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Manganese black pigments in prehistoric paintings: the case of the Black Frieze of Pech Merle (France)

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Different black pigments of natural origin (mineral or organic) have been examined by means of several analytical methods (colour measurements, elemental analysis and structural analysis). The results, after being compared with each other, then served as reference points in the study of the 'Black Frieze' of the cave of Pech Merle (Lot). After that, colour measurement was investigated in situ on the paintings as a means of displaying small differences (in hue or chroma) between the black colours. The aim of this study was to verify several hypotheses concerning the techniques used by the painters of Pech Merle, and specifically by the one(s) of the Black Frieze. A first objective was that of identifying the nature and, if possible, the origin of the black pigments used in these figures. A second objective was that of determining in which parts of the frieze one or the other (or one and the other) had been used; and the final objective was to provide new technical information that might help us better to understand how the Pech Merle frieze was produced, whether by a single painter and in one episode, for the most part, or, on the contrary, in several episodes and by a succession of different painters.

Keywords: prehistoric paintings, france, pech merle cave, black frieze, black pigments, colour measurements, neutron activation analysis, x-ray diffraction analysis, black manganese hydroxydes, carbon blacks, mixed blacks, burnt blacks

INTRODUCTION

Among its 700 parietal motifs, the cave of Pech Merle (Cabrerets—Lot) contains about 40 black figures depicting mammoths, bison and horses. Most of these motifs are found together in a huge panel called the 'Black Frieze', a group of 25 line drawings spread over a width of 7 m and a height of 2.5 m. Together with the group of the spotted horses, this panel, the best known in the great Quercy cave, constitutes one of the gems of Quaternary parietal art. Extensive archaeological studies, together with experimentation, have shown that this is probably a spiral composition that began in the middle of the panel with the execution of the central horse, and developed outwards through the addition of halos of bison, then mammoths and, finally, aurochs.

The collection of 25 figures, placed in a large natural alcove, displays particular graphic conventions and appears to have been the work of a single artist. It has not been possible to determine the exact age of this production through a direct radiocarbon date, but it seems

reasonable to place the Black Frieze in the middle artistic phase of Pech Merle, slightly more recent than the spotted horses, which have been dated to $24\,640 \pm 390$ BP (Gif A 95357) through carbon 14 (Lorblanchet 1981). Pigment analysis now brings an indispensable scientific complement to our knowledge of this famous frieze.

ANALYTICAL PROCEDURES

Visible absorption spectrometry and colorimetry

Colour measurements were carried out using a portable reflectance spectrophotometer. The spectrograph is built in a Czerny–Turner configuration with interchangeable gratings (400 g mm^{-1} or 600 g mm^{-1}) and interchangeable entrance slits ($25\text{ }\mu\text{m}$ or $100\text{ }\mu\text{m}$), allowing measurements with a resolution higher than 1 nm in the $380\text{--}900\text{ nm}$ range. The detector is a cooled 1024-diode array, linked through a converter to a portable computer for data acquisition and processing. A special mobile probe made of fibre optic bundles is connected to the entrance of the spectrograph and allows measurements without contact on a very small area (about 2 mm^2). The light source used here is a stabilized quartz/tungsten/halogen lamp (pseudo-source C). The measuring time is achieved within a few minutes after an accumulation of 100 runs. The software allows different functions, among which are displays of absorbance or reflectance spectra and of different colour data (for example, colour coordinates $L^*a^*b^*$ or dominant wavelength λ_d). The method is non-destructive.

Neutron activation analysis (NAA)

Elemental analysis was carried out by neutron activation (either by rapid or by thermalized neutrons). For Mn identification, we used thermalized neutron activation, since the use of rapid high-energy neutrons engenders several nuclear reactions, which consequently produce a great deal of interference. It is then difficult to interpret the measurements, since corrections have to be made for elements with consecutive atomic numbers, such as iron and manganese. With thermalized neutrons, the only reactions produced are reactions of type (n, γ) , so no interference is possible between the nuclei of elements of consecutive atomic number—that is, between iron and manganese. Moreover, through irradiation with thermalized neutrons, three elements have very high reaction cross-sections (the cross-section is proportional to the probability of reaction): indium, manganese and gold (and, to a lesser extent, sodium). Therefore, these elements have the advantage of maximum sensitivity in this analytical method. This high sensitivity allows us to carry out measurements on very small samples. Again, the method is non-destructive.

Energy dispersive analysis (EDS)

Elemental analyses of a few microsamples were also carried out by using X-ray microanalysis with an electron beam (EDS), the analysis being only qualitative, since the equipment used was not adapted for computing actual percentages of elements. The samples are also far from homogeneous, and the percentage of each element found can vary a great deal according to the chosen grain and the measurement point on that grain.

X-ray diffraction analysis (XRD)

Analyses were carried out by X-ray powder diffractometry, using a goniometer system and a Cu anode tube ($\lambda = 1.540\text{ \AA}$) operating at $40\text{ kV}/30\text{ mA}$, with a scanning angle of 2θ between 2° and

46°. A second experimental XRD layout involved a position-sensitive curved detector, a Mo anode tube ($\lambda = 0.709 \text{ \AA}$) with $0^\circ \leq 2\theta \leq 120^\circ$ and a tube power of 40 kV/20 mA, the sample being placed in a glass capillary in a configuration of Debye–Scherrer type; due to this layout, very small quantities of samples, less than 0.5 mg, could be measured.

Raman analysis

Analyses were carried out with a Raman microspectrometer using a 1200 g mm^{-1} holographic grating, a cooled CCD detector and a $\times 100$ microscope darkfield objective, adapted for measurements on solid grains as small as $20 \mu\text{m}$. The excitation source was the emission line $\lambda = 514.5 \text{ nm}$ of an Ar^+ laser with 3 mW power. The integration time was 300 s.

COLOUR MEASUREMENTS

Although it is difficult to speak of colours where black is concerned, whether in Antiquity or in the Middle Ages, blacks have been considered as colours (*Colorum alii sunt albi, alii negri, alii medii*...). These black colours even constitute one of the principal poles of a very ancient chromatic system which still survives today; and is used, for example, by painters such as Pierre Soulages. So it has been known for a long time that not all blacks are strictly neutral (in the colour technology sense of the term), and that they have their own tint, even when their distance from a neutral black remains slight. This feeble tint is generally measured for a dominant wavelength between 580 nm and 600 nm—that is, between yellow and orange red—but one can also find purple tints, as well as rather ‘bluish’ blacks. The latter generally originate in phenomena of diffusion linked to a very fine granulometry of materials such as lamp blacks.

Colour measurements carried out directly on the paintings

A first trial series of measurements, carried out in 1993, involved the prehistoric paintings in two Lot sites, the decorated cave of Cougnac and that of Pech Merle. The results were a little disappointing as far as the red line drawings were concerned, since they were all composed of the same iron oxide, Fe_2O_3 , but on the other hand the black lines revealed notable differences. Systematic distances could be observed on the chroma diagrams between the Cougnac blacks and those of Pech Merle and, among them, colour differences even appeared according to the places at which the measurements had been made. These measurements highlight significant differences between the left side and the central part of the frieze. Different black pigments seem to have been used.

However, as far as black colours are concerned, great care has to be taken with the measurements, trying to reduce any stray light to the minimum and taking into account different surface or ground layer conditions. At first, a glossy *calcin*—i.e., the translucent calcite deposits—produces some unwanted specular reflection with possible local variations. This *calcin*, which is unevenly thick, is also naturally more or less tinted by iron oxide. To take this into account, we took pains to measure the wall colour in the vicinity of each black spot that was studied, in order to be able to eliminate it from the final result. Hence variations pointed out by the measurements could be engendered by the presence of distinct black pigments, or even by the use of different techniques. Afterwards, we undertook to compare some $L^*a^*b^*$ colour coordinates from the Black Frieze to color coordinates from various reference blacks at our disposal in the laboratory, and measurable under similar operating conditions.

Colour measurements carried out on different reference blacks

Measurements then carried out in the laboratory involved several reference blacks that were presumed to have been used in the prehistoric paintings, with a view to comparing the results to the preceding examinations.

Four mineral blacks and three carbon blacks were examined:

- (i) BK1, a black deposit of the damp floor of the cave of Cougnac (probably brought in by man, according to archaeologists, since similar deposits can be found outside the cave, in the immediate vicinity);
- (ii) BK2, a black rock taken from a former quarry, near Cadouin (Dordogne);
- (iii) BK3, a black deposit enclosed in the limestone of the cave of Pech Merle, in the 'Bear's gallery';
- (iv) BK4, a black sample of powdered manganese dioxide, MnO_2 ;
- (v) BK5, a juniper charcoal (gathered close to Pech Merle);
- (vi) BK6, a soot black;
- (vii) BK7, a drawing charcoal.

The CIELAB chroma diagram (Robertson 1977) presents the results of the measurements (Fig. 1). It shows that soot black (BK6) with a dominant wavelength of 478 nm is a somewhat dark bluish purple (a tint resulting from its very fine granulometry), whereas the other blacks have a rather orangey hue; their dominant wavelength is on average 585 nm. One should also note that the Pech Merle black (BK3) and the manganese black MnO_2 (BK4) show higher chromas, which distinguish them from the other blacks, whose very closely packed dots on the diagram are close to the neutral zero point 0. In spite of these small distances, it does seem to be possible to differentiate the Cougnac black (BK1) and the Cadouin black (BK2), since the colour differences ΔE^*_{ab} in that reduced part of the chroma diagram involve very small ellipses (or approximated circles).

However, the colour differences observed between Cougnac and Cadouin blacks are mostly lightness differences ΔL^* ; these might come from unwanted specular reflection or stray light due to unsuitable operating conditions. In order to cross-check the results, we carried out new measurements on the same reference blacks after dispersing them in a certain quantity of white MgO ; that is, in the end we measured greys of the same origin, but which were made increasingly light by means of successive dilutions. The new chroma diagrams obtained in this way confirm the first results: colour points for each reference black and grey are in the same alignment, and one can observe that the black and the greys of Pech Merle and those of the manganese dioxide again show a relatively saturated orangey tint, while the Cougnac, Cadouin, juniper and soot blacks and greys are darker, the soot ones being indeed bluish black. These new colour measurements confirm the previous results and make them immediately available for interpretation of the paintings of the Black Frieze. The chroma diagram (Fig. 1) also shows that Black Frieze points FN1–FN5 and FN9 have much lower chroma than the reference blacks BK3 and BK4, and that most of them have a chroma that is a little higher than that of the carbon blacks BK5, BK6 and BK7. The Black Frieze pigments seem to be somewhere between the manganese blacks and the carbon blacks.

New colour measurements were then undertaken in the laboratory with mixed blacks: mineral black plus carbon black. For example, mixtures of about 50% soot black BK6 with manganese blacks BK2 and BK4, or with charcoal black BK5, show new colour points on the chroma diagram $L^*a^*b^*$. These points are very close to the neutral zero point (Fig. 2). Mixed blacks then have different, and sometimes very different, colour coordinates. In any case, the reference

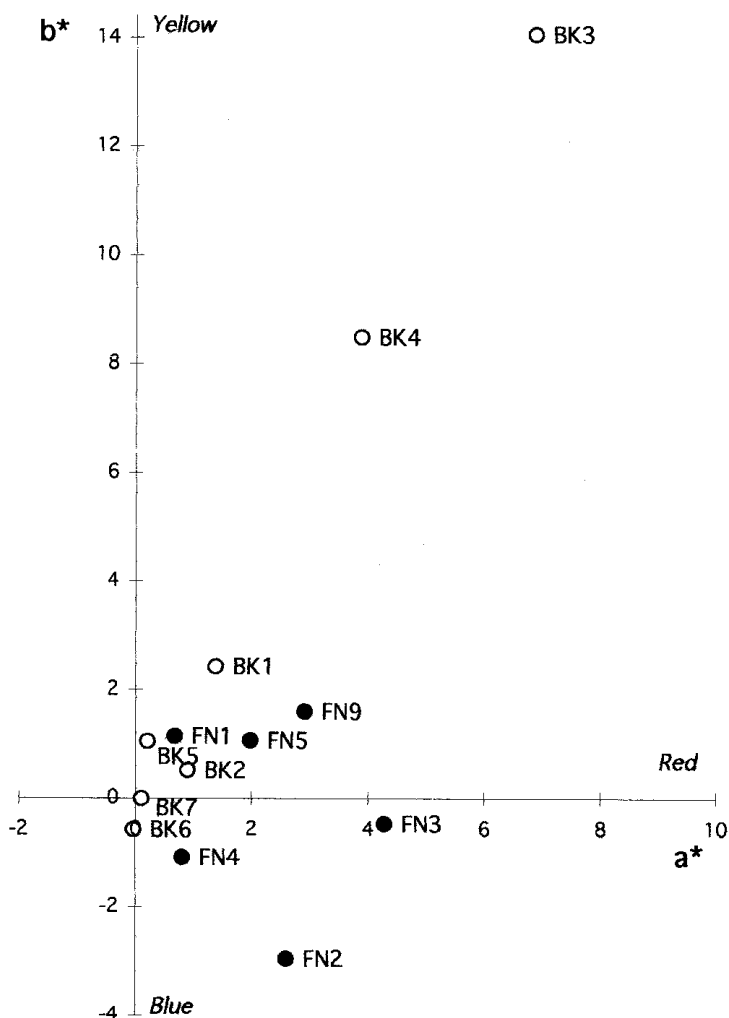


Figure 1 A CIELAB chroma diagram of reference blacks BK1–BK7, compared to measurement points FN1–FN5 and FN9 on the Black Frieze of Pech Merle.

blacks become much darker when mixed with a soot black. This observation suggests that some of the blacks of the Black Frieze might be mixed blacks. This hypothesis appears to be in concordance with the Raman results except for FN3, which appears with a higher chroma, perhaps due to its higher percentage of MnO_2 .

REFERENCE BLACKS

Manganese concentration

The analyses show that all of the mineral blacks contain a high percentage of manganese. Before being measured, the samples were precisely weighed to make it possible later to calculate the percentage of MnO_2 in each of them. In order to know this, measurements were taken at the same

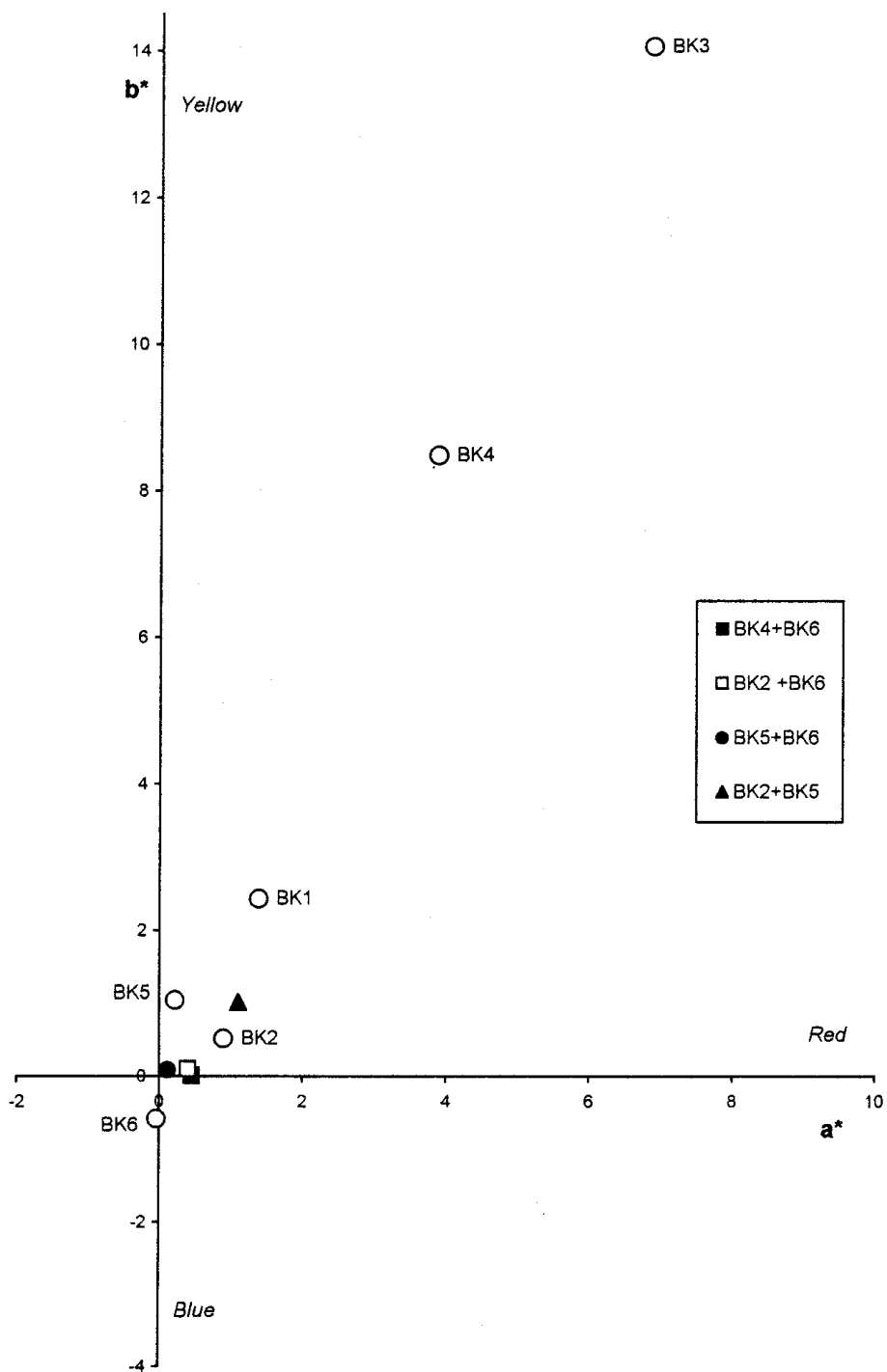


Figure 2 A CIELAB chroma diagram of four mixed blacks, BK2 + BK6, BK4 + BK6, BK5 + BK6 and BK2 + BK5, compared to reference blacks.

time, and hence in the same conditions, from three reference samples of manganese dioxide powder (BK4), weighing 0.606 mg, 0.424 mg and 0.204 mg respectively. Hence, after the measurements, it was possible to draw up a line of standardization. Next, by taking these samples of MnO_2 as yardsticks (reference 100%), one obtains $\text{MnO}_2 = 55\%$ for the black ochre of Cadouin (BK2), $\text{MnO}_2 = 54\%$ for the black ground of Cougnac (BK1) and $\text{MnO}_2 = 33\%$ for the black rock taken from the wall at Pech Merle (BK3).

As this method is very sensitive, it was applied to search for manganese in carbon blacks. Therefore, seven reference blacks of organic origin were measured under identical conditions. All of them were found to contain only a very tiny percentage of manganese dioxide. The greatest amount is found in the drawing charcoal from the spindle tree (BK7), with $\text{MnO}_2 = 0.21\%$, then the juniper charcoal (BK5), with $\text{MnO}_2 = 0.043\%$, and then the maritime pine charcoal (BK10), with $\text{MnO}_2 = 0.037\%$, and even less is found in other carbon blacks (soot black and vine black). Therefore one can immediately conclude that, in the analysis of a small sample carried out on a prehistoric painting, the contribution of manganese oxide to carbon black can always be considered to be totally negligible. The research was extended to a few other compounds which might be encountered in further studies; according to the same procedure, less than 0.05% of MnO_2 was found in gallnut extract, in a sample of parchment glue, in a sample of white of egg or in a sample of arabic gum.

Mineral compounds and mineralogy

XRD measurements, carried out on the reference blacks, enabled us to identify several manganese compounds. Among the possible candidates (Waychunas 1991; Post 1992), several black oxides had been selected beforehand which belong to the group of the ‘psilomelanes’—that is, different neutral or hydrate forms of manganese oxide or manganese dioxide and barium. Among the latter are the following:

- (i) Oxides or hydroxides $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ and $\text{Ba}_x\text{Mn}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$, the former known by the name of ‘romanechite’, from the eponymous site of Romanèche-Thorins in Burgundy. Romanechite has been identified in samples collected from the Lascaux cave (Vouvé *et al.* 1992).
- (ii) Oxides of type $\text{BaMn}_8\text{O}_{16}$, known by the name of ‘hollandite’ and, among these, oxide $\text{BaFeMn}_7\text{O}_{16}$ (ferrian hollandite) and oxide hydrate $(\text{BaK}_2)\text{Mn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$ (potassic hollandite).
- (iii) Oxide hydrate $\text{Al}_5\text{Mn}_{13}\text{O}_{28} \cdot 8\text{H}_2\text{O}$, a not very crystallized oxide, known by the generic name of ‘wad’, with the general formula $[\text{R}, \text{Mn}]\text{Mn}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, with R representing different metals such as aluminium, barium or cobalt, one or several metals being able to take each other’s place through ion exchange.

It is the oxide hydrate $\text{Al}_5\text{Mn}_{13}\text{O}_{28} \cdot 8\text{H}_2\text{O}$ that is identified in the sample (BK1) taken from the floor of the cave of Cougnac. The diffractograms were obtained by using the two different experimental layouts. Both show a common assemblage of three principal rays: 8.3 Å, 2.46 Å and 1.42 Å (Fig. 3). The rays are diffuse and of weak intensity: they have a very broad base, which indicates a poorly crystallized compound. The diffractograms also show that this black is mixed with quartz and some calcite and clay. Among the associated elements, one should note the presence of barium as revealed by elemental analysis.

With the sample taken from the black wall of Pech Merle (BK3), one can identify the same hydrate compound, $\text{Al}_5\text{Mn}_{13}\text{O}_{28} \cdot 8\text{H}_2\text{O}$. The latter is not mixed with calcite but with a lot of quartz and with a little hematite: the presence of quartz helps to make the sample very hard. Among the associated elements, one should again note the presence of a little barium as revealed by the elemental analysis.

As for the reference black from the Cadouin quarry (BK2), it is composed of a mixture of hollandite and romanechite: no calcite or quartz was detected, only some clays of illite type.

Diffraction data are shown in the appendix.

BLACK SAMPLES FROM THE BLACK FRIEZE

Six small samples (about 0.5 mg) were taken from the black lines: five come from the left part of the frieze (FN1–FN5), and the last (FN9) from the central horse. Figure 4 shows the exact location of the sampling. All of the samples contain a mixture of white grains and of grey black grains, the white grains being the more abundant. It should be noted that each of them has been sampled close to a point used for colour measurement carried out directly on the frieze. Additionally, four samples intended to serve as references were taken from the wall. These samples, listed as FN6, FN7, FN8 and FN10, are white to yellow white.

Elemental analyses

Neutron activation analysis revealed the presence of manganese in each of the samples taken from the drawn lines, the percentages being: $\text{MnO}_2 = 9.1\%$ for FN1, 9.3% for FN2, 13.2% for FN3, 10.3% for FN4, 6.1% for FN5 and 9% for FN9.

By EDS analysis, calcium is identified as a major element and the estimated percentages of calcite CaCO_3 are about 80% for FN2–FN5. One can also identify aluminium, manganese and barium in all samples and, depending on the sample, more or less important traces of silicon, iron, potassium and copper. One notices in particular that barium is more abundant in FN1 and FN9.

Moreover, with three samples taken from the wall, away from the drawn lines, calcium and, to a lesser extent, aluminium are the major elements: silicon and potassium are only present in very small quantities.

Mineral compounds and mineralogy

Analysis by X-ray diffraction makes it possible to specify the nature of the manganese compounds. The samples were subjected to the same examinations (and under identical conditions) as the reference blacks.

For example, one can identify the presence of hollandite $\text{BaMn}_8\text{O}_{16}$, and that of romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (see Table 1). These identifications are tentative, since calcite CaCO_3 is very abundant. These compounds are associated with quartz SiO_2 , but the latter is not very abundant. One can also detect the presence of clays (generally of illite type) and sometimes of goethite $\text{FeO}(\text{OH})$. One can also note in some diffractograms the presence, at small angles, of a high background noise (especially for the samples FN3, FN5 and FN9). Such a background noise is constituted in part by the diffusion of the glass capillary; it may perhaps also be another amorphous compound—an organic compound, for example, deriving from the presence of mould or fungi on the surface.

It can be seen here that one never finds the oxide hydrate $\text{Al}_5\text{Mn}_{13}\text{O}_{28} \cdot 8\text{H}_2\text{O}$ identified in the two reference blacks, those from Pech Merle and Cougnac. Nevertheless, we felt that it was possible that such a compound of local origin had been used, but perhaps after undergoing a transformation; for example, through the action of fire. Two fragments of this hydrate sample from Cougnac (BK1) were therefore burned in an oven, the first at 120°C and the second at 600°C . These burned samples were then subjected to new X-ray diffraction measurements. The

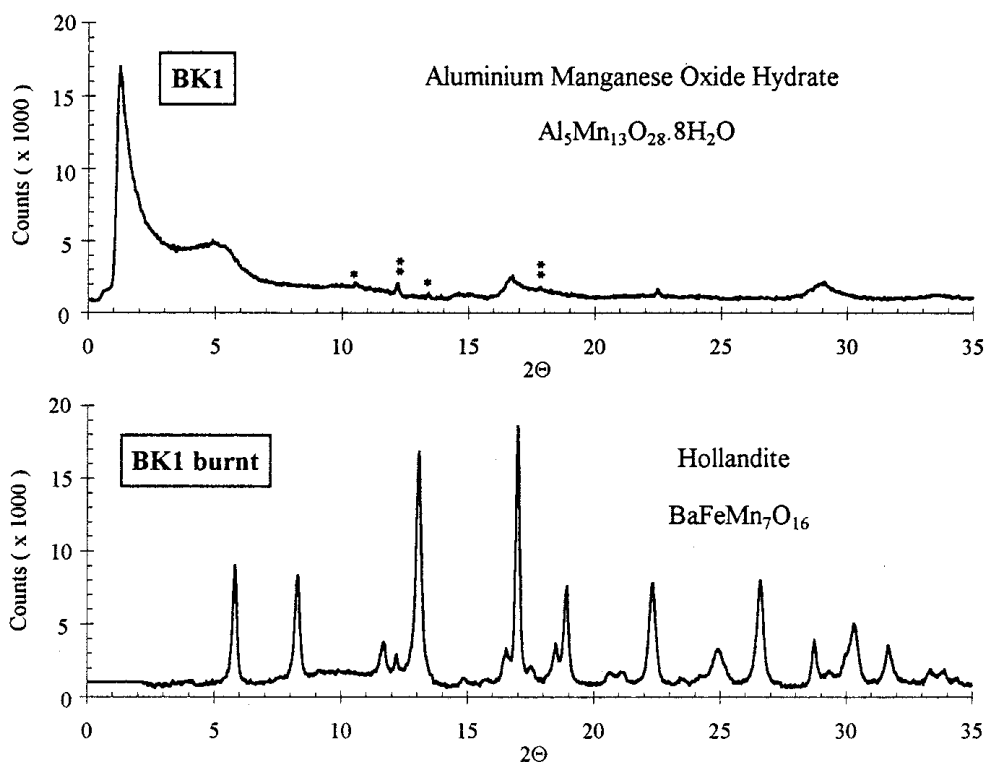


Figure 3 X-ray diffraction patterns for the reference black (BK1) taken from the damp floor of the cave of Cougnac and for the same sample burned at 120°C.

diffractograms obtained show that, at 120°C, the oxide hydrate transforms into a well crystallized compound of hollandite type. The diffractogram of the second sample, burned at 600°C, is identical to that of the 120°C sample (Fig. 3). These results fully confirm what has already been observed by other authors, that hollandites are formed by dehydration of wad (Wadsley 1950). As for the burned sample from Cougnac, that hollandite is identified as the compound $\text{Ba,FeMn}_7\text{O}_{16}$. These examinations were then complemented by measurements by Raman microspectrometry.

The presence of carbon black

Raman spectrometry is particularly well adapted to the study of carbon blacks. It should be recalled here that the presence of carbon can also be detected through elemental analysis (with special conditions). However, in that case, there is nothing to indicate the origin of this carbon, which could equally well come from an organic compound as from a mineral compound, and in the case that interests us here, as much from a carbon black as from a carbonate or another compound. Moreover, the presence of black from wood charcoal can, in certain cases, be observed with electron microscopy (Lorblanchet *et al.* 1990). Raman investigation can identify carbon blacks through the measurement of two bands located at around 1350 cm^{-1} and 1580 cm^{-1} . The intensity and the profile of these two characteristic bands depend not so much on the abundance of carbon but, above all, on its condition; a well graphitized carbon



Figure 4 The locations of the six microsamples (FN1–FN5 and FN9) from the Black Frieze of Pech Merle.

Table 1 *X-ray diffraction analyses of the six samples FN1–FN5 and FN9 taken from the Black Frieze of Pech Merle*

<i>Samples</i>	<i>Compounds</i>	
	<i>Manganese blacks</i>	<i>Other minerals present</i>
FN1	Hollandite $\text{BaMn}_8\text{O}_{16}$	Calcite CaCO_3 and clays; quartz SiO_2 (very little)
FN2	Hollandite $\text{BaMn}_8\text{O}_{16}$ and romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (traces)	Calcite CaCO_3 and illites; quartz SiO_2 (very little); goethite $\text{FeO}(\text{OH})$ (traces)
FN3	Hollandite $\text{BaMn}_8\text{O}_{16}$ and romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (traces)	Calcite CaCO_3 and illites; quartz SiO_2 (very little); goethite $\text{FeO}(\text{OH})$ (traces)
FN4	Hollandite $\text{BaMn}_8\text{O}_{16}$ and romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (traces)	Calcite CaCO_3 and illites; quartz SiO_2 (very little); goethite $\text{FeO}(\text{OH})$ (traces)
FN5	Hollandite $\text{BaMn}_8\text{O}_{16}$ and romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (traces)	Calcite CaCO_3 and illites; quartz SiO_2 (very little); goethite $\text{FeO}(\text{OH})$ (traces)
FN9	Hollandite $\text{BaMn}_8\text{O}_{16}$ and romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (traces)	Calcite CaCO_3 and illites; quartz SiO_2 (very little); goethite $\text{FeO}(\text{OH})$ (traces)

displays a narrow, intense band at 1580 cm^{-1} , whereas in the presence of a carbon that is semi-graphitized or close to amorphous, this band broadens and tends to become far less intense (Beny-Bassez and Rouzard 1985). However, it must be remembered that certain precautions need to be taken in order to avoid altering the sample during the measurement: since blacks are particularly absorbent, they run the risk of being altered under the impact of the laser beam. This is why, during the measurements, Raman bands could be observed corresponding to the oxide Mn_2O_3 , a mineral compound that was not found in any of the samples in the analyses carried out previously through X-ray diffraction (and for which identification by Raman analysis has sometimes been misinterpreted).

Hence, by using this Raman method, among the grains of calcite or quartz, we were able to identify the presence of carbon black in half of the six samples; that is, in samples FN1, FN3 and FN9. This carbon black is amorphous: it is particularly visible in sample FN1 (Fig. 5). This observation suggests that some blacks of the Black Frieze might be mixed blacks.

CONCLUSIONS

Although, due to lack of means and time, our investigations could not be extended to more samples, nor to all of the manganese black compounds, one can already see that the painters of the Black Frieze used a manganese black composed of hollandite $\text{BaMn}_8\text{O}_{16}$ and of a little romanechite $\text{BaMn}_9\text{O}_{16}(\text{OH})_4$ (perhaps, a late alteration of the anhydrous oxide). This manganese black is more or less mixed with a carbon black.

Such results can be interpreted in the following way. Whenever the presence of carbon black is very clear, this black was probably added intentionally and contributes to the darkening of the

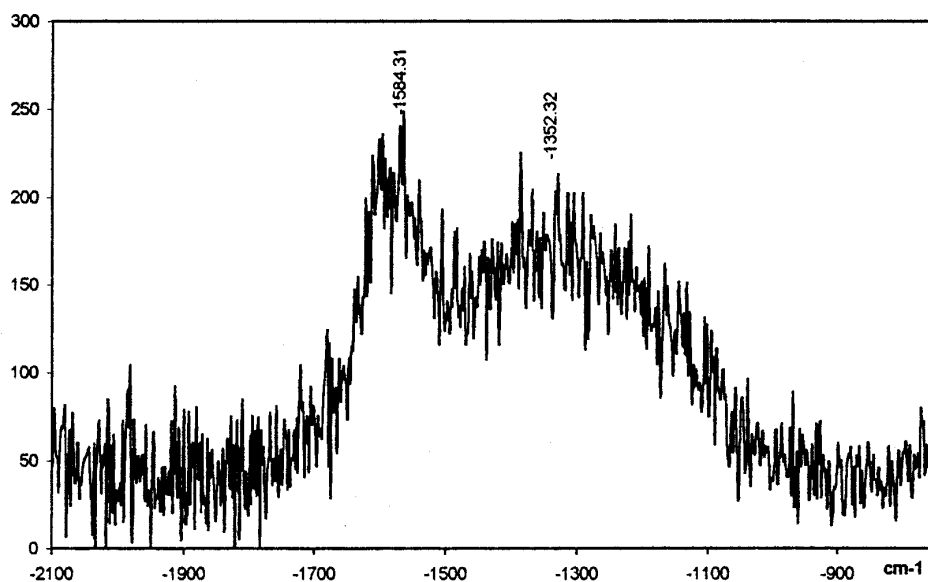


Figure 5 The Raman spectrum of the amorphous carbon black observed in the sample (FN1) taken from the Black Frieze of Pech Merle.

manganese blacks, as was indicated by colour measurements. When carbon black is only detected as traces, its presence can be attributed to burning of the manganese black, with remains of wood charcoal from this burning operation getting accidentally mixed with the manganese black. The first hypothesis had already been proposed by Lorblanchet and Labeau, on the basis of the results of the analysis of the burned ochres in the 'spotted horses' frieze at Pech Merle, since traces of wood charcoal black were recognized in these reds (Lorblanchet *et al.* 1990).

These results thus reinforce the hypothesis that the painters of Pech Merle used a manganese black of local origin, burning it beforehand as they did for the red or yellow ochres. It can be argued that two local manganese blacks (BK1 and BK3) are composed of amorphous manganese oxide hydrate (which might be transformed through heating into an artificial hollandite) and that carbon black has been identified in three samples of the Black Frieze. One may suppose that such a burning at least facilitated the crushing of the rock, just as it is now established that prehistoric man burned flint to facilitate its working, and thus to enable him to obtain a fine black powder that was easier to use. Moreover, one should not forget the important symbolic and even ritual aspect that such a burning may have had.

From this, it is possible to conclude that the Palaeolithic peoples carried out the burning of a wide variety of raw materials: the burning of goethites and limonites to obtain iron oxide reds is attested since the Acheulian of Terra Amata (Onoradini and Perinet 1985); that of flint to facilitate its working, and perhaps to modify its colour, is also known in the Upper Palaeolithic; and, in the same period, some human groups in Central and Eastern Europe began the firing of clay to make certain animal and human figurines (Lorblanchet 1999). Therefore, the burning of manganese was not an isolated phenomenon. The intervention of fire could have had both a practical use and a symbolic function.

This also means that the black pigments used by the painters of prehistory, including those of the Black Frieze of Pech Merle, still need to be the subject of much research before their precise

origin—and also the preparation that they may have undergone before use, or the alteration that they may have undergone over time—all become perfectly well known to us.

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REFERENCES

- Beny-Bassez, C., and Rouzaud, J. N., 1985, Characterization of carbonaceous materials by correlated electron and optical microscopy and Raman microscopy, *Scanning Electron Microscopy*, **1**, 119–32.
- Guineau, B., 1989, Non-destructive analysis of organic pigments and dyes using Raman microprobe, microfluorometer or absorption microspectrophotometer, *Studies in Conservation*, **34**, 38–44.
- Lorblanchet, M., 1981, Les dessins noirs de Pech Merle, *Congrès Préhistorique de France, XXIe session, Quercy 1979*, 178–209.
- Lorblanchet, M., 1999, *La naissance de l'Art, Genèse de l'art préhistorique*, Errance, Paris.
- Lorblanchet, M., Labeau, M., Vernet, J.-L., Fitte, P., Valladas, H., Cachier, H., and Arnold, M., 1990, Palaeolithic pigments in the Quercy, France, *Rock Art Research*, **7**(1), 4–20.
- Onoratini, G., and Perinet, G., 1985, Données minéralogiques sur les colorants rouges de Provence; démonstration que certains d'entre eux ont été obtenus par calcination de goethite, *Comptes Rendus, Académie des Sciences*, Paris, **301**, série II, 2, 119–24.
- Post, J. E., 1992, Crystal structures of manganese oxide minerals, *Catena Supplement* 21, Cremlingen, 51–73.
- Robertson, A. R., 1977, The CIE 1976 color-difference formulae, *Color Research and Application*, **2**, 7.
- Roux, J., and Volfinger, M., 1996, Mesures précises à l'aide d'un détecteur courbe, *Journal de Physique III, suppl.*, **6**, July, 127–34.
- Vouvé, J., Brunet, J., and Vouvé, F., 1992, De l'usage des minéraux de manganèse par les artistes de la grotte préhistorique de Lascaux, Sud-Ouest de la France, *Studies in Conservation*, **37**, 185–92.
- Wadsley, A. D., 1950, Synthesis of some hydrated manganese minerals, *American Mineralogist*, **35**, 485–99.
- Waychunas, G. A., 1991, Crystal chemistry of oxides and hydroxides, *Reviews in Mineralogy*, **25**, 46–55.

APPENDIX

X-ray diffraction data (d (Å)/ hkl) for romanechite (JCPDS 14-627), hollandite (JCPDS 12-514) and manganese oxide hydrate (JCPDS 4-0098), for reference blacks (BK1, BK2 and BK3), and for the sample blacks (FN1–FN5 and FN9) taken from the Black Frieze of Pech Merle

Romanechite $BaMn_9O_{16}(OH)_4$ (JCPDS 14-627)	Hollandite (ferrian) $BaFeMn_7O_{16}$ (JCPDS 12-514)	Manganese oxide hydrate $Al_5Mn_{18}O_{28} \cdot 8H_2O$ (JCPDS 4-0098)	BK1 (Cognac)	BK2 (Cadoun)	BK3 (Pech Merle)	FN1	FN2	FN3	FN4	FN5	FN9
9.68/30	–	9.78/100	8.3/100	10.2/16	9.65/15.5	13.5/1	–	–	142.1	–	–
6.96/55	6.96/15	7.46/10	7.491	6.99/45	7.60/19 ^p	–	10.0/2.5	9.7/6.6	9.7/3.1	9.7/2.5	–
5.55/25	–	–	–	–	–	8.4/1.1	–	8.4/5	–	8.4/2.4	–
4.84/20	4.94/20	4.85/35	–	4.92/36	4.80/11.3	6.25/1.1	6.96/2.4	6.96/5.9	6.95/2.5	6.96/2.5	6.96/2
–	–	–	–	4.47/22	4.44/13.5	–	5.76/2.5	5.75/5.4	–	–	5.76/1.9
–	–	–	–	–	4.25/43 [†]	–	–	–	–	4.88/3.1	4.80/3.6
–	3.52/40	–	3.86/42*	–	–	–	4.17/5	4.18/8	4.15/3.3	4.16/4.7	4.16/6
3.48/60	3.50/40	–	–	3.48/19	–	3.85/4.8*	3.85/13*	3.87/16*	3.85/15*	3.85/9*	3.85/14.5*
3.32/30	–	–	3.34/45 [†]	3.34/25	3.34/100 [†]	3.48/2.6	3.47/0.6	3.49/2.4	3.48/2.1	3.49/2.2	3.48/6.4
3.23/30	–	–	3.26/9	–	–	3.34/3 [†]	3.34/0.4 [†]	3.35/8 [†]	3.34/8 [†]	3.35/3.2 [†]	3.35/9.7 [†]
–	–	3.26/10 ^p	–	–	–	3.12/5	3.12/2.8	3.128/16	3.12/6.2	3.12/3.1	3.12/12
–	3.145/100	–	–	3.12/73	–	3.036/100*	3.035/100*	3.044/100*	3.036/100*	3.037/100*	3.035/100*
2.972/20	3.120/100	–	3.04/20*	–	–	2.843/2.8*	2.841/2*	2.845/6.5*	2.846/4*	2.843/0.9*	2.845/7.3*
2.882/40	3.000/7	–	–	–	–	–	–	2.75/4.9	2.72/3.9	–	2.71/2.9
2.687/8	2.880/15	–	–	–	–	–	–	2.500/10*	2.495/15*	2.493/8*	2.495/14*
–	2.500/10	–	2.79/20	2.74/8	2.70/11.4	2.492/4*	2.494/18*	2.412/35 ^p	2.405/13 ^p	2.408/1.4 ^p	2.403/11.5
2.426/30	2.467/20	–	–	2.58/18.8	2.50/11.8	2.405/2.4	2.405/7.5	2.289/17*	2.284/18*	2.284/13.5*	2.284/35.5*
2.408/100	2.415/60	2.46/50	2.45/73	2.46/19	2.46/23	2.284/10*	2.284/20*	2.196/5	2.193/2.5 ^p	–	2.178/5.4
2.366/50	2.330/7	–	–	2.40/100	–	–	2.192/3.3	–	–	–	–
2.257/35	2.295/5	–	2.29/34 [†]	2.34/11	–	–	–	2.164/3	–	–	–
–	2.225/40	–	–	2.24/12.5	2.28/18.8 [†]	2.099/37*	2.094/20*	2.098/17*	2.094/16*	2.093/14*	2.093/20*
–	2.210/55	–	–	–	–	–	1.928/14*	1.927/12.3*	–	1.929/5*	1.928/13.6*
2.188/85	2.180/70	–	–	2.21/19.5	2.23/13.5 [†]	1.914/7*	1.913/22*	1.879/29*	1.914/24*	1.913/20*	1.913/21.5*
2.151/35	2.165/60	–	–	–	2.13/15 [†]	1.877/11*	1.875/27*	1.83/3.1	1.876/26*	1.876/18*	1.875/24*
–	2.000/15	2.07/35	–	2.16/39	–	–	–	1.824/5.5 [†]	1.842/6	1.825/2.3	1.817/4.4
2.025/14	1.990/20	2.03/35	–	1.98/11.7	1.98/14 [†]	–	–	1.732/4.8	1.722/2.1	1.703/2	1.716/1.66
1.958/10	1.960/15	–	–	1.94/10.2	–	–	–	1.695/12	–	–	1.67/1.46
1.860/14	1.855/40	–	–	–	–	1.626/3	1.624/4.7	1.628/14*	1.625/2.5*	1.625/3*	1.626/6.3*
1.824/40	1.840/40	1.79/20 ^p	1.818/32 ^p	1.83/38.3	1.82/18 [†]	1.604/4.5*	1.604/10.6*	1.606/11*	1.604/10*	1.603/9*	1.604/10*
1.740/10	1.750/10	–	–	1.74/8	–	1.562/1.4	1.55/3.1	1.563/2	1.560/2.9	–	1.562/2.93
1.696/8	1.695/10	–	–	1.69/11.3	1.695/10.5	1.524/4*	1.522/13*	1.526/13*	1.526/7.5*	1.525/5*	1.524/8.5*
1.642/16	1.670/25	–	–	1.64/20 ^p	1.67/13 [†]	1.518/1.7*	1.518/11*	1.518/8.5*	1.518/14*	1.512/1.8*	1.513/5*

APPENDIX
(continued)

Romanechite $BaMn_9O_{16}(OH)_4$ (JCPDS 14-627)	Hollandite (ferrian) $BaFeMn_7O_{16}$ (JCPDS 12-514)	Manganese oxide hydrate $Al_5Mn_{15}O_{38} \cdot 8H_2O$ (JCPDS 4-0098)	BK1 (Cognac)	BK2 (Cadoun)	BK3 (Pech Merle)	FN1	FN2	FN3	FN4	FN5	FN9
—	1.650/20	—	—	—	—	1.474/1.6*	1.474/1.2*	1.477/1.6*	1.475/2*	1.474/1.4*	1.473/2.6*
—	1.630/25	1.63/10 ^D	—	—	—	1.441/10*	1.441/5.7*	1.444/8.5*	1.442/8*	1.441/6*	1.442/8*
1.561/30	1.555/60	—	—	1.543/41	1.54/16†	1.421/1.8*	1.421/4.8*	1.426/8.3 ^D	1.423/6*	1.421/4*	1.423/7.5*
—	1.547/60	—	—	—	—	—	—	1.40/6.3	1.40/3.1	—	1.40/3.1
1.498/12	1.508/10	—	—	1.505/13.3	—	1.357/1.5*	1.356/5.7*	1.359/3*	1.356/1.3*	1.356/0.9*	1.356/2.6*
1.423/30	1.440/30	1.42/100	1.415/57	1.429/23.3	1.418/13 ^D	1.340/4.2*	1.338/4*	1.339/1.8*	1.339/4.5*	1.338/1.5*	1.338/2.7*
—	1.370/30	—	—	1.373/18	1.374/48†	1.310/1.5	1.306/1.6	1.307/3 ^D	1.31/3.2	1.305/2.6	1.31/1.7
—	1.360/25	—	—	1.355/26.7	—	1.296/2.3*	1.296/5.2*	1.299/16*	1.297/8.5*	1.297/2.3*	1.297/5.2*
—	1.310/30	—	—	1.299/23.3	—	1.285/1.5	1.283/0.2	1.285/5.5	1.285/2.9	1.285/2.7	1.283/2.7*

* Calcite.

† Quartz.

D = diffuse.