

Spectroscopic characterisation of crusts interstratified with prehistoric paintings preserved in open-air rock art shelters[†]

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In situ micro-Raman spectroscopy (μ -RS) of rock art paintings in open-air rock shelters entails several difficulties: sunlight, wind, dust and crusts that mask Raman signals from the pigments and any other component of the paint recipe. These problems have been considered in the present work. Special attention has been devoted to the presence of crusts. Five rock art sites in the eastern Iberian Peninsula with outstanding difficulties to be analysed by this technique have been the object of this study. *In situ* energy dispersive X-ray fluorescence and diffuse reflectance infrared Fourier transform spectroscopy using portable instruments have provided important help. Moreover, microstratigraphic studies by μ -RS and scanning electronic microscopy combined with energy dispersive X-ray spectroscopy of micro-specimens from the painting panels have revealed the distribution of the different components. Dolomite and calcite are dominant minerals in the rock substrata. Whewellite, gypsum, calcite, clay, dolomite, α -quartz, anatase and haematite have been found on the surface of the painting panels or forming stratified layers in the crusts. Haematite and amorphous carbon have been detected in red and black pictographs, respectively. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: Raman microscopy; SEM/EDS; EDXRF; crusts; prehistoric paintings

Introduction

In situ micro-Raman spectroscopy (μ -RS) of rock art paintings in open-air rock shelters involves several problems:^[1–4] sunlight, wind, dust, no electric power lines and the presence of crusts interstratified with pigment layers that mask or hide their Raman signals. These problems are considered in the present work, but special attention is devoted to the last one because it is the most difficult to solve, although in some cases, it may be considered an advantage from the archaeological and preservation point of view. The microstratigraphic composition of these crusts, their possible origin, as well as their effect on *in situ* μ -RS and procedures to solve problems caused by these crusts in a number of representative sites are studied.

A large number of rock shelters with painting panels have been the object of μ -RS analyses by our research group, Fig. S1 (Supporting Information). Five of them, Fig. S1 1–5, have been selected in this work because of remarkable difficulties encountered applying *in situ* μ -RS, as well as for opportunities of scientific dating of their accretionary crusts and preservation concerns. These are the rock art panels found in the shelters of the Cova dels Rossegadors (La Pobla de Benifassà, Castellón), Cueva de la Vieja and Cueva del Queso (Alpera, Albacete), Abrigo de los Chaparros (Albalate del Arzobispo, Teruel) and Abrigo Riquelme (Jumilla, Murcia). They are distributed over the eastern

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[†] This article is part of the special issue of the Journal of Raman Spectroscopy entitled "Raman in Art and Archaeology 2013" edited by Polonca Ropret and Juan Manuel Madariaga.

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half of the Iberian Peninsula, in the area included in the UNESCO World Heritage List under the generic name of Rock Art of the Mediterranean Basin on the Iberian Peninsula.

The pictorial materials have been analysed by *in situ* μ -RS, *in situ* energy dispersive X-ray fluorescence (EDXRF) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In addition, micro-specimens of the painting panels close to the pictographs have been extracted for microstratigraphic studies by μ -RS, scanning electronic microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS) and the corresponding images and mappings of components obtained by these techniques.

The results of this study may benefit future studies on this field. They provide information on the materials used by prehistoric artists and can contribute to the scientific dating of the crusts as well as to rock art preservation.

Archaeological background

The five rock shelters indicated previously have significant examples of Levantine and Schematic art of the Iberian Peninsula;^[5] the open questions about chronology and relative seriation^[6] of these styles demands a greater number of scientific datings. These open-air rock art sites have natural conservation problems like flaking, biological activity or coatings that hide the paintings. Some anthropic factors like wetting of the motifs over decades and even vandalism have deteriorated seriously the paintings. The Cova dels Rossegadors has more than 200 Levantine art pictographs affected by flaking, biological activity and accretionary crusts.^[7] The Cueva de la Vieja was one of the first shelters with Levantine art that was discovered at the beginning of the 20th century.^[8] Here, several hundreds of well-preserved Levantine and Schematic pictographs have been recorded, but they cannot be easily observed because of the thick coating produced by decades of repeated wetting of the panels in order to see clearly the figures. The Abrigo de los Chaparros is a site with more than 100 pictographs of Levantine and Schematic styles with very significant superimpositions that could offer relevant information about seriation of these styles in Aragón.^[9] The site has several and important endogenous risks for the preservation of the motifs. The Abrigo Riquelme was discovered just 3 years ago, but it has attracted researchers since then for its particular kind of Schematic art.^[10] Very active processes of natural flaking and spallation are a serious concern for the preservation of this extraordinary rock art site. Finally, the Cueva del Queso is the worst preserved site. It was seriously damaged shortly after its discovery^[8] on 1911 by vandals that detached the majority of the paintings. Nowadays, only a couple of Levantine and Schematic figures can be observed.

Experimental

In situ Raman spectra of the painting panels have been obtained with a BWTEK innoRam 785H portable Raman microscope. An optical fibre cable connects the spectrometer to a handheld probe head with 10 \times magnification and alternatively to a microscope/videocamera set with 20 \times objective lens supported on an XYZ focusing system, Fig. S2 (Supporting Information). The laser line at 785 nm is used for Raman excitation with powers between 4 and 10 mW measured at the focus position. A spectral range of 65–2500 cm^{-1} (Stokes) can be recorded with a spectral resolution $\sim 3.5 \text{ cm}^{-1}$. Integration times of 1–2 s and up to 30 spectral accumulations were normally used to achieve an acceptable

signal-to-noise (S/N) ratio. Wavenumber shift calibration was accomplished with Hg-I lines, 4-acetamidophenol, naphthalene and sulphur standards^[11] over the range 150–2500 cm^{-1} . This resulted in a wavenumber mean deviation of $\Delta v_{\text{cal}} - \Delta v_{\text{obs}} = -0.01 \pm 0.05 \text{ cm}^{-1}$ (t_{student} 95%).^[11] The spectrometer is powered by a rechargeable Li battery 14.4 V (1 kg). The total weight of the instrument is about 10 kg. The software package GRAMS/AI v.7.00 (Thermo Electron Corporation, Salem, NH, USA) was used to assist in determining the wavenumber of the peaks.

The *in situ* elemental composition was carried out using an OXFORD Instruments handheld EDXRF XMET5100 spectrometer. The instrument implements a rhodium X-ray tube as excitation source, which works at a maximum voltage of 45 kV. The analyser has a high resolution silicon drift detector. The semi-quantitative analyses were performed using a method based on fundamental parameters, and spectra were acquired during 50 s. EDXRF spectra were collected and saved in a personal digital assistant (PDA) using the OXFORD Instruments X-MET programme. The semi-quantitative results were transferred as .txt files to a PC and converted into .xlsx files to perform the data treatment.

The infrared spectra were acquired with a 4100 ExoScan handheld FTIR spectrometer (A2 Technologies, nowadays Agilent Technologies), which implements a DRIFTS sampling head. A Michelson interferometer with 4 cm^{-1} of maximum resolution, a ZnSe beam splitter and a temperature stabilised DTGS detector are also implemented in the instrument. DRIFTS spectra were collected and saved in a PDA using the A2 Technologies MicroLab Mobile SoftwareTM. The spectra were transferred to a PC, opened with A2 Technologies MicroLab PC 2.5.7 software and finally converted into the more standard SPC format (Thermo Galactic). The spectral analysis was performed with GRAMS/A1 7.02 and OMNIC 7.2 software.

Some of the points that have been analysed *in situ* are indicated in Figs S3–S5 (Supporting Information). Specimens (size $\leq 2 \text{ mm}$) of the painting panels have been removed for laboratory microstratigraphic studies of the observed crusts. Polished thin cross sections of the specimens embedded in polyester resin were prepared. μ -RS spectra, SEM/EDS data and mappings of components were obtained by these techniques. The protocol used for micro-sample extraction, μ -RS and SEM/EDS studies of prehistoric paintings has been described elsewhere.^[12] Specific experimental details of this work are mentioned in the following. The μ -RS study of the samples has been carried out with a Jobin Yvon LabRam-IR HR-800 confocal Raman spectrograph coupled to an Olympus BX41 microscope. The 632.8 nm line of a He/Ne laser was used for Raman excitation with a power of 339 μW (50 \times LWD objective lens) measured at the sample position. The average spectral resolution in the Raman shift range of 100–1700 cm^{-1} was 1 cm^{-1} (focal length 800 mm, grating 1800 grooves/mm, and confocal pinhole 100 μm). These conditions involved a lateral resolving power of $\sim 5 \mu\text{m}$ (50 \times LWD objective lens) at the specimen. An integration time of between 1 and 20 s and up to 36 accumulations were used to achieve an acceptable S/N ratio. Wavenumber shift calibration applying the method indicated previously^[11] over the range of 150–3100 cm^{-1} resulted in a wavenumber mean deviation of $\Delta v_{\text{cal}} - \Delta v_{\text{obs}} = -0.01 \pm 0.17 \text{ cm}^{-1}$ (t_{student} 95%). Spectral smoothing was not applied to the observed spectra. The software package GRAMS/AI v.7.00 (Thermo Electron Corporation, Salem, NH, USA) was used to assist in determining the wavenumber of the peaks and the appropriated spectral baselines.

X-ray microanalyses of the samples were carried out with an EDS spectrometer Rontec Xflash Detector 3001, Peltier-refrigerated,

with the Be window removed and coupled to a Hitachi S-3000N scanning electron microscope (Everhart–Thornley detector of secondary electrons) with an operating resolution of 3 nm.

A petrographic microscope Leica DM2500 with polarised light was utilised to obtain microphotographs of the polished thin cross sections of the extracted micro-specimens.

Raman images of the thin cross sections were obtained with a Renishaw inVia Raman spectrometer coupled to a Leica DMLM microscope. A long-range objective 50× was used for the images. The microscope is equipped with a motorised XYZ positioning stage with integrated position sensors on the *x*-axis and *y*-axis. Raman chemical images were obtained with the Renishaw StreamLine™ Plus system. Renishaw WIRE 3.2 software controls all the system and collects the data. The 785 nm excitation laser line was used to acquire Raman spectra. Its power at the surface of the analysed sample was set at 100%, i.e. ~150 mW. The spectral resolution was around 1 cm⁻¹. In order to record the Raman images of the thin cross sections, the selected spectral ranges were 501–1628 cm⁻¹ (Cueva de la Vieja and Abrigo Riquelme), 557–1674 cm⁻¹ (Los Chaparros) and 1079–1100 cm⁻¹ (Cova dels Rossegadors).

Results and discussions

One of the first problems using portable Raman microscopes in open-air rock shelters is sunlight.^[2,4] The pre-focused probe head and the objective of the microscope collect sunlight even in shadow areas and Fraunhofer lines appear in the spectra, Fig. S6a (Supporting Information), complicating the detection of Raman signals from the painting panels. Instead of subtracting these lines from the collected spectra, a simple method consists in the use of an opaque foam rubber tube covering the head or the objective (that we call Càrol's cap), Figs S6b and S7 (Supporting Information). The external end of the Càrol's cap is adapted to the irregular surface of the rock and blocks sunlight entering the instrument. The flexibility of the cap enables focusing, while its soft contact with the rock avoids possible damages to the surface. Attempts of working at night demonstrate the presence of insects, caterpillars, spiders and other intrusive invertebrates moving over the painting panels and interfering the analyses. Thus, identification of proteins or other biological molecules on the surface of rock art pictographs must be considered carefully, because they must not be attributed immediately to original paint binders.

Wind is another problem. The base of the microscope must be complemented with heavy objects in order to increase its stability facing up to wind. In this way, blurred images from the video camera and microscope focussing improve, Fig. S8 (Supporting Information). Nevertheless, objective magnification higher than 20× (e.g. 50×) makes focussing in the shelters very difficult. An additional contribution to the stability of the microscope is given by the Càrol's cap, once it is well adapted to the rock surface. This cap protects also the probe head and objective from dust. In any case, whenever possible it is advisable to cover the shelter floor with polyethylene sheets (optical fibre contacts must always be free from dust particles), Fig. S9 (Supporting Information). However, one of the main difficulties applying *in situ* and laboratory μ -RS to study prehistoric paintings from open-air rock shelters is the presence of crusts and layers of fluorescent materials interstratified with the pigments. Five archaeological sites with this problem are going to be considered next.

Cova dels Rossegadors

A thick ochre-coloured crust covers the painting panels of this site, Fig. S8. The visible pictographs are painted in red. *In situ* Raman spectra of these figures excited at 785 nm show an intense spectral background of fluorescence radiation. Similar spectra are collected from points without figures. A precise focussing of the microscope and a careful selection of the operating conditions (laser power at the focus, integration time and number of spectral accumulations) made possible in some cases to detect gypsum

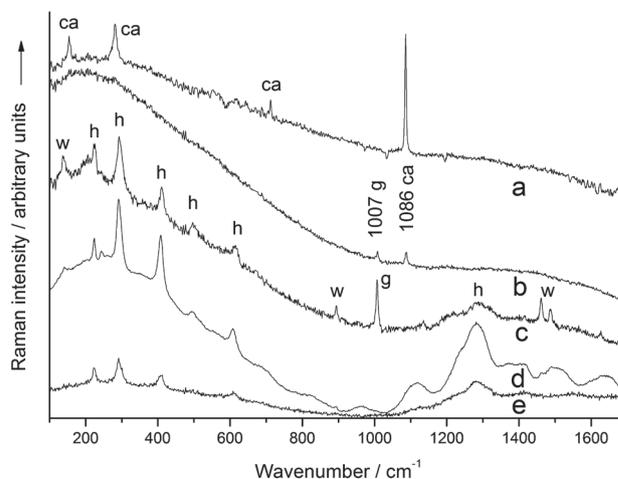


Figure 1. Representative raw μ -RS spectra obtained *in situ* from the painting panels of different rock shelters with a BWTEK innoRam 785H portable Raman microscope (laser line at 785 nm). No numerical treatment has been applied. Cova dels Rossegadors: (a) recent flaking area and (b) ochre-coloured crust that covers the panels (objective 20×, 9.58 mW at the focus, integration time 1 s and 25 spectral accumulations, s.a.). (c) Abrigo de los Chaparros: finger dots pictograph, Figs S7 and S20 (Supporting Information), (20×, 23.4 mW, 2 s, 10 s.a.). (d) Cueva de la Vieja: feathery crest of the great shaman, Fig. S4 (Supporting Information), point 005 (20×, 46.8 mW, 2 s, 20 s.a.). (e) Cueva del Queso: paint residues from a zoomorphic figure, Fig. S18 (Supporting Information), (10×, 130 mW, 1 s, 5 s.a.). Labels: ca, calcite; g, gypsum; h, haematite; and w, whewellite.

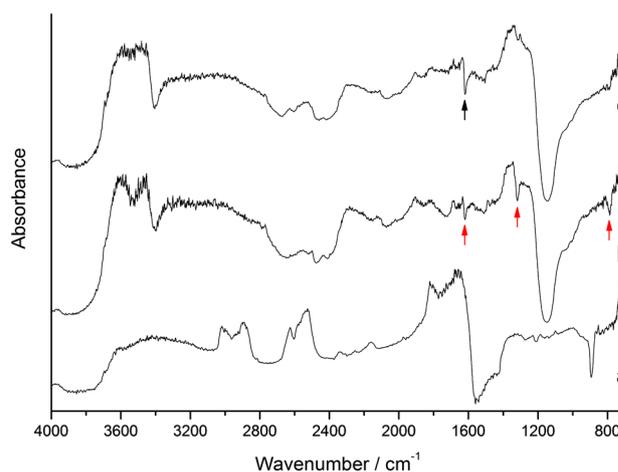


Figure 2. *In situ* DRIFTS spectra from the painting panel of the Cova dels Rossegadors. (a) Representative spectrum from white flaking areas with the typical profile of calcite from rough porous or fracture surface. Spectra (b) and (c) from the ochre crust showing bands of (b) whewellite at 1616, 1315, 779 and 662 cm⁻¹ (red arrows) and (c) gypsum at 1620 cm⁻¹ (black arrow). Both spectra show a broad and strong band at 1148 cm⁻¹ from α -quartz and clay minerals.

and calcite Raman bands from the intense background, Fig. 1(b). Raman bands from the red paint used in the pictographs were not detected. Nevertheless, locations of the panels that have suffered recent flaking are not covered with the crust. They show the original white colour of the rock where the paintings were created. *In situ* Raman spectra of calcite without the intense background are obtained in these locations, Fig. 1(a). DRIFTS spectra of the painting panels of this site collected *in situ* confirm the previous results, Figs 2(a) and (c). However, bands of whewellite at 1616, 1315, 779 and 662 cm^{-1} [Fig. 2(b)], as well as a broad and strong band at 1148 cm^{-1} from α -quartz and clay minerals are also observed. *In situ* Raman and DRIFTS techniques provide information from the surface of the painting panels, but *in situ* EDXRF analyses obtain elemental information from deeper layers. Thus, EDXRF can obtain data from the pigments used in the paintings

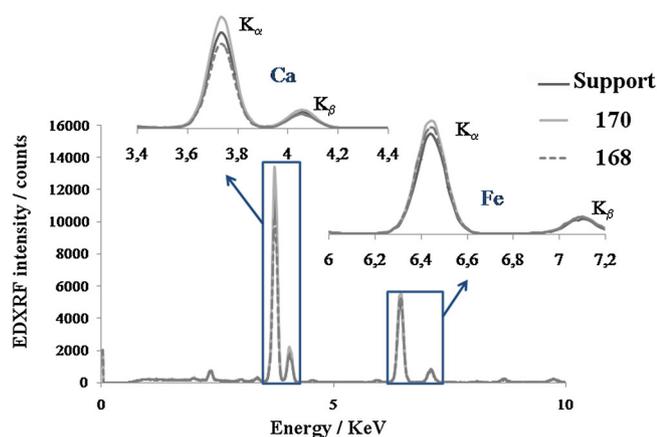


Figure 3. *In situ* EDXRF spectra of the rock supporting the paintings (Support), Fig. 168 (visible bowman) and 170 (invisible goat) from the frame of the Cova dels Rossegadors indicated in Fig. S10. Both figures contain more Fe than the support, but Fe dominates in the invisible goat. The crust is rich in calcite, whereas the support is dolomitic. Thus, the goat covered by the crust has the highest Ca content. On the contrary, the bowman is visible, and it has the lowest Ca content.

even when a crust is covering them. A recent revision of the imagery of this shelter using decorrelation stretch techniques (DStretch)^[13] to enhance visibility of pictographs identified two previously unknown figures, Fig. S10 (Supporting Information). An *in situ* EDXRF analysis of the area of these invisible pictographs, Fig. 3, indicates that the Fe contents is significantly higher than in their surroundings. This observation suggests that the identification of the two figures using DStretch was right, and that an iron pigment was used by the prehistoric artists. A specimen of the bedrock covered with a similar crust to that observed over the paintings was collected next to the shelter. It was the object of a microstratigraphic study. Besides calcite, gypsum, whewellite and clay minerals detected *in situ* using portable Raman (Fig. 1) and handheld DRIFTS (Fig. 2) instruments, dolomite, α -quartz and anatase were detected in this sample using the Jobin Yvon LabRam IR HR-800 confocal Raman microscope, Fig. S11 (Supporting Information). SEM/EDS spectra of this sample agree with these results, Fig. S12 (Supporting Information). Microphotographs of the thin section of the crust show several stratified layers of accretions containing calcite, dolomite and clay. They are distinguished using alizarin red as a differentiation stain, Fig. S13 (Supporting Information). SEM/EDS maps of the corresponding crust area are in agreement with this layer characterisation, Fig. S14 (Supporting Information). Raman images of this area, Fig. 4, show a microstratigraphic layer distribution of dolomite, calcite, α -quartz and clay minerals in the crust that agrees with the previous results. According to the Raman image of Fig. 4(b), the microphotographs (Fig. S13), the SEM/EDS maps (Fig. S14) and the spectra of the coatings (Figs 1, 2 and S11) calcite layers of the crust are interstratified with layers [upper black layers in Fig. 4(b)] containing clay minerals, α -quartz, gypsum, whewellite and anatase. This set of stacked layers on the pictographs is responsible of the difficulties to visualise the figures of this site, as well as the strong fluorescence radiation that masks the possible Raman signals from the pigment used. Wind-blown dust and surface water runoff could have contributed to form these layers. La Poble de Benifassà, where the site is located, is one of the strongest wind places in the Iberian Peninsula. This fact could have contributed to form the observed coatings.

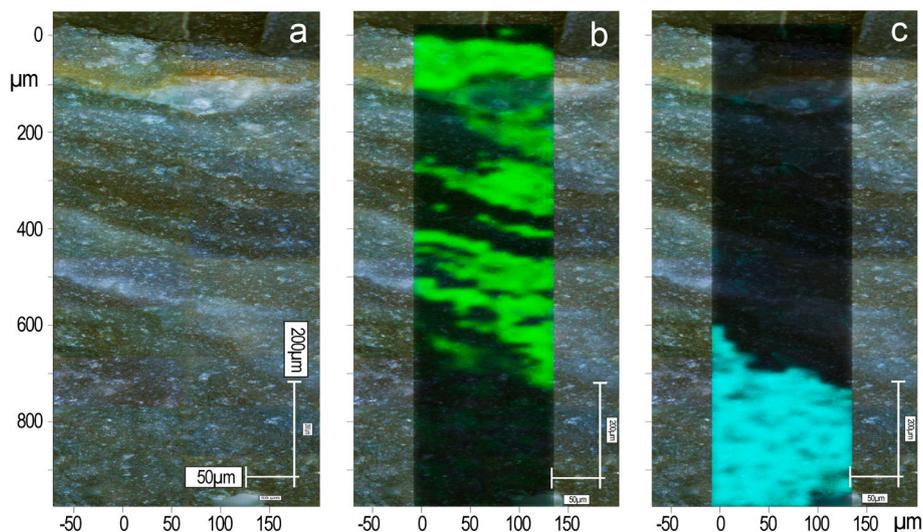


Figure 4. Optical image (a) and superimposed Raman images (b and c) of the cross section of the crust that covers the painting panels of the Cova dels Rossegadors. (b) Green layers: calcite (1079–1089 cm^{-1}) from the crust. (c) Blue region: dolomite (1089–1100 cm^{-1}) from the original rock.

Cueva de la Vieja and Cueva del Queso

Water spraying on the painting panels of rock art shelters has been a common practice to enhance visibility of the pictographs with the naked eye. Since the discovery of the Cueva de la Vieja site in 1912,^[8] this repeated practice dissolved salts and move materials from the underlying rock. They recrystallised and coated the surface of the painting panel. The result is that a white crust of anthropic origin is covering the paintings, and they are difficult to see nowadays, Figs S15 and S16 (Supporting Information). Very strong spectral background of fluorescence radiation was observed studying this panel by *in situ* μ -RS. Nevertheless, some points of the red figures indicated that haematite was used as pigment, Fig. 1(c). Detailed μ -RS analyses of a panel micro-specimen with the LabRam IR HR-800 confocal Raman

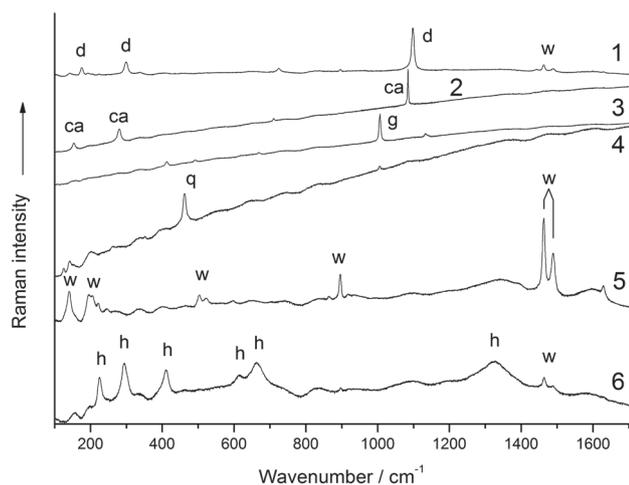


Figure 5. Representative μ -RS spectra from a panel specimen of the Cueva de la Vieja site obtained with the laboratory confocal Raman microscope Jobin Yvon LabRam-IR HR-800 (laser line at 632.8 nm). No numerical treatment has been applied. Labels: ca, calcite; d, dolomite; g, gypsum; h, haematite; q, α -quartz; and w, whewellite.

microscope revealed the presence of whewellite, dolomite, α -quartz, gypsum, calcite and haematite in the crust deposited over the paintings, Fig. 5. Small amounts of whewellite were detected together with dolomite, Fig. 5(1) and haematite, Fig. 5(6). Raman images of a thin cross section of the specimen, Fig. 6, indicate that calcite is concentrated in the part of the crust closer to the original rock, dolomite is distributed along the cross section and whewellite is concentrated on the crust surface. The latter result is very important from the archaeological point of view. This external layer of whewellite could be used to establish an *ante quem* date for the paintings by radiocarbon dating. In some cases, layers of calcium oxalate bracketed the pigment layer, and thus *ante quem* and *post quem* radiocarbon dating of these layers enclose the date of the pictorial event.^[6,12,14–16] SEM/EDS maps of the cross section, Fig. S17 (Supporting Information), show that Si, Al and K are concentrated on the most external layer of the crust, i.e. α -quartz and clay minerals are more abundant in this layer. Clay minerals give rise often to strong fluorescence radiation when excited by laser lines, even at 1064 nm.^[17] This could be the cause of the strong spectral background observed in the *in situ* μ -RS studies of the panel, and the difficulties arisen to characterise the pigments used.

The Cueva del Queso is located at about 300 m from the Cueva de la Vieja and in the same rock mass. Soon after its discovery, in 1911, most of the figures of the site were removed by vandals. The *in situ* Raman analyses of several paint remains, Fig. S18 (Supporting Information), showed that the pigment used was haematite, Fig. 1(e). The components identified in the crust of the painting panel of this site were similar to the components detected previously in the Cueva de la Vieja analyses, i.e. dolomite, calcite, gypsum and whewellite.

Abrigo de los Chaparros

The painting panel in this rock shelter is coated with an ochre-coloured crust similar to that found in Cova dels Rossegadors, Fig. S19 (Supporting Information). Strong spectral background of fluorescence radiation was also observed in the Raman spectra

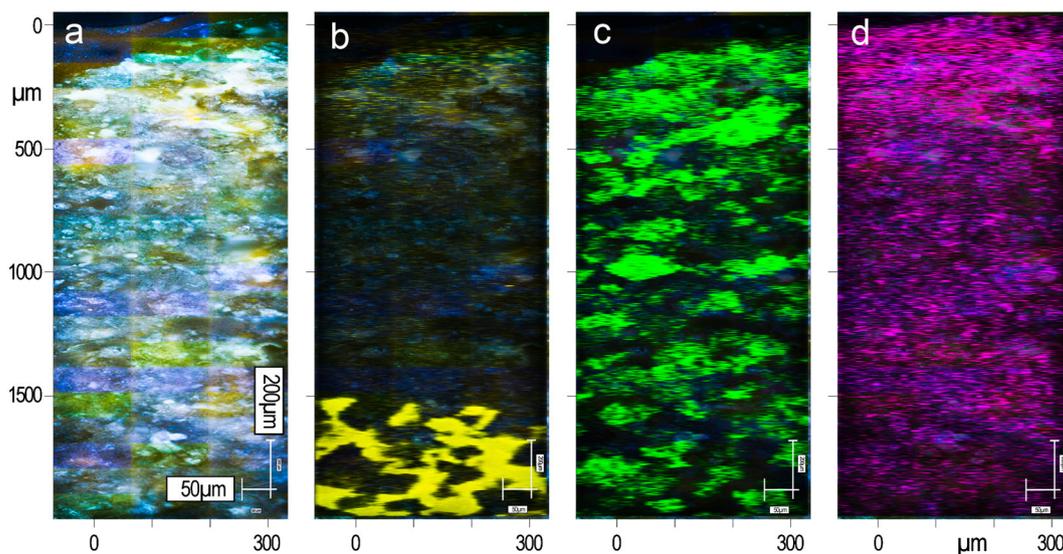


Figure 6. Optical image (a) and superimposed Raman images (b, c and d) of the cross section of the crust that covers the painting panel of the Cueva de la Vieja shelter. Colour code of different components: (b) yellow, calcite (1079 – 1089 cm^{-1}); (c) green, dolomite (1089 – 1100 cm^{-1}); and (d) magenta, whewellite (1440 – 1520 cm^{-1}).

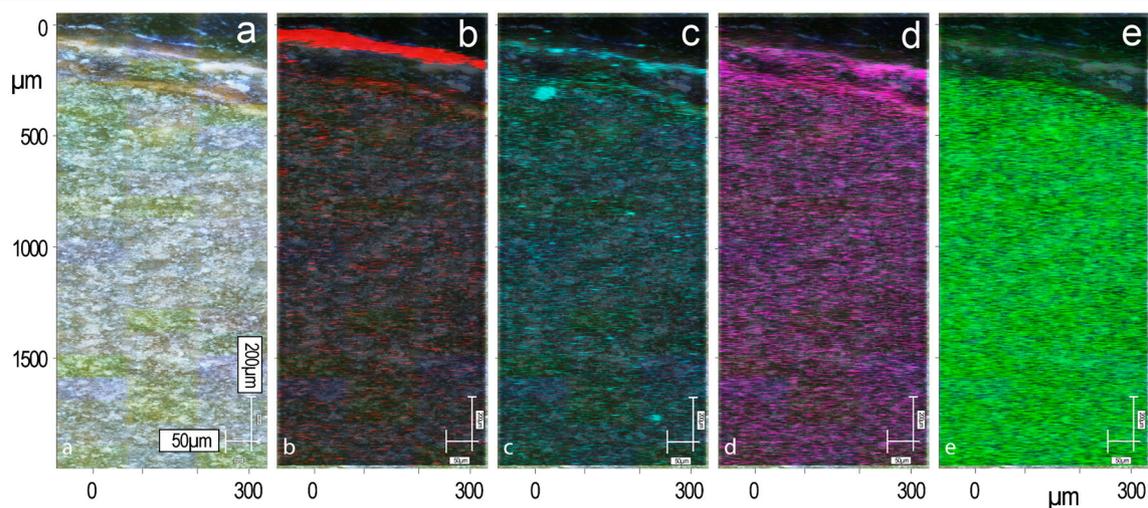


Figure 7. Optical image (a) and superimposed Raman images (b, c, d and e) of the cross section of the crust that covers the painting panel of the Abrigo de los Chaparros shelter. Colour code of different components: (b) red, gypsum ($1002\text{--}1010\text{ cm}^{-1}$); (c) blue, clay minerals ($1155\text{--}1205\text{ cm}^{-1}$); (d) magenta, whewellite ($1440\text{--}1520\text{ cm}^{-1}$); (e) green, dolomite ($1089\text{--}1100\text{ cm}^{-1}$).

of the crust recorded *in situ* and excited at 785 nm. Only one of the red pictographs not completely covered by the crust, Figs S7 and S20 (Supporting Information), provided Raman bands of its components: haematite, gypsum and whewellite, Fig. 1(c). The μ -RS study of the cross section of a micro-specimen of the painting panel, Fig. S21 (Supporting Information), detected dolomite, calcite, gypsum and whewellite in the crust, Fig. S22 (Supporting Information). Raman images of the cross section, Fig. 7, show two gypsum layers on the surface and two other layers of whewellite, one of them between the gypsum layers. Clay minerals are also observed on the surface. Dolomite is the main component of the rock where the paintings were drawn. Calcite is a minor component (not shown in Fig. 7). Like in the case of the Cueva dels Rossegadors, the detection of the external layers of whewellite is a first step to achieve radiocarbon dates for the rock art of the site. SEM/EDS maps of the cross section, Fig. S23 (Supporting Information), show that Si and Al are concentrated in the most external layer of the coating. This agrees with the Raman images and suggests that clay minerals are present on the crust surface. They could be the origin of the strong fluorescence radiation observed in the *in situ* Raman studies of the painting panel. Evidences of surface water runoff are observed on the walls of the rock shelter. The metabolic activity of microorganisms, fungi and lichens colonising the rock surface could have produced the whewellite layers.^[14,18] The site is in an arid valley and wind-blown dust could also have contributed to the formation of the observed crust.

Abrigo Riquelme

A large number of red and black Schematic figures were painted on the walls of this rock shelter, Fig. S24 (Supporting Information). Severe rock fracture and flaking processes are affecting the site. Ochre and grey crusts cover the walls, and figures are difficult to see. Enhanced images applying Dstretch software^[13] reveal clearly the characteristics of the figures, Fig. S25 (Supporting Information). *In situ* μ -RS analyses of the pictographs using the laser line at 785 nm collected spectra with strong spectral background of fluorescence radiation and no Raman band. Only by analysing the black figure no. 9, Fig. S25, it was possible

to achieve a spectrum *in situ* with significant Raman bands, Fig. 8. Despite the strong spectral background and poor S/N ratio, broad bands at 1313 and 1585 cm^{-1} from amorphous carbon indicate that soot or charcoal has been used as pigment. The absence of an additional band of the phosphate group ($\nu_s\text{ PO}_4^{3-}$) in the region of $960\text{--}980\text{ cm}^{-1}$ suggests that bone black was not used. Bands of calcite and whewellite are also observed. Calcite, gypsum, amorphous carbon and whewellite were identified by the μ -RS analyses of the cross section of a micro-specimen of the painting panel, Fig. S26 (Supporting Information). The presence of gypsum on the surface suggests a deterioration process that could contribute to the observed flaking and spallation of the painting panel.^[12,14] Raman images of the cross section, Fig. 9, show that calcite is dominant in the substrate. Some micro-particles of dolomite and clay minerals are observed in the rock. Nevertheless, crust layers are not observed. A very thin coating of the

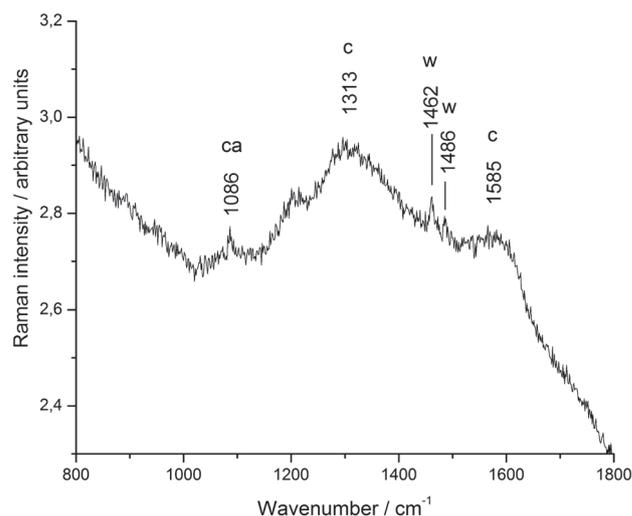


Figure 8. Raw μ -RS spectrum obtained *in situ* from the black figure no. 9 (Figs S24 and S25d–S25f, Supporting Information) of the Abrigo Riquelme with a BWTEK innoRam 785H portable Raman microscope (laser line at 785 nm). No numerical treatment has been applied. Conditions: objective $10\times$, 69 mW at the focus, integration time 2 s and 16 spectral accumulations. Labels: ca, calcite; c, amorphous carbon; and w, whewellite.

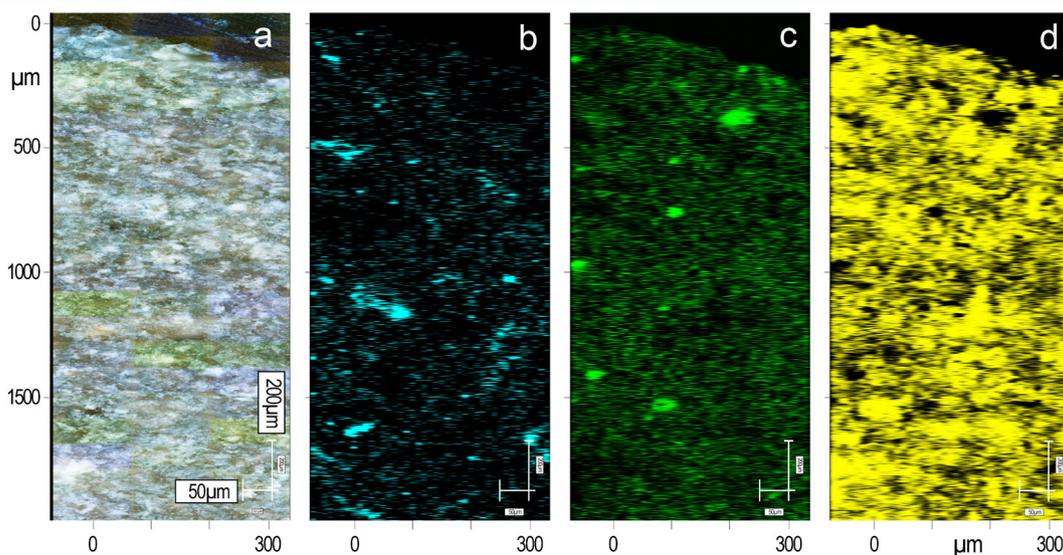


Figure 9. Optical image (a) and superimposed Raman images (b, c and d) of the cross section of a specimen of the painting panel of the Abrigo Riquelme shelter. Colour code of different components: (b) blue, clay minerals ($1155\text{--}1205\text{ cm}^{-1}$); (c) green, dolomite ($1089\text{--}1100\text{ cm}^{-1}$); (d) calcite ($1079\text{--}1089\text{ cm}^{-1}$).

Table 1. Components identified in the rock, crusts and pigments of the painting panels in five rock shelters of the Iberian Peninsula. Crust components are given in order of abundance

Rock shelter	Rock components		Crust components	Pigments
	Primary phase	Secondary phases		
Cova dels Rossegadors	Dolomite		Calcite, clay, α -quartz, gypsum, whewellite, dolomite and anatase	Iron pigment
Cueva de la Vieja	Calcite	Dolomite	Whewellite, dolomite, α -quartz, clay, gypsum, calcite and haematite	Haematite
Cueva del Queso	Calcite	Dolomite	Dolomite, calcite, gypsum and whewellite	Haematite
Abrigo de los Chaparros	Dolomite	Calcite	Dolomite, calcite, gypsum, clay, whewellite and gypsum,	Haematite
Abrigo Riquelme	Calcite	Dolomite and clay	Calcite, gypsum, clay and whewellite	Amorphous carbon

panel not well resolved by the images could be the reason. On the other hand, the use of red and black paints with a high content in clay minerals could contribute to the difficulties encountered to identify the used pigments.

The results obtained in these sites are summarised in Table 1. It is interesting to note that whewellite has been detected on the surface of all the studied painting panels. When the whewellite content is significant, it appears concentrated in stratigraphic layers adjacent to the rock surface, i.e. an inhomogeneous distribution has not been observed.^[19] A really relevant information regarding future opportunities to undertake a scientific dating of these rock art sites.

Conclusions

The portable μ -RS instrument used together with EDXRF and DRIFTS handheld spectrometers is an appropriated equipment to carry out *in situ* studies of rock art paintings in open-air rock shelters. The two last techniques are especially useful in those

cases where crusts covering the pictographs or strong fluorescence radiation hinder the detection of Raman signals from the pigments. The presence of concealed pictographs has been confirmed by *in situ* EDXRF. Nevertheless, extreme attention must be dedicated to the *in situ* μ -RS operating conditions: sunlight, wind, vibrations, objective lenses, focusing, dust, power supply, laser power at the focus position, integration time and number of spectral accumulations. Some proposals to face the difficulties found applying this technique in rock shelters have demonstrated to be efficient (such as Càrol's cap, stable support, handheld probe head or microscope/videocamera set). Microstratigraphic μ -RS and SEM/EDS studies of micro-specimens extracted from the painting panels have revealed that dolomite and calcite are the main components of the rocks supporting the paintings. Whewellite, gypsum, calcite, clay, dolomite, α -quartz, anatase and haematite have been detected in crusts that cover most of the studied painting panels. These materials appear normally distributed in interstratified layers. Haematite and amorphous carbon have been identified in red and black pictographs, respectively.

Acknowledgements

We gratefully acknowledge Dr S. Martin (UNED) for their help in recording SEM/EDX data, Carolina Allepuz for technical assistance in the sites, as well as Prof. J.M. Gavira (UNED), J. Royo (Parque Cultural del Río Martín), E. Hernández Carrión (Museo Arqueológico Municipal Jerónimo Molina, Jumilla), A.J. Medina Ruiz, F.J. Martínez Collado and M. San Nicolás del Toro (Centro de Estudios de Prehistoria y Arte Rupestre. Comunidad Autónoma de la Región de Murcia) for their contributions to the *in situ* analyses, images of the pictographs and interpretations of the observed results. Technical and human support provided by SGIker (UPV/EHU, MICINN, GV/EJ and ESF) is gratefully acknowledged. This work has been financially supported by the Ministerio de Ciencia e Innovación (MICINN, project CTQ2009-12489BQU), Consejería de Cultura de la Junta de Comunidades de Castilla-La Mancha (project Cal a.C.2008-10), The University of the Basque Country (project UFI11-26 Global Change and Heritage) and European Regional Development Fund (ERDF). We also thank Autonomous Communities of Valencia, Aragón, Castilla-La Mancha and Murcia permission to work in the archaeological sites.

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Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Spectroscopic characterisation of crusts interstratified with prehistoric paintings preserved in open-air rock art shelters.

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Supplementary Material

Fig. S1. Location of rock art shelters studied by our research group using μ -RS. This work: (1) Cova dels Rossegadors (Pobla de Benifassà, Castellón); (2) Abrigo de los Chaparros (Albalate del Arzobispo, Teruel); (3) and (4) Cueva de la Vieja and Cueva del Queso (Alpera, Albacete); (5) Abrigo Riquelme (Jumilla, Murcia). Previous studies: (6) Los Toros del Barranco de las Olivanas (Albarracín, Teruel); (7) and (8) Ceja de Piezarrodilla and Cabras Blancas (Tormón, Teruel); (9), (10), (11) and (12) Selva Pascuala, Peña del Escrito II, Marmalo III and Marmalo IV (Villar del Humo, Cuenca); (13) Cueva del Tío Modesto (Henarejos, Cuenca); (14) Hoz de Vicente (Minglanilla, Cuenca); (15) Abrigo Remacha (Villaseca, Segovia).

Fig. S2. The portable Raman microscope BWTEK innoRam 785H in the Cueva de la Vieja (upper left) and Cueva del Queso (upper right and down) rock shelters.

Fig. S3. Digital reproduction (scale length 10 cm) of one of the painting panels of the Cova dels Rossegadors shelter that have been analysed *in situ* using a portable μ -RS microscope, as well as handheld EDXRF and DRIFTS instruments. Pictographs studied are numbered. Additional images and their interpretation in J.F. Ruiz López, C. Allepuz García, *Zephyrus* **2011** ; LXVIII, 115.

- Fig. S4.** Digital reproduction (according original drawings from Juan Cabré on 1915; scale length 50 cm) of the painting panel of the Cueva de la Vieja shelter^[8] indicating locations from which acceptable spectra have been achieved by *in situ* μ -RS. Most of the figures are not visible today because of crust covering the pictographs.
- Fig. S5.** Digital reproduction (scale length 40 cm) of some pictographs from the Abrigo de los Chaparros shelter (according to A. Beltrán Martínez and J. Royo Lasarte, 1996) indicating locations that have been analysed *in situ* using a portable μ -RS microscope, in addition to handheld EDXRF and DRIFTS instruments.
- Fig. S6.** Raman spectra obtained *in situ* from the painting panel of the Cova dels Rossegadors with the portable Raman microscope BWTEK innoRam 785H using 20x objective in the microscope/videocamera set. (a) Sunlight spectral background with Fraunhofer lines entering through the objective. (b) Spectrum of the same point of the painting panel covering the objective with the Carol's cap, bands of gypsum (g) and calcite (ca) emerge from the strong background of fluorescence radiation.
- Fig. S7.** The microscope/videocamera set of the Raman microscope BWTEK innoRam 785H focussed on a pictograph of the Cova dels Rossegadors without sunlight protection (upper left). The same microscope focussed on a pictograph of the Selva Pascuala rock shelter (Villar del Humo, Cuenca, Spain) with the Carol's cap mounted on the objective (upper right). The probe head on a pictograph of the Abrigo de los Chaparros with the Carol's cap installed to avoid sunlight entering the Raman spectrometer (down).
- Fig. S8.** The portable Raman microscope in the Cova dels Rossegadors. Blurred images from the video camera, provoked by the wind, and microscope focussing improve hanging a heavy backpack from the tripod.
- Fig. S9.** The portable Raman microscope in Ceja de Piezarrodilla rock shelter (Tormón, Teruel, Spain). A polyethylene sheet is covering the floor to protect the instruments from du
- Fig. S10.** (Left) Pictographs 169 (anthropomorph) and 170 (goat) included in the frame of the digital reproduction (scale length 10 cm) of the painting panel corresponding to Lámina 11 of the Cova dels Rossegadors. These two figures cannot be visualised directly due to the crust that covers them. (Center) Photograph of the frame. (Right) DStretch enhanced image revealing the presence of underlying pictographs.
- Fig. S11.** Representative Raman spectra recorded from a specimen of the crust covering the painting panels of the Cova dels Rossegadors with a Jobin Yvon LabRam IR HR-800 laboratory Raman microscope. Labels: q, α -quartz; g, gypsum.
- Fig. S12.** Representative EDS spectrum of the crust specimen extracted from the painting panel of the Cova dels Rossegadors.
- Fig. S13.** Microphotographs of the thin cross-section of the crust covering the paintings of the Cova dels Rossegadors. (Left) Alizarine red staining affinity for calcite differentiates layers with calcite from those with silicates (grey) and dolomite (white rock). (Right) Image of other crust area not stained with alizarine to obtain Raman spectra (several studied points are numbered) and Raman maps.
- Fig. S14.** SEM/EDS maps of the crust area corresponding to the microphotograph of the Fig S15 (right). Si and Al are concentrated in the gray/black layer of silicates. Si concentration at the bottom of the image is due to the glass slide supporting the thin cross-section.
- Fig. S15.** Water spraying effect on the painting panel of the Cueva de la Vieja shelter since 1915 (Fig. S4). The goat and shaman in the frame are difficult to see due to the white crust that covers them nowadays.

- Fig. S16.** A zoomorph figure covered by the white crust of the painting panel of the Cueva de la Vieja site. This is another example of the water spraying effect..
- Fig. S17.** SEM/EDS maps of the cross section of the crust that covers the painting panel of the Cueva de la Vieja site. Si, Al and K are concentrated in the most external layer of the crust.
- Fig. S18.** One of the two painting remains that survived vandalism in the Cueva del Queso site shortly after its discovery on 1911.
- Fig. S19.** Pictograph of a deer covered by the ochre-coloured crust of the Abrigo de los Chaparros.
- Fig. S20.** Finger dots in the Abrigo de los Chaparros.
- Fig. S21.** Microphotograph of a thin cross section of the crust that covers the paintings of the Abrigo de los Chaparros. Some of the points studied by μ -RS are indicated.
- Fig. S22.** Representative Raman spectra from a thin cross section of the crust that covers the painting panel of the Abrigo de los Chaparros recorded with a Jobin Yvon LabRam IR HR-800 confocal Raman microscope. Labels: c, calcite; d, dolomite; g, gypsum; w, whewellite.
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- Fig. S24.** Photograph of the walls of the Abrigo Riquelme rock shelter. Locations and numbering of the figures are indicated. They are distributed in a surface of about 10 m².
- Fig. S25.** Two figures from Abrigo Riquelme site. Red finger dots, figure no. 3: (a) location; (b) photograph; (c) Dstretch enhanced image. Black traces, figure no. 9: (d) location; (e) photograph; (c) Dstretch enhanced image.
- Fig. S26.** Representative Raman spectra from a thin cross section of the painting panel of the Abrigo Riquelme recorded with a Jobin Yvon LabRam IR HR-800 confocal Raman microscope. Labels: ac, amorphous carbon; c, calcite; g, gypsum; w, whewellite.



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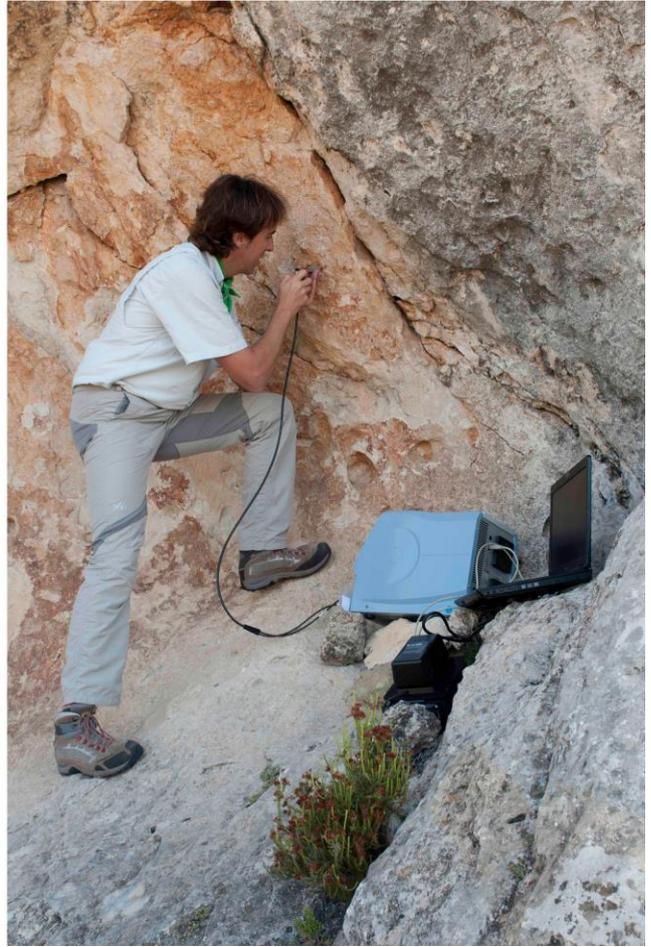


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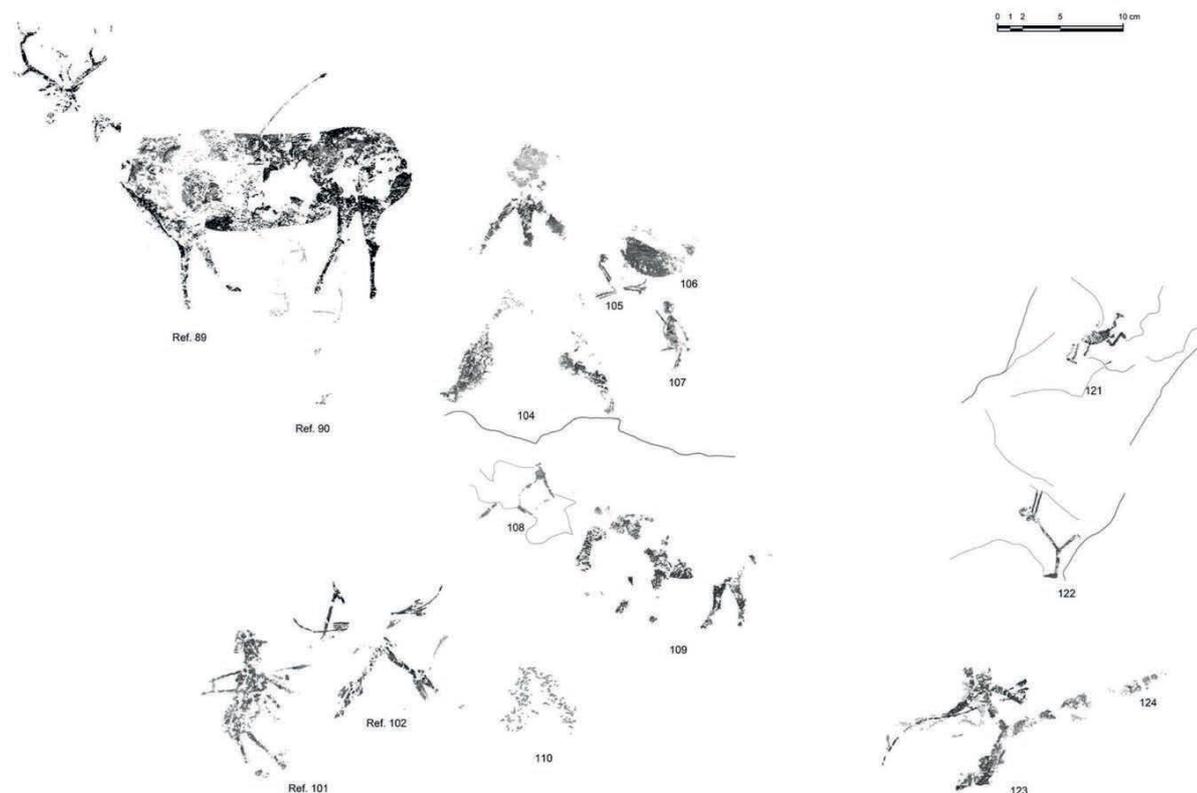


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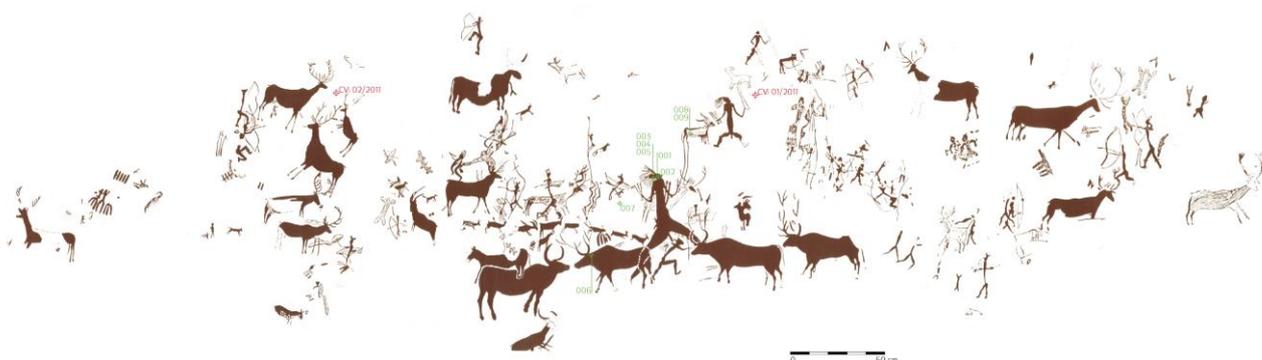


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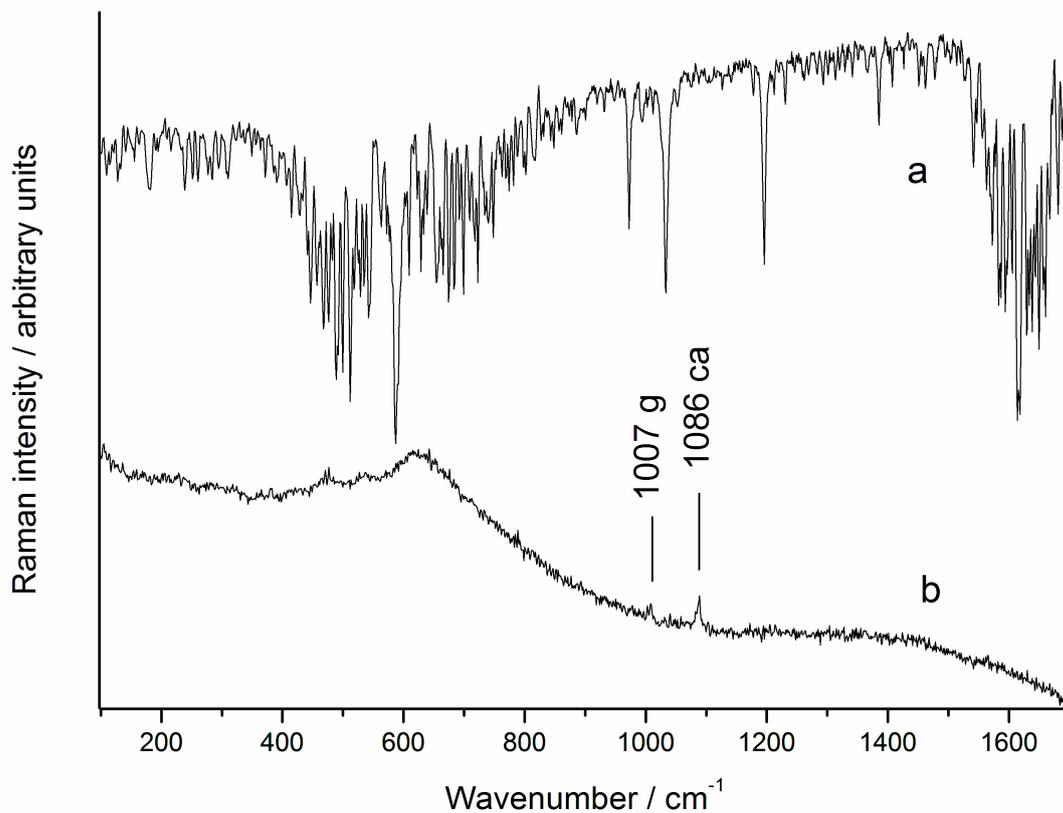


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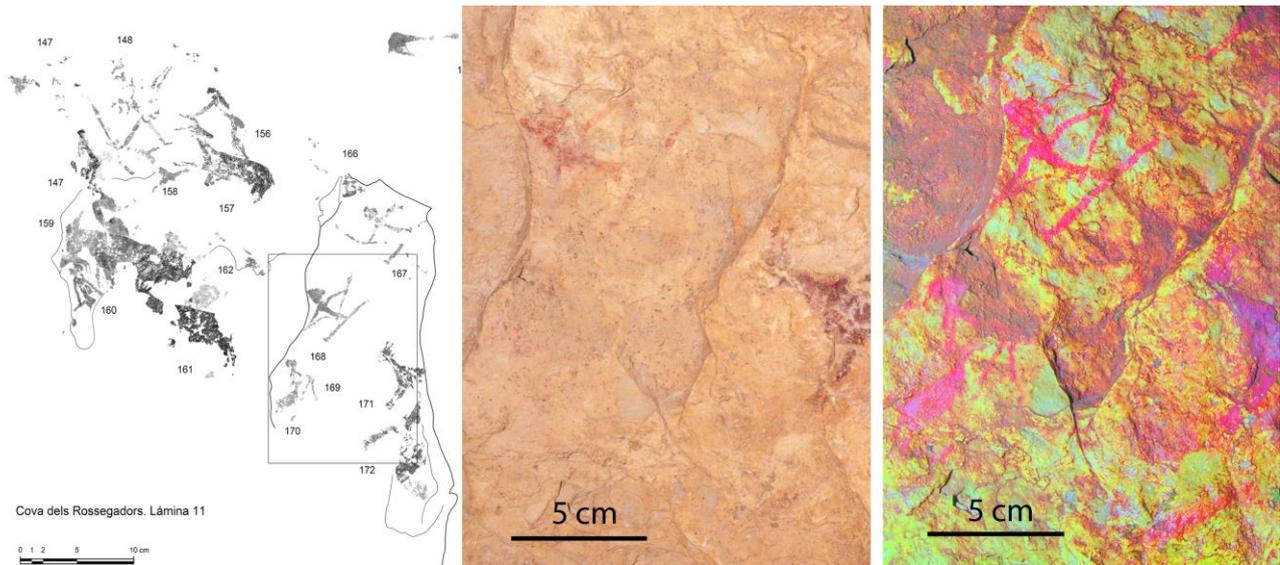


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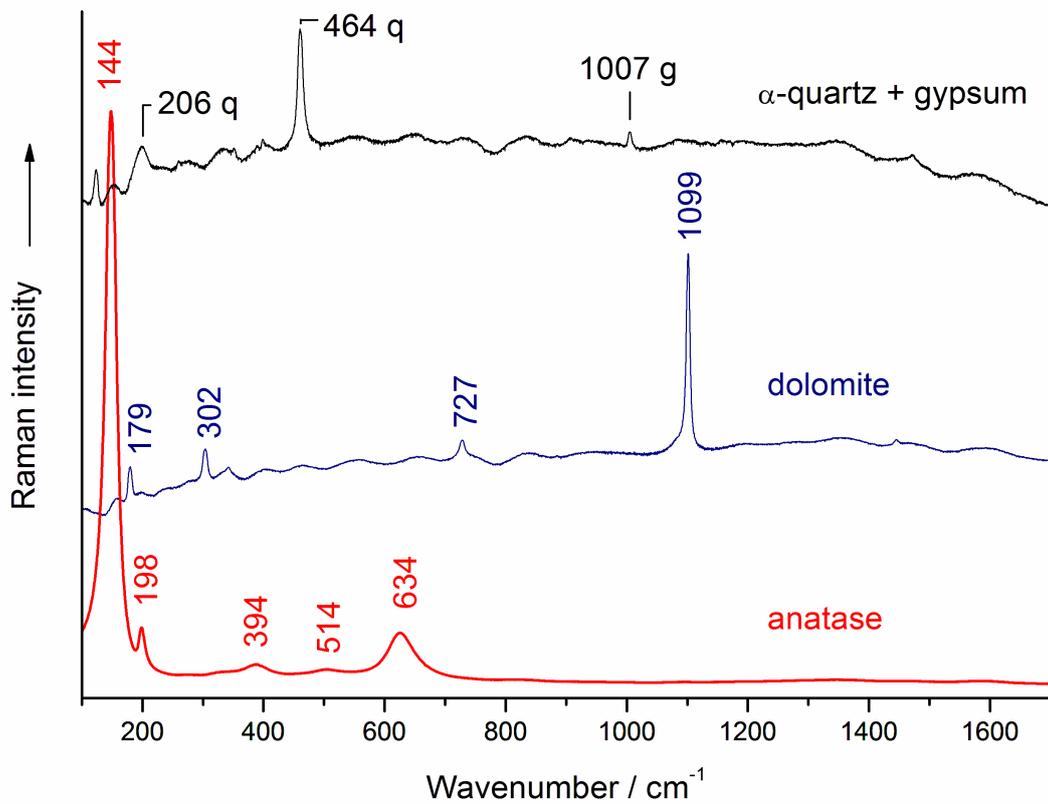


Figure S11. Representative Raman spectra from a specimen of the crust covering the painting panels of the Cova dels Rossegadors recorded with a Jobin Yvon LabRam IR HR-800 confocal Raman microscope. Labels: q, α -quartz; g, gypsum.

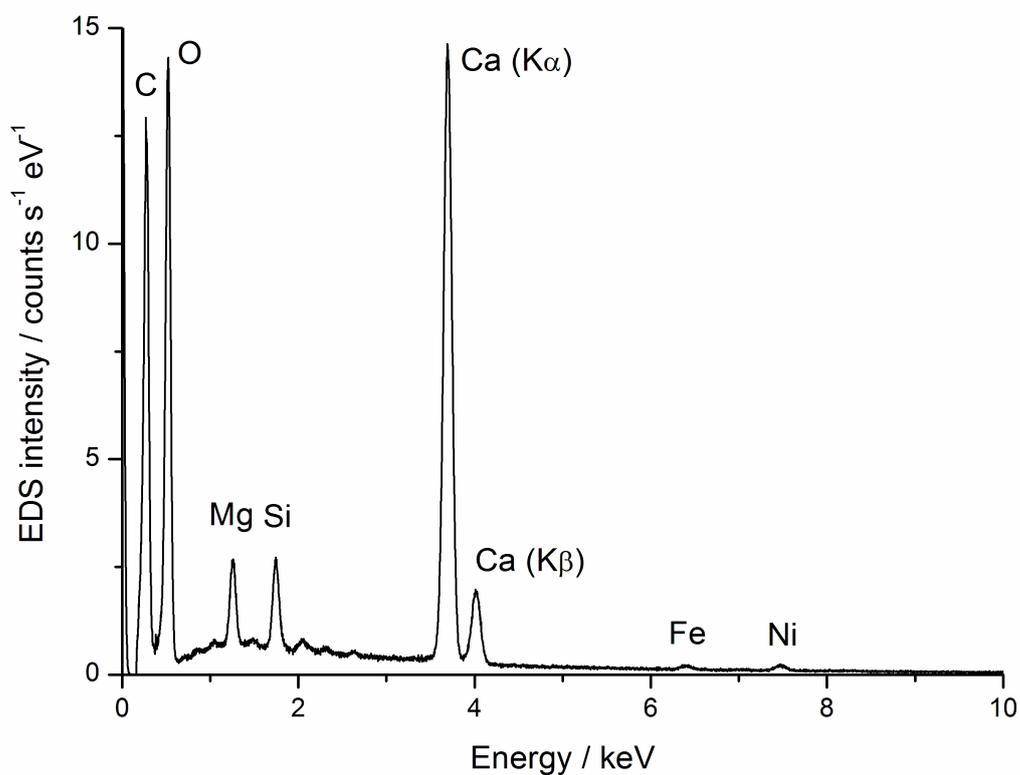


Figure S12. Representative EDS spectrum of the crust specimen extracted from the painting panel of the Cova dels Rossegadors.

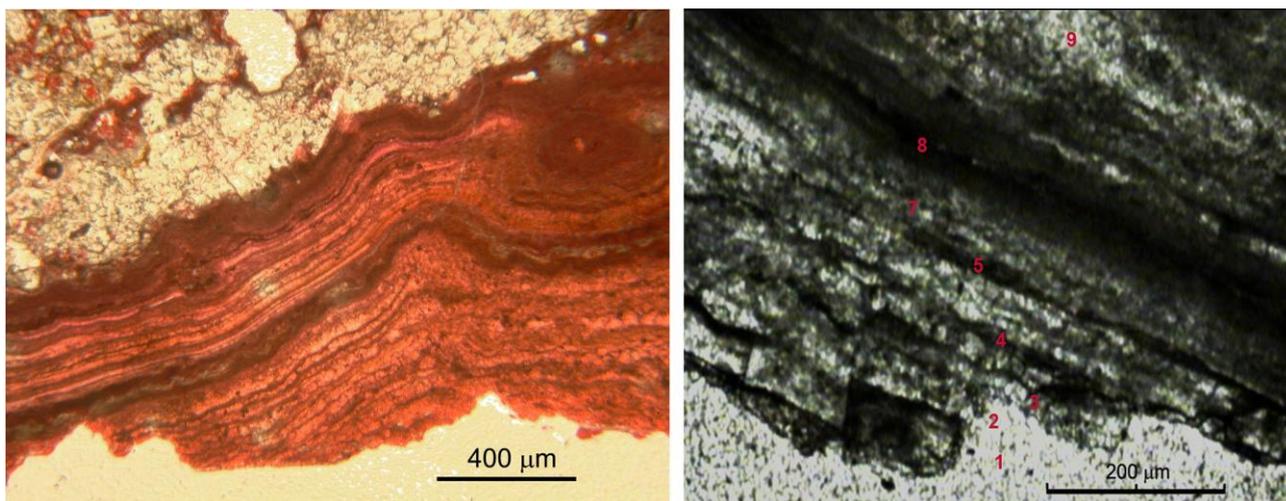


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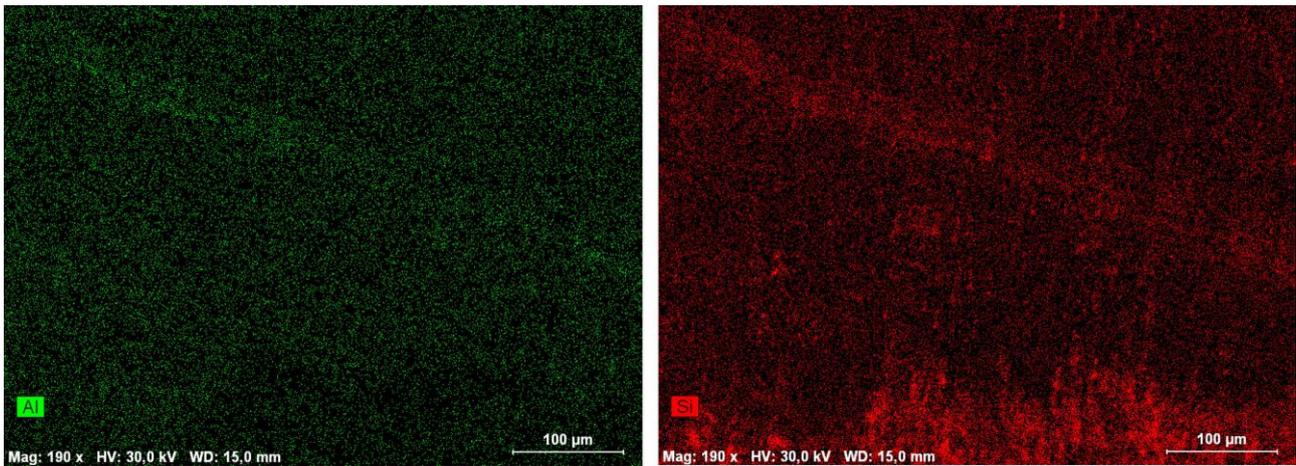


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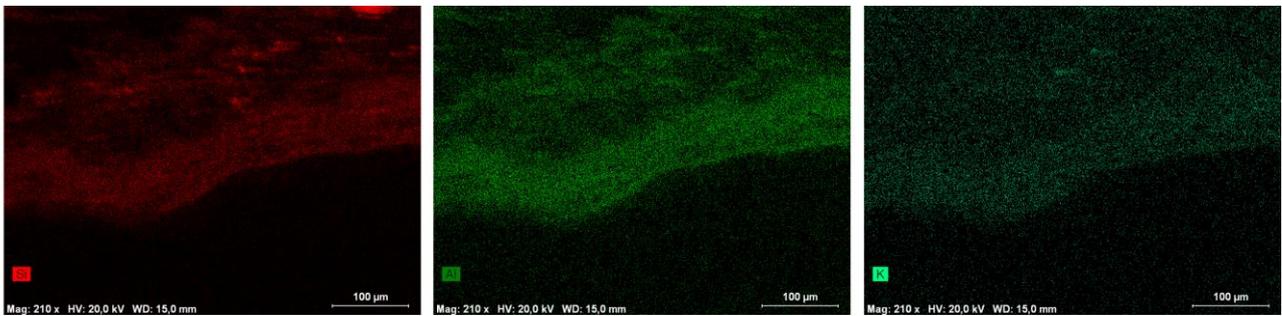


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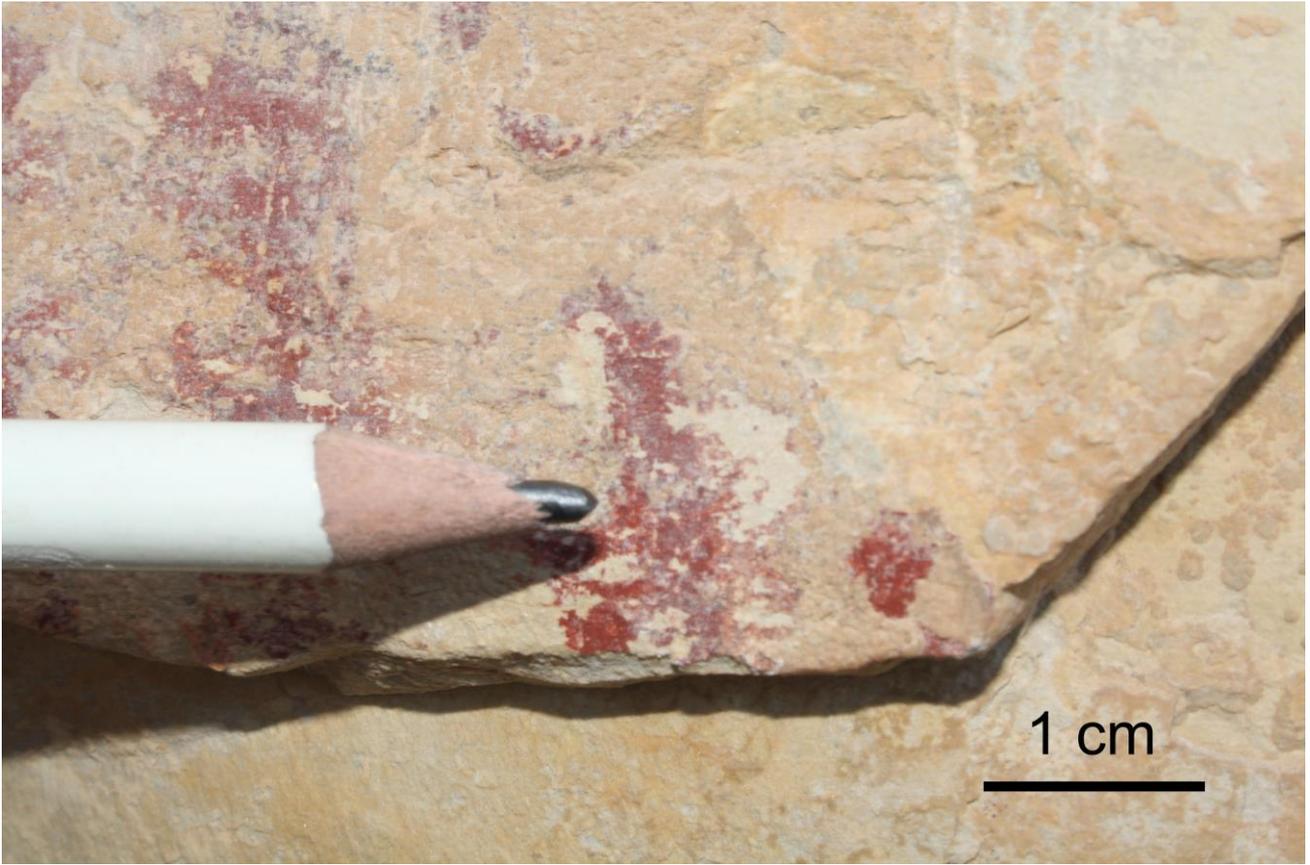


Figure S20. Finger dots in the Abrigo de los Chaparros.

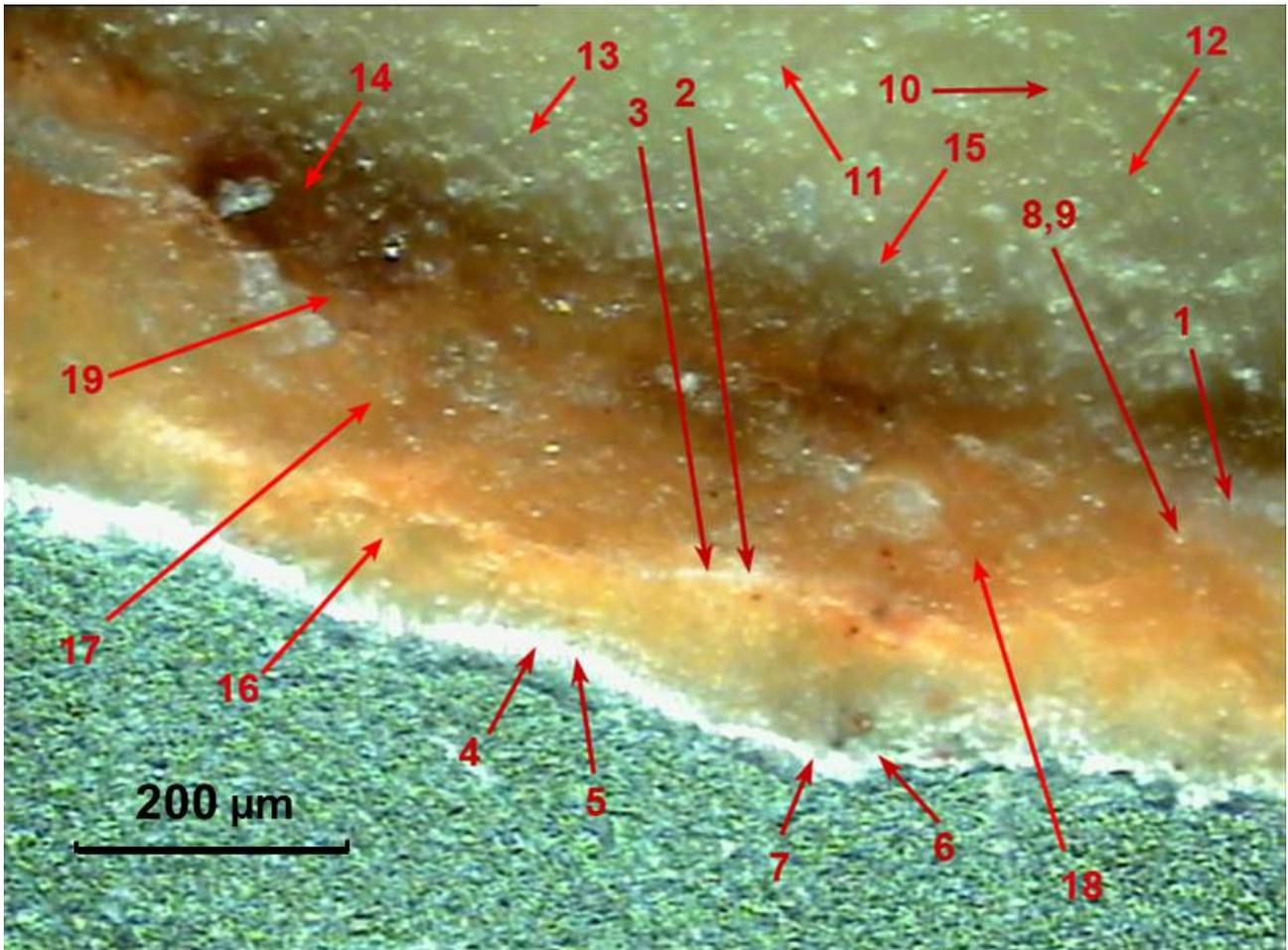


Figure S21. Microphotograph of a thin cross section of the crust that covers the paintings of the Abrigo de los Chaparros. Some of the points studied by μ -RS are indicated.

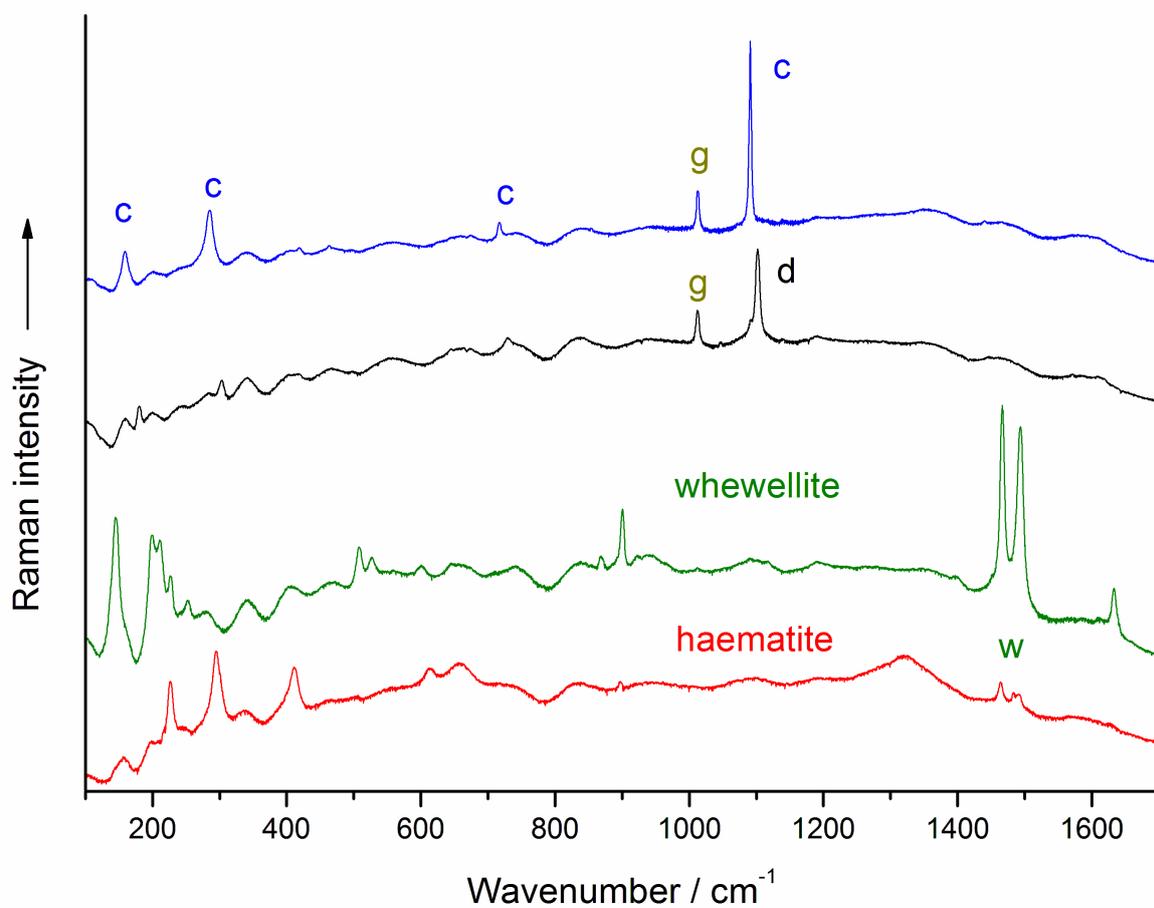


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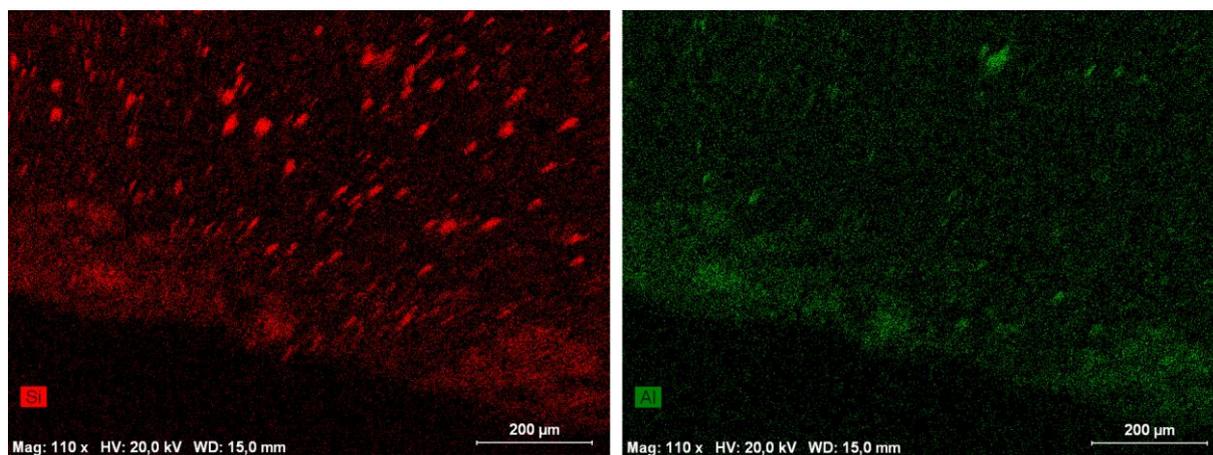


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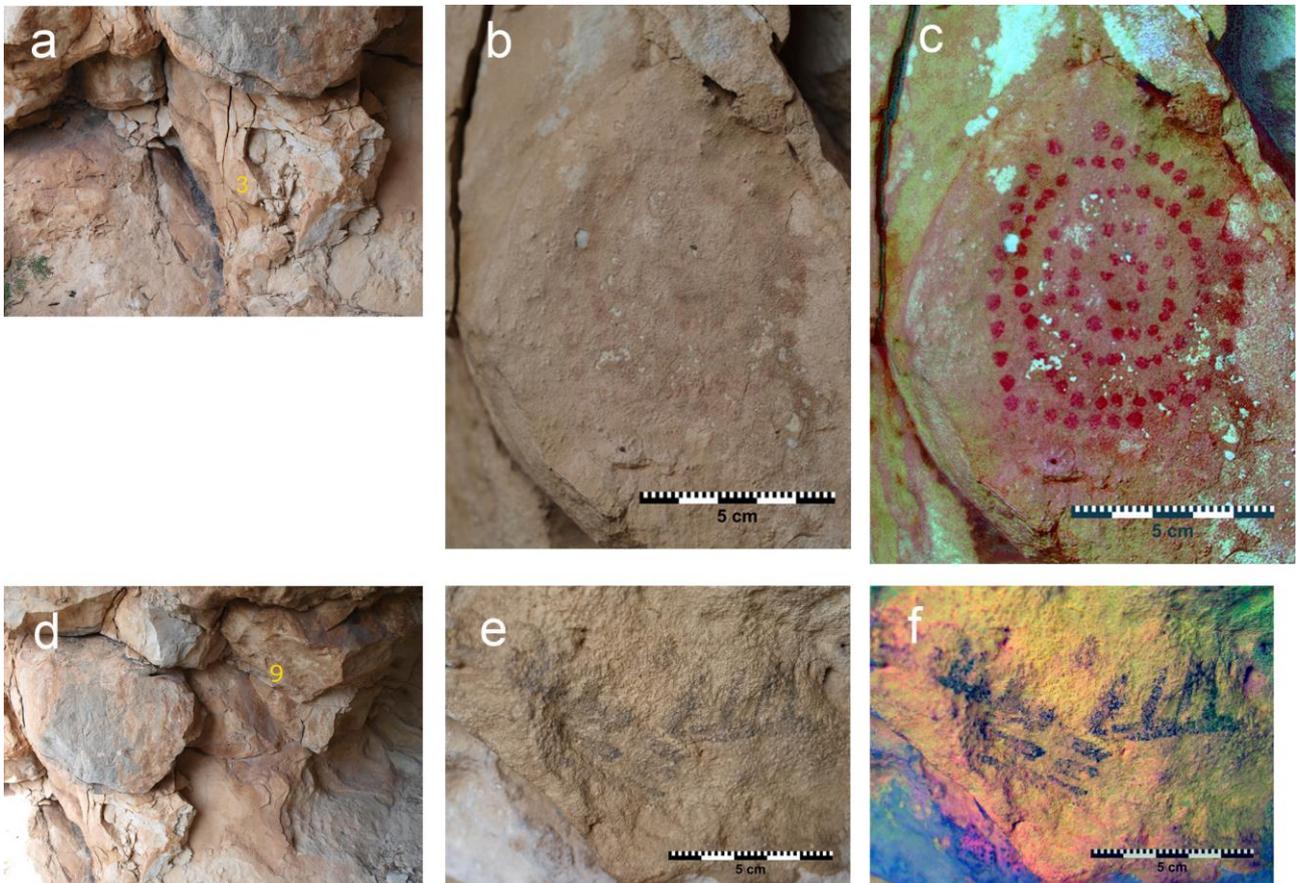


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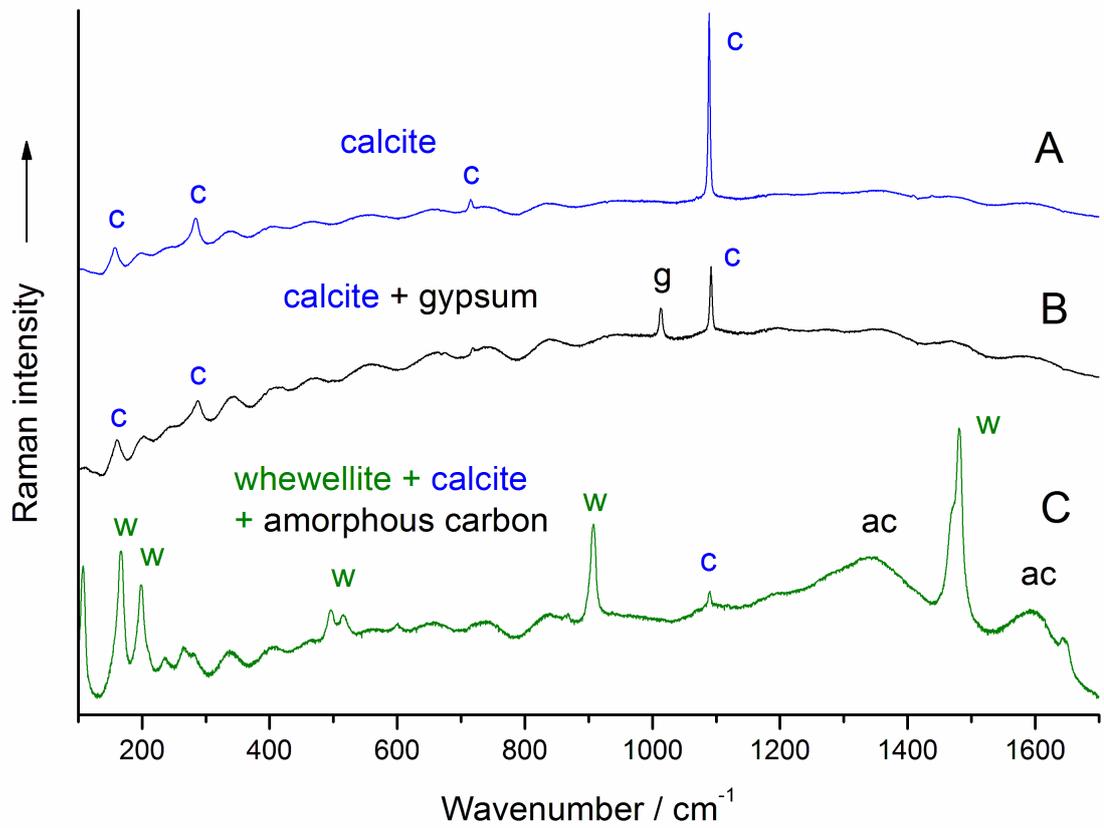


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