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Raman microscopy of prehistoric rock paintings from the Hoz de Vicente, Minglanilla, Cuenca, Spain†

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The third painted panel of the Hoz de Vicente rock shelter (Minglanilla, Cuenca, Spain) contains a series of prehistoric pictographs which were studied by Raman microscopy. Scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX) and petrographic polarised light microscopy were used as auxiliary techniques. The results obtained indicate that well-crystallised haematite (α-Fe_2O_3) of grain size less than 1 μm was used as red pigment. However, amorphous carbon, probably vegetable charcoal or soot, was used as the black pigment. A patina of whewellite and weddellite covers the areas of the painting panel with pictographs. The microstratigraphic study of a schematic figure revealed that the layer of pigment is sandwiched between layers of these hydrated forms of calcium oxalate produced by the activity of fungi and lichens. These products have also been detected in the layer of pigment. These findings will enable obtaining limiting radiocarbon ^{14}C accelerator mass spectrometry (AMS) dates for the corresponding pictorial events. On the other hand, crystallisation of gypsum in the external layers of the panel is related to the deterioration observed in the flaking areas. Gypsum and clayish minerals appear as the main components of an ochre-coloured accretion covering several parts of the panel.

Supporting information may be found in the online version of this article.

Keywords: Raman microscopy; SEM/EDX; rock art; pigments; prehistoric paintings

Introduction

In the eastern half of Spain there are around 1500 open-air rock shelters with paintings on their walls. In 1998, they were included in the UNESCO World Heritage List under the generic denomination of *Rock Art of the Mediterranean Basin on the Iberian Peninsula*. This exceptionally large group of painted and engraved rock shelters includes, at least, four different styles: palaeolithic art, levantine art, macro-schematic art and schematic art. Raman spectroscopy, combined occasionally with other techniques, is an efficient tool to determine the composition of the materials present in prehistoric paintings.[1–8] Our group is applying Raman microscopy assisted with scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM/EDX) and polarised light microscopy to study paintings from a series of archaeological sites within the indicated geographical and cultural areas[9–13] (Fig. S1,). The characterisation of the composition of the pigments, binders, substrata and accretions, as well as their microstratigraphy and chemical alterations, are the main objectives of this investigation. This information is fundamental to consider potential radiocarbon absolute dating,[14–19] to investigate degradation processes[9,10,13] and to undertake the appropriate conservation action of the paintings. In the present work, we study the painted panel 3, Fig. 1, of the Hoz de Vicente rock shelter. This site is located in Minglanilla municipality (Cuenca, Spain) (Fig. S2). Pictographs, accretions, substrata and alterations observed in this panel were analysed to identify the pigment palette composition and to determine the nature and origin of the accretions and alterations detected. The results will provide basic data on the technologies used by the prehistoric artists, and they are very important for the assessment of the dating and conservation of these remains of our past. Our previous studies revealed the presence of whewellite- and weddellite-forming crusts that extend over the painted panels of many rock shelters of Cuenca province.[10,12,13] This finding enabled the first radiocarbon ^{14}C accelerator mass spectrometry (AMS) dating of oxalate crusts related to Spanish prehistoric rock art.[19] Therefore, an additional objective of this work is to determine the stratigraphic relationship between any possible oxalate crust and the pictographs, from which a reliable dating of the art work can be undertaken.

Archaeological background

Hoz de Vicente rock art site was discovered by chance[20] in 1987. It is located inside the deep gorge opened by the Cabriel river

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Figure 1. Some pictographs from the painting panel 3 of the Hoz de Vicente rock shelter.

which nowadays forms the border between Cuenca and Valencia provinces and divides into two the high plateau of La Mancha and La Plana de Utiel. In the surrounding area there is no rock art, except for a shelter recently discovered (R. Martínez-Valle, personal communication 2009), so it is the main example of rock paintings in the area between Bicorp and Dos Aguas (Valencia) and the remaining rock art of the Cabriel valley in Villar del Humo and Pajaroncillo (Cuenca).

Shepherds have used this large shelter for long as a natural sheepfold, so in the lower part of it appears a large substratum which is very likely concealing an archaeological site still unearthed. Paintings of two styles appear along its walls: Levantine art and Schematic art, in some places with clear superimpositions of schematic pictographs over the Levantine ones. There are a large number of figures painted, but there is still no definite inventory of them, although it is absolutely certain that there are more than 100 individual motifs. They are distributed in at least three areas or panels, two of them on the southern face of the shelter and the third one on the eastern face. The latter (panel 3) is the more interesting one because of the high concentration of both styles of pictographs, the superimpositions between them and the overall good level of preservation. In the Levantine figures present here, we should highlight the absence of animal pictographs, the appearance of a pair of large antropomorphs, as well as the presence of a very interesting group that could be interpreted as female depictions. However, there are some hunting scenes, in some way related to the Levantine tradition, in the remaining panels. All of them were painted in different shades of red. There are also a large number of schematic motifs produced with several techniques and painted in red or black. We can observe some meaningful differences among them; the largest part, mainly human and animal depictions, are small figures painted with a feather or a small brush, and the remainder is a set of more typical schematic anthropomorphic figures of a larger size and painted with a wide brush.

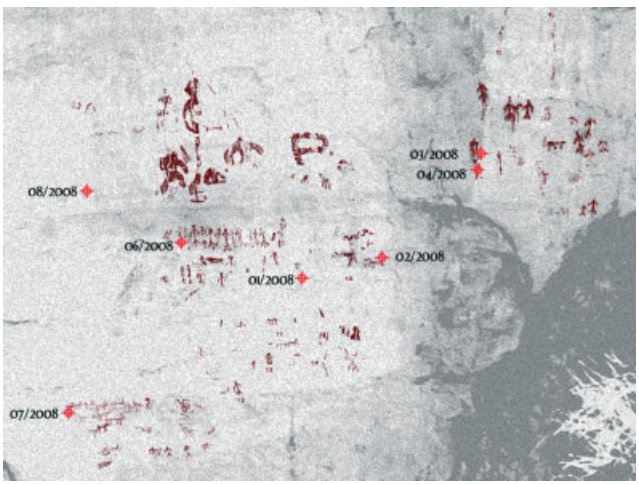

Figure 2. Digital reproduction of the panel 3 of the Hoz de Vicente shelter indicating the sampling points. Tracing based on Ref. [20].

Experimental

The experimental protocol followed in the study of these prehistoric paintings has been described elsewhere.[10,12,13] Only specific details of the present study are reported here. Pictographs, accretions, alterations and substrata have been selected for sampling according to criteria of archaeological interest, their state of conservation and the specific characteristics of the rock surface. The locations of the sampling points within the painting panel 3 are indicated in Fig. 2. The samples were labelled according to the code established for the Micr-Art database.[10] A zoomorphous schematic figure, painted in red, in the lower left part of the panel was sampled (07/2008-HVip3), Fig. 2. Similarly, a sample of black pigment was excised from the upper left part of the panel (08/2008-HVip3). An ochre-coloured crust covering the central

section of the panel was also sampled (01/2008-HVip3:alt and 02/2008-HVip3:alt). On the right of the panel a dark crust covers apparently some Levantine feminine figures, and some schematic figures seem to be painted on this crust. A sample of the substratum containing this crust was extracted (03/2008-HVip3:sus). Another specimen of substratum from the central section of the panel, and not covered by the indicated crust, was removed. In this case, the minute rock fragment bears a small amount of red pigment from the skirt of a feminine figure (04/2008-HVip3). A schematic line was painted over an old flaking of the rocky surface in the central section of the panel (06/2008-HVip3:sus), Fig. 2. This area appears now covered by a patina. Consequently, a fragment of the substratum with the patina was extracted. If a material suitable of radiocarbon dating is found in the patina, then an *ante quem* date for the pictorial event could be obtained. Finally, a polished, thin cross section (thickness 30 μm) of the sample of pigment 07/2008-HVip3 was prepared using a polyester resin matrix. This thin section was examined with a petrographic microscope using polarised light to observe its microstratigraphy.[12,13]

The micro-Raman spectroscopic study of the samples was carried out with a Jobin Yvon LabRam-IR HR-800 spectrograph coupled to an Olympus BX41 microscope according to the procedure described elsewhere.[10,12,13] The 632.8 nm line of a He–Ne laser was used for Raman excitation using effective powers of 566 μW (50× long-working-distance, LWD, objective) and 548 μW (100× objective) measured at the sample position to avoid sample degradation.[21,22] The average spectral resolution in the Raman wavenumber 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 gave a lateral resolving power of ∼1–2 μm (100× objective lens) and ∼5 μm (50× LWD objective lens) at the specimen. A spectral integration time of between 2 and 30 s and up to 36 accumulations were used to achieve an acceptable signal-to-noise ratio. The linearity (sine bar linearity) of the spectrograph was adjusted using the fluorescent lamps of the lab (zero-order position) and the lines at 640.22 and 837.76 nm of a Ne lamp. The confocality of the instrument was refined using the 519.97 cm^{-1} line of a silicon wafer. Wavenumber shift calibration was accomplished with 4-acetamidophenol, naphthalene and sulfur standards[23] over the range 150–3100 cm^{-1}. This resulted in a wavenumber mean deviation of $\Delta\nu_{cal} - \Delta\nu_{obs} = -1.05 \pm 0.54\ cm^{-1}$ ($t_{Student}$ 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 appropriate spectral baselines.

A petrographic microscope Leica DM2500 with polarised light was utilised to obtain microphotographs of the polished, thin cross section of a sample of pigment.

The micromorphology and distribution of the components in the samples were observed with a Hitachi S-3000N SEM equipped with an Everhart–Thornley detector of secondary electrons with an operating resolution of 3 nm. X-ray microanalyses (EDX) of the samples were carried out with an EDX spectrometer (Rontec Xflash Detector 3001) coupled to the SEM, Peltier-refrigerated and with the Be window removed. Coating of the samples with an Au–Pd alloy (Polaron Range SC7620 sputter-coating instrument) was made only when previous image tests revealed that it was strictly necessary.

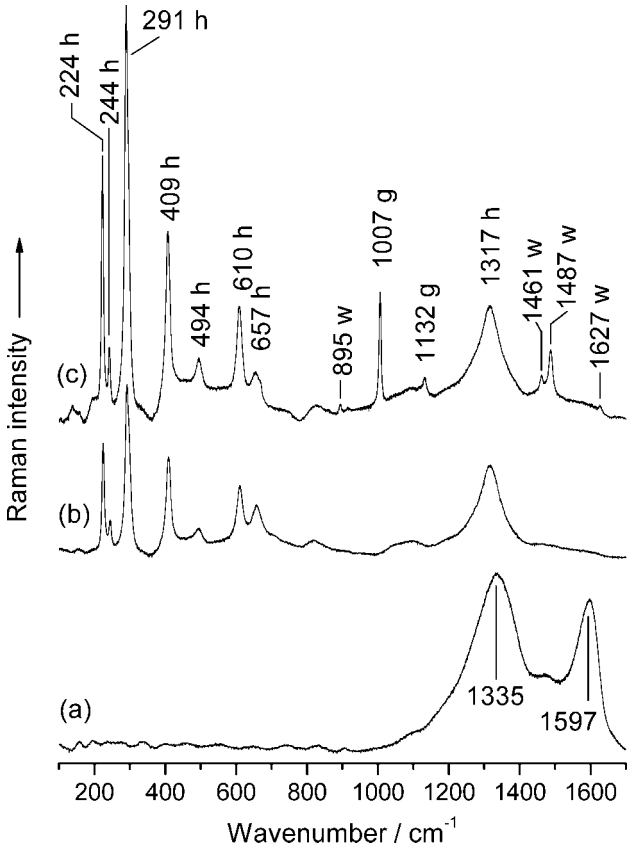

Figure 3. Raman spectra of representative points of the samples of pigments from the panel 3 of the Hoz de Vicente shelter: (a) 08/2008-HVip3 black pigment from the upper left part of the panel with broad bands of amorphous carbon; (b) 07/2008-HVip3 red pigment from a zoomorphous figure with the typical bands of haematite; (c) 04-HVip3 red pigment from the skirt of a feminine figure with bands of haematite, gypsum and whewellite. Labels: h, haematite; g, gypsum; w, whewellite. The spectra have been baseline-corrected from the background of fluorescence radiation.

Results and Discussion

Pigments

The Raman spectra of the samples of the red pigment 04/2008-HVip3 and 07/2008-HVip3 from this panel, Fig. 3(b) and (c), show that the pigment used is haematite.[3,9,10,13,21] No other iron oxide or oxyhydroxide, e.g. goethite, was detected.[21] The narrow band at 409 cm^{-1} indicates that well-crystallised haematite was used.[7] This is the red pigment commonly employed in the prehistoric paintings of the sites that we have analysed in SE Spain.[9,10,13] The particles of haematite cannot be distinguished by applying the maximum resolution of the optical microscope (objective magnification 100×). Using the magnification of the optical and SEM microscopes applied to obtain the images B and D of Fig. S1 in Ref. [13] we obtained in this case similar results. This indicates that haematite has been processed to reach a fine granular size, i.e. less than 1 μm. This size is similar to that used nowadays in commercial haematite powder (image B of Fig. S1, in Ref. [13]), an indication of the technological level achieved by the prehistoric artists. Some microscopic locations reveal the presence of pure haematite, Fig. 3(b). However, bands of whewellite ($CaC_2O_4{\cdot}H_2O$), weddellite ($CaC_2O_4{\cdot}(2 + x)H_2O$, $x \leq 0.5$) and gypsum appear usually together with the haematite bands in the different spectra

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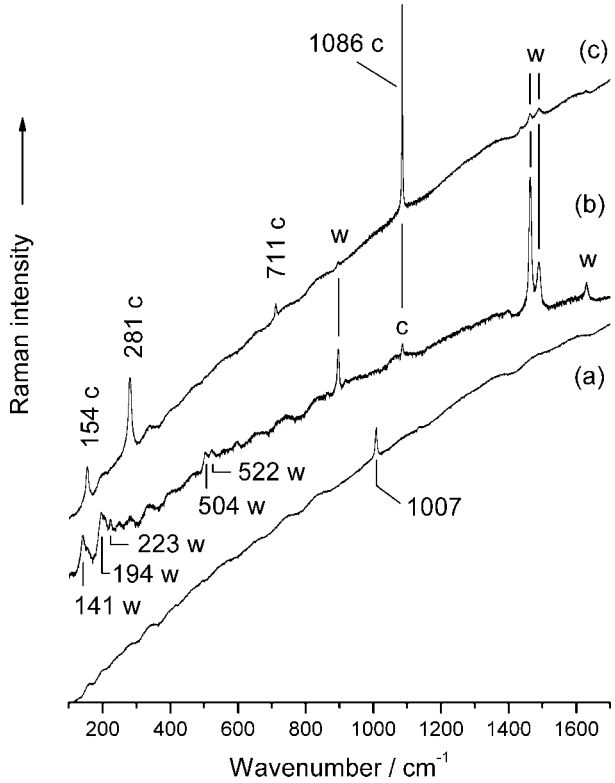

Figure 4. Raman spectra of representative points of the samples of substratum and accretions from the panel 3 of the Hoz de Vicente shelter: (a) 03/2008-HVip3 dark ochre-coloured crust from the right part of the panel showing the band of gypsum at 1007 cm^{-1}; (b) 06/2008-HVip3 substratum of calcite with a patina of whewellite; (c) substratum of calcite with traces of whewellite corresponding to the sample of red pigment 04-HVip3. Labels: c, calcite; w, whewellite. No baseline correction has been applied.

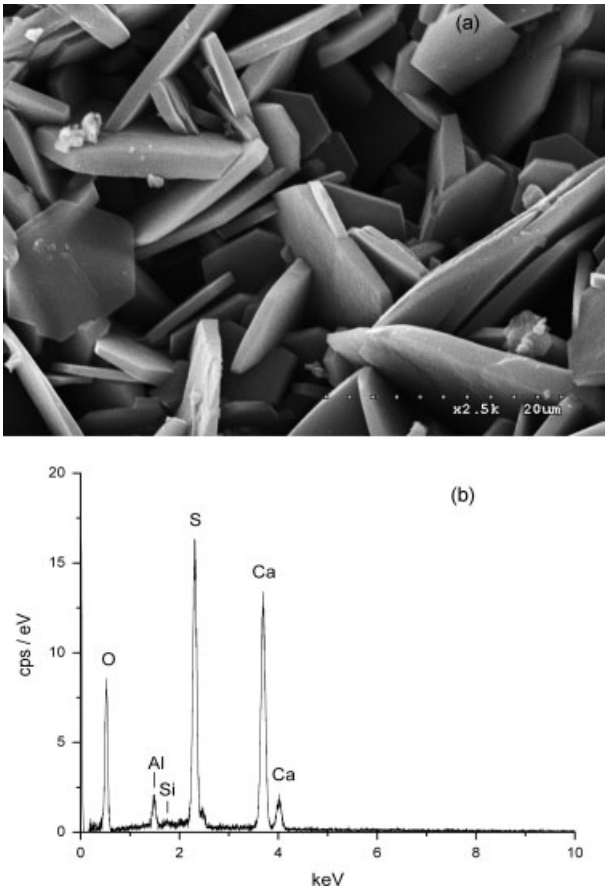

Figure 5. (a) SEM image of the 03/2008-HVip3:sus crust showing gypsum microcrystals. The dotted segment is 20 μm in length. (b) EDX spectrum corresponding to this crust.

of the red pigment, Fig. 3(c). The presence of these hydrated forms of calcium oxalate in the layer of pigment suggests that the biological activity of fungi or lichens has reached this layer and fungal hyphae could have penetrated this layer leaving oxalates as products of their metabolism,[12] a result that has also been observed in our previous studies on the pictographs of the Sierra de las Cuerdas.[10,13] On the other hand, water from rain or wet areas dissolve sulfates and the evaporation on the rock surface generates gypsum crystals. This process could be the origin of the flaking that is affecting some areas of the painting panel.[10,13]

The Raman spectra of the black pigment 08/2008-HVip3, Fig. 3(a), show the broad D1 (~1335 cm^{-1}) and G (~1597 cm^{-1}) bands typical of amorphous carbon.[1,3,9,13,24] Bands from phosphates are not observed and this excludes the use of calcined bone (bone black) as pigment and suggests the use of charcoal of vegetal origin or soot.

Substratum and accretions

Bands of calcite are clearly identified in the spectra of the substratum, together with bands of whewellite forming a patina of oxalates with variable thickness, Fig. 4(b) and (c). As anticipated previously, the detection of this patina in the sample 06/2008-HVip3:sus will enable achieving an *ante quem* date for the painting of the schematic line.[17,19,25] On the other hand, most of the Raman spectra obtained from the external face of the samples of this panel exhibit a noticeable background level due to fluorescence, Fig. 4. This is particularly significant in the spectra of surfaces covered with ochre-coloured accretions, i.e. the external face of the samples 01/2008-HVip3:alt, 02/2008-HVip3:alt and 03/2008-HVip3:sus. Even so, the strong band of gypsum at 1007 cm^{-1} emerges frequently from the background, Fig. 4(a). Therefore, gypsum is one of the components of these crusts. This result has been confirmed by SEM/EDX, Fig. 5. Gypsum microcrystals giving strong EDX peaks of Ca, S and O are detected in the surfaces previously indicated. The Al and Si peaks observed in the EDX spectrum of the external face of the sample 03/2008-HVip3:sus, Fig. 5(b), suggest that clayish materials could be considered as additional components of these crusts. They could also give rise to the high background level of the Raman spectra. Further SEM/EDX studies on the ochre-coloured accretions of this panel support their clayish composition. For example, the EDX spectrum of one of these crusts covering partially the sample of pigment 07/2008-HVip3, Fig. 6, reveals strong peaks of Si, O, Ca, Al and Mg together with peaks of K and Fe. All of these are also indicative of the existence of clays. The C and S peaks could be due to oxalates and gypsum, respectively. The presence of Fe could be the origin of the colour of these crusts. Supplementary studies to characterise these clayish minerals by X-ray diffraction are planned. Permission to extract samples from the panel that can be powdered for this purpose has been requested.

Calcite is also the main component of the substrate of the pictographs discovered in the Los Murciélagos cave (Zuheros, Córdoba, Spain).[9] Nevertheless, significant differences are found

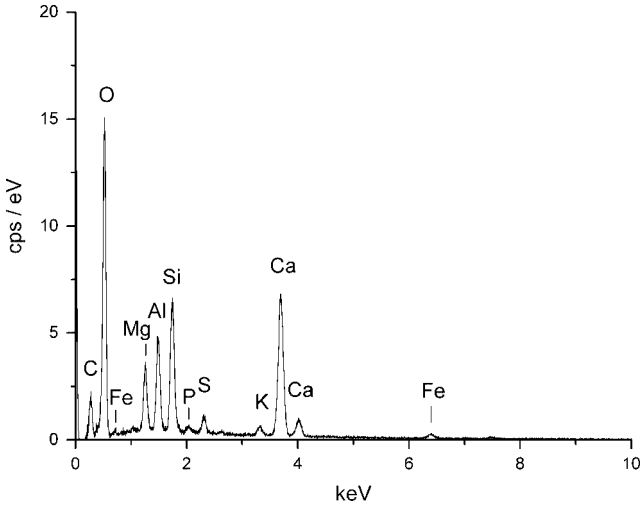

Figure 6. EDX spectrum obtained from the sample 07/2008-HVip3 and corresponding to the ochre-coloured accretion that frequently covers the pigment.

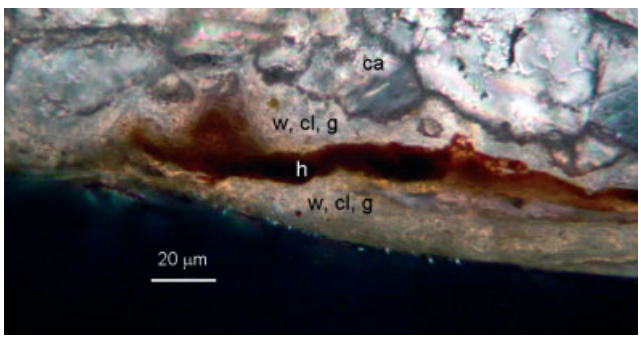

Figure 7. Microphotograph with polarised light of a thin section of pigment from a zoomorphous figure (sample 07/2008-HVip3) illustrating its microstratigraphy. The layer of red pigment, haematite (h), appears between layers containing whewellite (w), clay (cl) and gypsum (g). The substratum is basically calcite (ca). The composition of the layers was determined by Raman microscopy, Fig. 8, and SEM/EDX, Fig. 9.

between the surfaces of the painting panels in a cave and those in an open-air rock shelter as the Hoz de Vicente. The latter contain accretions of whewellite, weddellite, gypsum and clayish materials which have not been detected in Los Murciélagos cave. Conversely, nitrates are present only in the samples from the cave. Special environmental conditions, biological colonisation and geological structure would account for the different type of accretions observed on the surfaces of these rocky substrata.

Microstratigraphy

A microstratigraphic study of the distribution of components of the sample of pigment 07/2008-HVip3 from a zoomorphous schematic figure has been completed. The microphotograph with polarised light of a polished thin cross section of the sample reveals different layers, Fig. 7. The spectra obtained by Raman microscopy of these layers provide valuable information to determine the materials present in each layer, Fig. 8. The strong band of calcite at 1086 cm^{-1} is clearly detected in the spectra of the rocky substratum extracted together with the pigment, Fig. 8(a). Haematite is the main component of the layer of the red pigment, Fig. 8(b) and (c).

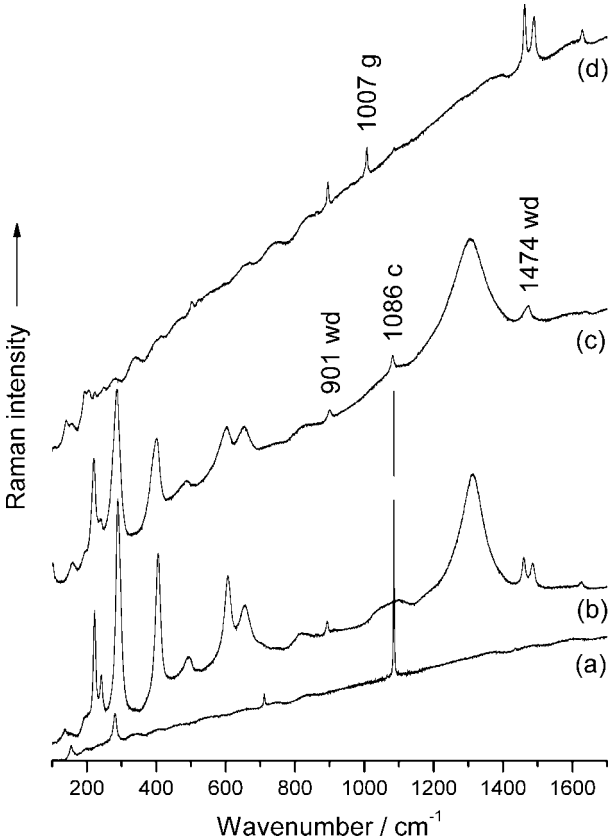

Figure 8. Representative Raman spectra obtained from the layers of the thin cross section of the sample 07/2008-HVip3: (a) calcite from the substratum, (b) haematite and whewellite from the pigment layer, (c) haematite, weddellite and calcite from the pigment layer, (d) whewellite and gypsum from the external layer. Labels: ca, calcite; wd, weddellite; g, gypsum. No baseline correction has been applied.

Nevertheless, weak bands of whewellite at 895, 1461, 1487 and 1627 cm^{-1} are frequently detected in this layer, Fig. 8(b). Traces of weddellite and calcite are also observed in some spectra of the layer of pigment, Fig. 8(c). As stated above, the presence of oxalates in this layer may be considered as a consequence of the activity of lichen or fungi colonies present on the surface of the rock. The two white layers adjacent to the red layer of pigment, Fig. 7, i.e. those between the substratum and the pigment and the more external one, are accretions of whewellite with some gypsum microcrystals, Fig. 8(d). The observed bracketing of the layer of pigment between oxalate layers is a result that will enable the radiocarbon ^{14}C AMS dating of these paintings. *Post quem* and *ante quem* dates for the pictorial event could be obtained in this way.[17,19,25] As indicated before, the marked background level observed in the spectra of the external layers may be ascribed to the content in clays. These results have been confirmed by EDX spectra obtained from these layers, Fig. 9. Peaks of Ca, O and C observed in the spectra of the substratum, Fig. 9(a), may be assigned to calcite; whereas the C peak, together with Ca and O peaks, in the spectra of the other three external layers may be ascribed dominantly to calcium oxalates, Fig. 9(b)–(d). The two Fe peaks are present in the spectra pigment layer, Fig. 9(c). As shown in Fig. 6, additional Si, Mg, Al, K and Fe peaks in the spectra of the three external layers, Fig. 9(b)–(d), suggest again the presence of clayish minerals. The S peak is not discernible as it overlaps with a broad Au peak from the Au–Pd coating of the sample.

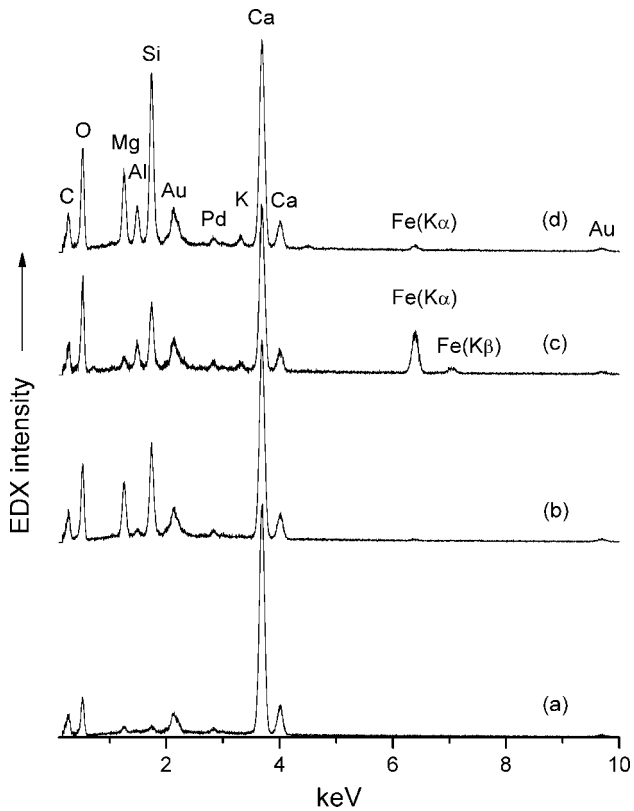

Figure 9. Representative EDX spectra obtained from the layers of the thin cross section of the sample of pigment 07/2008-HVip3: (a) substratum, (b) layer between the substratum and the pigment, (c) pigment layer, (d) external layer. Peaks from the Au–Pd coating are also observed.

Conclusions

Well-crystallised haematite, α-Fe_2O_3, powdered to achieve a granular size less than 1 μm, was used to paint the red pictographs of the panel 3 of the Hoz de Vicente shelter. Whewellite and weddellite have frequently been detected together with haematite. These hydrated forms of calcium oxalate have also been detected making a patina on the substratum and accretions. This suggests that colonies of fungi or lichens have left these products of their metabolic activity on the indicated surfaces; even they have penetrated into the layer of pigment. Gypsum has also been detected in the pigment, external layers of the pictographs and external faces of substrata and accretions. Crystallisation of gypsum in these surfaces and layers from water containing sulfates can be the origin of the flaking observed in some areas of the painting panel.[10,13] Hence, it is imperative that the panel should be preserved from humidity. Amorphous carbon, probably vegetable charcoal or soot, was used as black pigment. No binder has been detected. Calcite is the basic component of the rock used as substratum of the paintings. Indications of the presence of clayish minerals in an ochre-coloured accretion, which is present in several areas of the panel, have been obtained by EDX spectroscopy. The microstratigraphic study of a sample of pigment from a schematic figure revealed that the pigment is between layers of whewellite and weddellite. This finding, as well as the detection of a patina of whewellite covering another pictograph, will enable obtaining significant radiocarbon ^{14}C AMS dates for these representations of the schematic art.[17,19,25]

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Supporting information

Supporting information may be found in the online version of this article.

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Figure S1. Location of rock art sites with prehistoric paintings that have been studied by our group until 2009. Labels: 1, Selva Pascuala; 2, Peña del Escrito II; 3, Marmalo III and Marmalo IV; 4, Cueva del Tío Modesto (1-4, Sierra de las Cuerdas, Cuenca); 5, Hoz de Vicente (Minglanilla, Cuenca); 6, Cueva de los Murciélagos (Zuheros, Córdoba).

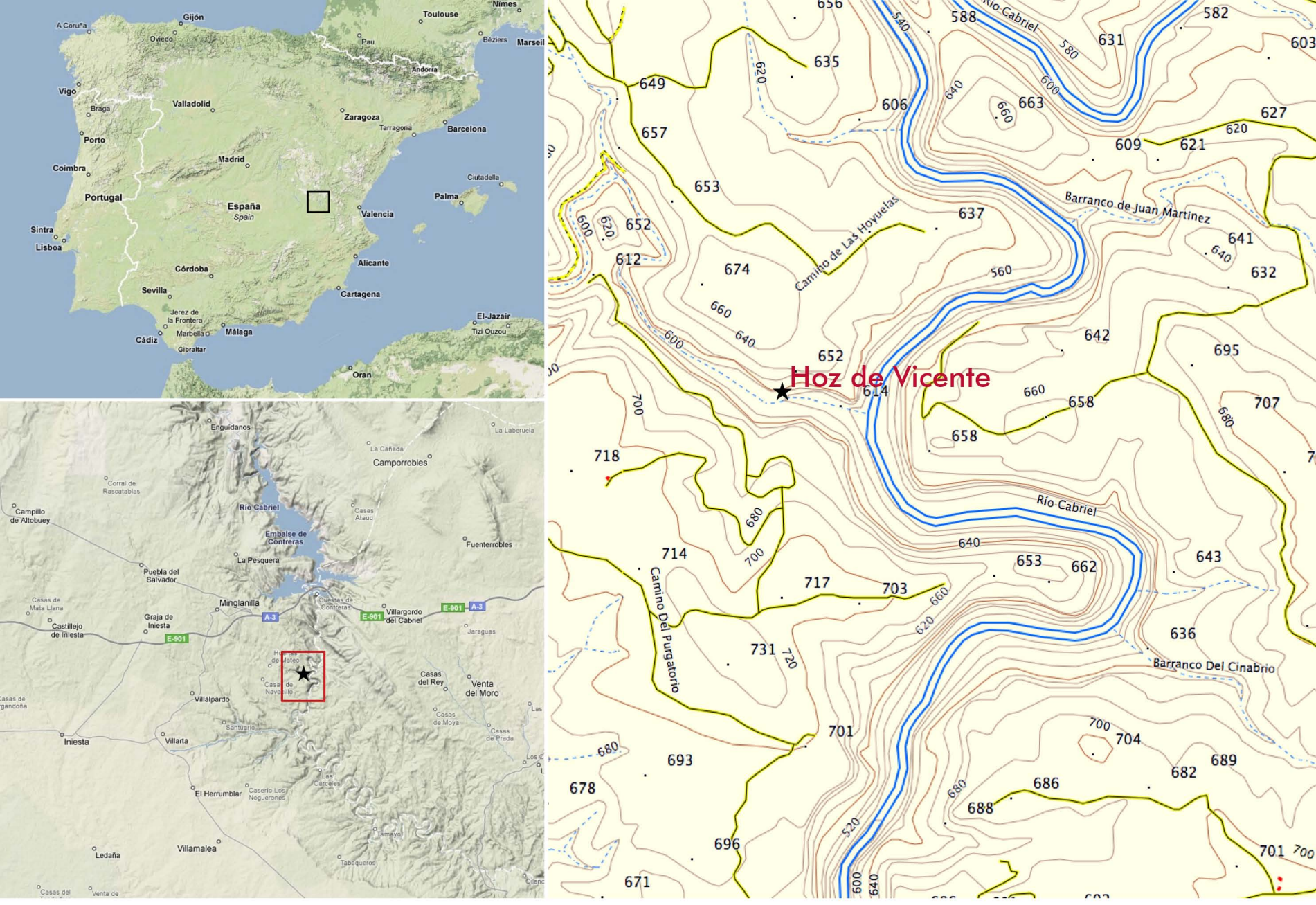

Figure S2. Location of the Hoz de Vicente rock shelter. The black square indicates the area in the iberian Peninsula and the black star the rock art site.