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# Discovery of Unusual Minerals in Paleolithic Black Pigments from Lascaux (France) and Ekain (Spain)

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**Abstract.** Analyses of archaeological materials aim to rediscover the know-how of Prehistoric people by determining the nature of the painting matter, its preparation mode, and the geographic origin of its raw materials. This study deals with identification of manganese oxides in black pigments by micro-XANES (X-ray absorption near-edge structure) based on previous TEM (transmission electron microscopy) studies. Complex mixtures of the manganese oxides studied are present in some of mankind's oldest known paintings, namely those from the caves of Lascaux (Dordogne, France) and Ekain (Basque country, Spain). Scarce manganese oxide minerals, including groutite, hausmannite, and manganite, were found for the first time in Paleolithic art at these archaeological sites. Because there are no known deposits of such minerals in these areas, more distant origins and trade routes are inferred. The closest known Mn-rich geological province for Lascaux is the central Pyrénées, which is ≈ 250 km from the Dordogne area.

**Keywords:** manganese oxides, Paleolithic rock art, pigment, micro-XANES
**PACS:** 61.10.Ht, 68.37.Lp, 91.65.Rg, 83.80.Nb

## INTRODUCTION

Paleolithic rock art is known in southwestern Europe where it is preserved in limestone caves. Modern-day conservation of these patrimonial artifacts requires an accurate knowledge of the materials comprising them as well as the factors causing their potential degradation (*e.g.*, tourism and pollution). Archaeologists have also been concerned about the paleoethnologic interpretation of this rock art and constituent pigments since its discovery in 1902 [1,2]. Based on recent research and discoveries, Paleolithic artists used mainly red, yellow, and black colors. Reds were provided by hematite ($Fe_2O_3$), either as raw ore or included in red-colored clays and ochre. Yellows were provided by iron oxyhydroxides such as goethite (FeOOH) and ferrihydrite. The black color was provided by either charcoal [3] or manganese oxides [4]. These pigments could be prepared in different ways: by grinding, by mixing with an extender and/or a binder, or by heating. Archeological studies clearly show that these processes were performed to enhance the pigments' properties (such as color, texture, adhesion, and layout).

In addition to TEM, XANES methods are very useful for detecting subtle changes in manganese speciation related to heat treatment, for example. Also, in some cases, identification of the various Mn oxyhydroxides phases is not always straightforward with TEM because of the poor crystallinity of some samples as well as potential sample damage by the electron beam. Here we present mineralogical findings for various highly valuable manganese oxide pigments from two caves located in Lascaux (Dordogne, France, 17000 B.P.) and Ekain (Basque country, Spain, 16500-12500 B.P.), which display some of mankind's oldest and most exquisite paintings.

## EXPERIMENTAL METHODS

Mn K-edge XANES spectra for model compounds and archeological pigments were collected under high resolution conditions (~ 0.6 eV) at SSRL (Stanford, USA) using beamline 11-2 with a Si(220) double-

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crystal monochromator. In parallel, micro-XANES spectra were collected on beamline ID21 at ESRF (Grenoble, France) in order to map the speciation of manganese at the micron scale. A Si(111) double-crystal monochromator and a Fresnel zone plate were used to obtain a monochromatic, 5 µm x 5 µm beam.

Energy calibrated (± 0.05 eV) XANES spectra were normalized in intensity using conventional methods (xafs3 code [5]). Pre-edge features were modeled following [6]. We used a series of pseudo-Voigts of fixed width (0.7 eV) and of fixed Gaussian percentage (45%), chosen based on theoretical calculations and experimental studies for well-known models of Mn(II), Mn(III), and Mn(IV) [7]. Figure 1 lists reference manganese oxides used in this study.

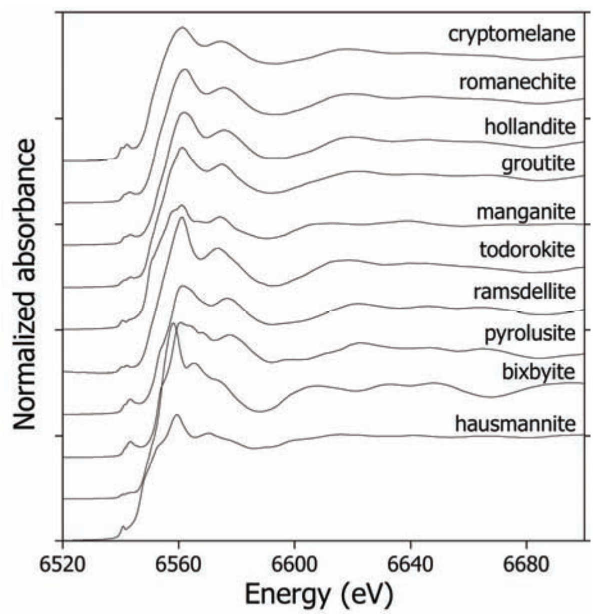


**FIGURE 1.** XANES spectra of manganese oxides: Mn K-edge normalized spectra (data collected at SSRL, beamline 11-2). Model compounds: cryptomelane (K, Ba)$Mn_8O_{16}$•n $H_2O$, hollandite $BaMn_8O_{16}$•n$H_2O$, romanechite $Ba_2Mn_5O_{10}$•n $H_2O$, groutite α-MnOOH, manganite γ-MnOOH, todorokite (K,Ba,Ca,Na)$Mn_6O_{12}$•n$H_2O$, ramsdellite β-$MnO_2$, pyrolusite β-$MnO_2$, bixbyite $Mn_2O_3$, hausmannite $Mn_3O_4$.

## PAINTING MATTER CHARACTERIZATION

### The Great Bull of Lascaux

The "great bull" shown in Figure 2a is mainly black in color but has some red pigment on its flanks. To reveal the nature of the painting matter preparation specific to the mode of application, two micron-sized samples were extracted: one from the "chignon" (between the ears) and the second from the "muffle" (snout). Archaeologists have shown that the chignon was painted by brush and the "muffle" was painted by blowing the pigments. For the chignon, µ-XRF mapping was performed at the ESRF on beamline ID21 (Fig. 2b). Mn K-edge µ-XANES collected for several spots from this sample are characteristic of a mineral related to romanechite (see Fig. 1). TEM observation revealed minor amounts of todorokite (undetected by µ-XANES). The presence of additional minerals such as quartz, clay, and iron oxide and the distribution of each component seem to indicate that a deliberate mixture was prepared before the pigment was applied. The pigment present in the "muffle" sample was not clearly identified, but its unique XANES features are similar to those of hausmannite (see Fig. 1) mixed with another Mn-containing compound not yet identified (Fig. 2c). This pigment is mixed with large amounts of calcite and Fe-rich clays.

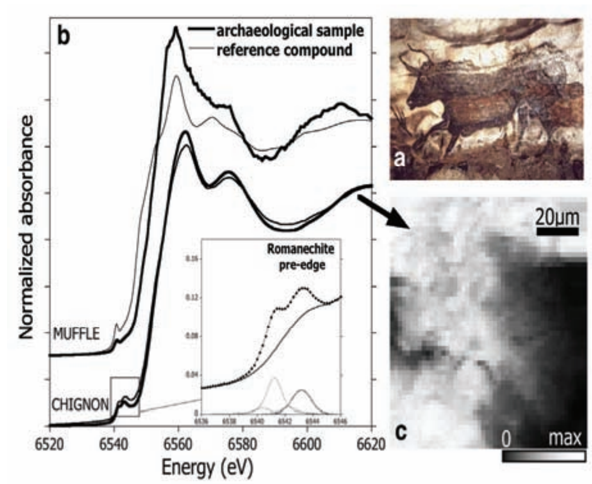


**FIGURE 2.** (a) The Great Bull from Lascaux cave © C2RMF, (b) Mn distribution in the "chignon" sample, (c) Mn *K*-edge XANES spectra of the "muffle" and "chignon" samples compared to those of romanechite and hausmannite.

These results indicate that two distinct manganese oxides and pigment preparations were used in painting the Great Bull of Lascaux. Our observations are consistent with hypotheses concerning changes in pigment preparation and its mode of application. The most intriguing finding is the presence of hausmannite ($Mn_3O_4$), which has never been encountered before in prehistoric pigments. Hausmannite is a relatively rare manganese oxide, which is usually formed at high temperature (>1000°C [8]). Lower temperature $Mn_3O_4$ is also known but requires specific chemical or microbiological processes [9]. $Mn_3O_4$ is more typically formed by heat-treatment of Mn-oxyhydroxydes over 900°C [10]. However, this high temperature could not be reached by open-pit fires in a prehistoric settlement. Another possibility is that the hausmannite is natural and was imported from the Hautes-Pyrénées (250 km from Dordogne [11]).

## The Ekain Case: Local Supply of Mn Ore?

The black pigment used in the majority of the paintings of the Ekain cave (Basque Country, Spain) is charcoal [3]. Nevertheless, two paintings were made with manganese oxide pigment: one horse (Fig. 3a) and two bears (not shown). The presence of Mn pigments seems to be linked to the black natural deposit inside the cave, which shows evidence of mining activity. To determine if Paleolithic men worked this deposit as a source of Mn pigment, samples were taken from each figure and the deposit.

Unfortunately, no definitive electron diffraction patterns could be obtained for these samples because of their low crystallinity. Mn K-edge XANES spectra were collected to help identify the phases present. Groutite ($\alpha$-MnOOH, see Fig. 1) was identified in both the deposit and the horse samples (Fig. 3b, µ-XANES collected on ID21). In addition, µ-XRF mapping was performed to check sample homogeneity (Fig. 3c).

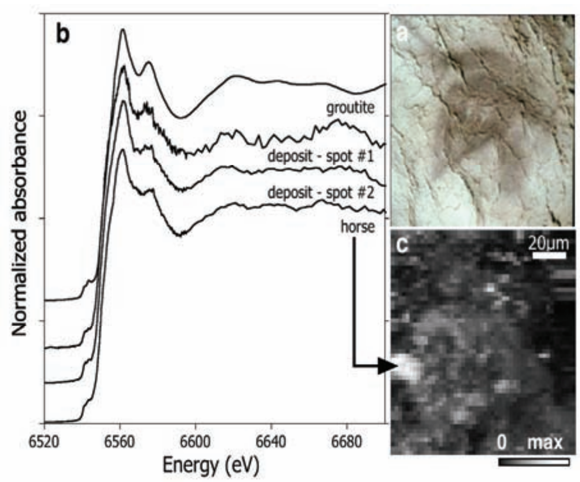


**FIGURE 3.** (a) The horse head from the Ekain cave © J. Altuna, Aranzadi, (b) Mn K-edge spectra, and (c) XANES map of the horse head (Ekain)

Although groutite was present in both the deposit and the horse painting, we cannot conclude unambiguously that the Paleolithic people extracted Mn ore from this unique deposit to prepare the pigment. Further studies of this deposit's paragenesis are necessary to provide an answer to this question. Noteworthy is the relative scarcity of groutite, particularly in the Spanish Basque country. Finally, the presence of this Mn-oxyhydroxide suggests that this pigment was not subjected to significant heat treatment (otherwise the hydroxide would have modified into pyrolusite, a dehydrated oxide that forms at temperatures above 300°C).

## CONCLUSIONS

Through these examples and because of parallel studies on other caves or settlement sites [4], an unanticipated variety of Mn-containing minerals was found, which significantly enrich the Paleolithic palette. Further, the presence of new pigments used by the Paleolithic artists, such as groutite and hausmannite, has been revealed. The rare occurrence of these Mn-oxides in the southwest region of Europe highlights the potential origins and supply of these pigments. It is possible that a regional source of raw material was exhausted or forgotten and can no longer be located. Alternatively, we can use mineralogical arguments to constraint possible metallogenic provinces of these manganese ores, such as the central Pyrénées manganese province (Vieille-Aure area in Ariege or the Labiat region in the Hautes Pyrennes area). Accordingly, we propose a local Mn-ore trade or a supply route of these ores to explain the presence of these unusual Mn-oxide minerals in the Lascaux painting materials.

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