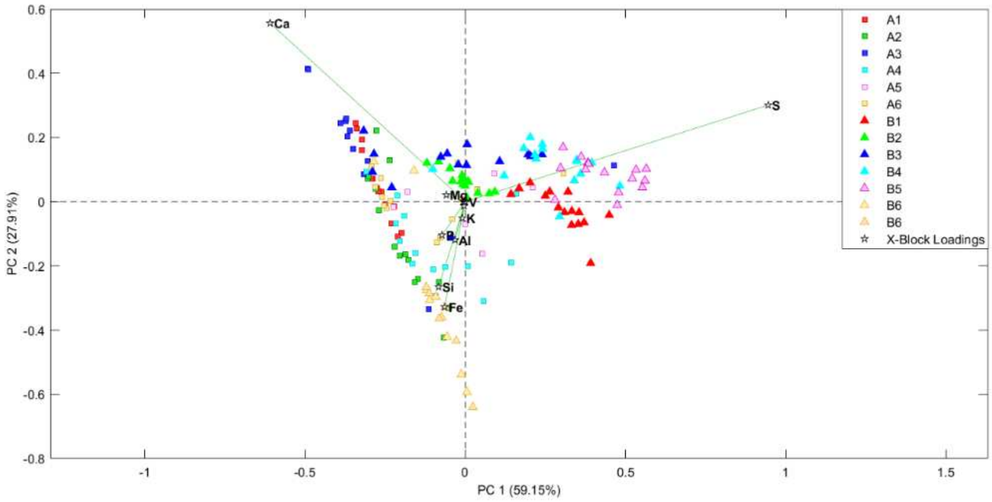

Figure 8. PCA bi-plot of EDXRF spectra obtained from the sample analysis before and after the conservation treatment. B) PC2 loading plot. C) PC3 loading plot.

On the other hand, bi-plot perfectly shows the relationship between the samples and their elemental composition. On the one hand, all the non-treated samples are highly correlated with sulfur as observed in the XRF spectra study. However, it must be highlighted that B6 sample is located near the treated samples even if it is a non-treated one. The reason for this is that this sample comes from a red pictographs and, therefore, has a red coat on its surface. This red coat is composed mainly by iron shifting this sample to the area where iron dominates.

In addition, in this bi-plot is appreciated that the treated samples are distributed depending its Ca and Fe content. This can help understanding the different hues observed in the rocky support going from whitish to reddish.

These plots also show some samples or some replicas of the same sample which are instead of being non-treated are located nearer the treated samples and vice versa. This fact is again explained by the heterogeneity of such a natural system that a rock-shelter is. Considering that EDXRF analysis were performed collimating the X-ray beam to 25 microns, analyses are subjected to microscopic variation. In this way, it is logical to think that the surface of the rock walls was not perfectly treated and minor points remained with a high concentration of sulfur. Likewise, in non-treated samples some microscopic points with low S presence were located. In anyway, these cases are just anecdotal comparing with the majority of the analysed points from all the samples (15 point for each sample were recorded).

3. Materials and Methods

3.1. Materials

The rock shelter *Cueva de la Vieja* is located to the east of the province of Albacete, 5 km away from Alpera town and it was discovered in 1910. It was included in the UNESCO World Heritage list in 1998, being one of the most significant sites of the Rock Art of the Mediterranean Basin of the Iberian Peninsula property. The rock shelter is a relatively deep painted panel, in full sunlight, where are preserved paintings with a large variety and large number of figures (human figures, archers, female representations, deer, goats, bulls, horses) distributed along a surface of 10 meters with a size of the figures ranging from 40 cm to 5 cm. All these figures painted in red-ochre belongs to the Levantine style. Even a group of abstract and geometric motifs were present that correspond to Schematic style. The most ancient figures in Levantine style are dated in the Epipaleolithic, in the transition from the Paleolithic to the Neolithic. (8000 and 6000 B.C.). while the most modern, in Schematic style, belong to a period between the 6000 and the 3000 B.C.

The pictographs were barely visible before the cleaning treatment. A whitish layer of concretion, covered most of them. The paintings located at both ends of the panel presented a lower incidence of this alteration and, in general, could be observed much better. On the other hand, alterations such as runoff areas, plaques, small scales, fissures, alveolization, dissolution, remains of animal activity were also noted. Diagnosis of these alterations and of the processes that generate them was key for verifying whether the panel would withstand cleaning of the whitish crust that makes it difficult to see the cave paintings.

Six samples were analysed before the cleaning treatment. Five of these belonged to the support and the other one have traces of pigmentation. They were collected in degraded areas where a flaking of support was clearly visible. After the cleaning, other six samples were collected again. Three of these last samples were collected from an insoluble greyish crust that remained after the cleaning procedure. These areas were located around natural holes in the support, through which water could flow periodically.

Figure 9. 3D reconstruction de la *Cueva de la Vieja* after de cleaning treatment.

3.2. Methods

3.2.1. Micro-Energy Dispersive X-ray Fluorescence Spectroscopy (Micro-EDXRF)

The elemental maps were acquired using a M4 TORNADO EDXRF spectrometer (Bruker Nano GmbH, Berlin, Germany). The analyses were performed under vacuum (20 mbar) in order to improve the identification of the lighter elements. The lateral resolution used for spectral acquisitions was 20 micrometers. The maps were obtained using M-QUANT software. To obtain the quantitative maps, the assignment of the elements and the deconvolution of the spectral information were carried out. The maps were obtained by considering the K-alpha line of each element.

3.2.2. Micro-Raman Spectroscopy

The micro-samples were analysed for the molecular characterization using a confocal Renishaw InVia Raman spectrometer, coupled to a Leica DMLM microscope. The spectra were acquired with the Leica 50× N Plan (0.75 NA) lens with a 2 µm spatial resolution. The minimum theoretical spot diameter, using the 532 nm laser was, for the Leica 50×, 0.9 µm while using the 785 nm laser it was 1.7 µm. Additionally, for visualization and focusing, another Leica 5× N Plan (0.12 NA) and a 20× N Plan EPI (0.40 NA) lens were used. For focusing on and searching for points of interest, the microscope implements a motorized stage (XYZ). The power applied was set at the source at a maximum of 50 mW while on the sample was always less than 20 mW to avoid possible thermodecomposition of the samples. Normally, 10-300 scans, each lasting 1-20 s, were accumulated to achieve a suitable signal-to-noise ratio at an operating spectral resolution of 1 cm^{-1}.

3.2.3. X-ray Diffraction

The mineralogical composition was characterized by means of the Analytical Xpert PRO X-Ray Diffractometer (XRD, PANalytical, Netherlands). The XRD system is equipped with a copper tube, a vertical goniometer (Bragg–Brentano geometry), a programmable divergence slit, a secondary graphite monochromator and a Pixcel detector. The measurement conditions were set at 40 kV, 40 mA and a scan ranging between 5 and 70 °2theta. Diffractograms interpretation was performed using Win- PLOTR software, by comparison with the PDF-4 standards database.

3.2.4. Chemometrics

EDXRF data was analysed using chemometric methods. Two kind of analysis were performed with different aims. On the one hand, PCA analysis were performed using all the EDXRF spectra. After an outlier study, data were meancentered. On the other hand, a semi-quantitative elemental estimation was calculated from the EDXRF spectra. With this dataset and once again after an outlier study, data was meancentered. By this means, a bi-plot study was performed relating scores and loadings. In this case, the entire XRF spectrum while a further statistical treatment was carried out by considering the semi-quantitative data obtained with the aim of finding similarities at elemental levels between all samples. For PCA, we used the PLS-Toolbox v.7.0.2 (Eigenvector Research, USA) implemented in MATLAB 2010 software (The MathWorks, MA, USA).

4. Conclusions

According to the results obtained on the micro-samples, it seems evident that the nature of the analysed stone was dolomitic limestone, with aggregates of silica or aluminosilicates as well as the presence of iron oxides, mainly hematite. In addition, it has been possible to identify aggregates of anatase or formed by titanium, copper, zinc, manganese. In any case, a much-differentiated composition between the samples was not found. The only sample that presented red pigmentation demonstrated that the pictographs were done mainly with hematite mixed with amorphous carbon and calcined bones.

Regarding the external and internal analysis, the significant difference for the micro-samples taken before the cleaning, was the presence of a whitish formation, in the form of a crust on the external part. Raman and XRD analyses demonstrated that it was mainly composed of gypsum with a minor amount of epsomite. The presence of both sulfates was explained as reaction products of the original material (dolomitic limestone), as well as the observed relative presence of both degradation compounds. Thus, it appears that a dissolution phenomenon of the original carbonate was taking place and the following reprecipitation as sulfates. This reactivity of the material favoured the loss of the consolidant and therefore its weakening. Anthropogenic factors and weathering processes contributed to the formation of sulphates on the surface of the painted panel. According to our knowledge on the history of the rock shelter, the practice of humidification the panel could be considered as principal reason of sulfates formation, even due to the distribution of the white patina that was exactly on the central area where the pictographs were made.

In addition, it was possible to observe in almost all the samples analysed the presence of compounds that showed the presence of biological activity by to the identification of calcium oxalates monohydrate and dihydrate, as well as some pigments such as scytonemin or astaxanthin. This indicates that microorganisms, which may also be favouring the dissolution of the original material, and/or the acidification of the support, was affecting the material. On the other hand, it is known from previous studies that the presence of calcium oxalates is not harmful to paints and would preserve their integrity over the years. Therefore evaluating the dangers of the activity of microorganisms for the conservation of paintings can be complex.

To the naked eye, this whitish layer was removed thanks to the desalting treatment carried out by the restorers. since microanalytical techniques have been applied to the study they still detected the presence of sulfur after the cleaning, although in much smaller quantities. In fact, analyses performed on the samples collected after the desalination treatment showed the presence of calcium oxalates, predominantly whewellite, and calcium carbonate as the main compound. This showed that the treatment removed most of the sulphate compounds without affecting the oxalate patina that is probably one of the main factors that have enabled the pictographs to be preserved.

Statistical treatment of the XRF data using principal component analysis (PCA) confirmed the effectiveness of the treatment and highlighted the elemental composition of each sample before and after treatment. An increased presence of iron, manganese, zinc, copper and potassium belonging to the rocky substrate is acxtually evident in the treated samples revealing the original nature of the panel.

Long-term monitoring will be carried out in the future, by means portable instrument to check the conservation status of the panel months after the desalination treatment and to verify the influence of weathering processes on patina formation.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

Acknowledgments: This work has been financially supported by the DEMORA project (Grant No. PID2020-113391GB-I00), funded by the Spanish Agency for Research (through the Spanish Ministry of Science and Innovation, MICINN, and the European Regional Development Fund, FEDER). Technical and manpower support provided by SGIker (UPV/EHU, MICINN, GV/EJ, ERDF and ESF) is gratefully acknowledged in XRD analysis. The authors would like to thank the restorers Eudald Guillamet and Laura Ballester. I. Costantini gratefully acknowledges to the UPV/EHU for her postdoctoral contract.

References

1. Brumm, A.; Oktaviana, A.A.; Burhan, B.; Hakim, B.; Lebe, R.; Zhao, J.; Sulistyarto, P.H.; Ririmasse, M.; Adhityatama, S.; Sumantri, I.; et al. Oldest Cave Art Found in Sulawesi. *Science Advances* **2021**, *7*,
2. Robbins, L.H.; Murphy, M.L.; Brook, G.A.; Ivester, A.H.; Campbell, A.C.; Klein, R.G.; Milo, R.G.; Stewart, K.M.; Downey, W.S.; Stevens, N.J. Archaeology, Palaeoenvironment, and Chronology of the Tsodilo Hills White Paintings Rock Shelter, Northwest Kalahari Desert, Botswana. *Journal of Archaeological Science* **2000**, *27*, 1085-1113.
3. Sampietro-Vattuone, M.M.; Peña-Monné, J.L. Application of 2D/3D Models and Alteration Mapping for Detecting Deterioration Processes in Rock Art Heritage (Cerro Colorado, Argentina): A Methodological Proposal. *Journal of Cultural Heritage* **2021**, *51*, 157-165,

4. Morillas, H.; Maguregui, M.; Bastante, J.; Huallparimachi, G.; Marcaida, I.; García-Florentino, C.; Astete, F.; Madariaga, J.M. Characterization of the Inkaterra Rock Shelter Paintings Exposed to Tropical Climate (Machupicchu, Peru). *Microchemical Journal* **2018**, *137*, 422-428.
5. Tan, N.H. Rock Art Research in Southeast Asia: A Synthesis. *Arts* **2014**, *3*, 73-104.
6. Chazine, J.-M.; Setiawan, P. DISCOVERY OF A NEW ROCK ART IN EAST BORNEO: NEW DATA FOR REFLEXION.
7. Black, J.L.; MacLeod, I.D.; Smith, B.W. Theoretical Effects of Industrial Emissions on Colour Change at Rock Art Sites on Burrup Peninsula, Western Australia. *Journal of Archaeological Science: Reports* **2017**, *12*, 457-462.
8. Aramendia, J.; de Vallejuelo, S.F.-O.; Maguregui, M.; Martinez-Arkarazo, I.; Giakoumaki, A.; Martí, A.P.; Madariaga, J.M.; Ruiz, J.F. Long-Term in Situ Non-Invasive Spectroscopic Monitoring of Weathering Processes in Open-Air Prehistoric Rock Art Sites. *Anal. Bioanal. Chem.* **2020**, *412*, 8155-8166.
9. Ravindran, T.R.; Arora, A.K.; Singh, M.; Ota, S.B. On-and off-Site Raman Study of Rock-Shelter Paintings at World-Heritage Site of Bhimbetka. *Journal of Raman Spectroscopy* **2013**, *44*, 108-113.
10. Mazel, V.; Richardin, P.; Touboul, D.; Brunelle, A.; Richard, C.; Laval, E.; Walter, P.; Laprévote, O. Animal Urine as Painting Materials in African Rock Art Revealed by Cluster ToF-SIMS Mass Spectrometry Imaging. *Journal of Mass Spectrometry* **2010**, *45*, 944-950.
11. Gomes, H.; Collado Giraldo, H.; Martins, A.; Nash, G.; Rosina, P.; Vaccaro, C.; Volpe, L. Pigment in Western Iberian Schematic Rock Art: An Analytical Approach. *Mediterranean Archaeology and Archaeometry: International Scientific Journal* **2015**, *15*, 163-175.
12. Pitarch, À.; Francisco Ruiz, J.; Vallejuelo, S.F.-O. de; Hernanz, A.; Maguregui, M.; Manuel Madariaga, J. In Situ Characterization by Raman and X-Ray Fluorescence Spectroscopy of Post-Paleolithic Blackish Pictographs Exposed to the Open Air in Los Chaparros Shelter (Albalate Del Arzobispo, Teruel, Spain). *Analytical Methods* **2014**, *6*, 6641-6650.
13. Iriarte, M.; Hernanz, A.; Ruiz-López, J.F.; Martín, S. μ-Raman Spectroscopy of Prehistoric Paintings from the Abrigo Remacha Rock Shelter (Villaseca, Segovia, Spain). *Journal of Raman Spectroscopy* **2013**, *44*, 1557-1562.
14. Hernanz, A.; Ruiz-López, J.F.; Madariaga, J.M.; Gavrilenko, E.; Maguregui, M.; Fdez-Ortiz de Vallejuelo, S.; Martínez-Arkarazo, I.; Alloza-Izquierdo, R.; Baldellou-Martínez, V.; Viñas-Vallverdú, R.; et al. Spectroscopic Characterisation of Crusts Interstratified with Prehistoric Paintings Preserved in Open-Air Rock Art Shelters. *Journal of Raman Spectroscopy* **2014**, *45*, 1236-1243.
15. Hernanz, A.; Ruiz-López, J.F.; Gavira-Vallejo, J.M.; Martin, S.; Gavrilenko, E. Raman Microscopy of Prehistoric Rock Paintings from the Hoz de Vicente, Minglanilla, Cuenca, Spain. *Journal of Raman Spectroscopy* **2010**, *41*, 1394-1399.
16. Pozo-Antonio, J. s.; Rivas, T.; Carrera, F.; García, L. Deterioration Processes Affecting Prehistoric Rock Art Engravings in Granite in NW Spain. *Earth Surface Processes and Landforms* **2018**, *43*, 2435-2448.
17. Hernanz, A.; Gavira-Vallejo, J.M.; Ruiz-López, J.F.; Edwards, H.G.M. A Comprehensive Micro-Raman Spectroscopic Study of Prehistoric Rock Paintings from the Sierra de Las Cuerdas, Cuenca, Spain. *Journal of Raman Spectroscopy* **2008**, *39*, 972-984.
18. Peña-Monné, J.L.; Sampietro-Vattuone, M.M.; Báez, W.A.; García-Giménez, R.; Stábile, F.M.; Martínez Stagnaro, S.Y.; Tissera, L.E. Sandstone Weathering Processes in the Painted Rock Shelters of Cerro Colorado (Córdoba, Argentina). *Geoarchaeology* **2022**, *37*, 332-349.
19. Rousaki, A.; Vargas, E.; Vázquez, C.; Aldazábal, V.; Bellelli, C.; Carballido Calatayud, M.; Hajduk, A.; Palacios, O.; Moens, L.; Vandenabeele, P. On-Field Raman Spectroscopy of Patagonian Prehistoric Rock Art: Pigments, Alteration Products and Substrata. *TrAC Trends in Analytical Chemistry* **2018**, *105*, 338-351.
20. Ilmi, Moh.M.; Maryanti, E.; Nurdini, N.; Lebe, R.; Oktaviana, A.A.; Burhan, B.; Perston, Y.L.; Setiawan, P.; Ismunandar; Kadja, G.T.M. Uncovering the Chemistry of Color Change in Rock Art in Leang Tedongnge (Pangkep Regency, South Sulawesi, Indonesia). *Journal of Archaeological Science: Reports* **2023**, *48*, 103871.
21. Ruiz López, J.F. El Abrigo de los Oculados (Henarejos, Cuenca). In Proceedings of the Actas del Congreso de Arte Rupestre Esquemático en la Península Ibérica: Comarca de los Vélez, 5-7 de Mayo 2004, 2006, ISBN 84-611-2821-4, págs. 375-388; Julián Martínez García, 2006; pp. 375-388.
22. Ruiz, J.F.; Hernanz, A.; Armitage, R.A.; Rowe, M.W.; Viñas, R.; Gavira-Vallejo, J.M.; Rubio, A. Calcium Oxalate AMS 14C Dating and Chronology of Post-Palaeolithic Rock Paintings in the Iberian Peninsula. Two Dates from Abrigo de Los Oculados (Henarejos, Cuenca, Spain). *Journal of Archaeological Science* **2012**, *39*, 2655-2667,
23. Lofrumento, C.; Ricci, M.; Bachechi, L.; De Feo, D.; Castellucci, E.M. The First Spectroscopic Analysis of Ethiopian Prehistoric Rock Painting. *Journal of Raman Spectroscopy* **2012**, *43*, 809-816.
24. Hedges, R.E.M.; Ramsey, C.B.; Klinken, G.J.V.; Pettitt, P.B.; Nielsen-Marsh, C.; Etchegoyen, A.; Niello, J.O.F.; Boschin, M.T.; Llamazares, A.M. Methodological Issues in the 14C Dating of Rock Paintings. *Radiocarbon* **1997**, *40*, 35-44,

25. Russ, J.; Kaluarachchi, W.D.; Drummond, L.; Edwards, H.G.M. The Nature of a Whewellite-Rich Rock Crust Associated with Pictographs in Southwestern Texas. *Studies in Conservation* **1999**, *44*, 91–103, doi:10.1179/sic.1999.44.2.91.
26. Russ, J.; Palma, R.L.; Loyd, D.H.; Boutton, T.W.; Coy, M.A. Origin of the Whewellite-Rich Rock Crust in the Lower Pecos Region of Southwest Texas and Its Significance to Paleoclimate Reconstructions. *Quaternary Research* **1996**, *46*, 27-36.
27. López-Montalvo, E.; Villaverde, V.; Roldán, C.; Murcia, S.; Badal, E. An Approximation to the Study of Black Pigments in Cova Remigia (Castellón, Spain). Technical and Cultural Assessments of the Use of Carbon-Based Black Pigments in Spanish Levantine Rock Art. *Journal of Archaeological Science* **2014**, *52*, 535-545.
28. Domingo, I.; Chieli, A. Characterizing the Pigments and Paints of Prehistoric Artists. *Archaeol Anthropol Sci* **2021**, *13*, 196.
29. Beltrán, A. El arte rupestre levantino, cronología y significación.
30. Domingo Sanz, I.; Vendrell, M.; Chieli, A. A Critical Assessment of the Potential and Limitations of Physicochemical Analysis to Advance Knowledge on Levantine Rock Art. *Quaternary International* **2021**, *572*, 24-40.
31. Roldán, C.; Murcia-Mascarós, S.; Ferrero, J.; Villaverde, V.; López, E.; Domingo, I.; Martínez, R.; Guillem, P.M. Application of Field Portable EDXRF Spectrometry to Analysis of Pigments of Levantine Rock Art. *X-Ray Spectrometry* **2010**, *39*, 243-250.
32. Mas, M.; Jorge, A.; Gavilán, B.; Solís, M.; Parra, E.; Pérez, P.-P. Minateda Rock Shelters (Albacete) and Post-Palaeolithic Art of the Mediterranean Basin in Spain: Pigments, Surfaces and Patinas. *Journal of Archaeological Science* **2013**, *40*, 4635-4647.
33. Iriarte, M.; Hernanz, A.; Gavira-Vallejo, J.M.; de Buruaga, A.S.; Martín, S. Micro-Raman Spectroscopy of Rock Paintings from the Galb Budarga and Tuama Budarga Rock Shelters, Western Sahara. *Microchemical Journal* **2018**, *137*, 250-257.