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Abstract: The Carrer Paris site is located in Cerdanyola del Vallès (Barcelona, Spain). It is a Chalcolithic hypogeum dated between 3800-4100 BP with more than 60 individuals distributed in four burial levels. We study the remains of Individual 5 from burial level II. It is an adult skeleton, preserved in anatomical position and buried with Campaniform pottery. During the excavation, we identified red pigment on the mandibular symphysis region of the individual 5. In this work we present the preservation state and conservation methodology to restore the individual 5 cranium and mandible. At the same time, we present the results of the pigment composition analyzed by non-destructive methods. These analyses were conducted directly on the pigments and the bone surface with environment electronic microscopy (ESEM-EDS) X-ray micro-diffraction (μ-DRX) before the conservation treatments. The objective of the analysis was to characterize the pigments, the bone and the clays to apply the best methodology to conserve the pieces. The combination of both techniques allows us to analyze the area of interest without removing samples. These analyses were performed directly, without affecting the bone and pigments and assuring the integral preservation of the objects. The results reach us new data on the use of pigment in funerary rituals during the Chalcolithic.

Résumé : *L'hypogée du Chalcolithique de la Rue Paris (Cerdanyola del Vallès, Barcelona, Espagne) a été daté entre 3800 et 4100 BP. Les restes anthropologiques fouillés étaient distribués sur quatre niveaux et dépassaient les 60 individus. Ceux étudiés ici proviennent du deuxième niveau d'inhumation et appartiennent à un squelette adulte (individu 5), préservé en connexion anatomique et inhumé avec de la céramique campaniforme. Au cours de la fouille, des restes de matière colorante rouge ont été identifiés sur la région de la symphyse mentonnière. Dans ce travail sont présentés l'état de conservation et la méthodologie de restauration du crâne et de la mandibule de l'individu 5. De même, sont présentés les résultats des analyses non destructices faites directement sur les matières colorantes et l'os. Les analyses ont été réalisées avant la restauration du crâne et de la mandibule à l'aide d'un microscope électronique à balayage environnemental (ESEM-EDS) et micro-diffraction de rayons X (μ-DRX). L'objectif des analyses est la caractérisation des pigments, de l'os et du sédiment afin de choisir la meilleure méthodologie à appliquer pour la conservation des pièces. La combinaison de ces techniques favorise l'analyse des zones d'intérêt sans la prise d'échantillons. Ces analyses ont été faites directement sans abîmer l'os ni les pigments et, en conséquence,*

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la préservation intégrale des objets est assurée. Les résultats obtenus apportent une information importante à propos de l'utilisation de quelques matières colorantes dans les rituels funéraires au Chalcolithique.

Keywords: Chalcolithic, conservation, cinnabar, hypogeum, Environmental Scanning Electron Microscope, X-ray diffraction.

Mots clé : *Chalcolithique, conservation, cinnabar, hypogée, microscopie électronique à balayage environnemental, diffraction de rayons X.*

1. Introduction

The Carrer Paris hypogeum is located in Cerdanyola del Vallés (Vallès Occidental, Barcelona, Spain) (Figure 1). The site was discovered accidentally during the foundation works of new housings constructions. It is a funerary structure with oval plant. The north part of the site was destructed by the constructing works but the south side kept preserved. During the excavation processes were identified different levels of burials. In the second burial level we located four individuals, three of them in a primary position and the fourth displaced and lying close to the west wall of the structure (Francés Farré *et al.*, 2004; Gibaja *et al.*, 2006). One of these primary burials belongs to individual 5 which has been restored and has been sampled for this study.

Individual 5 is an adult skeleton buried in lateral decubitus position. The longitudinal axis of the body was oriented north-south with the crania looking to the east. During the excavation we identified red pigment remains over its mandible, in the soil of the burial level II and inside of the ceramic glass found together with the skeleton, possibly as a funerary present (Figure 1).

2. Methods

The skull was extracted in block with sediment and it was transported to the Restoration Laboratory in IPHES. The conservation procedures involved the cleaning and reconstruction to achieve the anthropological study, to observe the pigments distribution and to analyze the composition. The chemical analyses of the colouring materials were performed with non-destructive methods to guarantee the complete preservation of the pigments.

Figure 1: (See colour plate) A) Individual 5 during the excavation process in Carrer Paris Chalcolithic hypogeum. B) Detail of the cranium and the mandible of Individual 5 with red pigments remains "in situ". C) Geographical situation of Carrer Paris site (Cerdanyola del Vallès, Barcelona).

Figure 1 : (Voir planche couleur) A) Individu 5 durant la fouille de l'hypogée Chalcolithique du Carrer Paris. B) Détails du crâne et de la mandibule de l'individu 5 avec les pigments rouges pendant l'excavation. C) Situation géographique de Carrer Paris (Cerdanyola del Vallès, Barcelone).

Documentation and sampling

We documented the state conservation of the bone using high resolution photographies. We also conducted an observation study using a binocular microscope to distinguish more signs of colouring material. We took control samples of the sediment to test if the red material was present on the sediments.

Analytical techniques

We analyzed the pigments on the left mandibular fragments from individual 5, four samples of the sediment recovered during the cleaning of the cranium and one mineral standard sample of cinnabar from Almadén mines (Spain) to compare with the archaeological samples.

The analyses on the mandibular fragments (CP1 and CP2) were done before the restoration processes with environmental scanning electron microscope (ESEM) and X-ray microdiffraction (µ-DRX). We present the analyzed areas in Figure 2.

The Environmental Scanning Electron Microscope used was FEI Quanta 600 (ESEM) with an attached X-ray Energy Dispersive Spectroscopy (EDS) of Oxford Instruments. The samples were evaluated under 0,68 Torrs of chamber pressure, 20kV of beam energy and 10 mm of working distance. We used simultaneously detectors of the secondary electrons (SE) and the backscattered electrons (BSE). We documented the distribution of the pigments and sediment presents over the surface of the mandible and we analyzed the elemental composition of pigments.

Microdiffraction (µ-DRX) measurements were made using a Bruker-AXS D8-Discover diffractometer equipped with parallel incident beam (Göbel mirror), vertical θ-θ goniometer, $Cu_{k\alpha}$ radiation, XYZ motorized stage and with a GADDS (General Area Diffraction System). The samples were placed directly on the sample holder and the area of interest was selected with the aid of a video-laser focusing system. An X-ray collimator system allows us to analyze elliptic areas of 500 x (500/sinθ_1) microns. We collected *frames* (2D XRD patterns) covering 15-70º 2θ from three different detector positions (θ_1: 16.27, 25.25 and 34.2º) at

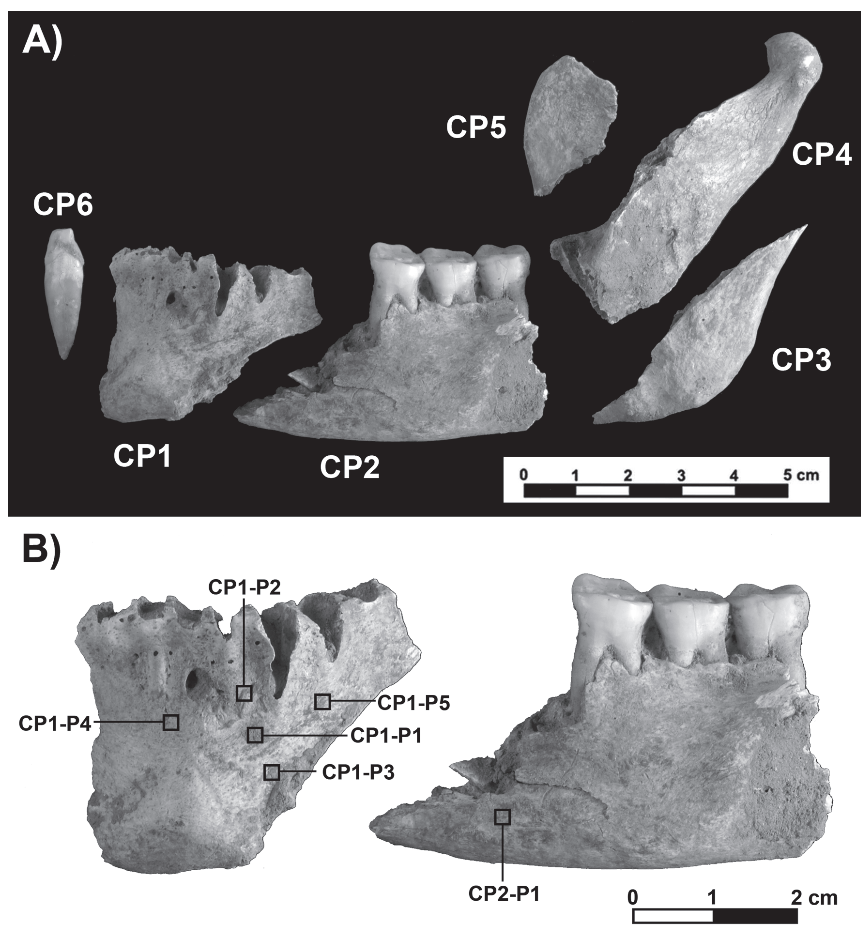

Figure 2: (See colour plate) A) Left side of Individual 5 mandible before the conservation treatments. B) Detail of the red pigment concentred in fragments CP1 and CP2 and areas analyzed by ESEM-EDS and X-ray diffraction.

Figure 2 : (Voir planche couleur) A) Coté gauche de la mandibule de l'individu 5 avant les traitements de restauration et détail du pigment rouge concentré sur les fragments CP1 et CP2. B) Zones analysées par ESEM-EDS et micro-diffraction de rayons X (µ-DRX).

a distance of 15cm from the sample. The exposition time was 120s per *frame* and it was chi-integrated to generate the conventional 2θ vs. intensity diffractogram.

The identification of the minerals was achieved by comparison of the XRD diffractogram with the ICDD data base (release 2007) using Diffrac^{plus} Evaluation software (Bruker, 2007).

Conservation treatments

Once we known the nature of pigments (and their implication for the archaeological study) and sediment, we proceeded to planning a methodology of conservation. We documented that the cranium has diagenetic modifications due to the sediment pressure and humidity: deformations of the bone, crushing, distortions, displacements, fissures and cracks filled by sediment. The facial region has important missing parts and some teeth have been lost. The cranium was very broken, it has modern fractures, cracks and some parts of the bone have cohesion problems due to the vibrations from the transport and possibly by the action of plant roots. The mandible was fragmented in five pieces and one isolated teeth. All the fractures were old and only one showed a recent breakage. The fragments preserved some sediment adhered to the surface but we could observe abundant patches of red colouring material.

We performed some cleaning tests in localized areas to determine which cleaning system was the most adequate. The removal of the sediment was done with deionized water, paintbrushes, cotton swabs and wood-sticks. The areas with pigment were cleaned under a stereo microscope Zeiss Stemi 2000C using magnification between 6.5 and 50x. Occasionally, in the regions without cohesion or broken we used the acrylic resin Paraloid B72 dissolved with acetone at 5-10% to consolidate and 20% to glue. This synthetic resin is well-known in conservation and is the most recommended to preserving bones. It has showed the best long-term stability in test but at the same time it was demonstrated that it is not completely reversible (Johnson, 1994; Shelton & Chaney, 1994; Johnson, 2001), so we only used it when it was completely necessary for the bone preservation and we didn't used it directly over the pigments.

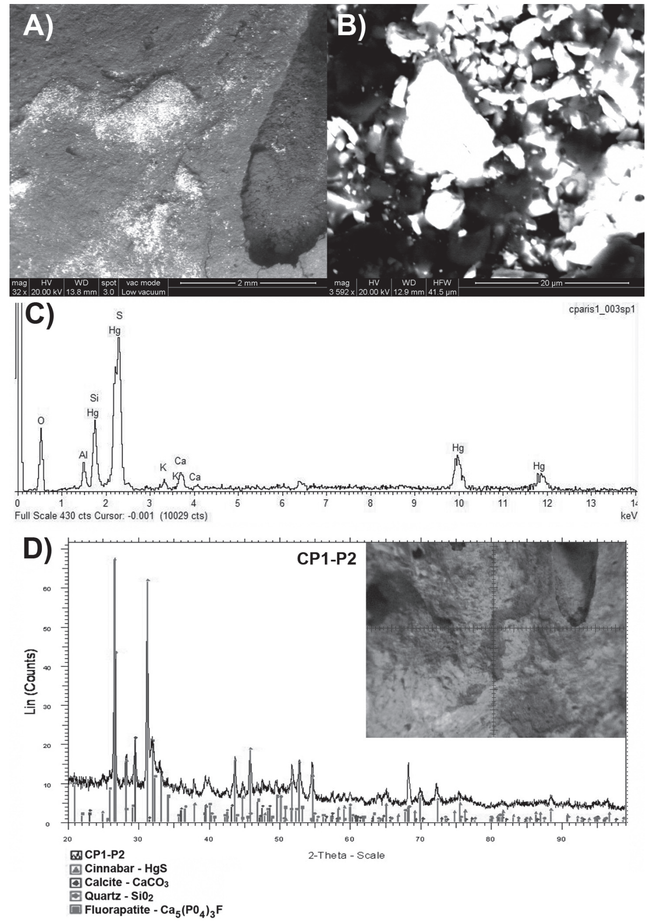

Figure 3: (See colour plate) ESEM-EDS and X-ray diffraction results of sample CP2-P1**.** A) ESEM-EDS analysis: location of pigments between the bone and site sediment with BSE detector. B) Detail of cinnabar crystals (BSE) in the same site of interest. As shown in the image, the cinnabar crystals present a maximum size of 15 µm and are defined as equidimensional or elongated with subhedral forms. Their roundness is subangular and the habits are tabular (Bullock et *al.*, 1985). C) Elemental spectrum of the biggest cinnabar crystal shown in image B. The elements Hg and S of the cinnabar (HgS) are associated to O, Al, Si, K and Ca. D) X-ray diffractogram and site of interest. The most abundant compounds detected are cinnabar, calcite, quartz and fluorapatite.

*Figure 3 : (Voir planche couleur) Résultats des analyses avec ESEM-EDS et de la micro-diffraction de rayons X obtenus pour l'échantillon CP2-P1***.** *A) Analyses ESEM-EDS: situation des pigments entre l'os et le sédiment avec detector BSE. B) Détail des cristaux de cinabre (BSE) au même endroit. Les cristaux de cinabre montrés sur cette figure présentent une taille maximale de 5 µm et sont décrits comme équidimensionels ou allongés avec une forme subhédrale. Leur rondeur est subangulaire et leurs habitudes sont tabulaires (Bullock et al., 1985). C) Spectre élémentaire du plus grand cristal de cinabre de l'image B. Les éléments Hg et S du cinabre (HgS) sont associées aux éléments O, Al, Si, K and Ca. D) Diffractogramme de rayons X et lieu d'intérêt. Les composés les plus abondants détectés sont du cinnabre, de la calcite, du quartz et de la fluorapatite.*

3. Results

The ESEM observation allows us to document the distribution of the pigments between the bone surface and the sediment from the site (Figure 3). The elemental microanalysis (EDS) in the different analysis points permit us to identify that the red pigment is composed mainly by minerals with the elements S and Hg in association. These results allowed us to characterize that the base of red pigment is cinnabar (HgS). The size and shape of cinnabar crystals are described Figure 3. We have detected other elements associated oxygen (O), aluminium (Al), silicon (Si), calcium (Ca) and depending the areas magnesium traces (Mg), potassium (K) and iron (Fe). These elements are related possibility to calcite, quartz and aluminiumsilicates.

Using the µ-DRX we can confirm that the composition of the coloring materials of the mandible is composed principally by cinnabar (HgS) and quartz (SiO_2). We also detected the bone fluorapatite ($Ca_5 (PO_4)_3F$) and the calcite ($CaCO_3$) of the sediment (Figure 3). As the archaeological samples, the geological cinnabar sample is composed mainly by cinnabar and quartz (Figure 4). We have not located cinnabar on the sediment samples and all of them are composed by calcite, dolomite, quartz, muscovite and chlorite. We present the all results of the X-ray diffraction on Table I.

During the conservation processes we did not find colouring material in other regions of the cranium bones. Once restored the mandible, it was possible to manipulate it to study and describe the pigment distribution. The colouring material is concentrated on the left mandibular body. There are some red pigments inside the teeth alveolus and some very small remnants of pigment in the internal side of the mandible and in the right side (Figure 5).

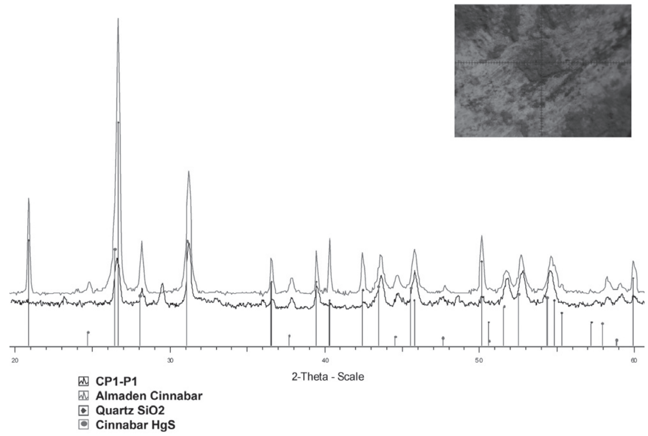

Figure 4: (See colour plate) Comparison of the X-ray diffractogrammes of CP1-P1 and the geological reference of Almadén cinnabar. Both samples present cinnabar and quartz as principal components.
Figure 4 : (Voir planche couleur) Comparaison des diffractogrammes de rayons X de CP1-P1 et de l'étalon géologique du cinabre d'Almadén (Spain).

4. Discussion and conclusions

In Iberian Peninsula the use of Ferric oxide as red coloring material has been documented in funerary ritual since the Paleolithic period (Duarte, 2002). The early use of cinnabar for funerary rituals dates from the Middle Neolithic in Gavà mines (Barcelona, Spain) (Gómez-Merino & Gispert-

Sample	Analysis Point	Material	CN	C	D	F	Q	m	M	CL
CP-01		Sediment		x	x		x	x	x	X
CP-02		Sediment		x	x		x		x	x
CP-03		Sediment		x	x		x		x	x
CP-04		Sediment		x	x		x		x	x
Sample 5		Almadén-cinnabar	x				x			
CP1	P1	Pigment	x	x		x				
CP1	P2	Pigment	x	x		x	x			
CP1	P3	Pigment	x	x		x	x			
CP1	P4	Os		x		x	x			
CP1	P5	Pigment	x	x		x	x			
CP1	P5	Pigment	x	x		x	x			
CP2	P1	Pigment	x	x		x				

CN: Cinnabar; C: Calcite; D: Dolomite; F: Fluorapatite; Q: Quarz; m: Microcline; M: Muscovite; CL: Clinochlore (Chlorite).

Table I: X-ray diffraction results in pigment, bone and sediment from Carrer Paris Individual 5.
Tableau1 : Résultats de diffraction de rayons X obtenus sur le pigment, l'os et le sédiment de l'individu 5 de Carrer Paris.

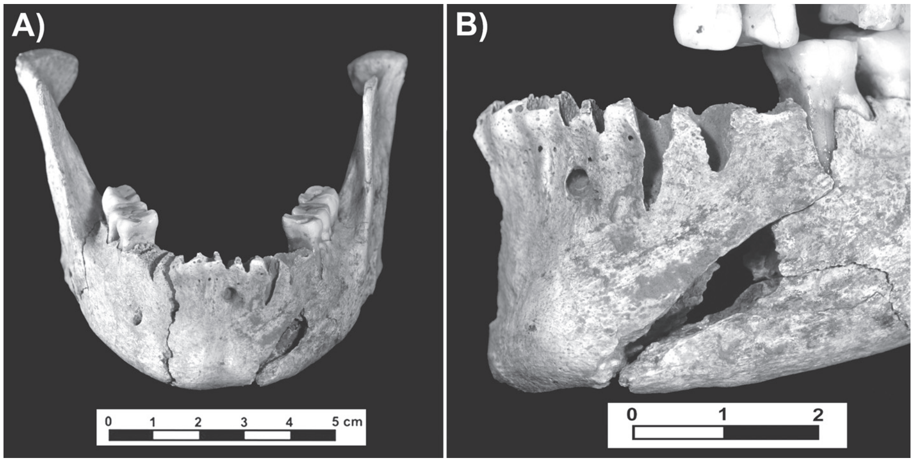

Figure 5: (See colour plate) Mandible after the conservation treatments. A) General view of the piece. B) Detail of the pigment distribution concentrated on the left side.
Figure 5 : (Voir planche couleur) Mandibule après les traitements de restauration. A) Vue générale de la pièce. B) Détail de la distribution des pigments concentrés sur le coté gauche.

Guirado, 2010). The cinnabar has been used frequently in funerary rituals during Bronze Age and it has been documented in several sites, where it has been documented the use of cinnabar to paint the funerary structures and human skeletons (Martín Gil *et al.*, 1995; Delibes de Castro, 2000). The use of cinnabar during the Calcolithic in north-east of Iberian Peninsula is not well documented. The most important mines of this mineral are located far away in other regions (Casanova & Canseco, 2002; Calvo, 2008). The identification of cinnabar in Carrer Paris hypogeum is interesting because it indicates a selection or preference in using this coloring material, which is not abundant in the territory. The closest mines are Garralda (Navarra), Albarracín (Teruel) and Espadán (Castelló) which are located between 280 km and 320 km in NW, W and SW direction, respectively (Delibes de Castro, 2000). Thus, this mineral must be obtained by travelling long distances or by exchange with other groups. We have analyzed a sample of Almadén cinnabar to compare with our archaeological samples, but it does not mean that Almadén was the origin for the cinnabar of Carrer Paris site. To determine the origin of this raw material, we require further studies and a systematic analysis of all possible sources. The cinnabar is a poisonous substance and in low concentration has sedative properties. Martín Gil *et al.* (1995) and Delibes de Castro (2000) had suggested that cinnabar was used in Bronze Age in funerary ritual to preserve the bodies. Currently, cinnabar has been used in traditional medicine and as cosmetic in China (Chuu *et al.*, 2007; Huang *et al.*, 2007) and in the Arabic Peninsula (Hardy *et al.*, 1995). We think that the cinnabar identified in the mandibular symphysis of the individual 5 seems to be linked to the funerary context but we cannot rule out other possibilities.

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