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2003 Meas. Sci. Technol. 14 1590

(http://iopscience.iop.org/0957-0233/14/9/310)

Meas. Sci. Technol. **14** (2003) 1590–1597 PII: S0957-0233(03)56719-4

Analysis of rock art painting and technology of Palaeolithic painters

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Received 27 November 2002, accepted for publication 17 February 2003
Published 29 July 2003
Online at stacks.iop.org/MST/14/1590

Abstract
Archaeologists have attempted the interpretation of rock art, but have often disregarded the technical aspects of paints. Analysing paint samples for preparation techniques and studying the various compounds used, allows us to determine the technology of early painters. Palaeolithic artists used two main colours: red (iron oxide: natural hematite or heated goethite) and black (charcoal or manganese oxides). These pigments could be prepared in different ways (grinding, mixing with extender and/or binder or by heating) in order to enhance the properties of the paints. Analyses attempt to determine the physicochemical nature of the matter and its preparation mode, and to get an idea of its geographic origin. This paper presents techniques and methods used in the C2RMF laboratory for manganese oxide pigments. Distinction between manganese oxides with or without other cations is made and heat treatment of manganese oxide minerals is described. Results obtained for black pigment in Lascaux and Ekain caves are presented and discussed. From paint analyses, several conclusions are drawn concerning the technical level of Palaeolithic artists.

Keywords: rock art, black paint, manganese oxide, heat treatment, Lascaux, Ekain

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Different cultures such as Chatelperronian, Aurignacian, Gravettian, Solutrean, Magdalenian, contributed to the Upper Palaeolithic period (35 000–10 000 BP[4]) (figure 1). Hunter–gatherer people from this period created the most ancient art currently known due to its conservation in limestone caverns. This rock art is particularly abundant in southwestern Europe: central France and northern Spain (figure 2). Hundreds of sites have been discovered since the beginning of the 20th century and each year new sites are brought to light, among them Chauvet, the most ancient cave (35 000–26 000 BP, (1) in figure 2), in 1994 and Cosquer, a sub-marine cave (27 000–19 000 BP, (2) in figure 2), in 1992. Since its recognition in 1902 [1], palaeolithic art has provoked many questions and great interest as well as controversies, especially concerning its interpretation. A stylistic approach has been utilized by the archaeologist, Leroi-Gourhan [2], who established graphic codes for the representations he knew: animals, signs and anthropomorphs. Several investigators have attempted to understand the meaning of these representations as, for example, hunter codes or, more recently, shamanic figures as proposed by Clottes and Williams [3]. Debate is still on-going. Another approach consists in careful examination of the minute tracks and marks left by the Palaeolithic people on painting matter. Analysing the techniques used and studying the various components of this matter allow us to determine the technology of the ancient artists who worked during the longest period of art history. Only three colours are used

[4] BP: before present (before 1950–C14 dating).

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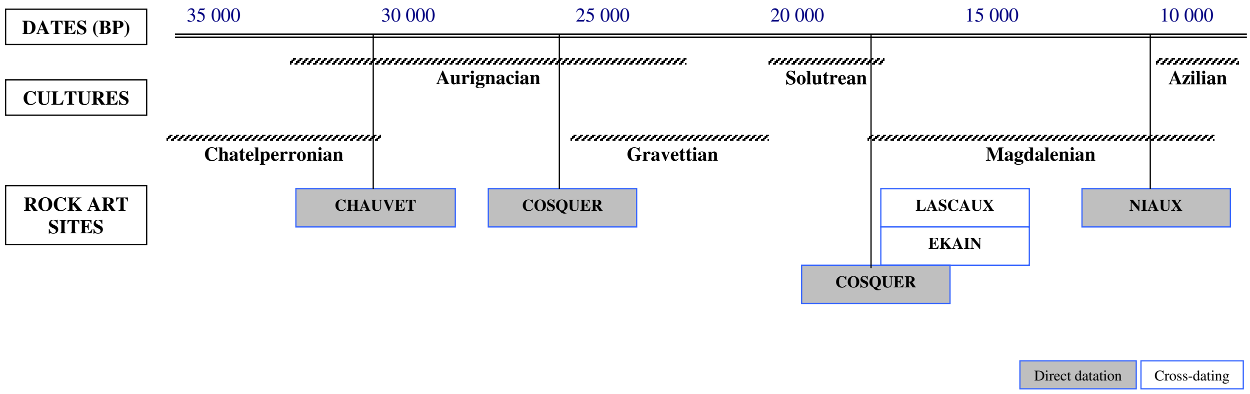

Figure 1. Chronology of Upper Palaeolithic [20].

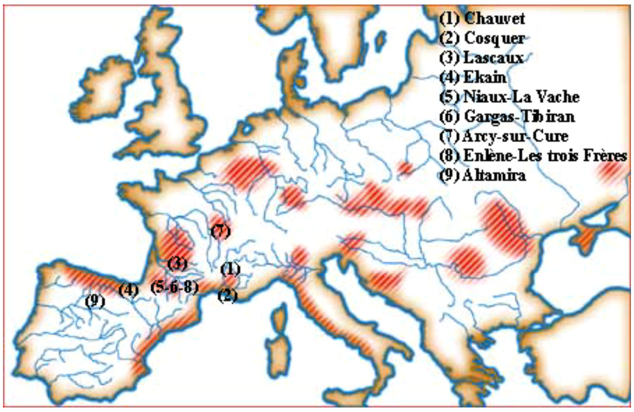

Figure 2. Most famous sites of rock art in Europe and most important areas of habitation (shaded). (©Valérie Féruglio).

in Palaeolithic representation: red (hematite, Fe_2O_3), black (charcoal, soot, bone charcoal or manganese oxide) and yellow (goethite, FeOOH). Red pigment has been widely studied, as the transformation of yellow goethite into red hematite under heat treatment was known by prehistoric people [4]. Until now, black pigments, and especially manganese oxides, have been less analysed [5, 6]. In this paper, the protocol used to study manganese oxide as a Palaeolithic pigment is developed and results obtained for two caves will be presented: Lascaux (Dordogne, France, (3) in figure 2) and Ekain (Basque country, Spain, (4) in figure 2). Both of these are dated by cross-dating[5] as Magdalenian caves (16 000–12 000 BP).

2. State of the art

Study of cultural heritage material calls for non-destructive and micro-analytical methods. Materials are often precious and fragile. An extensive physicochemical study of ancient paints enables us to identify the elemental and structural compositions and a possible geographic origin. Analysis attempts to determine pigment preparation methods such as grinding, mixing or heating and application modes of the paint on the rock. Thus, pigment may be mixed with extenders (clay, calcite, quartz, bone, talc, potassium feldspar, etc) and with a binder (water, vegetable oil or animal fat). Preparation may enhance the adhesive properties of paints, change the textures and consistency or provide better coverage and perhaps even better preservation. In Niaux (Ariège, (5) in figure 2), several types of extender were determined by Menu *et al* [7]: potassium feldspar, talc and biotite. No extender was observed in the Gargas and Tibiran caves (Hautes-Pyrénnées, (6) in figure 2) [8]. In Arcy-sur-Cure (Yonne, (7) in figure 2), black drawings were made with charcoal without extender, but in red pigments, clay seems to have been deliberately added [9].

Binders can be detected by gas chromatography coupled with mass spectrometry, but there is only one, very preliminary, rock art study in this field done on black pigments from the Enlène and 'Les Trois Frères' caves (Ariège, (8) in figure 2) [10]. Nevertheless, experimentation has shown that water is the most practical and common binder [11].

The first study in rock art involved the survey of stylistic representations, based on Leroi-Gourhan's [2] characterization and comparison between different sites. Then, examinations of rock figures were performed at macroscopic scale. A careful survey of rock surface may identify the mode of pigment deposition and allow differentiation between charcoal, used primarily to draw, and manganese oxide used to paint. Charcoal black is darker than the shiny manganese oxide and its grain size is larger.

At the C2RMF laboratory, the nature of a pigment is determined with elemental analysis (EDX) coupled with a scanning electron microscope (SEM). Elemental composition and crystal morphology are simultaneously determined. With SEM analysis, we attempt to distinguish between

[5] Cross-dating: indirect dating from stylistic comparison.

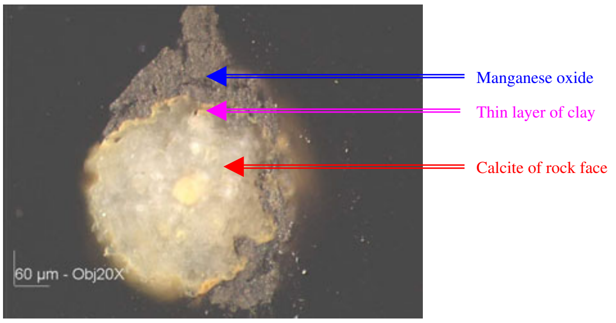

Figure 3. Cross-section of the rhinoceros sample from 'Scène du Puits', Lascaux, by optical microscopy.

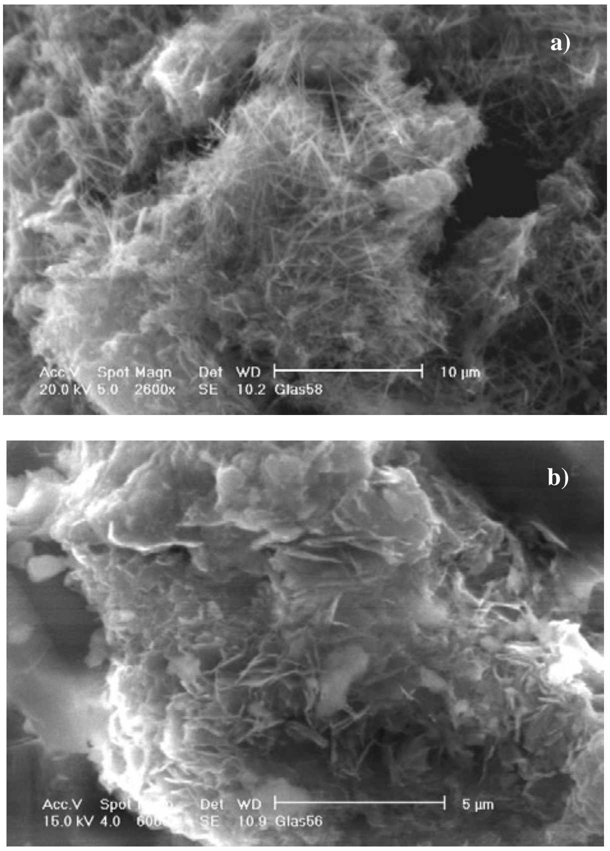

Figure 4. SEM micrograph of two samples from 'Scène du Puits' of Lascaux: (a) rhinoceros: needles of cryptomelane and (b) bison: leaf agglomerate of hollandite and cryptomelane. Experimental conditions: Philips XL3CP, secondary electron image, accelerating voltage 20 kV for (a) and 15 kV for (b).

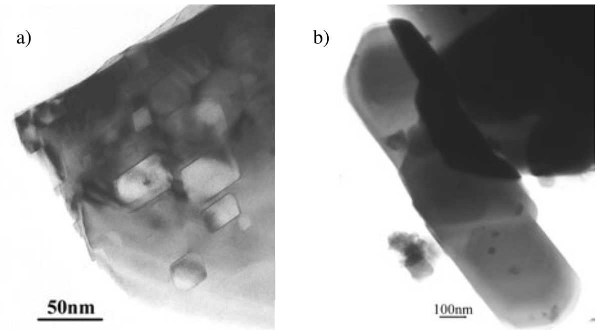

Figure 5. Manganite crystals after heat treatment for 18 h at (a) 700 °C and (b) 960 °C by TEM. Experimental conditions: Jeol 2000FX, accelerating voltage 200 kV.

deliberate human mixing and natural mixing, according to the distributions and proportions of the mineral phases. Other clues may be found, like chips of bone or hairs from the pad or brush used by an artist. From SEM analysis, we can determine the application mode of the paint onto the cave walls by ancient artists.

Quantitative elemental analysis can be accomplished by non-destructive PIXE analysis (proton-induced x-ray emission) in front of the external beam of AGLAE (analytical system of the C2RMF based on a small electrostatic accelerator). This method yields trace elements as possible geological markers, specific to a pigment source or to a geological formation [12, 13].

The crystalline structure of iron or manganese oxides can be distinguished by x-ray diffraction (XRD) or transmission electron microscopy (TEM). XRD analysis indicates the relative proportions of each mineral phase, characteristic of natural or human mixtures in paint samples. TEM may provide microscopic results when the available quantity is not sufficient for XRD method.

Archaeological observations suggested that Palaeolithic artists might have used the colour changes accompanying dehydration of yellow goethite (FeOOH) to hematite (Fe_2O_3) to make red pigment [14]. TEM is very useful for observing pores in hematite. These pores, filled with structural water, are generated during dehydration of the oxyhydroxide crystal, FeOOH. Heating processes could be used to modify optical properties such as colour, but also to allow easier grinding or better adhesion to the wall.

Other laboratories have examined paint samples using similar techniques. Other approaches have been used such as colour measurements [6] and, more recently, micro-Raman spectroscopy on samples from les Fieux, Les Merveilles and Pergouset (Quercy district, SW France) [15].

3. The particular case of manganese oxide pigment

The purpose of our study was to identify the nature of the raw materials, their origin, the techniques of production and their use, in the particular case of manganese oxide pigment using the various techniques available in the C2RMF laboratory as presented in table 1. The analytical study was made in parallel with geological references, synthetic samples and archaeological samples. The reference minerals came from environment deposits inside or outside the caves and from mineral collections. Synthetic samples were generated by heat treatment.

3.1. Structure identification, heat treatment indication

Manganese oxides are present in several mineralogical forms on the earth's surface. Different kinds of minerals can be distinguished by their chemical composition, oxidation degree (II, III, IV or mixed) and crystalline structure (tunnels of various sizes, larger ones containing cations or water molecules or layers) [16]. Mineralogists have identified about 20 different naturally occurring manganese oxides. This study was limited to two main families, presented in table 2: (1) manganese oxides without any associated other cation (such

Table 1. Methods used in the C2RMF laboratory.

Methods	Advantage/disadvantage	Applications
Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDX)	Non-destructive Needs sampling Cross-section preparation	Chemical and morphological nature Extender nature Distinguishing between natural or deliberate mixture Thickness of paint layers
PIXE	Non-destructive Needs sampling	Chemical analysis Trace elements
X-ray diffraction (XRD)	Non-destructive Needs sampling	Crystallographic nature Phase proportions Heat treatment
Transmission electron microscopy coupled with energy dispersive spectroscopy (TEM)	Needs sample preparation	Chemical, morphological and crystallographic characterization Heat treatment
Infrared spectroscopy	Non-destructive Needs sampling	Identification of crystalline phase Detection of OH^- and H_2O molecules.

Table 2. Manganese oxides studied.

Mineralogical name	Formula	Symmetry	Tunnel size
Manganite	MnOOH	Monoclinic	1×1
Pyrolusite	MnO_2	Tetragonal	1×1
Bixbyite	Mn_2O_3 (or natural $(Mn, Fe)_2O_3$)	Cubic	—
Hausmannite	Mn_3O_4	Tetragonal	—
Romanechite	$Ba_2Mn_5O_{10}{\cdot}xH_2O$	Monoclinic	2×3
Hollandite	$BaMn_8O_{16}{\cdot}xH_2O$	Monoclinic	2×2
Cryptomelane	$(K, Ba)Mn_8O_{16}{\cdot}xH_2O$	Monoclinic	2×2
Todorokite	$(Ba, Ca, K, Na)Mn_6O_{12}{\cdot}xH_2O$	Monoclinic	3×3

as manganite MnOOH, pyrolusite MnO_2, bixbyite Mn_2O_3 and hausmannite Mn_3O_4) and (2) manganese oxides enriched in barium and other cations in tunnel structures (romanechite $Ba_2Mn_5O_{10}{\cdot}xH_2O$, hollandite $BaMn_8O_{16}{\cdot}xH_2O$, cryptomelane $(K, Ba)Mn_8O_{16}{\cdot}xH_2O$, todorokite (Ba, Ca, K, Na) $Mn_6O_{12}{\cdot}xH_2O$). These manganese oxides have already been identified as Palaeolithic pigments [5] and are the more common ones found in soils.

By optical microscopy, we distinguished between different mineral phases and components of paints according to their colour. When paint material is sampled, part of the rock surface may be extracted as well. Therefore the distinction between components from the rock surface and genuine painting matter is important (figure 3).

The parallelepipedic crystal morphology of pyrolusite was easily identified with SEM. Romanechite, hollandite or cryptomelane structures, with large tunnels containing cations and water molecules, present two typical morphologies—an acicular (needle-like) type (figure 4(a)) and a leaf type (figure 4(b)).

Naturally, manganese oxides are frequently encountered in clays, quartz, calcite and iron oxides. SEM observation of a cross-section aims at distinguishing between natural or deliberate mixtures.

XRD and TEM give access to crystallographic structures of different oxides with or without extraneous cations. Crystalline identification is performed by the indexing of the point patterns obtained by electron diffraction or XRD diffractograms in combination with the elemental analysis.

Natural manganese oxide structures were studied in our laboratory as a function of the temperature of the heat treatment. Oxyhydroxide manganite is transformed into pyrolusite between 360 and 560 °C. Disappearance of bands corresponding to OH^- vibrations at 2662, 2061, 1153, 1115 and 1086 cm^{-1}, specific of manganite, were observed by infrared spectroscopy. Over 560 °C, pyrolusite is transformed into bixbyite, Mn_2O_3. Characteristic pores were observed by TEM (figure 5(a)) in this 'secondary' bixbyite phase. These pores result from dehydration of manganite, MnOOH. Moreover, 'heated' bixbyite does not contain iron atoms, contrary to the natural rare bixbyite phase that is always enriched in Fe ($(Mn, Fe)_2O_3$). So if 'pure' bixbyite (that is without any Fe cations) is identified in an archaeological sample and/or it contains dehydration pores, we assert that the pigment results from manganite or pyrolusite heating. When heated over 800 °C, bixbyite turns into hausmannite, Mn_3O_4, and the beginning of the recrystallization process is observable by TEM (figure 5(b)). Formation of 'secondary' hausmannite is unlikely at temperatures in a Palaeolithic fireplace.

Romanechite, a manganese oxide with Ba cations, is a frequent natural black mineral lacking a metallic aspect, as compared to pyrolusite or manganite. Its acicular crystals, observed by TEM, turn into hollandite crystals without morphological change at temperatures over 450 °C. This transformation does not lead to the formation of pores: it is a topotactic[6] transformation and not dehydration as for

[6] A topotactic transformation is a conversion of a crystalline phase into another one with simple crystallographic orientation relations. The initial and final crystalline phases have relatively close structure.

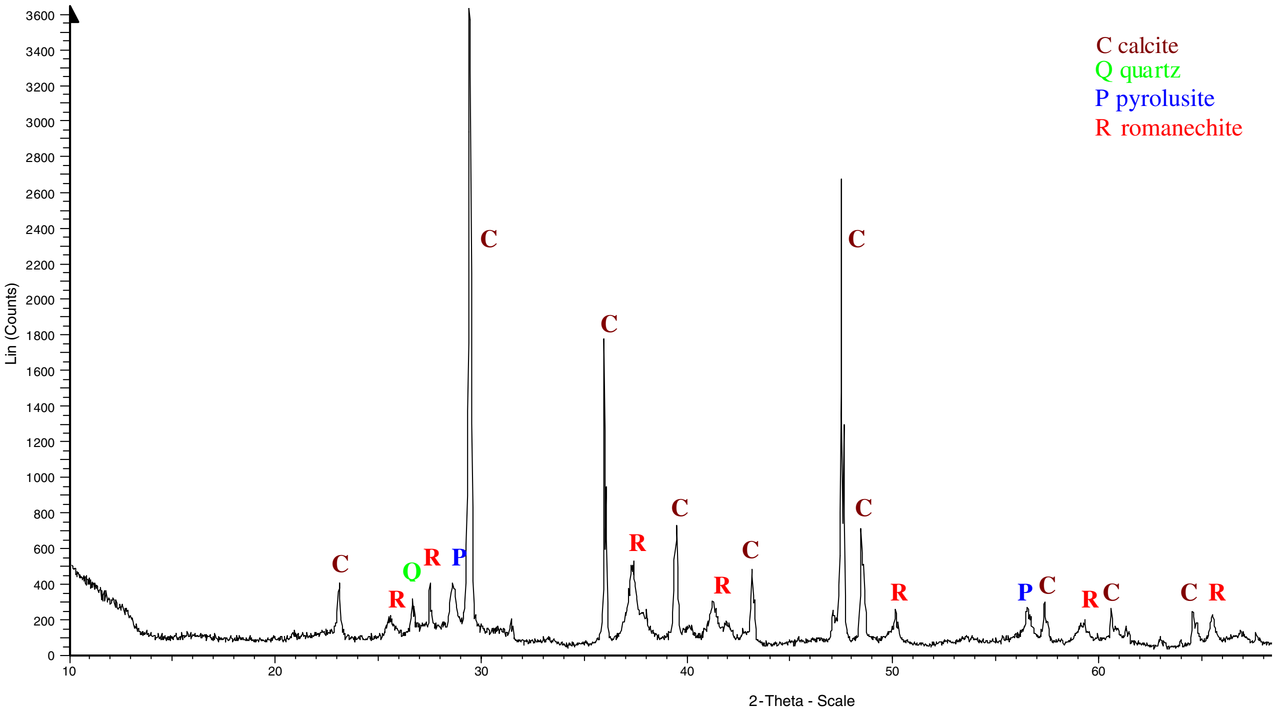

Figure 6. Diffractogram of minerals from the environment of Lascaux (Pech de Bord, Vallée de la Vézère, Dordogne). Experimental conditions: Cu Kα radiation, step 0.003°, steptime 8 s, 10°–70°.

'secondary' bixbyite. So 'secondary' hollandite is hard to distinguish from the natural one, but the presence of cations like Fe^{2+} or Pb^{2+} indicates a geological origin.

Natural manganese oxides can exist mixed together in nature. For example, one can find pyrolusite mixed with romanechite and todorokite. Hollandite is frequently found in mixtures with romanechite or cryptomelane. Concerning todorokite, crystal lattice morphology and characteristic electron diffraction patterns are identified by TEM, even in the minority phase.

The diffractogram presented in figure 6 regarding a mineral extracted from the region of Lascaux (Dordogne) shows pyrolusite and romanechite mixed with abundant calcite and a little quartz. This mineral, considering the purity of archaeological samples, seems to be too rich in various impurities to have been used by Palaeolithic artists.

3.2. New results concerning the black colour in the Lascaux and Ekain caves

3.2.1. Lascaux. Several black representations were sampled in Lascaux and analysed with the protocol described above. Black crayons (figure 7) coming from Glory's excavations in Lascaux in the 1960s [17] and which were supposed to have been used to paint the cave walls, have also been sampled.

A cross-section of a sample from the black chignon of the 'Grand Taureau' in the axial diverticule was analysed by SEM (figure 8). The paint layer is thick (750 μm) and composed of a mixture of barium manganese oxide, iron oxide (appearing lighter than the other components), clay and quartz. Figure 8 shows a heterogeneous compound distribution with a minority of manganese oxide with copious clay and quartz.

All representations of the famous 'Scène du Puits' (figure 9) were sampled and analysed to illuminate the nature of the black pigment, painting preparation and application [18]. The paints were made with Ba manganese oxide, well crystallized and pure, not mixed with any extender. The application mode was determined by observation of the rock walls and with macrophotographs. In this way, we showed that this black pigment was applied with a brush or by blowing through an hollow tube, depending on the part of the scene. Figure 3 shows an external manganese oxide layer (20–170 μm), a thin layer of clay and an internal nucleus of calcite coming from the cave wall substrate. The rhinoceros figure has needle morphology (figure 4(a)) compared to leaf agglomerates (figure 4(b)) observed for the other figures. For the rhinoceros, the manganese oxide was identified as natural cryptomelane (characterized by its potassium content) with a little todorokite. For the bison, a natural mixture of hollandite and cryptomelane was found. The presence of natural cryptomelane allows us to conclude that no heat treatment of these pigments was performed.

The crystallographic study was aimed at understanding the use of 'crayons' discovered on the ground of Lascaux cave (figure 7). These 'crayons' are composed of both raw pigments and prepared painting matter, modelled or scraped by Palaeolithic hands, with consequently a great variety of hues. The study of the black blocks enabled us to identify a great variety of manganese oxides used singly or in mixtures like pyrolusite, romanechite, hollandite and todorokite. TEM observations of some samples did not reveal any trace of heat treatment such as dehydration pores and/or characteristic crystal structure.

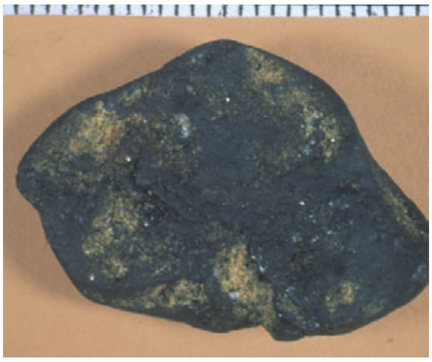

Figure 7. One black 'crayon' from Glory's excavation in Lascaux (Institut de Paléontologie Humaine, photo ©C2RMF).

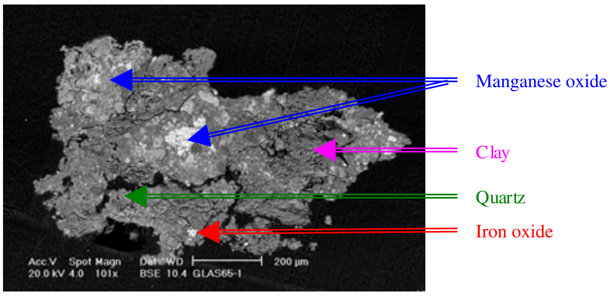

Figure 8. Cross-section of the chignon sample of 'Grand Taureau', Lascaux, by SEM. Experimental conditions: Philips XL3CP, back scattering electron image, accelerating voltage 20 kV.

3.2.2. Ekain. In Ekain cave (Basque country, Spain), several black, red and brownish samples were studied [19]. Ekain is a cave particularly devoted to horses; black colour is dominant. A majority of black pigments were charcoal, applied directly on the wall, or ground before application. Nevertheless two samples collected were manganese oxide mixed with calcite (from the wall), quartz and iron oxides. Inside the cave, a geological manganese deposit with evidence of prehistoric use is still present. Elemental analyses and SEM observations showed that rock art samples are different from those of the geological deposit. Moreover the two figures are not made of the same paint since crystal size and mixtures are different for the manganese oxide. Crystalline structure was not determined by XRD because of the small amount of matter and of the poor crystallinity of the manganese oxides. But from TEM observations, we can ascertain that heat treatment was not performed to prepare the paint. Concerning the red and brownish representations, paint is composed of iron oxide crystals or clays coloured by iron oxide.

4. Discussion and conclusion

Results obtained on Lascaux paint samples can be interpreted at different levels. Concerning the preparation mode of the paint, different cross-sections showed that raw pigment was used for the representation of 'Scène du Puits', but deliberately mixed in the chignon of 'Grand Taureau'. Pigment preparation depends on the subject or, rather, on the execution period. In Lascaux Cave, 'Scène du Puits' is far from the axial diverticule and not easily accessible. So we may assume that these two paintings were made at two different times.

Figure 9. 'Scène du Puits' of Lascaux (photo ©Norbert Aujoulat).

A stylistic survey of 'Scène du Puits' determined by different archaeologists showed the lack of homogeneity due to the presence of the rhinoceros. In fact we showed the specific needle morphology of manganese oxide crystals from the rhinoceros paint, and our analyses converge with its peculiar graphic style. The rhinoceros was created with another paint 'pot'[7] containing a manganese oxide coming perhaps from another deposit. The time of its execution must be different from the other paintings, but only direct dating will prove this.

We compared samples of Lascaux black painting and samples coming from crayons found in front of the cave walls. Results from black crayons are similar to those for painted figures. Many manganese oxides are used in both cases, with or without mixing and always without heat treatment. This similarity suggests that crayons were used to make these figures, and moreover that they constituted a reserve or remainder of unused pigment. No direct connection has been made between a specific crayon and a specific figure.

In Ekain, charcoal is the primary black pigment used to create black horses (more than 75%). In this cave, association of painting and engraving is frequent. Paints could have been prepared or not, according to the location of the panel. We assume that different paint 'pots' were used and/or that the figures were done by several artists. Style homogeneity leads us to conclude that execution time was limited. Figures made with manganese oxide are peculiar because of their theme (two bears in a small cavity near the manganese deposit) or of their application mode (a big horse head in the entrance was painted, whereas the other horses were drawn). Analytical results and archeological studies lead to the same conclusion concerning the originality of both the horse head in the entrance and the two bears. This practice is in contrast to the use of manganese oxide in Lascaux for all black representations. If we consider the 'crayons' left on the ground at Lascaux, we can assume that Palaeolithic people considered painting matter as abundant and common. In fact, we know that manganese was extracted from a number of tiny mines during the 19th C in the near-Lascaux environment. But in Ekain, the use of manganese oxide being limited to uncommon figures suggests that this pigment was precious or symbolic. However, archaeologists attribute both caves to the same Magdalenian culture despite the geographical distance between them. Horse representations are similar in

[7] Material used by prehistoric people, characterized by pigment nature, texture, morphology, grain size and impurities; it changes with time.

both caves, but Lascaux is a painted cave, whereas in Ekain drawing is predominant.

Concerning heat treatments, archaeologists have made many hypotheses. Our analyses determined that heat treatment was not exploited for making black paint in the caves we studied. Concerning iron oxides, modern experiments show that heating was known and used to obtain red hematite in Troubat, Hautes Pyrénées, [4–12] which is a living shelter or in a funeral context as at Bois-Ragot in Charente. But no red or black heated pigments were found in the rock painting samples included in this study. The Palaeolithic people used heated hematite, perhaps for its prophylactic property and particularly for funeral rites, but the Palaeolithic artists preferred the use of natural materials rather than transformed pigment in these two sites.

From paint analyses in our laboratory, several conclusions were drawn concerning the technical level of prehistoric artists. In Ariège, the presence of biotite, talc and feldspar in the environment governed the preparation of painting matter with the addition of extenders to the pigment. So paint recipes[8] in the caves of Ariège are homogeneous and contain biotite, talc or feldspar [7].

Paint analysis showed links between Palaeolithic living areas (outside caves) and inside caves where rock art was produced. Study of black pigment in Enlène (Ariège) identified the presence of organic binder in the black sample from 'Le Sorcier' in the decorated cave 'Les Trois Frères' (Ariège) [10–13]. Similar links were determined between la Vache, a place of paint preparation and Niaux, a Magdalenian sanctuary [7]. In Arcy-sur-Cure (Yonne) [9] where the prehistoric living area coexists with rock art area, the presence of red pigment on the ground testifies that it may have been a workshop to prepare the paints. TEM experiments showed that this hematite does not come from dehydration of goethite present in the neighbouring cave of Saint Moré. These observations are crucial to understand work organization and task partitioning. Preparation could have been executed outside the caves (Niaux, Les Trois Frères) or inside, as in Lascaux or Arcy-sur-Cure and can be complex or simple using only native raw pigments as in Ekain. We become increasingly aware that paint recipes, a direct reflection of technical ability, differ depending on the group or the culture. They are governed by specific local minerals from the region and can be developed during time.

Timescales are difficult to evaluate through material analysis, but we can make hypotheses, as for 'Scène du Puits'. Another example, the Gargas cave (Ariège) is well known for the large number of negative hands, realized with different colours (red, black, yellow and one white), different preparations (with and without extender) and different application modes (with a pad or blowing through a hollow tube). Analyses indicate the existence of different paint 'pots' for individual hands and the same one for a pair of hands. Pigment nature is connected to the mode of application, like manganese oxide dabbed on the surface or charcoal blown through a blowpipe. This variety of paints allows access to the notions of 'short time', about the realization of each hand, and 'long time', for the entire realization of the cave [13].

[8] Everything required to develop a new material with specific properties that can be controlled and are reproducible.

Acknowledgments

The authors wish to acknowledge Françoise Pillier (Laboratoire de Physique des Liquides et Electrochimie, UPR 15 du CNRS, Paris) and Marie–Pierre Pomiès (Laboratoire de Céramique et des Matériaux minéraux, ESPCI, Paris) respectively for their help in TEM and XRD analysis. The archaeologists Norbert Aujoulat (Centre National de Préhistoire, Périgueux) and Jesus Altuna (Société des Sciences Aranzadi, Donostia, Spain) are gratefully acknowledged for the sample study of, respectively, the Lascaux and Ekain caves. We also thank le Musée de Minéralogie de l'Ecole des Mines de Paris and more particularly J M Le Cleac'h as well as le Musée de Minéralogie de l'Université Pierre et Marie Curie (Paris) for the geological references.

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