Journal of Archaeological Science 38 (2011) 1165–1172

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Characterization and origin of black and red Magdalenian pigments from *Grottes de la Garenne* (Vallée moyenne de la Creuse-France): a mineralogical and geochemical approach of the study of prehistorical paintings

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ARTICLE INFO

Article history:
Received 28 September 2009
Received in revised form
23 December 2010
Accepted 24 December 2010

Keywords:
Parietal art
Pigments
Chemical analysis
Mineralogy
Origin

ABSTRACT

Pigments sampled from wall paintings and from crayons taken on the floor, at the *Grottes de la Garenne* (Saint-Marcel – Indre, France) have been analyzed and characterized by infrared spectroscopy, Raman micro-spectroscopy, X-ray diffraction, ICP/MS and analytical TEM. The red pigment used for the wall paintings is mainly composed by hematite, clays, carbon matter and carbonates. Results on the red pigments show that the compositions of the paintings are similar to that of some crayons. Regarding these analyses, their origin is compatible with local siderolithic facieses. Analysis of black pigments shows that they are made of cryptomelane, pyrolusite, clays, carbonates and carbon matter. It shows also that paintings and some crayons compositions are compatible. On the contrary of red pigments, the origin of black pigments is probably allochtonous. Indeed, the traces of thallium detected in cryptomelane, the cerium anomaly and the absence of iron are not compatible with local facieses or other sites from the French Massif Central.

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1. Introduction

35 000 years ago, prehistorical men gave the first major art forms, stones or bones bearing simple incisions, followed by schematic geometrical and animals figures. Time after time, this prehistorical art is becoming increasingly sophisticated and precise to achieve the exceptional quality of wall paintings such as Lascaux cave paintings. This parietal art has been extensively studied by archaeologists, but inputs of sciences like chemistry, biology or geology can be fruitful for several reasons. Numerous studies have been conducted on paintings to understand the nature of the materials and for the understanding of the techniques used by prehistoric men. Thus different authors have used various analytical techniques to analyze prehistorical paintings such as optical microscopy, SEM-EDS (Garate et al., 2004; Chalmin et al., 2002, 2004a, 2006; Vignaud et al., 2006), Gas-Chromatography coupled to Mass spectroscopy (GCMS) (Pepe et al., 1991), TEM-EDS (Chalmin et al., 2004a; Chalmin et al., 2006), X-Ray diffraction (XRD) (Chalmin et al., 2006; Vignaud et al., 2006), IRTF and Raman spectroscopies (Van Der Weerd et al., 2004; Edwards et al., 2000), and synchrotron radiation spectroscopies (XANES, EXAFS, XRF) (Chalmin et al., 2006; Reiche and Chalmin, 2008; Farges et al., 2005). Some authors have tried to determine how prehistorical men prepared and used these pigments, and they suggested for example that red pigments can sometimes be obtained by dehydrating goethite to transform it into hematite (Chalmin et al., 2004b; Pomies et al., 1998, 1999). In contrast, no thermal treatments have been detected on black pigments obtained from manganese-based minerals (Chalmin et al., 2004b).

The *Grottes de la Garenne*, located at Saint-Marcel, Indre – France (Fig. 1) are a set of Magdalenian living sites (Despriee et al., 2001). These caves take place in a karstic context, belonging to an entrocs-containing bajocian limestone level that overlooks the river *Creuse* valley. The caves are located on the southern shore of the river *Creuse*, in a hill called *Coteau de la Garenne*. Known prehistoric sites are located on the west part of the hill. The first parts of this site have been discovered in 1848, during the building of the Paris – Toulouse railway. Several caves have been opened since this date. This site is a set of 9 archaeological levels, opened in the middle of the hill, at an altitude of approximately 120 m (Fig. 2). These levels seem to be a succession of spaces, living places and other places, successively occupied from the bottom to the top of the hill. The different levels have been dated (^{14}C dating) from

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doi:10.1016/j.jas.2010.12.014

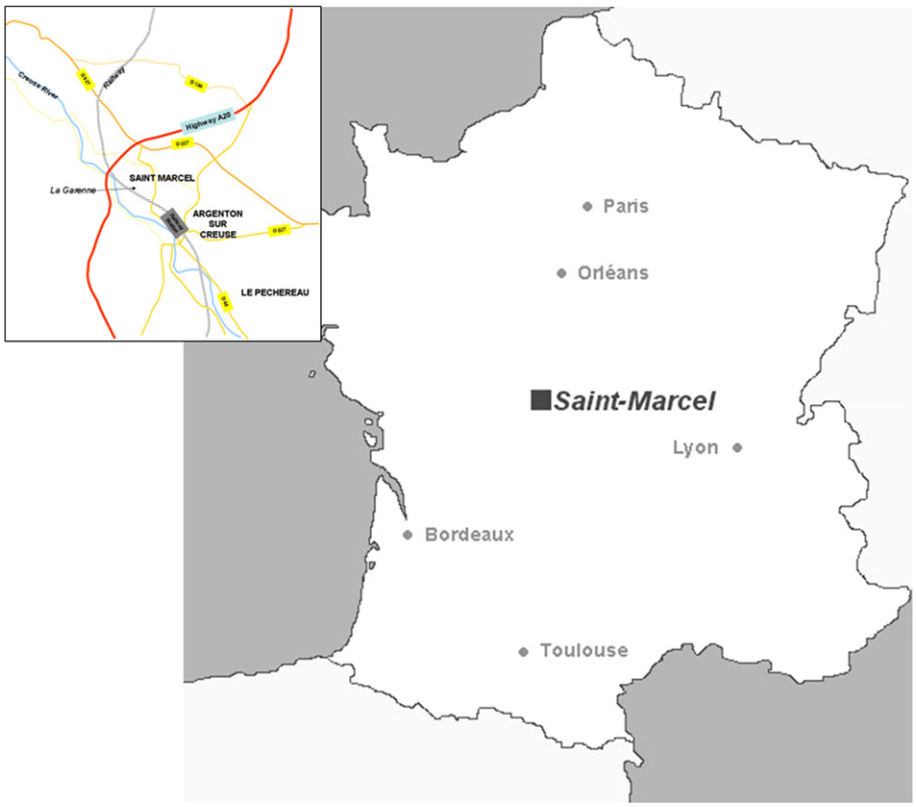

Fig. 1. Location of Saint-Marcel, France.

15290 BP to 11920 BP (Despriee et al., 2001). Some of these places are sometimes well equipped (flooring, fireplaces…). An important set of objects has been discovered in the different levels, such as tools made with reindeer antlers, animals' bones (reindeers, horses, wolves, rodents or fishes). The analysis of pollens and animals remains shows that this period corresponds to a cold steppes climate.

The walls of these caves are covered by a substantial set of paintings whose study may allow archaeologists to obtain information or confirm hypothesis about the techniques and tools used by men from the Magdalenian age (Vignaud et al., 2006). The study of these paintings can also be used to link painting materials to local or external supply sources. Several objects that could have been used as "crayons" have been found on the floor during explorations of the caves. Moreover, the answers obtain from this study can help to understand the risk of degradation of prehistorical painted caves like Lascaux cave (Allemand, 2003), Gargas cave (Mangin et al., 1999) or Arcy-Sur-Cure cave (Chalmin et al., 2008). A study of pigments samples taken on the prehistoric site of the *Coteau de la Garenne* at St Marcel allowed us to determine the

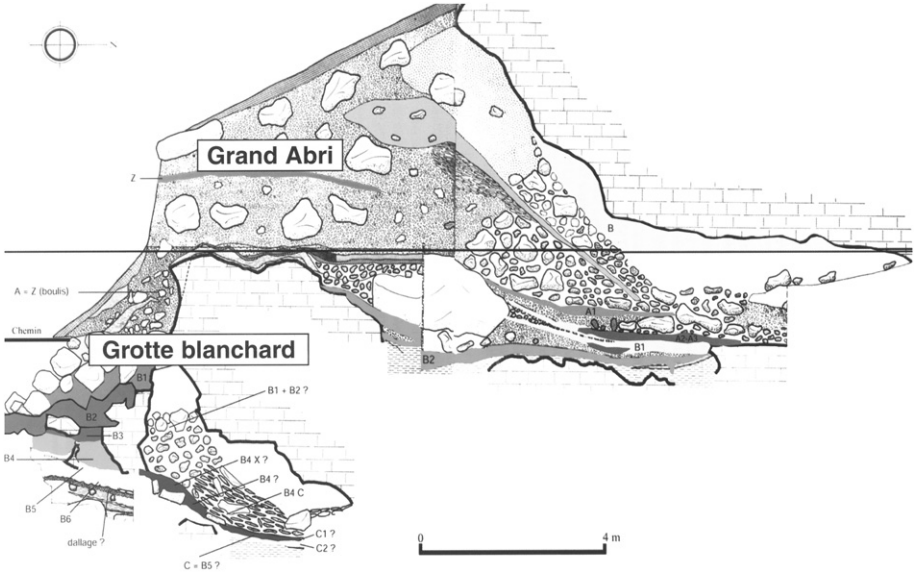

Fig. 2. The Grand Abri and the Grotte Blanchard (Despriee et al., 2001).

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