

# Fourier Transform Raman Spectroscopic Study of Prehistoric Rock Paintings from the Big Bend Region, Texas

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Samples of prehistoric rock paintings from the Big Bend region of Texas were analysed using Raman microscopy. This was the first chemical/mineralogical study of ancient paints from the region, and thus allowed us to test the utility of Raman microscopy as the principal tool for analysing pictograph rock paintings. The method is non-destructive and non-invasive, two extremely important criteria for the study of these artifacts. The Raman study was followed by scanning electron microscopic, Fourier transform IR spectroscopic, powder x-ray diffractometric, and gas chromatographic–mass spectrometric analyses to test the results obtained from the Raman analysis. It was concluded that the combination of Raman microscopy and scanning electron microscopy provided the most information and required the least amount of sample. Mineralogical, chemical and elemental information was obtained on the paint materials, including the pigments and binders. Furthermore, it was possible to identify and establish the relationship between the paints and the natural surrounding matrix, which included calcium sulphate (gypsum) and calcium oxalate monohydrate (whewellite). Copyright © 1999 John Wiley & Sons, Ltd.

## INTRODUCTION

A resurgence of interest in prehistoric rock art has occurred recently owing to advances in analytical techniques that provide information on the composition of ancient paints and the natural matrices surrounding the paints. The greatest problem in studying ancient rock art was the inability to affiliate the artifacts to specific cultures, which severely limited our knowledge of the origin and role of art within prehistoric societies. It is now possible to date directly many pictograph paints if organic matter was utilized in the original paint mixture and residual organics remain in the paint,<sup>1–3</sup> or if the paints are incorporated with natural rock crusts such as calcium oxalate or silica skins that are datable.<sup>4</sup> Furthermore, it is now realized that inorganic constituents of pictograph paints can be used to compare motifs, themes and painted panels based on chemical characteristics of the paints,<sup>5</sup> in addition to providing information regarding the substances available and utilized by early people for their art.

Aside from archaeological information gained by the chemical analyses of ancient paints, conservation strategies aimed at preserving and/or enhancing the artifacts also require knowledge of the relationship between paint components and the surrounding rock matrix. Most ancient rock paints are encapsulated within natural crusts produced by geochemical and biogeochemical weathering

processes that obscure or cause the artifacts to appear faded, and affect the integrity of the rock substrate and the adherence of the applied paint layers. Increased erosion from ultraviolet radiation exposure and from biodeterioration is particularly fuelled by pollution; there are now reports of the obliteration of artwork in frescoes and murals by microorganisms, fungi and lichens.<sup>6–8</sup> Hence there is an important need for new analytical methods to study prehistoric paints, especially techniques that are non-destructive and non-invasive, and which require only minute quantities for analysis.

Hitherto, Raman microscopy has not been widely used in studies of pictograph paints. The potential of Raman spectroscopic and Raman microscopic techniques for the analysis of pigments in manuscripts has been clearly demonstrated,<sup>9,10</sup> and in earlier studies in our laboratory we monitored the deleterious effects of the environmental biodeterioration of frescoes and ecclesiastical architecture.<sup>11–13</sup> Furthermore, we have examined prehistoric rock art specimens from the Lower Pecos region of Texas, and obtained results consistent with earlier studies.<sup>14</sup>

The aim of the study reported here was to investigate the utility of Raman microscopy as the primary tool for the analysis of prehistoric rock paintings by first drawing conclusions from the Raman analysis, then testing the results using scanning electron microscopy with an energy-dispersive x-ray analyser (SEM–EDS), Fourier transform infrared (FTIR) spectrometry, powder x-ray diffractometry (XRD) and gas chromatography–mass spectrometry (GC–MS).

The samples used for this study were from prehistoric pictographs in the Big Bend region of southwestern Texas (Fig. 1). Although there are an estimated 300 rock art

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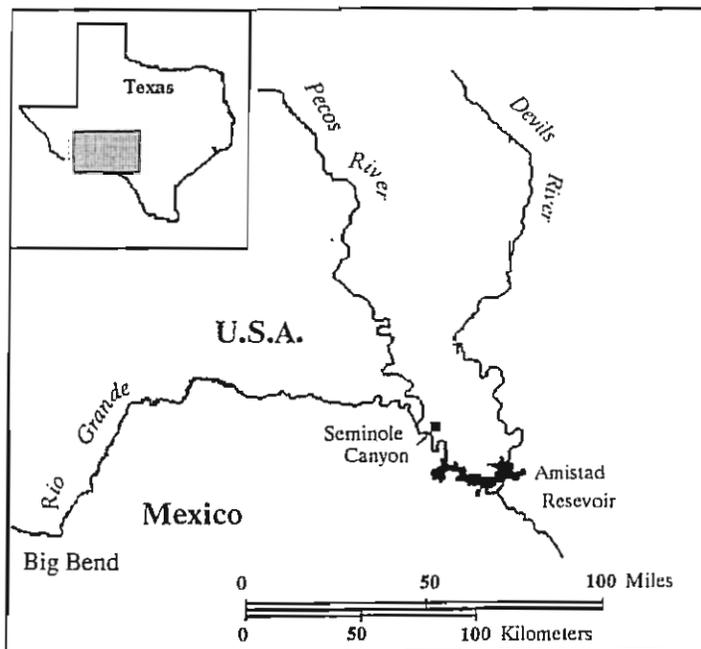


Figure 1. Map of USA (Texas)—Mexico region, showing location of the Pecos River Culture, Seminole Canyon and Big Bend pictographs.

sites within the region, until now the study of prehistoric rock paintings had been limited to categorizing styles and recording rock art panels;<sup>15</sup> therefore, the chemical content of the paints and surrounding matrices was completely unknown. This provided us with the opportunity to demonstrate the degree of utility of Raman microscopy for the study of these invaluable artifacts.

## EXPERIMENTAL

### Samples

The samples used in this study were from site 41PS114 (the number 41 represents the state of Texas, PS the county and 114 the archaeological site number), a dry rock shelter in a volcanic tuff formation in the Big Bend region of Texas. The site contains approximately 20 pictographs, all of which appear to be in the same style and composed of a paint with a black (2.5YN) and brown (5Y4/2) component. The samples studied had naturally exfoliated from a shield-like pictograph (Fig. 2) and were collected from the shelter floor during field work in March 1994 under Texas Antiquity Permit No. 1407. The samples included portions of paint adhered to spalled fragments of the substrate. Non-painted samples for controls were collected directly from the shelter wall *ca* 0.3 m from the pictograph.

### Instrumental methods

FT-Raman spectroscopy was carried out using a Bruker IFS66 infrared instrument with an FRA106 Raman module and Raman microscope attachment. Excitation was effected using an Nd:YAG laser with a nominal maximum power of 700 mW at 1064 nm. A 100 $\times$  microscope objective gave a sample spot diameter of about 10  $\mu$ m. Wavenumbers are

correct to  $\pm 1$   $\text{cm}^{-1}$  and the instrument response was correct for white light. Spectra were accumulated at 4  $\text{cm}^{-1}$  spectral resolution from 2000 to 12 000 scans to provide suitable signal-to-noise ratio enhancement.

The SEM-EDS analysis was performed using a JEOL 6400 scanning electron microscope equipped with a Noran I-2 integrated imaging x-ray microanalysis system. We studied broken-sectioned paint samples which provided top and cross-sectional views of paint and substrate. Samples were mounted on 1 cm Al stubs and Au/Pd coated prior to analysis.

We also analysed paint and control samples using a Nicolet 5PC FTIR instrument to determine whether oxalates were present. The samples were prepared by scraping material from areas of interest, then grinding and pressing the material into a KBr pellet. The mineralogy of the paint components was further investigated using a Philips PW1729 powder XRD system. Paint materials were removed from samples using a dental pick and ground in an agate mortar and pestle prior to analysis. Finally, we tested the paint for the presence of organic matter using an HP 5800 GC-MS instrument. Samples were prepared using two protocols. The first was a Soxhlet extraction using polar solvents that were directly injected into the GC-MS instrument. The second method involved digesting samples in 1.0 M HCl, followed by solvent extraction of the organic components. The extracts were saponified then derivatized using boron(III) fluoride to convert fatty acids into their methyl esters for the GC analysis. Lipid and fatty acid standards applied directly to control samples were used to test the methodology.

## RESULTS AND DISCUSSION

### FT-Raman microscopy

The Raman microscope spectra of the prehistoric rock paint samples show several features of interest regarding

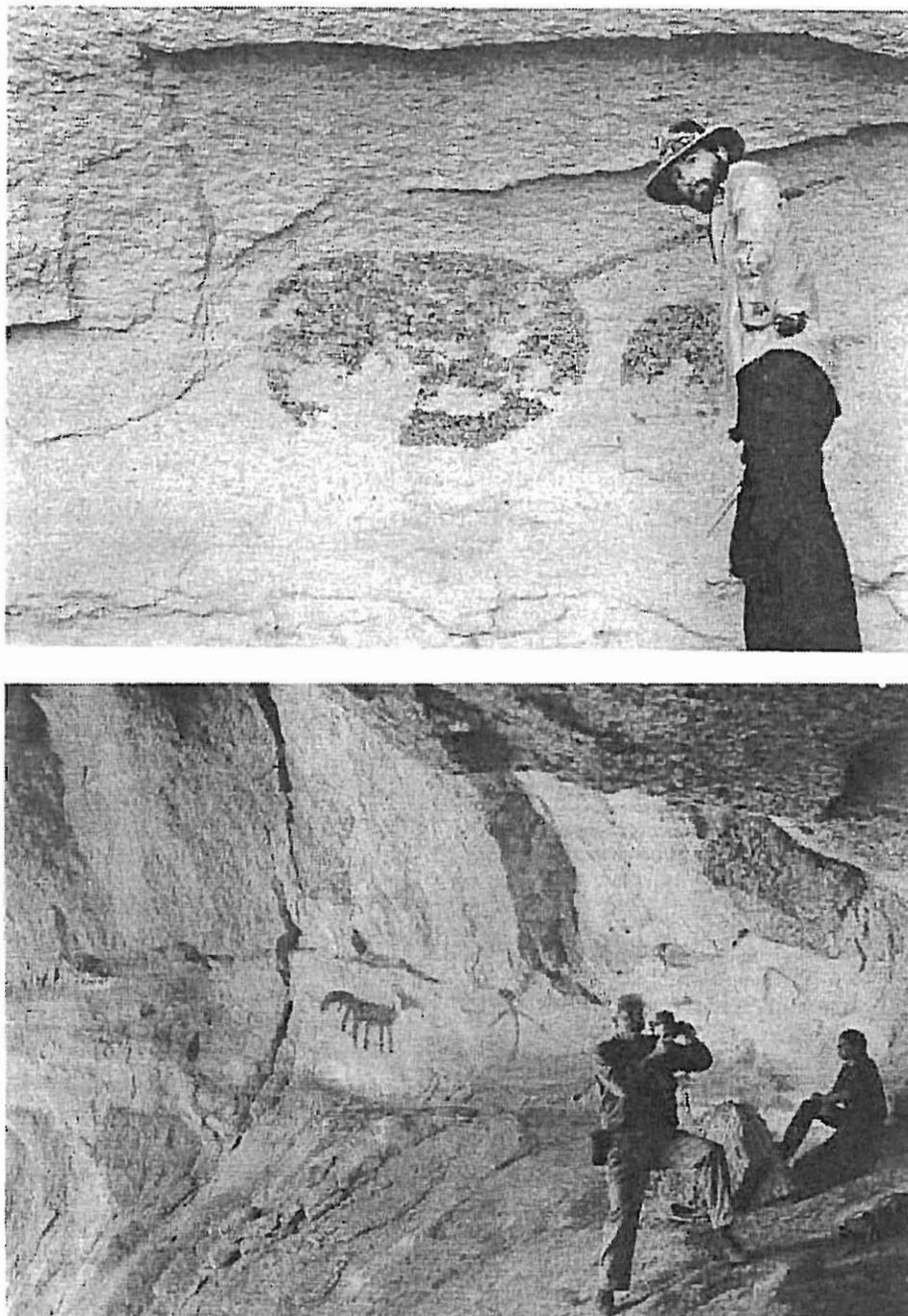


Figure 2. Big Bend pictographs in site 41PS114. The samples studied were from the shield-like pictograph shown here.

the pigment composition and its substrata. The first comment to be made relates to the heterogeneity of the samples; visual microscopic examination clearly demonstrates the presence of black pigment interspersed with white and some red-brown coloration (Fig. 3). None of the specimens studied showed Raman scattering in the wavenumber region  $2700\text{--}3600\text{ cm}^{-1}$  characteristic of  $\nu(\text{CH})$  stretching modes; hence we conclude that there are no organic materials or binders present in the pigments used in these samples. This observation is very important for assignment of observed features in the region  $1200\text{--}1600\text{ cm}^{-1}$  where organic compounds and amorphous carbon have vibrational modes.

The wavenumber region  $1200\text{--}2000\text{ cm}^{-1}$  is important for the identification of the white material in the

specimens, which gives bands at  $1630\text{ cm}^{-1}$  (weak),  $1490\text{ (m)}$  and  $1462\text{ (m)}\text{ cm}^{-1}$ , characteristic of calcium oxalate monohydrate (whewellite) (Fig. 4). The presence of whewellite in lower layers of the specimens is ascribed to earlier colonization by lichens, which probably indicates a previous biodeterioration of the rock substrata. One sample (41PS114-3) showed spectroscopic evidence of whewellite at the sample surface.

In the  $700\text{--}1200\text{ cm}^{-1}$  region, the characteristic features of calcium sulphate dihydrate (gypsum) with a weak band at  $1135\text{ cm}^{-1}$  and a strong band at  $1007\text{ cm}^{-1}$  were clearly indicated, as was the presence of calcium carbonate by the  $\nu(\text{CO}_3^{2-})$  mode at  $1086\text{ cm}^{-1}$  and a  $\delta(\text{CO}_3^{2-})$  mode at  $712\text{ cm}^{-1}$ . The control sample 41PS114-Acc 1 also showed gypsum, calcite and  $\alpha$ -quartz ( $463\text{ cm}^{-1}$ ) (Fig. 5).



**Figure 3.** Optical micrograph of Big Bend sample showing the black painted areas, white crystalline areas and areas of brown pigmentation.

The region  $100\text{--}700\text{ cm}^{-1}$  provides the major identification for the pigment(s), along with the whewellite bands at  $895$  and  $502\text{ cm}^{-1}$ , corresponding to  $\nu(\text{CC})$  and  $\delta(\text{CO}_2)$ , respectively, and calcite ( $281\text{ cm}^{-1}$ ). The black pigmented areas (2.5YN) of the specimens 41PS114-3 and 4IPS114-5/6 are manganese(IV) oxide (pyrolusite) with characteristic features due to  $\nu(\text{Mn-O})$  at  $670$  and  $620\text{ cm}^{-1}$  (Fig. 6). Brown areas (5Y4/2) found in conjunction with the black pigment associated with whewellite have characteristic features at  $413$  and  $300\text{ cm}^{-1}$ ; these bands are ascribed to iron(III) oxide (haematite). The haematite could have arisen either from the application of red ochre to the walls by the artists or to localized concentrations of iron(III) oxide in the substratum. In another study, that of the cryptoendolithic communities in the Antarctic Dry Valleys, Raman spectroscopic evidence was used to demonstrate the ability of the lichens and fungal hyphae to leach out iron oxides from layers in Beacon sandstones.<sup>16,17</sup> We therefore suggest that the presence of the brown regions is due to a localized concentration of iron(III) oxide, rather than to a deliberate application of iron(III) oxide in the form of red ochre by the ancient artists.

A composite table of Raman band wavenumbers is given in Table 1, including the PS114-Acc 1 rock substrate control sample. To summarize the Raman results, we conclude that (1) the samples are heterogeneous; (2) calcium oxalate monohydrate (whewellite) and calcium sulphate dihydrate (gypsum) were the primary substances in the natural crust covering the paint pigments; (3) the paint was composed of a black manganese oxide (pyrolusite) and iron oxide (haematite), the latter likely the result of

**Table 1.** Raman band wavenumbers and vibrational assignments for the Big Bend pictograph specimens

Specimen code			Approximate assignment of mode
PS114-3 $\tilde{\nu}/\text{cm}^{-1}$	PS114-5/6 $\tilde{\nu}/\text{cm}^{-1}$	PS114-Acc1 $\tilde{\nu}/\text{cm}^{-1}$	
1630 w	1630 w		$\delta(\text{OH})$ whewellite
1490 m	1490 m		$\nu(\text{CO}_2)$ whewellite
1461 m	1462 m		$\nu(\text{CO}_2)$ whewellite
1136 mw	1135 mw	1135 mw	$\nu(\text{SO}_4^{2-})$ gypsum
1086 w	1085 m	1086 m	$\nu(\text{CO}_3^{2-})$ calcite
1007 m	1007 m	1007 ms	$\nu(\text{SO}_4^{2-})$ gypsum
900 mw	902 mw		$\nu(\text{CC})$ whewellite
	711 mw	712 mw	$\delta(\text{CO}_3^{2-})$ calcite
670 mw	670 mw		$\nu(\text{MnO})$ ; manganese(IV)oxide
620 m, br	620 m, br		$\nu(\text{MnO})$ ; manganese(IV)oxide
	509 mw		$\delta(\text{CO}_2)$ whewellite
	463 mw	463 mw	$\nu(\text{SiO})$ ; $\alpha$ -quartz
413 mw	412 mw		$\nu(\text{Fe-O})$ ; haematite
300 mw	302 mw		$\nu(\text{Fe-O})$ haematite
	281 mw	280 m	Calcite
	155 mw	153 m	Calcite

lichen or fungal activity; (4) there was no evidence of organic matter in the paint; and (5) the control samples consisted of gypsum, calcite and  $\alpha$ -quartz.

#### SEM-EDS, FTIR, XRD and GC-MS analysis

The next phase of this research was to investigate the conclusions drawn from the Raman study using standard instrumental methods. (1) SEM-EDS showed clearly the heterogeneous nature of the paint and substrate. There was a smooth coating that covered much of the paint, followed by a complex paint layer that was intermingled with the upper basal rock. (2) The smooth coating that covered the paint surface was composed mainly of calcium and sulphur, as indicated by EDS (Fig. 7). This suggested that the coating was primarily gypsum, which was confirmed using XRD. There was no evidence of oxalate minerals in the XRD diagram; however, FTIR analysis demonstrated that a significant fraction of the crust was indeed oxalate (Fig. 8). (3) The XRD analysis demonstrated that the primary mineralogy of the paint was  $\text{MnO}_2$  (pyrolusite), but measurable quantities of manganese were also in the mineral forms  $\text{CaMn}_3\text{O}_7$  and  $\text{Ca}_2\text{Mn}_3\text{O}_8$ . The high concentration of calcium throughout the sample, including the pigment area (Fig. 9), suggests a weathering reaction between the substrate and the original pigment. A significant iron peak observed in the EDS spectra of the brownish area (Fig. 10) was confirmed by characteristic  $d$ -spacing peaks for haematite and goethite in the XRD analysis. Thus we firmly established the presence of an iron component in this paint phase, but did not necessarily confirm the mineralogy. (4) There were no organic compounds in the paint or substrate extracts as determined using GC-MS. (5) The mineralogy of the control sample was indeed mostly silicate (zeolites), as established using XRD, and, as noted previously, a secondary gypsum component. The presence of a carbonate (e.g. calcite) was not confirmed using FTIR but was found in the XRD patterns.

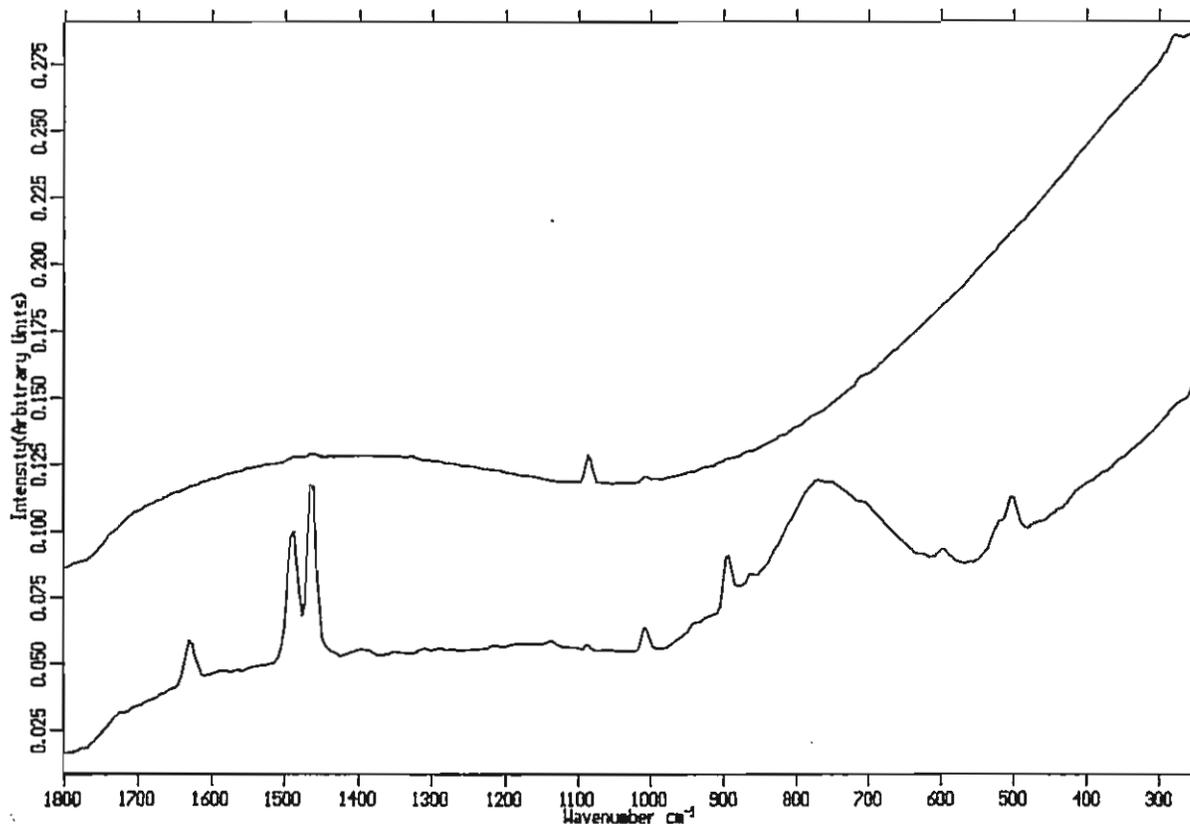


Figure 4. Raman spectra of surface of PS114-3 specimen. Conditions: 1064 nm excitation; 100 × microscope objective; 2000 scans; 4  $\text{cm}^{-1}$  spectral resolution. Lower spectrum, white crystalline deposits at surface; upper spectrum, cluster of beige particles at the surface.

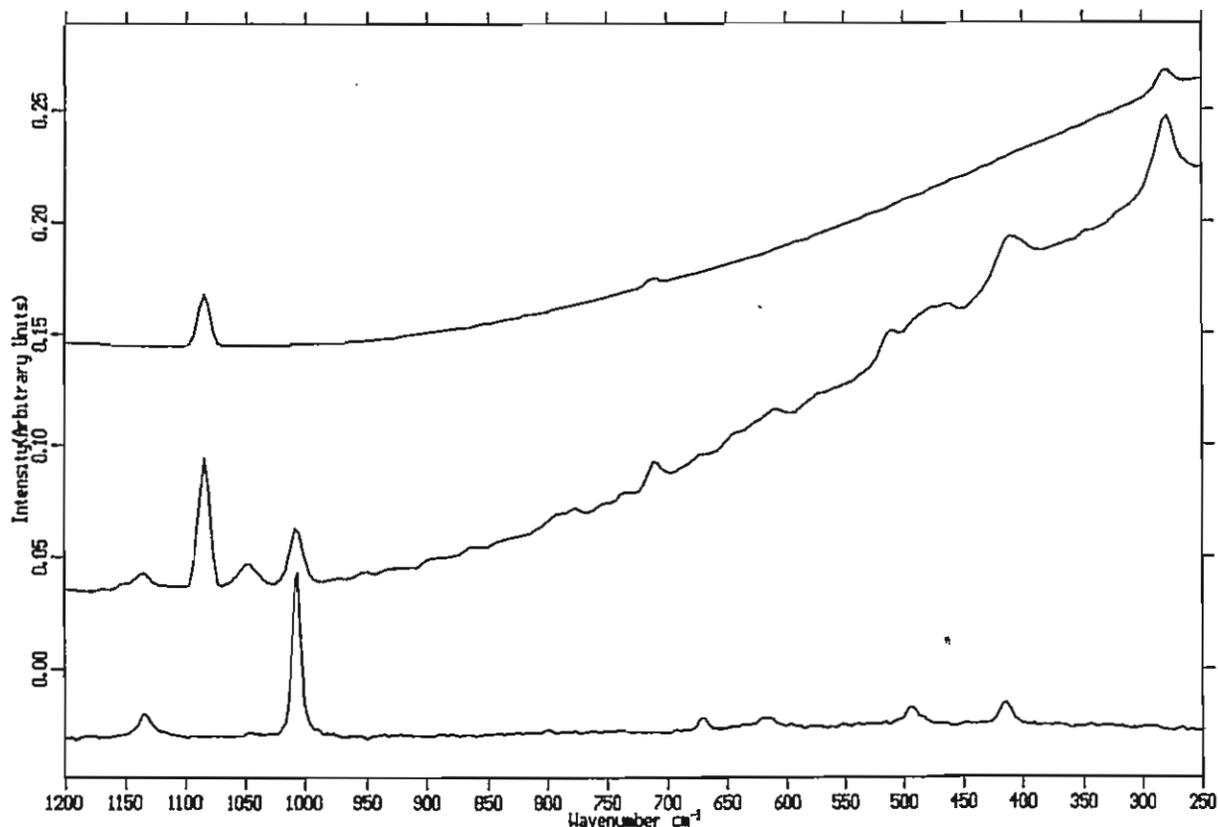


Figure 5. Raman spectra of different regions of the substratal accretion PS114-Acc1 (upper, lower spectra). Middle spectrum: PS114-5/6 black painted specimen with brown edges, showing the matching of features with calcite, gypsum accretions but with additional weaker bands at 1050, 520 and 460  $\text{cm}^{-1}$ . Conditions as in Fig. 4.

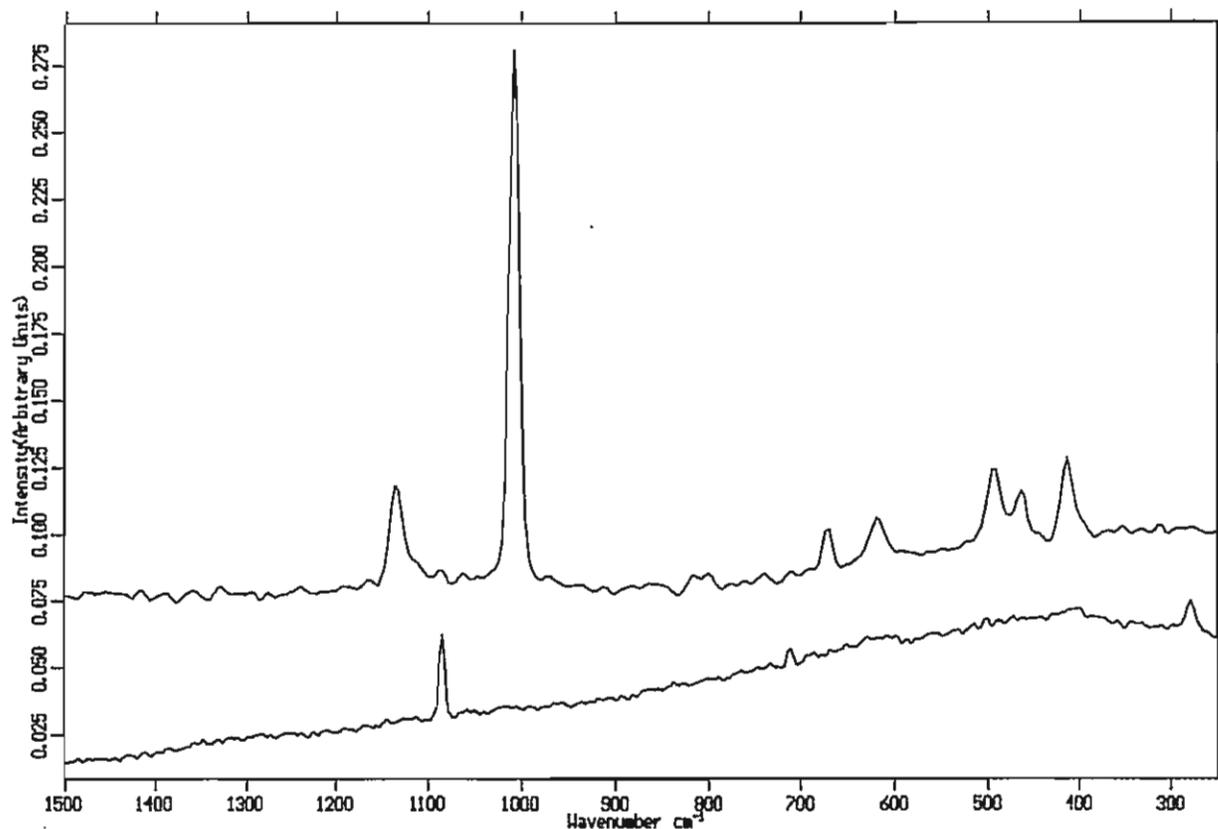


Figure 6. Black pigmented area of PS114-5/6 and 114-3 specimens (upper Raman spectrum), with incorporated calcite particles (lower spectrum). Conditions as in Fig. 4.

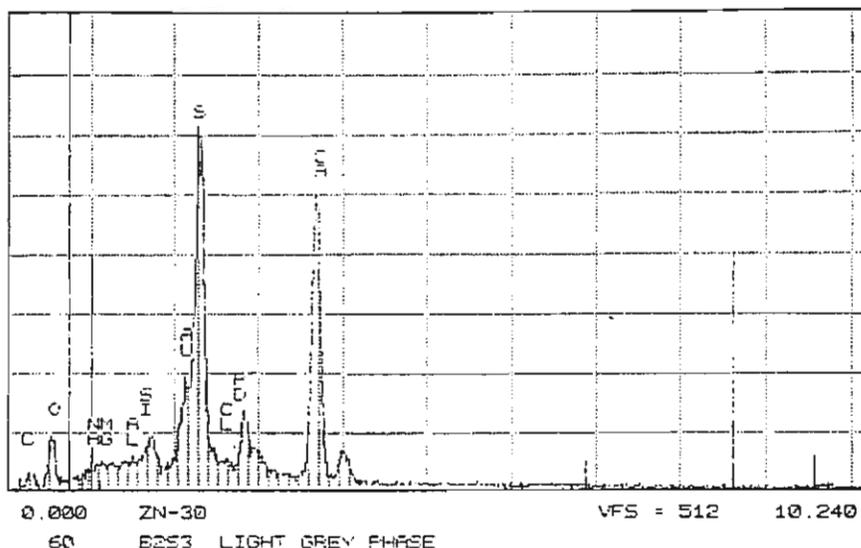


Figure 7. EDS spectrum of smooth surface crust covering the paints. The high concentrations of calcium and sulphur are indicative of gypsum.

### Further results

The SEM images showed that the manganese paint components had a botryoidal morphology, which was partly covered by the gypsum/oxalate coating. Furthermore, the morphology of the substrate appeared as individual rectangular particles of the order of 15  $\mu\text{m}$  in length, with an elemental composition consistent with silicates. The lack of cementation between the particles (Fig. 11) is a likely

cause of the friable nature of the substrate and the reason for the exfoliation of portions of the pictographs.

### CONCLUSIONS

The multiple conclusions gleaned from the Raman spectroscopic analysis were found to be consistent with the results obtained from the other standard instrumental

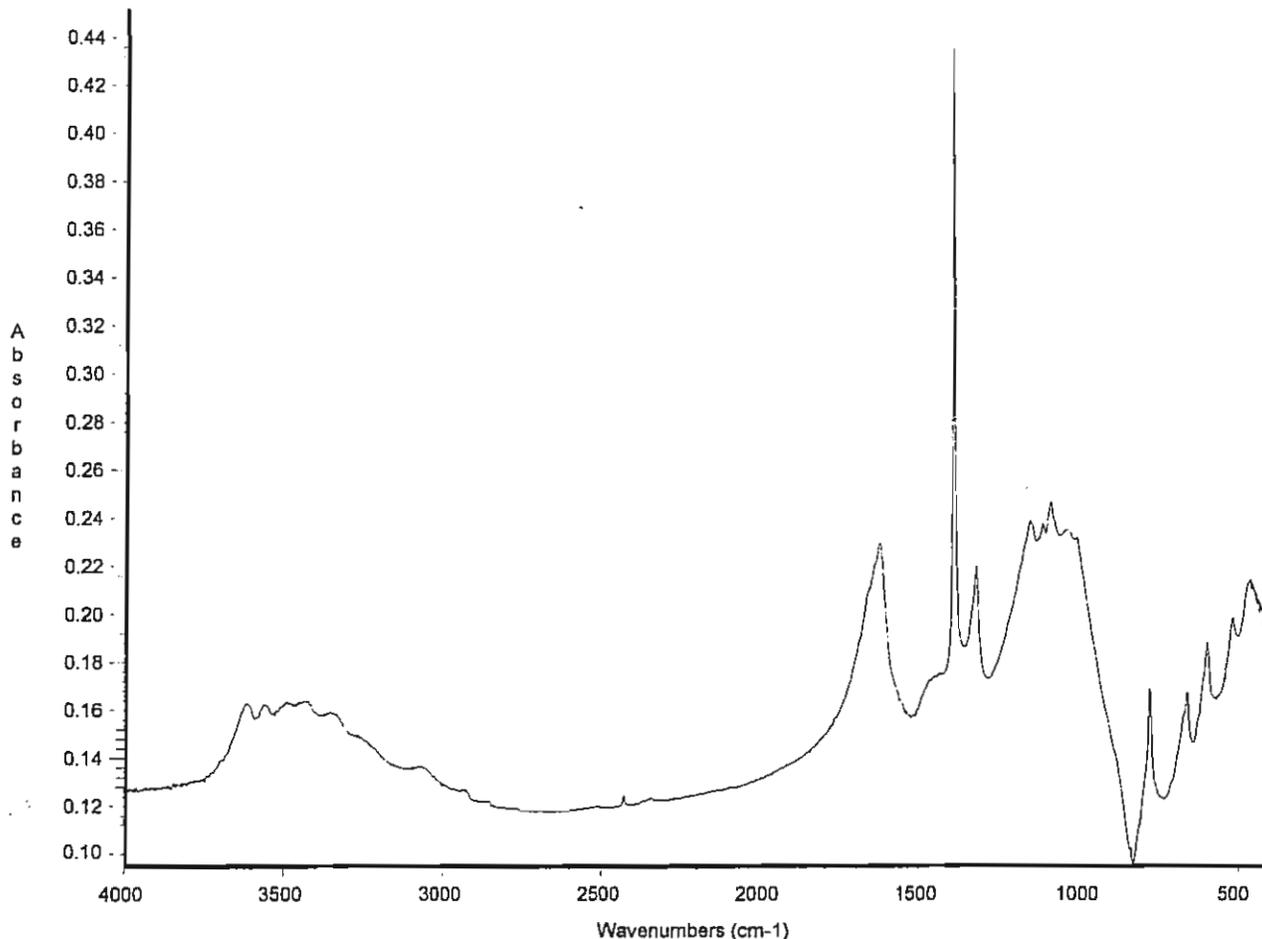


Figure 8. FTIR spectrum of scraping from Big Bend paint sample. The peaks at  $1325$  and  $1610\text{ cm}^{-1}$  and the four peaks between  $525$  and  $795\text{ cm}^{-1}$  are characteristic of oxalate ion.

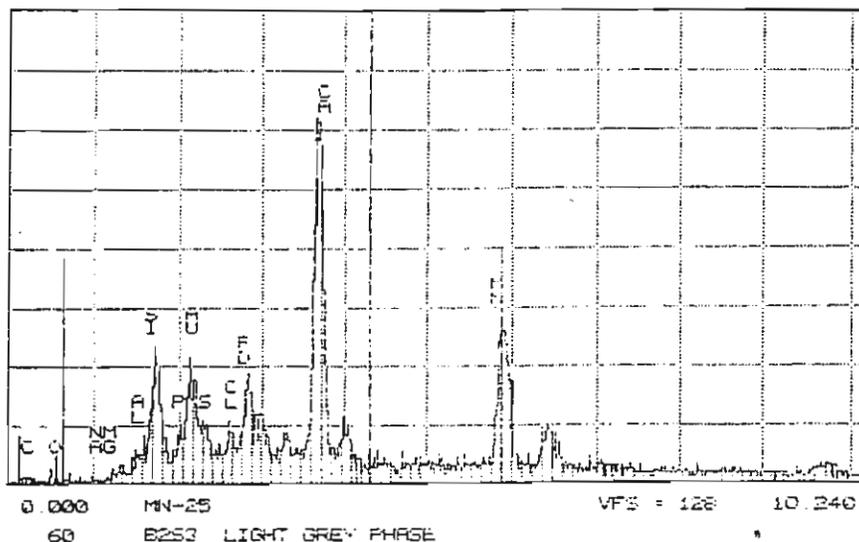


Figure 9. EDS spectrum of pigmented area showing high concentrations of calcium and manganese.

methods, thus demonstrating that this single, non-invasive, non-destructive technique can provide information that in other circumstances requires limited data and which involves the destruction of the samples. Since the SEM-EDS technique provided highly magnified details of paint-substrate systems and elemental data that were used for comparison with Raman results, we conclude that the Raman microscopy-SEM-EDS combination

provided the maximum information with the least sample requirement.

We have clearly demonstrated the utility of Raman microscopy for the study of ancient rock paintings by characterizing the most important features of the ancient paints, including the chemical nature of the natural rock coatings, pigments, organic media and substrata. Furthermore, since the samples studied using Raman

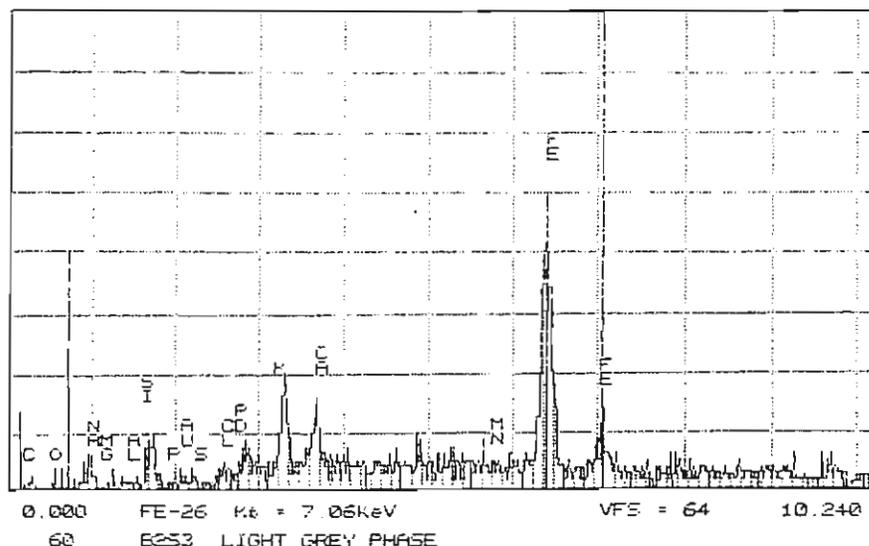


Figure 10. EDS spectrum of brownish component in paint showing high concentration of iron.

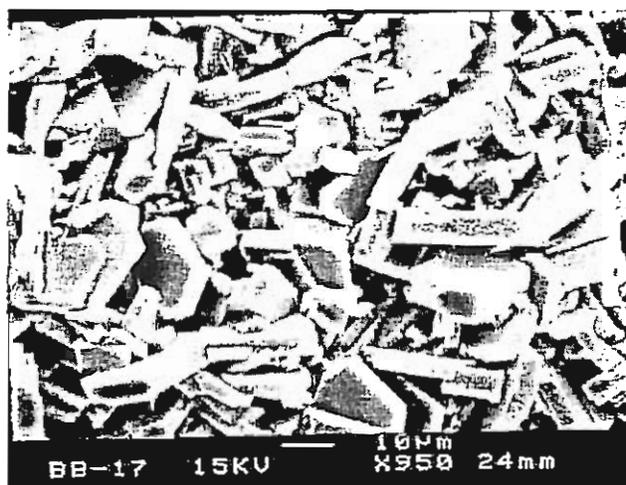


Figure 11. Photomicrograph of substrate showing planar grains without evidence of cementation.

spectroscopy can be subjected to further analyses using other methods, it should prove to be an important tool for the initial investigation of these invaluable artifacts. For example, Raman microscopy can provide data on the presence and nature of organic material in paint samples, in addition to that in the substrata (which in the case of  $^{14}\text{C}$  analysis would represent background contamination), prior to subjecting the sample to dating experiments which then destroy the sample. The Raman results coupled with SEM-EDS results allowed us to characterize effectively the Big Bend paints, with the possible exception of mineralogical details.

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