

Raman spectroscopic analysis of pigments and substrata in prehistoric rock art[☆]

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Abstract

The application of Fourier-transform Raman spectroscopy to the analysis of pigments in samples of prehistoric cave art is reported. Despite the limitations of a restricted colour palette used by the artists, the nondestructive identification of natural mineral pigments is accomplished and the unique information provided by the Raman technique is highlighted. The observed deterioration in cave art sites caused by local environmental, biochemical and geochemical changes is a cause for concern among conservationists and historians; the role of Raman spectroscopy in the identification of chemical products of bio-deterioration, in particular, can assist in the elucidation of agencies which may be responsible for site instability. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, the capability of Raman spectroscopy for the identification of pigments on ancient manuscripts and paintings has been elegantly demonstrated through the work of Clark and others [1,2]. From Raman microscopic spectra of historiated letters in particular, a range of mineral, natural organic and synthetic pigments and colourants has been characterised; colour changes resulting from unstable mixtures, the adoption of experimental pigments and reaction of the pigments with their support materials

have been catalogued [3], e.g. the blackening of a basic lead carbonate pigment through contact with egg white used as a mediaeval binding agent, and the inherent instability of lead tetroxide and cinnabar mixtures in strong sunlight which was recognized even in Roman times [4].

Nowhere is the deleterious effect of environmental exposure of pigments with time more noticeable than in prehistoric rock art; localised climatic changes of temperature, humidity and air pollution affect not only the pigments themselves but also their interaction with their substrata. Over several thousand years, the colonisation of prehistoric caves and shelters by bacteria, algae, fungi and lichens can be significant; there are now reports of hydrocarbon emissions into the atmosphere assisting the growth processes leading to environmental biodeterioration [5]. Reactive chemical metabolic products released by organisms

[☆] Dedicated to Professor James R. Durig on the occasion of his 65th birthday.

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into their rock substrata, such as oxalic acid, can cause substantial erosion and fragmentation of sedimentary geological formations [6]; in previous studies [7], we have calculated that over 1 kg/m^2 of calcium carbonate substratum in Renaissance frescoes has been eroded in less than 20 y by the aggressive lichen *Dirina massiliensis* forma *sorediata*, which contains up to 50% of its biomass as calcium oxalate monohydrate. Experimentally, we have identified fungal hyphae and cyanobacteria more than 10 mm below the surface of the substratal rock [8,9]. Hence, the destabilisation of prehistoric rock art tableaux resulting in spallation, a breaking away of the pigmented areas from the surrounding rock, is a very real observation which is causing concern to conservators [10].

Hitherto, most information relating to pigment composition and the interaction of pigments with their rock substrata has come from studies using either infrared spectroscopy, X-ray diffraction or a combination of these techniques [11]; perhaps, the most important aspect of the infrared spectroscopic analyses carried out hitherto has been the attempt to identify organic material in the pigments or rock encrustations on which the paintings are based [12–14]. Since most inorganic natural mineral pigments are expected to have infrared absorption bands in the low-frequency region, the observation of pigment composition in rock art samples is not usually a prime target for the infrared technique [10]. However, the identification of carbonaceous and organic material by infrared spectroscopy does afford the possibility of undertaking ^{14}C -radiocarbon dating on the samples [15]. This is very often the only possibility one has of dating accurately the rock art since associated artefacts are rare or of dubious provenance because suitable cave shelters may well have been occupied for extensive periods of time, before and after the rock art had been undertaken. In contrast, the XRD technique can provide information about elemental composition but it is insensitive to amorphous organic matter and especially carbon itself [10]. Also, it is difficult to be certain about the pigments used merely through the identification of elemental composition of the heterogeneous samples which comprise the cave art specimens [16]. An illustration of this is provided by our work in the related area of mediaeval church frescoes, where Raman and

infrared spectroscopy clearly indicate the presence of basic copper(II) acetate, verdigris, whereas XRD techniques show the presence of copper, iron, silicon and oxygen from the same sample [17]. Clearly, identification of the pigment is not possible using the diffraction technique as material such as copper(II) silicates and carbonates cannot be excluded.

The application of Raman spectroscopy, especially Raman microscopy, to the analysis of prehistoric rock art has provided some novel information in several areas which have not been accessible hitherto:

1. The heterogeneity of the rock-art specimens has been noted and probed using Raman techniques; the involvement of substratal chemistry has been recorded [10].
2. Significant compositional changes between samples taken at the same site have been noted, which are attributed not only to the pigments used, but to interactions with the environment and prevailing geology [10,11].
3. Raman spectroscopy has demonstrated a capability of showing the presence of organic and inorganic materials in rock art specimens. This is especially important when it is realised that organic dyes are themselves fugitive; the presence of organic moieties in cave art specimens, whilst important for archaeometric dating procedures, has relevance also for studies of ancient technologies and palaeoclimatology.
4. An apparently limited colour palette used by ancient artists should not be confused with simplicity of pigment selection, e.g. whereas it is tempting to assume that the most easily available black pigment was carbon, the use of pyrolusite and magnetite cannot be ruled out. Indeed, the source of carbon could often be important—and Raman spectroscopy can clearly distinguish between charcoal or soot and bone black by the phosphatic stretching mode near 960 cm^{-1} in the latter [17].

In this paper, we will demonstrate the application of Raman spectroscopic and Raman microscopic techniques to the following aspects of prehistoric rock art:

1. the identification of pigments and pigment mixtures used by prehistoric artists; generally, the colour palette is limited to red, white, yellow and black;
2. the construction of a database of minerals commonly encountered in prehistoric art;
3. the characterisation of products of biodeterioration, past or present.

Three prehistoric rock art sites were sampled namely:

- Pecos River Culture (North American, Texas (Val Verde), Seminole Valley);
- Big Bend site (Texas, USA);
- Catamarca Cave (South American, Argentina).

2. Experimental

2.1. Sites and samples

2.1.1. Lower Pecos, Texas, USA

Ten samples of rock-art and non-pigmented pieces of cave shelter wall were obtained from Seminole Canyon, near the edge of the Edwards Plateau, at the confluence of the Pecos and Devils Rivers with the Rio Grande. This region provides one of the longest continuous records of human occupation ($\sim 10^4$ years) in North America and contains over 250 sites, with over five different art styles [18,19]. The oldest is the Pecos River Style, for which radiocarbon assay gives ages ranging from 3000 to 4200 y BP. The samples studied here came from a localised Val Verde site for which AMS dating [20] gave 3355 y BP (Fig. 1). An average sample area was 1 cm^2 and all samples were obtained from exfoliated spalls. The predominant pigmentation was red, followed by black and white, but there was extensive specimen heterogeneity especially of the white pigmentation, with some yellow areas seen under the microscope. The collection of the samples was performed under State Park Scientific Study Permit No.49-93 and National Park Service Permit No.93-1.

2.1.2. Big Bend, Texas, USA

The site contained approximately 20 pictographs in a dry rock shelter, all composed of black and brown pigments. They are believed to be of a similar age to the Seminole Canyon samples. In all, six samples were obtained from this site; an example of the

specimen heterogeneity obtained from a spalled black pigmented region is shown in Fig. 2, also demonstrating the serious preservation condition which some rock-art is facing. The samples studied had been naturally exfoliated from a shield-like pictograph and were collected during field work in March 1994 under Texas Antiquity Permit No.1407.

2.1.3. Catamarca, Argentina

Several rock art sites on the eastern slopes of the Sierra de Ancasti, near San Fernando del Valle de Catamarca are known [15]. The two samples studied here were obtained from La Candelaria Cave and consisted of predominantly white pigment applied to a darker metamorphic granite rock base; pottery associated with the cave dates from the Aguada culture, ca 1100–1500 y BP. The samples were provided by Professor R.E. Hedges of the Laboratory for the History of Art, University of Oxford.

2.2. Raman micro-spectroscopy

FT-Raman micro-spectroscopy was undertaken using a Bruker IFS66 instrument with FRA 106 Raman module attachment and Raman scope microscope facility. Excitation was effected using a Nd/YAG laser with a nominal maximum power of 700 mW at 1064 nm. A $100\times$ microscope objective lens gave a sample “footprint” or spot diameter of about $10 \mu\text{m}$. Normally, spectra were obtained with about 40 mW of laser power at the sample and with accumulation of about 2000 to 10,000 scans to provide suitable signal-to-noise enhancement. Band wavenumbers are accurate to $\pm 1 \text{ cm}^{-1}$ and the instrument response is corrected for white light.

3. Results and discussion

Table 1 gives a listing of minerals which are found naturally and which can be considered as a good starting base for cave art; the colours or colour ranges of specimens are also provided. The inclusion of materials such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcite or aragonite (CaCO_3) arises because of the use of these as white pigments, but also because of their commonly found presence in the rock substrata. Likewise, quartz ($\alpha\text{-SiO}_2$) can be found as localised crystalline deposits in substrata, but there is also



Fig. 1. The prehistoric pictographs in a rock shelter at Seminole Canyon, Texas. The predominant colour palette is red, black and white. There has been some deterioration in the paintings and considerable spallation has occurred onto the shelter floor. The darker areas of “desert varnish” which obliterates part of the artwork should also be noted.

evidence that fine river sand was used as an aid to the grinding process, whereby natural minerals such as haematite (Fe_2O_3) could be mixed with clay to form red ochre. Whewellite and weddellite, the hydrated naturally occurring forms of calcium oxalate, are often found as white encrustations remaining on rock surfaces, resulting from the chemical attack by

oxalic acid from the lichen invasion of calcareous substrata [21]. An alternative suggestion for their presence in ancient rock art, however, arises from the use of cactus juice in desert areas as a paint preparation medium [15]. The presence of calcium oxalate monohydrate and/or dihydrate in rock art although providing a useful means of dating rock

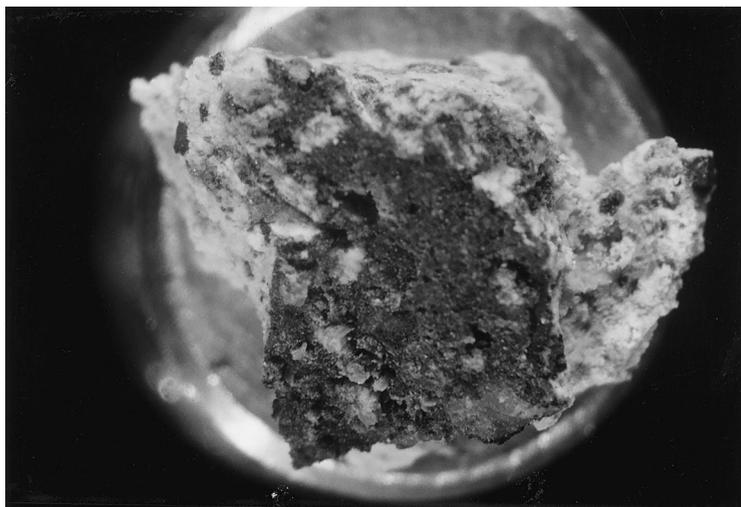


Fig. 2. Spallated fragment of Big Bend pictograph material, showing the heterogeneity of the sample; there are black, brown and white pigmented areas in the sample, with crystalline regions. Sample diameter, approximately 10 mm.

Table 1
Minerals providing a database for rock-art and their characteristic Raman bands

Mineral	Chemical formulation	Pigment colour	Characteristic Raman bands (cm ⁻¹)
Haematite ^a	α -Fe ₂ O ₃	Red	224 mw, 244 mw, 292 ms, 409 m, 610mw
Goethite	α -FeO(OH)	Red-brown	118 m, 203 w, 241 w, 299 m, 393 s, 553 ms
Lepidocrocite	γ -FeO(OH)	Red-yellow	251s, 378s, 527 ms
Magnetite	Fe ₃ O ₄	Black	612 ms, 412 ms, 292 ms
Pyrolusite	β -MnO ₂	Black	620 m, 640 mw
Quartz	α -SiO ₂	Colourless	148, 357 w, 465 s
Calcite	CaCO ₃	White	154 s, 282 m, 712 m, 1086 s
Gypsum	CaSO ₄ ·2H ₂ O	White	140 m, 181 m, 493m, 619 m, 679 m, 1007 s, 1132 m
Anhydrite	CaSO ₄	White	124 m, 415, 496, 674mw 1015 s, 1127, 1160 m
Rutile	TiO ₂	White	147 s, 242 s, 440 s, 611 s
Anatase	TiO ₂	White	144 s, 201 s, 397 s, 512 s, 634 s
Whewellite	CaC ₂ O ₄ ·H ₂ O	White	1496 s, 1464 s, 906m, 506 m
Weddellite	CaC ₂ O ₄ ·2H ₂ O	White	1472 s, 900 m, 502 m
Lampblack/soot ^b	C	Black	1590 m, 1360 m
Bone black ^b	C	Black	1590 m, 1360 m, 1070 w, 964 s, 670mw
Graphite	C	Black	1590 s, 1360 m
Cinnabar	α -HgS	Red	252s, 282m, 345ms
Massicot	PbO	Yellow	144s, 280 mw

^a The admixture of haematite with clay and sand produces ochres, with a range of pigment colours—predominantly red, but orange and yellow are known. Variable Fe(II)/Fe(III) ratios and coordinated oxygen and hydroxide content are believed to contribute to the source of these colour changes, reflecting a different thermal history of preparation of the mixture.

^b These non-mineral materials are included here since they were produced by the burning of wood or bone in ancient cultures.

accretions, should also be treated with concern since the work of our laboratory and others has shown the deleterious effect the production of this material by organisms has on the integrity of the rock surface [7–9]. Hence, our previous studies [7] of the aggressive lichen colonization of the Palazzo Farnese frescoes in Caprarola, Italy, have revealed that *Dirina massiliensis* forma *sorediata* is capable of converting 1 m² of calcite substratum into calcium oxalate, with the loss of 1 kg of substrate over a period of about 10 y. On historical timescales, therefore, the destruction of rock art and murals by lichens, fungi and algae must be appreciated. From a spectroscopic study of European mediaeval wall-paintings, we now have evidence that parts of the artwork have been restored within 200 y of its creation using inferior materials—the most likely reason from architectural and local climatic grounds being invasion through non-glazed apertures by the lichen *Diploschistes scruposus* [22].

Generally, the colour palette of ancient rock art is limited by the availability of materials locally. The preponderance of red, yellow, black and white there-

fore reflect the presence of easily available minerals such as haematite, clay, charcoal or soot and gypsum. The vibrational spectra consequently provide a good means for the unequivocal identification of these materials which is nondestructive of sample. Some examples of the FT-Raman spectra of the coloured paint samples from Seminole Canyon and Big Bend Sites in North America are shown in Figs. 3–8. Whereas it is generally realised that one does not expect to see organic dyestuffs or plant extracts used in ancient rock art, because these colourants are fugitive and prone to attack by adverse microclimates pertaining to caves and shelters, the presence of organic material is clearly evident in the Raman spectrum of a black-pigmented sample from Seminole Canyon (Fig. 5). This has now been identified from DNA profiling as bone-marrow extract from bison or deer [23]; its presence within the paint layer of the rock art sample, therefore, points to the use of organic extracts of this sort perhaps for ritualistic purposes, in addition to egg albumin and wine as possible binders to assist in the adhesion of the pigments to the rock substrata.

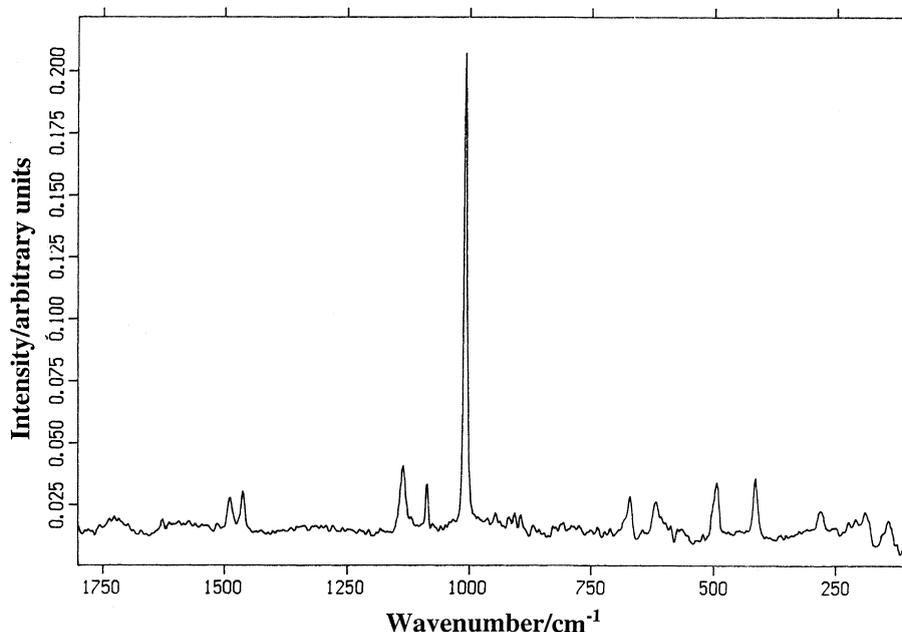


Fig. 3. FT-Raman spectrum of a black-pigmented specimen (41VV576-46) from Seminole Valley, Val Verde, pictographs; 2000 scans, 1064 nm excitation, 4 cm^{-1} spectral resolution; $100\times$ microscope objective wavenumber regions $100\text{--}1750\text{ cm}^{-1}$; the pigment contains white micro-crystalline particles which are composites of calcium oxalate monohydrate, calcite and gypsum. There is also possibly a trace of rutile present.

There are still some surprises to be found, however, even from the simple palettes described above. Hence, the FT-Raman spectrum of the red paint sample 41VV576-5a from Seminole Canyon shown in Fig. 7, does not show the vibrational bands expected for red ochre, calcite and gypsum. Instead, the Raman spectrum exhibits a complex arrangement of bands which bears little relation to a mixture of minerals, but which would be better described as a natural product; a sharp feature at 3112 cm^{-1} (not shown) is assignable to a $\nu(\text{NH})$ mode, which along with bands near 1400 and 1200 cm^{-1} , points to the presence of CHN moieties. The band at 1673 cm^{-1} is characteristic of an aromatic quinonoid structure similar to atranorin, an orange-red pigment found in some natural plant species. The wavenumbers and relative intensities of the bands at 1549 and 1185 cm^{-1} are suggestive of a conjugated ($-\text{C}=\text{C}-\text{C}=\text{C}-$) structure as possessed by the carotenes and lycopenes. However, the bands at 107 , 162 , 202 , 397 , 495 and 561 cm^{-1} , with the strongest band in the spectrum at 649 cm^{-1} all point to a hitherto unidentifiable mineral.

An interesting sequence of bands is that at ~ 1492 (sh), 1467 and 905 cm^{-1} which indicates the presence of calcium oxalate in the sample. Calcium oxalate monohydrate has been observed in several spalled fragments of cave art from Seminole Canyon and may be ascribed to previous lichen colonisation of the shelter walls. The iron oxide, oxy-hydroxide system provides a good illustration of a range of materials with different colours and compositions which are generically termed “red or yellow ochres”. In admixture with clay and sand, which assisted the preparation of fine pigment powders, and followed by simple heating processes, a range of colours could be produced with minimal technology from red, orange, yellow through to brown; some mineral conversions produced by heat in the iron oxide and oxy-hydroxide system are shown in Fig. 9. Whereas haematite, $\alpha\text{-Fe}_2\text{O}_3$, is usually thought to be the major iron oxide component of red ochre, Fig. 9 shows that goethite, $\alpha\text{-FeO.OH}$, can be converted into haematite on heating [24] but the β - and $\gamma\text{-FeO.OH}$ are converted into $\gamma\text{-Fe}_2\text{O}_3$ and the latter is converted into haematite

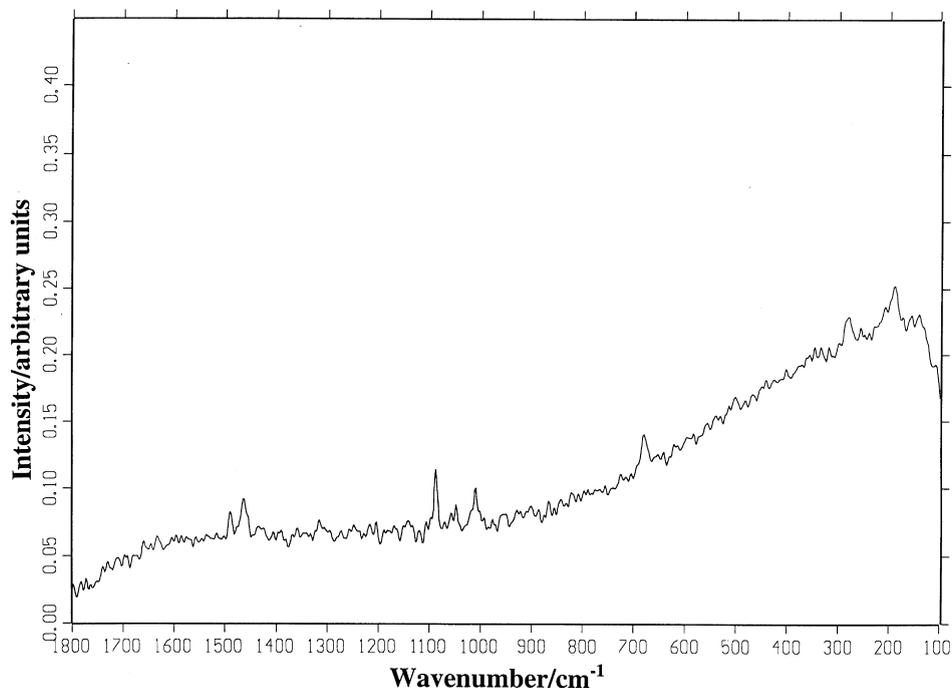


Fig. 4. FT-Raman spectra of a black-painted specimen (41VV576-1a) from Seminole Valley, Val Verde pictographs; conditions same as in Fig. 3, but compositional differences for the whewellite, gypsum and calcite are noted here. Also, there is no rutile present, but another species with a band at 1048 cm^{-1} , probably BaCO_3 , is evident.

on further heating at 600°C . Furthermore, treatment of these oxy-hydroxide minerals with bone ash in boiling water provides another series of brownish-black pigments of indefinite composition represented by $(\text{FeO})_x \cdot (\text{Fe}_2\text{O}_3)_y \cdot (\text{H}_2\text{O})_z$, where the $y:x$ ratio ranges from 1 to 3. Another major mineral oxide in Fig. 9 is the black pigment magnetite, Fe_3O_4 , with a spinel structure in which one third of the metal is Fe(II) and the remainder Fe(III)—hence its representation alternatively as $\text{Fe}^{\text{III}}(\text{Fe}^{\text{II}}\text{Fe}^{\text{III}})\text{O}_4$. An interesting conclusion from Fig. 9, is the relatively low-temperature conversion of $\gamma\text{-Fe}_2\text{O}_3$ to magnetite at 250°C ; this conversion is also believed to result naturally from bacterial attack on haematite and its oxy-hydroxides, to form “desert varnish”. The important oxy-hydroxides goethite and lepidocrocite are intermediate in composition between iron(III) hydroxide and iron(III) oxide, both mineral structures being characterised by strong hydrogen bonds and layer lattices.

The FT-Raman spectra of some of the important mineral species identified in Fig. 9 are shown stack-

plotted in Fig. 10; here the metal–oxygen vibrational modes for species in the iron(III) oxide–hydroxide system are shown for haematite (upper spectrum) and lepidocrocite (lower spectrum). The differences between these mineral pigments are significant; hence, it is possible now to establish a protocol for the identification of those materials in prehistoric rock art as shown in Table 1.

The Catamarcan rock art specimens are also not as straightforward as might first appear. Here, the predominant pigmentation in the caves is white. The FT-Raman spectra of a white pigment specimen (LC2) and of the basal substratum (LC1) are shown in the stack-plot in Fig. 11. The most significant points to be concluded from these spectra is the presence of a large, broad feature, centred on 800 cm^{-1} which is characteristic of a limewash which was identified previously in our studies of mediaeval wall paintings as a wall-preparation agent [25]. Other clearly identifiable features in the LC2 spectrum are the bands at 1007 and 1086 cm^{-1} (Table 1) which are characteristic of gypsum and calcite, respectively.

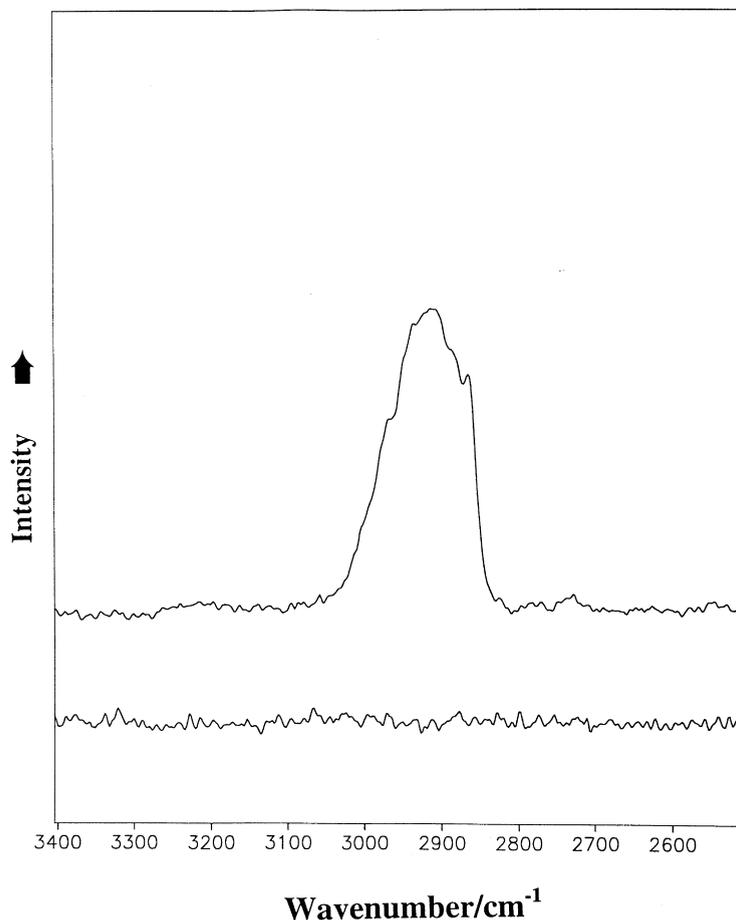


Fig. 5. $\nu(\text{CH})$ stretching region of Seminole Valley pictograph specimens, wavenumber region 2500–3400 cm^{-1} ; conditions as in Fig. 4. Upper spectrum, black pigmented 41VV576-1a specimen; lower spectrum, red pigmented 41VV576-2a specimen. Clearly, the black-pigmented specimen contains an organic component, which the red-painted specimen does not.

The doublet at about 1468 and 1490 cm^{-1} is characteristic of calcium oxalate monohydrate (whewellite), which is not native to the geology of the region. Its presence is therefore indicative of either metabolic products from lichen invasion in ancient times or to the addition of cactus juice (which contains significant quantities of whewellite) to the powdered calcite and gypsum as an aid to adhesion. No other organic binding agents could be detected in these samples, using spectroscopic and other analytical techniques [15]. Clearly therefore, the Catamarcan cave-painters used a mixture of calcite and gypsum as a pigment in their rock art.

Finally, we should make reference to the predominantly black pigment specimens from the Big Bend shelter site on the Texas–New Mexico border of the Rio Grande. Here, Raman spectroscopic studies, which have been supported by SEM, infrared and XRD studies identified the black pigment as manganese(IV) oxide (pyrolusite) with characteristic broad Raman bands at ~ 620 and 670 cm^{-1} . However, here too there is evidence for whewellite; the location of calcium oxalate monohydrate at the surface of the paint fragments suggests a lichen colonisation source as the main purpose of a binding agent would be the adhesion of paint to the rock substratum. The deleterious

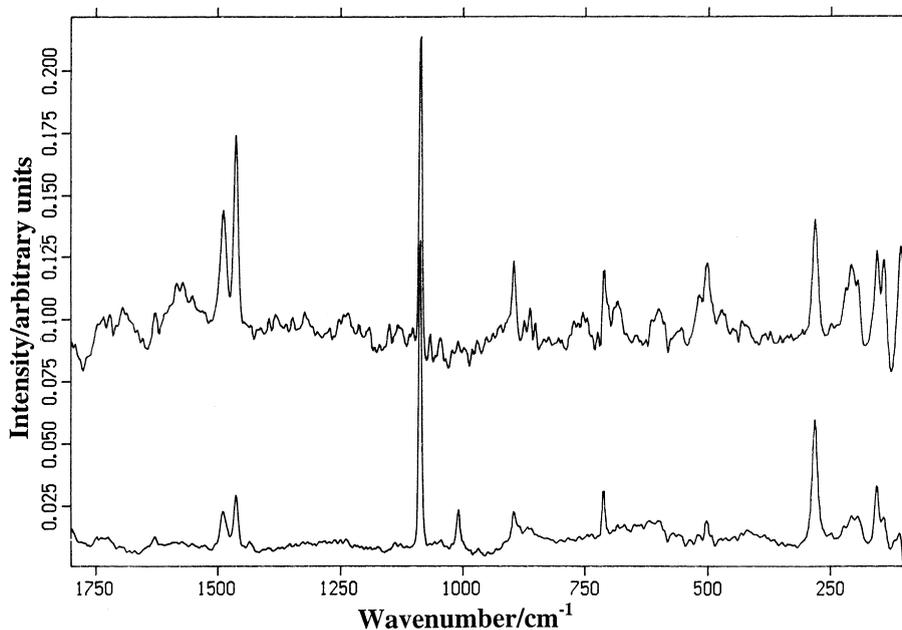


Fig. 6. FT-Raman spectra of red-painted specimens from Seminole Valley, Val Verde pictographs 41VV576-2a; conditions as in Fig. 4; wavenumber region 100–1750 cm⁻¹. Upper spectrum, central underside; lower spectrum, edge, underside. Evidence for calcium oxalate monohydrate and calcite is seen in both spectra, but there is also a gypsum component (1007 cm⁻¹) in the lower spectrum. A significant finding here is the absence of spectral bands due to haematite or goethite, despite the visual colour of the specimens.

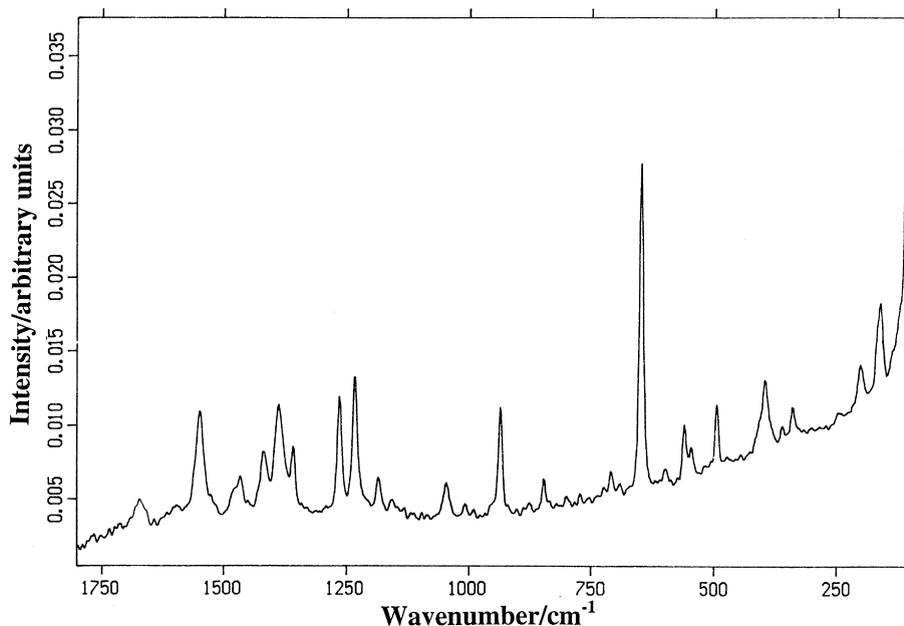


Fig. 7. FT-Raman spectrum, 100–1800 cm⁻¹ region, of 41VV576-5a red-painted sample from Seminole Valley pictographs; 20× microscope objective, 4000 scans accumulated at 4 cm⁻¹ spectral resolution. This spectrum is unique of all those studied and indicates a major organic composition for this pigment.

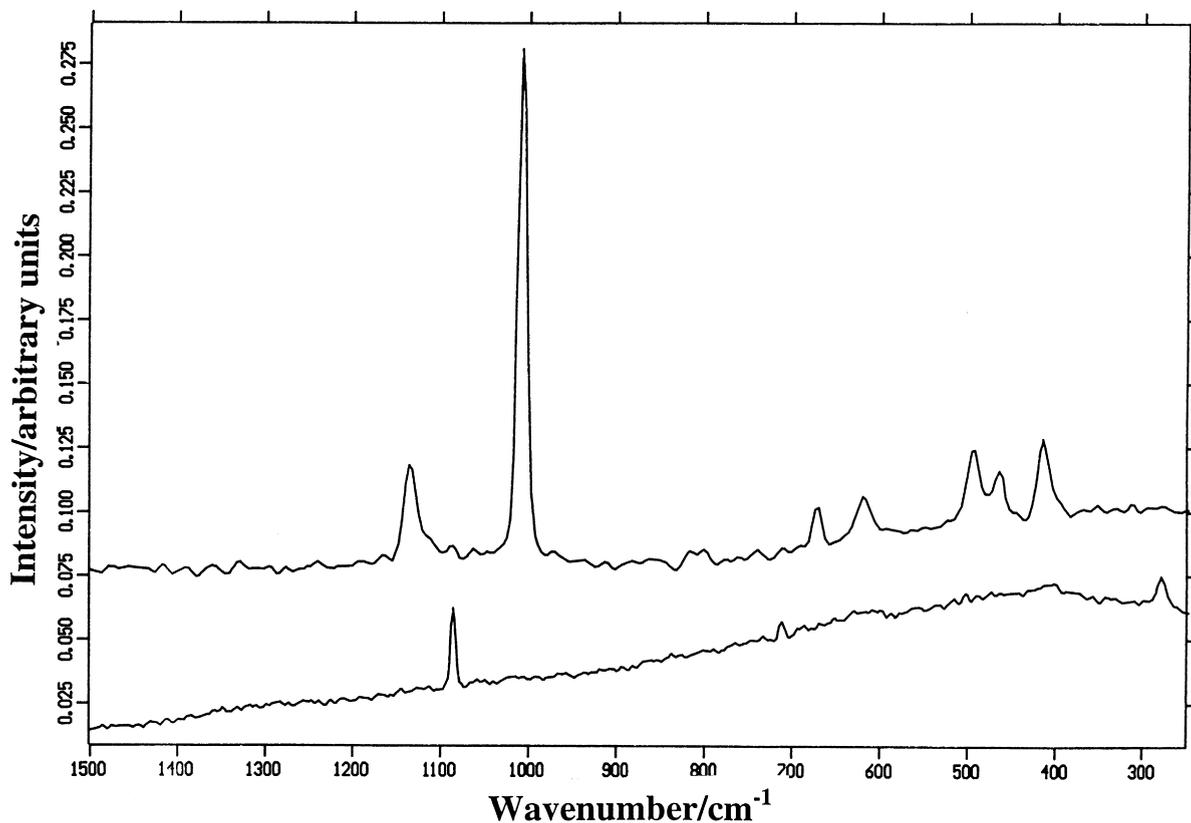


Fig. 8. FT-Raman spectra of black-pigmented area of PS114-5/6 (upper spectrum) and PS114/3 (lower spectrum) specimens of Big Bend, Pecos River, pictographs. Conditions as in Fig. 4. Clearly, there is evidence of gypsum in the upper spectrum, with manganese(IV) oxide and some bands in the 400–500 cm^{-1} region which may be ascribed to calcium/manganese oxide species, identified from EDAXS and SEM data.

effects of lichen invasion and colonisation of the surface of the Big Bend pictographs is observable in the erosion of the images and heavy spallation which has occurred there.

The brown pigments from Big Bend show a mixture of pyrolusite and haematite, with characteristic bands at 413 and 297 cm^{-1} , mixed with quartz particles which were probably used to aid the pulverisation of the minerals.

4. Conclusions

Raman spectroscopy provides a useful technique for the analysis of mineral pigments in prehistoric artwork. The identification of organic components in the specimens can often be related to either the

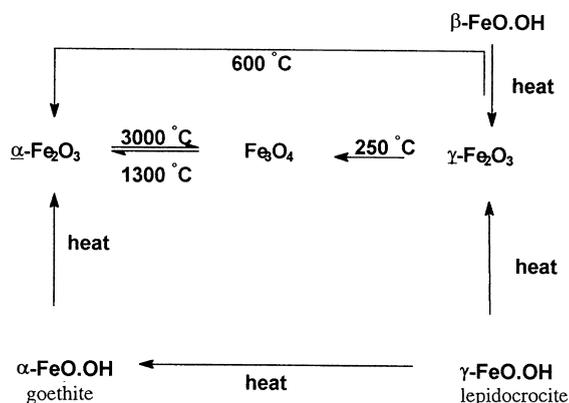


Fig. 9. The iron(III) oxide–hydroxide system.

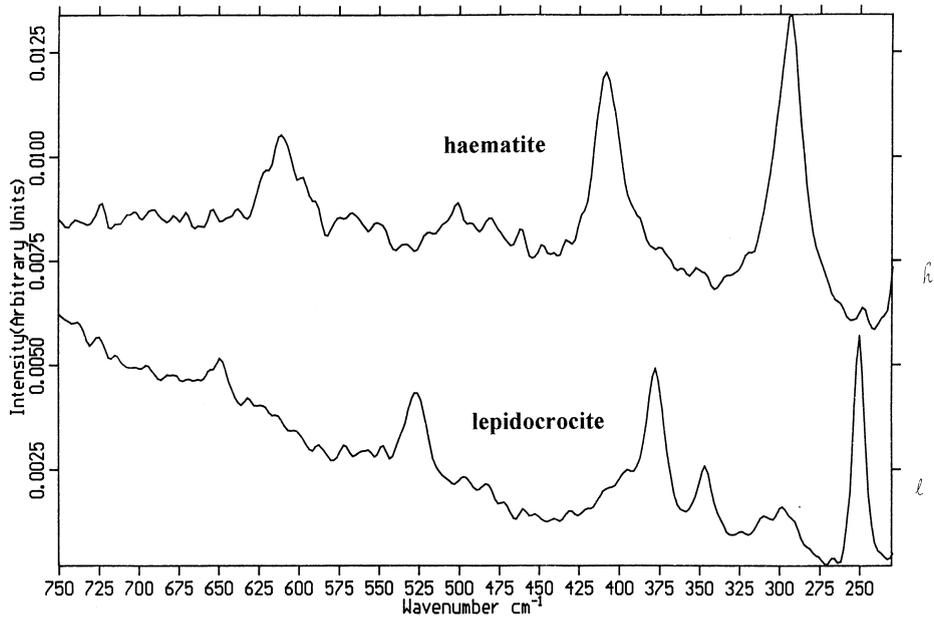


Fig. 10. FT-Raman spectra of some important mineral species based on the Fe(III) oxide–hydroxide system.

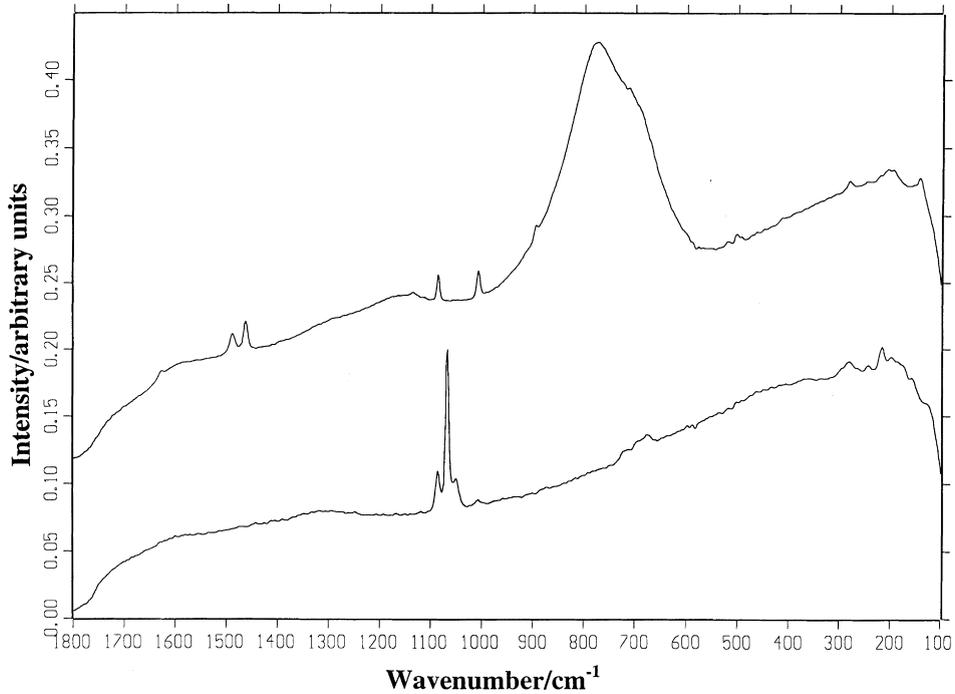


Fig. 11. The lower spectrum shows the presence of calcite in the rock accretion specimen. FT-Raman spectra of Catamarcan samples, Candelaria Cave, Argentina. Conditions as for Fig. 4. Upper spectrum, white-pigmented area, showing evidence of calcium oxalate monohydrate, calcite, gypsum and limewash component. The lower spectrum is of the substrate rock accretion, which shows the presence of calcite and a trace of gypsum, with two bands at 1067 and 1050 cm^{-1} .

use of binders or as an indication of more recent biodeteriorative processes, which may require recognition by conservators from the restoration point of view. In conjunction with other techniques, particularly SEM and EDAXS elemental analysis, the use of the nondestructive Raman spectroscopic technique first provides molecular information to reinforce and complement the findings of the destructive techniques. As more prehistoric rock art samples become available for analysis, it will be possible to expand the current Raman mineral database and this will itself mean that more definitive information can be forthcoming about pigment mixtures and their possible pretreatment in primitive technologies.

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