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Preliminary analysis of Palaeolithic black pigments in plaquettes from the Parpalló cave (Gandía, Spain) carried out by means of non-destructive techniques

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ABSTRACT

Parpalló cave (Gandía, Spain) is one of the most important Palaeolithic sites in the Spanish Mediterranean region. It is characterized by a mobiliary art whose archaeological sequence covers a dilated period (26,000–11,000 BP) and includes plaquettes decorated with black and different shades of red and yellow pigments. The aim of this paper is to present the results of analyses of the nature of black pigments used in the decoration of Parpalló plaquettes. The analyses were carried out by a non-destructive technique, by means of EDXRF. Furthermore, a colorimetric data bank has been created for conservation purposes. EDXRF measurements directly identify the use of manganese black pigments and indirectly the use of wooden charcoal based black pigments, in both zoomorphic motifs and undefined signs. No differentiation between manganese and non-manganese based black pigments was found from colorimetric measurements, but the data obtained will prove to be a useful reference for further studies as pigments fade with time.

1. Introduction

Within the large variety of Palaeolithic mobiliary art supports, plaquettes and pebbles make up a particular domain. This is mostly due to the fact that they are decorated objects with no defined functionality, in contrast to antler or bone points and other implements that are often decorated with figurative or geometric motifs. Mobiliary art on lithic support has been found in all the European Upper Palaeolithic, but only a few sites have yielded large collections of pieces (Limeuil, La Marche, Gönnersdorf) and most of them are of Magdalenian chronology. Parpalló's painted and engraved plaquettes present outstanding features and make a remarkable collection. The number of plaquettes found is very high; 5612 pieces associated to a very long archaeological sequence that covers practically the whole of the regional Upper Palaeolithic (26,000–11,000 BP). Among these plaquettes, those with painted motifs are quite abundant, especially in the Solutrean (Villaverde, 1994). The collection includes 81 painted animal figures and almost 2000 pieces painted with non-figurative motifs. Most of the latter do not present clearly defined motifs, and in many cases could just be plaquettes used for grinding pigment or pieces coloured by contact with materials deposited at their level. But a considerable number of pieces have signs and that shows that paint was used for the execution of those motifs. 194 non-figurative motifs have been identified. Among them there are different types of painted bands and spots, some rectangles, triangles and branch like shapes. Parpalló painted motifs are either monochrome or have just two colours: black and different shades of red and yellow.

Work concerning painted mobiliary art lithic pieces has been published in recent years; examples of these are Riparo Villabruna A (Broglio, 1998) and Riparo Dalmeri (Dalmieri et al., 2005), from the Late Epigravettian in the North of Italy. Likewise, references have been made to lines of engravings filled with paint in some bone and antler objects: La Vache (Buisson et al., 1989), La Garma scrapper (Arias et al., 2011) and, reference has also be made to the dots on a scrapper found in Abri Pataud (Beck et al., 2011). But it must be acknowledged that, generally speaking, most pigment characterization studies have focused on parietal rather than mobiliary art (Menu, 2009).

The Parpalló collection offers very good possibilities for the study of pigments. Paint was much used throughout the sequence, in the representation of both figurative and geometric motifs. Considerable variety in colours and techniques can be observed in pieces that often show similarities to motifs painted in parietal art. Furthermore, most of the pieces have sufficiently precise chronology because they have been associated to sequences studied

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Fig. 1. Geographical situation of the Parpalló cave.

through archaeological materials. Although pieces with absolute dating are not abundant, contrast with other sites in the region has helped to establish the Parpalló sequence with precision (Villaverde, 2005a; Villaverde et al., 2010; Fullola et al., 2005). So chronological precision for Parpalló mobiliary art pieces is not that different from chronological precision of parietal art figures. The time segments the pieces were referred to were defined with similar precision to that obtained from sigma calibration for direct dating of parietal figures.

The results obtained from technical, stylistic and thematic studies of the Parpalló mobiliary art collection have been corroborated by parietal art findings in nearby sites, or on the walls of the site itself. Parpalló's long sequence is unique in that it offers the possibility of establishing the characteristics of Palaeolithic art in Southeast Europe, particularly for the Solutrean periods. Moreover, the study of Parpalló has shown a lineal evolution in Palaeolithic art and has contributed to establishing the importance of studying regional cultural processes throughout the Upper Palaeolithic sequence, particularly in connection to Magdalenian art (Bicho et al., 2007).

Many studies of the pigments used in parietal and mobiliar rock art have been carried out (Clottes et al., 1990; Menu and Walter, 1996; Pomiès et al., 1999; Edwards et al., 2000; Chalmin et al., 2003; Sanoit et al., 2005; Iriarte et al., 2009; Menu, 2009). But a pigment study of the Parpalló collection was lacking. The style of the pieces is well known (Villaverde, 1994) but the characteristics of the pigments are yet to be studied. An analysis of pigments identifies the materials used and can be an excellent complement to stylistic studies. Given the artistic and historical value of this fragile art form, in-situ non-destructive analytical techniques have been used.

The preliminary research described in this paper is part of a wider project that has the objective of identifying the nature of the pigments used in the decoration of the plaquettes and to study their evolution over the extensive chronological sequence of Parpalló. This preliminary study was undertaken over a limited (selected) number of plaquettes motifs executed in black, in order to test the capability of portable and non-destructive techniques (X-ray fluorescence spectrometry and colorimetry) for the characterization of the pigments used in Parpalló mobiliary rock art. The aims were to establish a protocol which enables the distinction between carbon based pigments and manganese based ones by means of EDXRF spectrometry, to create a colorimetric data bank of the black pigments used in the figures of the Parpalló plaquettes, and to carry out complementary FTIR analyses of a small and selected set of plaquettes.

2. Material and methods

2.1. Archaeological site and sample description

Parpalló cave is on a south facing slope of the Mondúver Range, located near Gandía, in the Valencia province, 450 m above sea level and a few kilometers away from the current coastline (Fig. 1). This is a small cave, excavated by L. Pericot between 1929 and 1931, has three chambers and a narrow vertical entrance facing south. The main chamber is the largest, 5 by 6 m, and the other two are rather small.

Table 1
Analyzed plaquettes from the Parpalló cave with black motifs.

Slab identification number	Chronology (years BP)	Size (mm)[a]	Description
16014	Lower Solutrean (21500–20500)	67, 37, 10	Undefined sign
16061 (face A)	Lower Solutrean	191, 129, 42	Zoomorphic motif: female cervid
16061 (face B)	Lower Solutrean	191, 129, 42	Zoomorphic motif: female cervid
16129	Lower Solutrean	73, 81, 3	Spot on the leg of an undefined zoomorphic
16157	Lower Solutrean	100, 77, 7	Legs of an undefined zoomorphic motif
16170	Lower Solutrean	151, 116, 12	Undefined sign
16171	Lower Solutrean	155, 89, 11	Undefined sign
16319	Ancient Middle Solutrean (20500–20000)	165, 120, 16	Zoomorphic motif: female cervid
16452	Evolved Middle Solutrean (20000–19500)	170, 107, 21	Zoomorphic motif: ibex
16700	Evolved Middle Solutrean	130, 76, 10	Undefined zoomorphic motif
16754 (face A)	Evolved Middle Solutrean	83, 42, 12	Undefined zoomorphic motif
17251	Upper Solutrean (19500–18500)	82, 50, 18	Undefined sign
17261 (face A)	Upper Solutrean	29, 25, 2	Undefined sign
17279	Upper Solutrean	70, 42, 15	Undefined sign
17351	Upper Solutrean	68, 59, 10	Undefined zoomorphic motif
17873	Solutreo-Gravetian I (18500–17500)	142, 85, 7	Legs of an undefined zoomorphic motif
19359 (face A)	Ancient Magdalenian	29, 25, 2	Sign (painted band)
20345 (face A)	Upper Magdalenian (13500–12000)	112, 107, 7	Sign (spot on an ibex head)
20345 (face B)	Upper Magdalenian	112, 107, 7	Undefined sign
20004 (face B)	Upper Magdalenian	150, 120, 30	Non-figurative line

[a] Width, height, thickness.