

# An Initial Raman Microscopic Investigation of Prehistoric Rock Art in Caves of the Quercy District, S. W. France

D. C. Smith,<sup>1\*</sup> M. Bouchard<sup>1</sup> and M. Lorblanchet<sup>2</sup>

<sup>1</sup> Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle, CNRS–UPRESA 7058, 61 Rue Buffon, 75005 Paris, France

<sup>2</sup> Unité Toulousaine d'Archéologie et d'Histoire, Université de Toulouse–Le Mirail, CNRS–UMR 5608, 5 Allées Machado, 31058 Toulouse, France

**Raman microscopy, with its unique versatility and special advantages of no sample preparation and non-destructive analysis of both inorganic and organic materials, is now well established as the best technique for studying pigments and their fillers in ancient or recent paintings. Here this technique was applied for the first time to prehistoric rock art. Microsampling was carried out on red and black parts of Palaeolithic paintings in the three caves Les Fieux, Les Merveilles and Pergouset in limestone of the Quercy District, Lot Department, France. The initial results are: (a) the identification of 'normal' haematite pigment in red microsamples from each cave; (b) the discovery of an additional, but rare, orange–red phase (A) which seems to be a disordered form of goethite; (c) the confirmation of amorphous carbon in some black microsamples; and (d) the recognition of Mn oxide/hydroxide in some other black microsamples. Hence Raman microscopy is sufficiently powerful for distinguishing different red and different black pigments *without* the use of additional complementary techniques. Hence it is now reasonable to envisage analysis with optical fibres and a remote sensor inside the caves in order to avoid damaging prehistoric rock art by microsampling.** Copyright © 1999 John Wiley & Sons, Ltd.

## INTRODUCTION

Setting aside for separate detailed attention the artistic, social and chronological aspects of an overall archaeological study of pigments in wall paintings in general (rock art in caves, frescoes in temples, non-artistic wall coverings, etc.), the principal questions remaining concern the geological/biological and physico-chemical nature and history of the pigments. These can be summarized as follows.

First, from a crystallographic and/or molecular point of view, what are the physical structures and chemical compositions of the coloured material(s), of the associated filler(s) and/or binder(s), of the successive layers of substrate upon which the pigment was applied and of any layers of material which were later deposited on top of the pigment?

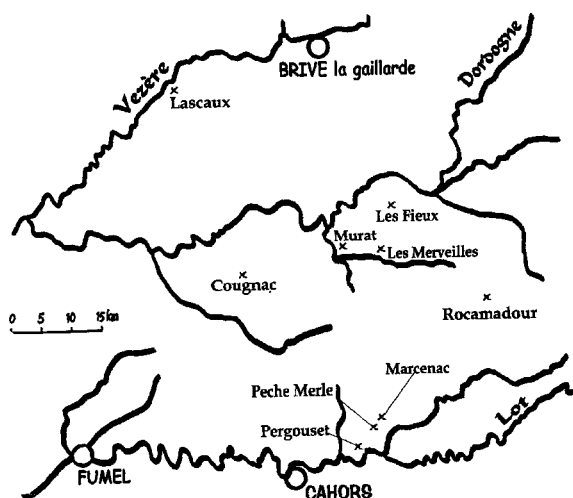
Second, concerning the mentioned petrographic contexts, what are the microtextural relationships of the associated phases (sizes/shapes of grains, proportions of phases and their microcartographic interrelations)? In the case of the co-existence of two or more colouring phases, was the mixture accidental or deliberate? Also, given the existence of a particular pigment, how can we distinguish that its arrival at its present archaeological emplacement was due to geological, biological or human processes?

Third, with regard to the mineralogical/petrogenetic evolution of the pigment (pre-, syn- and post-application), what can be deduced about the provenance of the raw materials used and the techniques of preparation and application of the pigments? Moreover, is there any evidence of infiltration and/or reaction of the pigment and the other layers at, or soon after, its application? Furthermore, is there any evidence of physico-chemical or geological/biological deterioration of the pigment by climatic or other means (fire, flood, lichen, vandalism, etc.)?

Since Raman microscopy is so readily applicable to the non-destructive physico-chemical analysis of geological/biological materials of archaeological interest,<sup>1,2</sup> and especially of pigments,<sup>3–9</sup> this research project was started to examine parietal decoration in prehistoric caves in limestone in the Quercy District, Lot Department, France (Fig. 1). Although the final objective is to carry out routine analysis *in situ* inside the caves using optical fibres and a remote sensor without any microsampling, the project was begun with the laboratory study of sub-millimetre microsamples scraped off parts of the paintings. This paper describes the results from the first stage of the project which explored several of the above-mentioned topics and also searched for differences between pigments in the same cave and in distinct caves.

It is well known, from other chemical or physical analytical techniques, that in prehistoric rock art in general the red and black pigments usually involve respectively Fe oxide/hydroxide(s) and Mn oxide/hydroxide(s) or carbon, but precise physico-chemical characterizations are often lacking. This is also the case in certain caves in Quercy.<sup>10</sup> This new study was undertaken using *only*

\* Correspondence to: D. C. Smith, Laboratoire de Minéralogie, Muséum National d'Histoire Naturelle, CNRS–UPRESA 7058, 61 Rue Buffon, 75005 Paris, France.  
E-mail: smith@mnhn.fr



**Figure 1.** Map of Quercy, Lot Department, S. W. France. Principal rivers, towns (large open circles) and caves in which traces of prehistoric occupation have been demonstrated (crosses).

Raman microscopy (textural analysis along with spectral analysis) in order to test the capability of the technique used alone, since the pigment samples studied here had not previously been analysed by any technique.

Archaeometric problems which may arise when dealing with wall paintings in general include: superposition of some paintings; muddy patches of anthropogenic or natural origin; growth of concretions; crusts of recent 'lamp black' from candles or other lamps; (in)voluntary dispersion of pigment elsewhere on the walls; traces of damage by impact or rubbing; and more recent drawings including graffiti. All of these matters may perturb the analytical data obtained by any technique, and of course also the representativity and interpretation of the data. However, all the microsamples mentioned here were of course extracted with special care to avoid any of these problems.

## ARCHAEOLOGICAL BACKGROUND

The wall paintings in the caves of Les Fieux (Miers, Lot), Les Merveilles (Rocamadour, Lot) and Pergouset

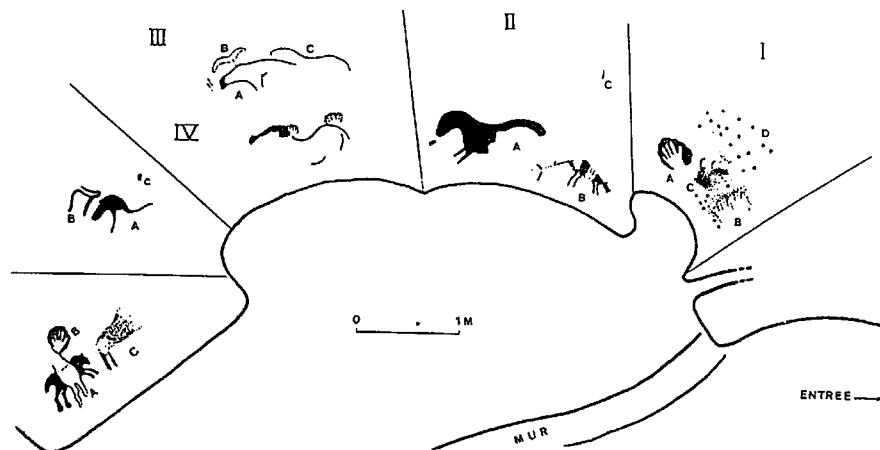
(St Gery, Lot) may belong partly or entirely to the oldest phase of Palaeolithic rock art of Quercy, that is to say to the Aurignacian and Perigordian periods.<sup>11,12</sup>

Les Merveilles and Les Fieux contain stencilled hands, fingerprint dots and animal figures in red or black pigment (Fig. 2) applied with the spitting technique; these art forms are typical of the first art phase of this region, even if a few motifs of Les Fieux are probably more recent.<sup>13</sup>

In contrast, Pergouset is rich in very beautiful engravings, realistic or fantastic (e.g. a splendid deer, an acephalous man, a vulva); more than 150 engravings have been recorded and traced.<sup>13</sup> The paintings are rare and reduced to simple lines and dots and a black cross. Moreover a special technique was used for the panel I in room IV: a piece of solid red pigment was used as a tool to engrave a set of geometric motifs. Also, it is important to note the complete absence of any archaeological artefacts (unlike the two other caves) despite 18 test excavations in different parts of the cave. The cave was almost certainly frequented only for a short time by very few people, just enough to execute the engravings. Most of the engravings seem to be Magdalenian, according to the depicted themes and the technostylistic approach; however, one radiocarbon date ( $32\,850 \pm 520$  BP [Gif 96675]) for a piece of charcoal found during an excavation on a rock ledge just below a panel of geometric engravings and red drawings raises the question of the chronological homogeneity of this decorated cave (M. Lorblanchet, unpublished data).

The different kinds of red and/or black figures that have been examined in the three decorated caves are as follows:

- (i) from the Les Fieux cave:
  - a red line [sample F2];
  - a red dot [sample F3];
- (ii) from the Les Merveilles cave:
  - a black horse [sample M1] from panel IIa;
  - a black incomplete horse [sample M2] from panel IV;
  - a red dot [sample M6] from panel Id;
- (iii) from the Pergouset cave:
  - a black line [sample Pt1] from room II;
  - a red engraving [sample Pt6] from room IV;
  - a painted black cross [sample Pt8] over which a human figure was engraved, from room IV;



**Figure 2.** Reproduction of rock art on panels I–VI near the entrance of the Les Merveilles cave (© M. Lorblanchet) showing the locations of three of the analysed microsamples: the red dots [M6] at the top right of panel I; the horse [M1] of panel IIa; and the incomplete black horse [M2] of panel IV.

a sample of the piece of the radiocarbon-dated charcoal [sample Pt5] found on a ledge occurring below Pt6 a few metres away from Pt8 from room IV.

A few microsamples from the walls of the caves, but in the vicinity of paintings, were also analysed [Mp1, M2p, M3p, M4p, M5p, Pt2, Pt3, Pt7, Pt9].

## RAMAN MICROSCOPY

The Raman microprobe (RMP) employed was a DILOR XY instrument. After wavenumber calibration using the diamond peak at  $1332 \pm 1 \text{ cm}^{-1}$ , the samples were simply placed in turn in the exciting laser beam under the microscope objective. The Raman spectra were measured with the following operational conditions: He-Ne laser excitation at 632.8 nm; 30 mW laser power at the source reduced considerably by various filters and by the optical trajectory;  $\times 10$ ,  $\times 50$  or  $\times 100$  objective; 300  $\mu\text{m}$  slits; multichannel CCD detection; integration time 50–400 s; and 2–7 accumulations. For the black pigments in Fig. 7,  $\text{Ar}^+$  laser radiation at 514.5 nm was used with variable but low laser power to reduce heating of the sample. For routine analysis,  $\pm 3 \text{ cm}^{-1}$  is considered to be the accuracy when comparing spectra from different samples, on different days, or from different instruments; the precision of RMP being around  $\pm 1 \text{ cm}^{-1}$ . The spectra published here were sometimes established by the simple addition of one spectrum obtained with the laser beam polarization vertical and one with the laser beam polarization horizontal, without moving the sample at all, in order to take account of the crystal axis orientation effect and of the optical trajectory orientation effect.<sup>14</sup> The spectra presented in Figs 3–7 were sometimes treated by baseline correction and/or minor smoothing.

## RESULTS

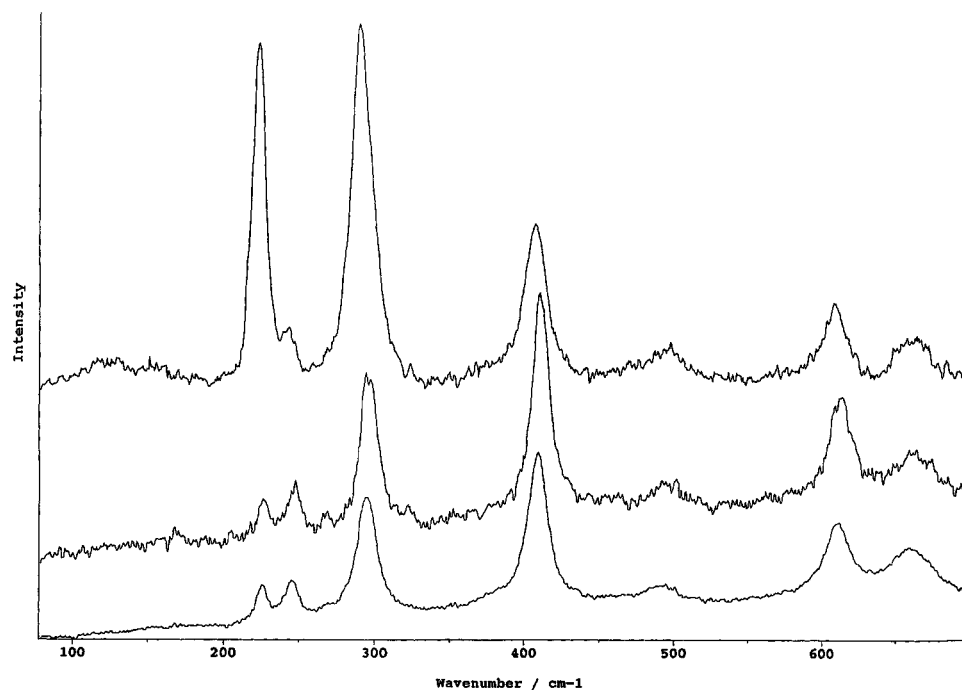
### Red pigment 1

'Normal' haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) was found to occur in pigment samples F2, M6, Pt6 and hence from all three caves (Fig. 3), being identified by eight bands at the characteristic Raman wavenumbers<sup>1,5,15</sup> 225, 244, 293, 299 (shoulder), 410, 494, 610 and 661  $\text{cm}^{-1}$ , which varied only slightly within the usual experimental limits. The intensity of the 225  $\text{cm}^{-1}$  band is usually relatively weak in most haematites; in the case of the uppermost spectrum the crystal orientation was clearly ideal for the expression of this band. Sample F3 did not give any result owing to a very intense fluorescence from the constitutive crystals. Traces of haematite were also detected in the charcoal block Pt5, and occasionally in the wall in the vicinity of paintings (sample Pt3).

Again in all three caves, the adjacent brilliant white, grey (dull or shiny) or colourless transparent grains were usually of calcite, identified by its characteristic Raman wavenumbers<sup>1,5,15</sup> at 156, 282, 714 and 1086  $\text{cm}^{-1}$ ; these bands occasionally appeared as contaminants in other spectra measured on the red pigments. In sample Pt6, minor quartz was also detected by its principal band<sup>1,15</sup> at 467  $\text{cm}^{-1}$ .

### Red pigment 2

Another colouring phase (referred to here as phase A) is sometimes present, along with 'normal' haematite, in red pigment microsamples M6 and Pt6 from the Les Merveilles and Pergouset caves, respectively. This phase A appears in the form of dispersed micrometre-sized orange-brown grains for which most analytical techniques are inapplicable. However, it is also found in



**Figure 3.** Raman spectra of 'normal' haematite: Les Merveilles (M6-AOHT05BA) (top), Les Fieux (F2-APHT04LD) (middle) and Pergouset (Pt6-APHT14LD) (bottom).

microsamples M2p, Pt3, Pt7 and Pt9 which came from the walls of the two caves, but always nearby a painting. Even some black paintings (microsamples M1, M2, Pt1 and Pt8) sporadically revealed traces of phase A. Hence, although phase A occurs in several distinct environments, it is always in a minor quantity. It is nevertheless of significant interest, both geologically and archaeologically, as it may represent a stage in the hydration/dehydration evolution of Fe oxides/hydroxides.

All the Raman spectra obtained gave bands at 92 (wide), 245 (weak), 299 (wide), 400 (very wide), 485 (weak), 559 (very wide) and *ca* 670  $\text{cm}^{-1}$  (weak and very wide) (Fig. 4). This superposition of different spectra obtained for phase A emphasizes their similarities: the 92, 299 and 400  $\text{cm}^{-1}$  bands are the most significant and frequently observed, whereas the bands close to 245, 485, 559 and 670  $\text{cm}^{-1}$  are less pronounced; hence a certain uniformity exists concerning the relatively great width of all the bands and their overall wavenumber position (whose centre is difficult to establish).

All spectra obtained from phase A show the band at 92  $\text{cm}^{-1}$ , which apparently has never been recorded before in any Fe oxide/hydroxide, perhaps because Raman wavenumbers below 100  $\text{cm}^{-1}$  are often not measured. Whereas in 'normal' haematite the 299  $\text{cm}^{-1}$  band is always a shoulder on the predominant 293  $\text{cm}^{-1}$  band, here the 299  $\text{cm}^{-1}$  band occurs alone, as has been recorded for goethite ( $\alpha\text{-FeOOH}$ ) and for  $\text{Fe}(\text{OH})_3$ .<sup>1,5,16</sup> The 400  $\text{cm}^{-1}$  band is so wide (*ca* 375–425  $\text{cm}^{-1}$ ) that it encompasses the total width of the bands recorded for haematite, hydrohaematite, protohaematite, goethite and feroxyhyte.<sup>1,16,17</sup> The 559 and 670  $\text{cm}^{-1}$  bands are difficult to relate to any well characterized Fe oxide/hydroxide.

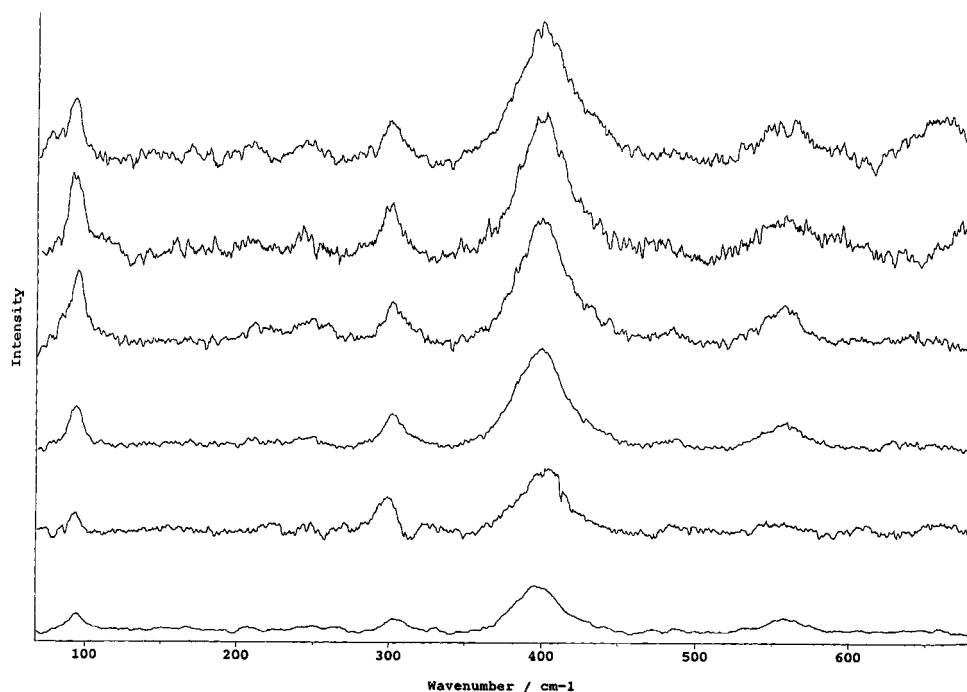
Figure 5 displays, at the top, an artificial addition of two spectra: a standard goethite and a haematite (from Fig. 3); this clearly reveals a minimum between the 387 and 410  $\text{cm}^{-1}$  bands of goethite and haematite respectively. At

the bottom, one of the spectra of phase A is reproduced (from Fig. 4). This demonstrates that its maximum intensity (crest) at *ca* 400  $\text{cm}^{-1}$  corresponds in wavenumber to the above-mentioned minimum in the upper spectrum; hence this phase cannot represent a simple addition of the spectra of haematite and goethite which would be obtained by the exciting laser beam simultaneously impinging upon adjacent crystals of these two minerals.

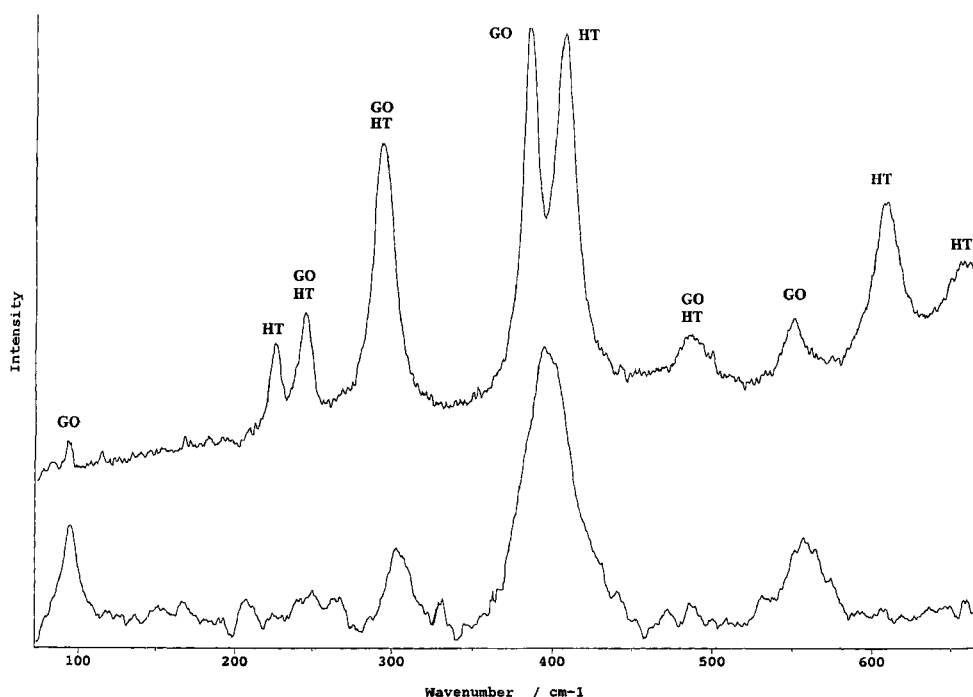
Since the mineral species haematite and goethite share the same topology of hexagonal close-packed oxygens and differ essentially only in the distribution of  $\text{Fe}^{3+}$  cations with the addition of some protons,<sup>18</sup> it seems most reasonable that in an intermediate structure the  $\text{Fe}^{3+}$  cations may be irregularly situated, with some in typical haematite positions and some in typical goethite positions.

It may be noted that all the other significant peaks in our extra phase are at the same positions as in goethite (92, 299  $\text{cm}^{-1}$ ) or are rather close thereto (559  $\text{cm}^{-1}$ ; goethite: 553  $\text{cm}^{-1}$ ) rather than of haematite (Fig. 5). Furthermore they are all also relatively wide, as is the principal band at 400  $\text{cm}^{-1}$ . This leads to the conclusion that phase A of Figs 4 and 5 is best described as "disordered goethite". On the other hand, some bands typical of 'normal' haematite were barely recognizable in other spectra (not shown); it is possible that those spectra represent a different stage of evolution when more cations are in the proper positions for haematite.

The linear binary system  $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$  [including polymorphs and various degrees of crystallinity and of cation ordering, but excluding  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$ , and also the isomorphous cations ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ )] contains many chemical compounds. Between the two chemical end-members haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) / maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and ice / water, these include the IMA-recognized species called goethite ( $\alpha\text{-FeOOH}$ ), akaganéite ( $\beta\text{-FeOOH}$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), feroxyhyte ( $\delta\text{-FeOOH}$ ), ferrihydrite and bernalite. These different structures can all be



**Figure 4.** Six different spectra for the extra phase A, referred to here as 'disordered goethite': Pergouset (Pt9-AWPR19BU, Pt9-ATUN07BU, Pt1\*-AWUN04BU, Pt3-AWPR14BU, Pt7-AQUN11BU) and Les Merveilles (M1\*-AZPR05CF), where \* denotes a black pigment which is not carbon.



**Figure 5.** A computerized addition of spectra of haematite (Pt6-APHT14BD) and of a goethite standard (BAGO11BU) (top) and a spectrum of 'disordered goethite' (AZPR05CF) (bottom).

simply related chemically in terms of polymorphism or of hydration/dehydration reactions. In addition, there exist some species such as hydrohaematite, protohaematite and  $\text{Fe}(\text{OH})_3$  which are not IMA-recognized (poorly characterized or non-natural). Unfortunately, reference Raman spectra of most of these phases are either non-existent or inconsistent.<sup>1,5,16</sup> To complicate the situation further, the terminology in the literature is often neither standardized nor coherent; this is because many old discredited mineralogical names are still used by non-mineralogists and, of course, they are still found when consulting old publications by mineralogists; these include synonyms (e.g. oligiste, przibramite), varieties (e.g. titanohaematite, aluminogoethite) and improper mineralogical terms, improper because they involve not minerals but rocks or powdered mixtures (e.g. red ochre, laterite). There are yet more problems as certain names appear with different compositions (e.g. turgite, limonite, xanthosiderite, as well as the IMA-recognized species ferrihydrite and bernalite). It is thus evident that in order to interpret Raman spectral data correctly, it is essential to create an adequate data bank of Raman spectra of as many as possible of these phases (work in progress). With the data at our disposition, it appears that the extra phase A is a 'disordered goethite', but this does not exclude the possibility that it is the same phase as one or other of those mentioned above, especially protohaematite or ferrihydrite mentioned by various workers.<sup>16,18,19</sup>

### Black pigment 1

Near to these red paintings, a series of black paintings exists in all three caves. The samples can be separated into two categories differing in their morphological aspect.

Samples Pt8 (wall painting) and Pt5 (black small block on a ledge) from Pergouset are both very dark and without any metallic aspect. These properties are typical of carbon black, but of course other materials were possible.

Raman microanalysis revealed spectra showing a large massif with two summits around the characteristic positions of  $sp^2$  (ca 1580  $\text{cm}^{-1}$ ) and  $sp^3$  (ca 1330  $\text{cm}^{-1}$ ) carbon (Fig. 6); this spectral morphology, which is essentially identical for both samples, is characteristic of amorphous carbon,<sup>1,5,8,20</sup> which is often given other names when dealing with pigments or with carbon precipitated in laboratory experiments: 'carbon black', 'lamp black,' 'disordered graphite,' etc. Since the band at ca 961  $\text{cm}^{-1}$  typical of  $\text{PO}_4^{3-}$  is not present, then this is not 'ivory black' created by burning bones which contain hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ ].

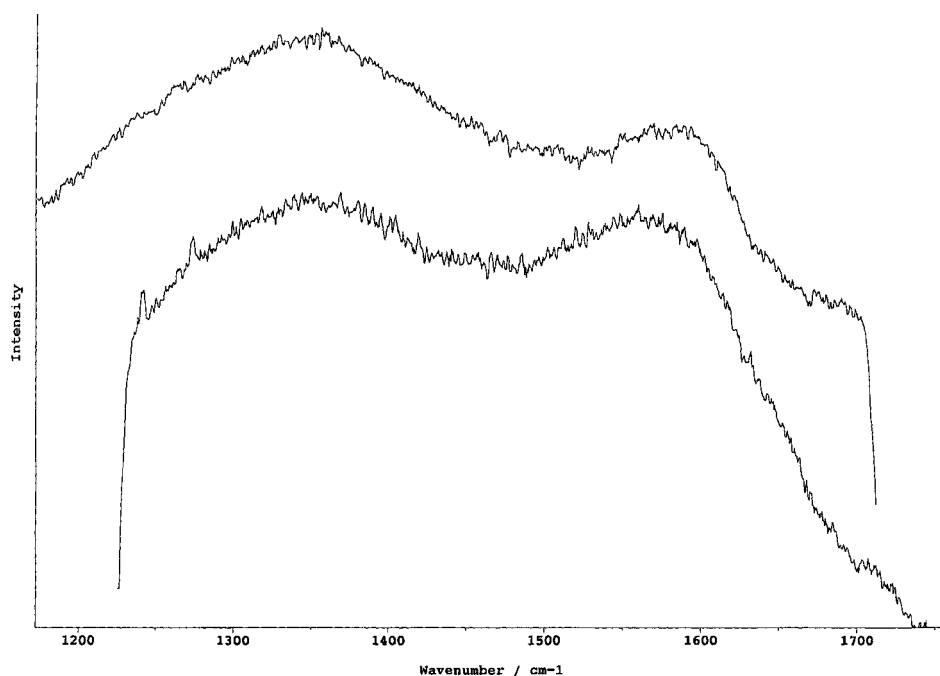
The identification of carbon in a pigment by Raman microscopy can thus contribute to increasing the efficiency of an archaeological programme by selecting for radiocarbon dating only those black pigments known to contain carbon.

A sample (Pt9) of the wall occurring ca 3–4 cm from the black cross was also examined by Raman microscopy. It showed only calcite with minor 'disordered goethite,' i.e. without carbon. This leads to the conclusion that the painting Pt8 was drawn by the application of a charcoal pencil (e.g. Pt5) and not by using any other more dispersive method, such as the spitting or the blowing techniques explained elsewhere.<sup>13</sup>

In sample Pt5, minor quartz was also detected by its principal bands<sup>1,15</sup> at 128 and 467  $\text{cm}^{-1}$ . Rutile ( $\text{TiO}_2$ ) was also detected on the basis of its characteristic bands<sup>1,15</sup> at 144, 239, 446 and  $613 \pm 3$   $\text{cm}^{-1}$ . These may represent contaminants as they were both found, amongst other phases, in a sample of mud (Pt4) collected from the floor of the cave.

### Black pigment 2

In contrast to samples Pt5 and Pt8, samples M1, M2, M3, M4 and M5 (from the Les Merveilles cave) and sample



**Figure 6.** Raman spectra of 'carbon black' from the Pergouset cave: the painted black cross (Pt8-AWBL12BU) (top); and the piece of charcoal found on the ledge a few metres away (Pt5-AUBL17BU) (bottom).

Pt1 (from the Pergouset cave) have a very marked grey-metallic coloration. They did not produce spectra typical of amorphous carbon and hence have a different constitution. Since manganese is well known in prehistoric paintings in some caves in Quercy<sup>10</sup> and elsewhere, it is probable that these black pigments are constituted of one or more Mn oxides/hydroxides. These are notoriously difficult with Raman spectroscopy because of their great opacity and hence great thermal absorption,<sup>21</sup> even in compact mineral form. In the powdered form of pigments, which drastically reduces thermal conductivity, the situation is worse and may lead to photodegradation which in turn may (a) create one or more new mineral phases under the laser beam yielding spectra which do not correspond to the original material before analysis<sup>21</sup> or (b) create an amorphous material which yields no spectrum at all or sometimes an ultra-high fluorescence. It is therefore necessary to employ a low laser power and hence a long counting time.

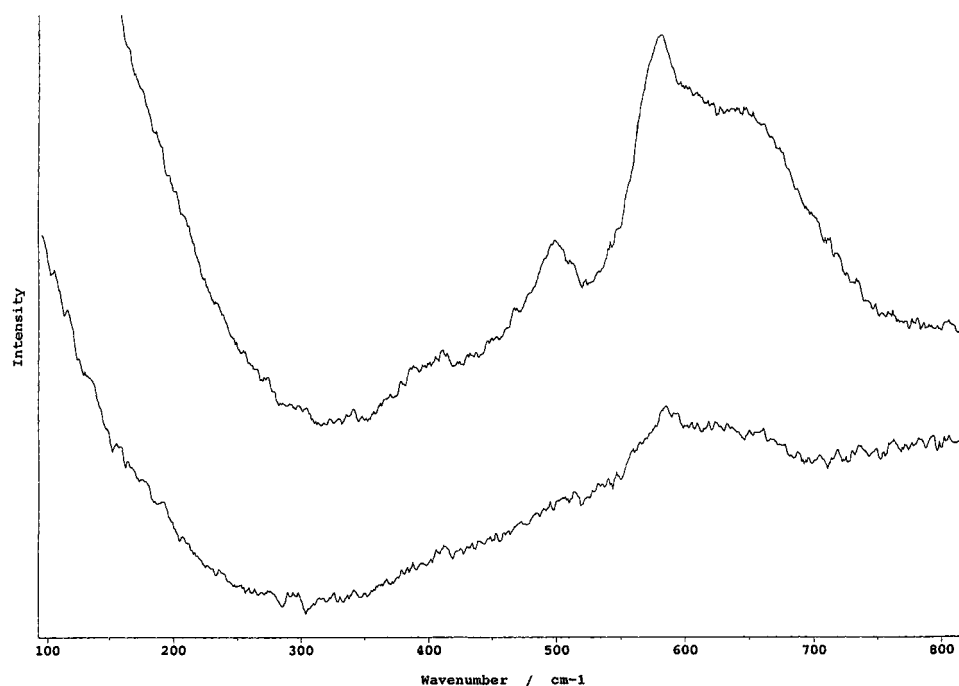
It is also relevant to mention here that Mn oxides/hydroxides present more variety, and hence more problems, than their Fe counterparts for three reasons: (i) the opacity/photodegradation problem described above is greater with Mn; (ii) in addition to  $\text{Mn}^{2+}$ , which can make pure  $\text{R}^{2+}$  or mixed  $\text{R}^{2+}/\text{R}^{3+}$  phases such as magnetite ( $\text{Fe}_3\text{O}_4$ ) and hausmannite ( $\text{Mn}_3\text{O}_4$ ), there is now also  $\text{R}^{4+}$  to extend the range of possible chemical compounds, notably to  $\text{MnO}_2$  in several polymorphic forms; (iii) Mn oxides/hydroxides provide many kinds of tunnels in their crystal structures which are suitable for occupancy by large low-valent cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Pb}^{2+}$ ; these can enter the Mn–O network in sufficient quantity to create true mineral species such as birnessite, romanéchite, todorokite and the hollandite series,<sup>18</sup> several of which are common in Nature.

Several of these grey-metallic powders were examined and no spectrum was obtained with the He–Ne laser or with the  $\text{Ar}^+$  laser. However, satisfactory results were obtained with the  $\text{Ar}^+$  laser by covering the microsample

with a few drops of water, as is often recommended for fragile or opaque samples.<sup>21</sup> The benefits are twofold: (i) the water rapidly disperses the heat generated by the laser; and (ii) the water disperses some of the laser light away from its intended trajectory so that a wider sample surface is analysed (this is in part equivalent to defocusing the exciting beam, a method often used with other techniques such as electron microprobe analysis).

Both of these aspects allow a higher laser power (at the objective) and hence a shorter counting time. It is fortunate that the Raman spectrum of water does not interfere in the low-wavenumber range of interest for Fe or Mn oxides. It may be noted that this procedure can lead to the creation of minute gas bubbles which may disturb the analysis (e.g. deflection of the laser beam; physical movement of the microsample). Whereas in the case of pigments from other kinds of painting, especially modern art containing organic colorants or soluble inorganic colorants where the presence of water could affect the pigment, this should not be the case with prehistoric rock art. The pigments have already survived many millennia in a damp atmosphere, often with occasional flooding, such that they should remain stable.

Figure 7 presents the results from sample Pt1. Three bands are observed at 498 (wide), 580 (strong) and 650  $\text{cm}^{-1}$  (wide shoulder) with some additional Raman intensity between the last two values; these correspond closely in morphology, but less so in precise wavenumber positions, to those characteristic of bixbyite ( $\text{Mn}_2\text{O}_3$ ):<sup>21</sup> 509 (wide), 581 (strong), and 650  $\text{cm}^{-1}$  (shoulder) with some Raman intensity between the last two values. The correspondence is equally good, or even better, with the spectra created in solution (and deduced to be  $\text{Mn}_2\text{O}_3$ ) during electrochemical studies involving changing the valency of Mn between  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$ .<sup>21</sup> This correspondence with bixbyite is better than that with any of the other Mn oxides/hydroxides provided in their comprehensive reference study,<sup>21</sup> most of which have their main Raman bands in the range 350–650  $\text{cm}^{-1}$ . However,



**Figure 7.** Raman spectra from black pigments of Mn oxide/hydroxide: Pergouset (Pt1-BHMN05LE) (top) and Les Merveilles (M2-BHMN14LE) (bottom).

comparable Raman data on the heavy element-bearing Mn oxides/hydroxides apparently do not exist. No other Raman bands were detected except for some intensity around  $400\text{ cm}^{-1}$ .

Samples M1 and M2 from the Les Merveilles cave produced lower quality spectra (Fig. 7) with a similar morphology for the massif between  $550$  and  $700\text{ cm}^{-1}$  but with the first band at *ca*  $500\text{ cm}^{-1}$  at the limit of visibility. It is thus less certain that this is pure bixbyite. It is, however, highly probable that all of the pigments of Fig. 7 are constituted by  $\text{Mn}^{3+}$  oxide in which bixbyite is the major constituent, and in which some impurities such as  $\text{Mn}^{2+}$ ,  $\text{Mn}^{4+}$  and/or  $\text{H}^+$  are present, either within the bixbyite crystal structure or within independent co-existing minor phases.

These data are significant for several reasons. First, bixbyite (even impure) in sample Pt1 proves absolutely the presence of Mn such that distinction from carbon is possible by Raman microscopy alone. Second the presence of a thin covering layer of water seems indispensable for analysing Mn oxides/hydroxides; hence when analysing rock art *in situ* in caves using optical fibres, it will be necessary to maintain a continuous but fine spray of water on the painting *during* the analysis. Third, as explained above, it is not certain that the bixbyite identified by Raman microscopy is the true phase present in the original pigment; in this case the identity of the true phase would remain to be established. Fourth, the bixbyite may be the true pigment phase, but this raises two intriguing possibilities: either a natural source of bixbyite was found and exploited by prehistoric man (but bixbyite is not very common geologically), or he created the bixbyite, most probably simply by heating and dehydrating Mn hydroxides such as groutite or manganite (both  $\text{MnOOH}$ ); cf. the well known synthesis of haematite ( $\text{Fe}_2\text{O}_3$ ) by heating and dehydrating goethite ( $\text{FeOOH}$ ).<sup>16</sup> Such a heating process may have been voluntary (e.g. to modify the colour) or involuntary (e.g. proximity of fire).

### Binders and/or fillers

The binder is an important constituent of many paints since it allows adherence between the different particles of colorant and between these and the support. For example, it has been established recently that vegetable oil was employed as a binder in rock art in the French Pyrénées.<sup>22</sup>

No binder has yet been discovered in rock art from Quercy.<sup>13</sup> However, nearby in the famous Lascaux cave in the Dordogne Department (Fig. 1), it has been shown that the water of the cave, full of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ , served as the unique binder by precipitating calcite.<sup>23,24</sup> In fact, it was because of the imprisonment by calcite crystals on the wall of the Fe and Mn oxides/hydroxides in the paintings that the latter have been conserved for so long.

In this work, many sorts of calcite have been differentiated under the microscope (microcrystals  $\leq 3\text{ }\mu\text{m}$ ; macrocrystals *ca*  $1\text{ mm}$ ; pink, orange, grey, white translucent or opaque). A few crystals of Fe oxide are imprisoned in a calcite matrix at Pergouset (sample Pt6). It would obviously be most useful if it became possible to distinguish physico-chemically the numerous different types of calcite mentioned in the Introduction in order to establish if one or other type of the observed calcite was a binder or a filler in Quercy's rock art.

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### CONCLUSIONS

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This study of prehistoric paintings by Raman microscopy is apparently the first in this field. The next logical step is to analyse rock art *in situ* inside the caves by means of a transportable Raman spectrometer coupled by optical fibres to a remote sensor. However, before carrying out such an operation, it is essential to have an adequate database of reference Raman spectra of standard mineral species (e.g. polymorphs and different states of

order/disorder or of valency in Fe hydroxides) and also of optimum analytical configurations (e.g. photosensitive powdered opaque Mn oxides).

It was emphasized above that these databases must be accompanied by a substantial improvement in terminological usage which can only be achieved by more scientific exchanges between the three major groups of disciplines involved: art/archaeology/ethnology; geology/petrology/mineralogy/cystallography; physics/chemistry/spectroscopy. It is now possible to be more precise in differentiating the various pigments employed in prehistoric rock art such that vague terms like 'red ochre' may be avoided in the future. It should also be possible to avoid incorrectly using precise terms such as 'haematite' for red pigments which have not been strictly identified.

Despite these database and terminological problems, this initial study nevertheless demonstrates that the Raman

microprobe *alone* can indeed non-destructively detect spectral differences corresponding to distinct mineral species in rock art from prehistoric caves, whether concerning the pigments (haematite, 'disordered goethite,' amorphous carbon, Mn oxide/hydroxide), or the substrate (calcite) or trace minerals (quartz, rutile). In particular, it has been shown that Raman microscopy can distinguish between haematite and non-haematite red pigments, and between carbon and Mn oxide/hydroxide black pigment. The latter point demonstrates the characterization of both organic and inorganic materials, something which cannot be done with most other physico-chemical analytical techniques.

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