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Characterising the pigment on a Mesolithic cranium from Corsica using ion beam analysis

M. Lambert [a,*], P. Courtaud [b], F.-X. Le Bourdonnec [c], Q. Lemasson [d], L. Pichon [d], F. Leandri [e,f], J. Cesari [g], C. Bressy-Leandri [e,f], R. Skeates [a]

[a] Department of Archaeology, Durham University, United Kingdom
[b] PACEA, Université Bordeaux I, France
[c] Archéosciences Bordeaux UMR 6034, Université Bordeaux Montaigne, France
[d] AGLAE, Palais du Louvre, Paris, France
[e] DRAC Corse, France
[f] TRACES UMR 5608, Université Toulouse, France
[g] LAMPEA UMR 7269, Université Aix-Marseille, France

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ABSTRACT

Characterising thin mineral layers on heterogeneous media is a significant challenge in archaeometry. Nevertheless, obtaining such geochemical and mineralogical data can, in many cases, provide valuable information about the original raw-material procurement strategies and document the chaîne opératoire leading to the finished object. In this contribution, we report on the geochemical analysis of a thin layer of red mineral pigment found on a skull from the Mesolithic burial of Campu Stefanu, Corsica. A proton ion beam analysis was conducted at the New AGLAE facilities (Palais du Louvre, Paris) to determine major, minor and trace element compositions. Contribution from the pigment's elemental composition is statistically differentiated from that of the bone and the sediment. Furthermore, the composition of the pigment is shown to be compatible with that of iron-oxide rich mineral blocks found within the mortuary deposits.

1. Introduction

The site of Campu Stefanu is located in the village of Sollacaro in South Corsica (Fig. 1). Excavations conducted underneath a large taffonu (i.e. a large granitic boulder eroded by winds, Fig. 2) brought to light several burial layers, especially a collective burial dated to the Mesolithic period [1]. Direct dating of well-preserved bone collagen from a humerus provided a chronological range of 8260–7970 cal B.C. [2], which currently makes the Campu Stefanu burial the oldest secure human presence of the island. In turn, the presence of a red colouration on the skull of an individual from this level provides the earliest dated context for the potential use of pigments in Corsica. Two additional single Mesolithic burials have also been uncovered at Torre d'Aquila (Pietracorbara) [3] and at Araguina Sennola (Bonifacio, South Corsica) [4], although ochred bones were reported only at the latter. At Araguina Sennola, a mineralogical analysis of the brownish powder laid on the bones had revealed its altered granitic nature, which contrasts with the miocene calcareous environment of Bonifacio [5].

In Europe, the phenomenon of ochre usage – or at least its presence – within or nearby a Mesolithic burial is reported to concern about half of the 200 Mesolithic burials [6]. However, very few analytical studies have been dedicated to the confirmation of the presence of a pigmenting matter and its geochemical characterisation [7]. This is of particular importance in granitic environments where geological degradation processes can be responsible for the formation of haematite and thus, for the red colouring of the burial.

Here, we address the question of confirming the presence of a pigmenting matter on the Campu Stefanu skull and identifying its composition using ion beam analysis. In addition, about ninety iron-oxide rich blocks have also been uncovered in Mesolithic levels, the majority of which bear use-wear traces related to grinding activity. The geochemical composition of a sample of these was determined to establish a comparison with that of the potential pigment on the skull.

2. Materials and methods

The lower layer of the burial contained a number of bones, of which the skull (Fig. 3) features an almost uniform colouration that can be

Abbreviations: ML, Maryline Lambert; FXB, Francois-Xavier le Bourdonnec; PC, Patrice Courtaud; QL, Quentin Lemasson; LP, Laurent Pichon; FL, Franck Leandri; CBL, Celine Bressy-Leandri; RS, Robin Skeates; JC, Joseph Cesari

* Corresponding author.
E-mail address: maryline.lambert@durham.ac.uk (M. Lambert).

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Fig. 1. Corsican Mesolithic sites with human remains mentioned in the text. 1. Campu Stefanu (Sollacaro). 2. Torre d'Aquila (Pietracorbara). 3. Araguina-Sennola (Bonifacio).

visually distinguished from the granitic sediment deposit. First and foremost, given the heritage value of the skull as the oldest human remain in Mesolithic Corsica, strictly non-destructive techniques were required. The particle-induced X-ray emission (PIXE) technique was selected as it enables a non-touch analysis of the cranium.

A 3 MeV proton beam with a 50 μm diameter was employed at an intensity of 5 nA. This ensured a relatively low penetration depth of the proton beam, estimated to about 104 μm by the SRIM software [8]. The GUYLS module further indicates that these conditions lead to a depth from which 95% of X-rays are detected of 10 μm for Si, 34 μm for Ca and 55 μm for Fe. These values indicate that the PIXE analysis mainly captured the upper pigmented layer, although the depth of this latter remains difficult to evaluate as it is not homogeneous and some areas may be free of pigment.

Due to the fragility of the skull, a bespoke hard foam coffin was created to maintain the skull in place and avoid deforming it. A silk paper was placed in-between to avoid any loss of material, especially some deposited sediment which allows the skull to remain steady. The assemblage was then tilted at an angle of about 30° to enable the ion beam to be focused onto the areas of interest on the object. Finally, metallic bars were fixed in front of the motorised table on which the setup lies, allowing for an additional protection in case of movement during the analysis.

We followed the protocol developed by L. Beck and collaborators [9, 10] for the study of iron-oxide-rich artefacts using PIXE. A set of monochromatic filters was thus used to minimise fluorescence effects due to iron. These consisted in a 20 μm thick chromium filter along with a 50 μm thick aluminium one. Seven areas of 4×4 mm were analysed on the skull, four of in the reddish pigmented areas. The acquisition time was between 10 and 20 min per zone. Three additional 5-minute punctual measurements were also collected.

To better understand the origin of the iron concentrations, three samples of sediment collected on the thorax, below and away from the cranium, during the excavations were analysed. In addition, seventeen blocks coming from the same Mesolithic levels were also selected to compare with the sediment. In particular, one of the blocks (number 17) was cleaned with distilled water to remove the sediment and enable a better discrimination. The sediment samples and the blocks were observed using a scanning electron microscope (SEM, Hitachi TM3000), which is equipped with a SwiftED 3000 energy dispersive X-ray spectrometer (EDX) to extract compositional data. A minimum of five measurements were collected for each block. As the current analyses are part of a larger programme aiming at characterising iron-oxide rich archaeological artefacts from Corsica, it has not been possible to study all of the Campu Stefanu blocks using PIXE. Nonetheless, five of the blocks were also studied using PIXE to ensure the SEM-EDX measurements for major elements Al, Si, K, Fe were comparable. X-ray diffraction (XRD) spectra of the sediments were also obtained using a Panalytical Aeris spectrometer and phases were identified using Profex software [11]. The collected PIXE spectra were mapped into compositional data using GUPIX and TrauPIXE software [12].

3. Results

Chemical elements for which more than half of the PIXE measurements either had a high statistical error or were below detection limits were discarded from the analysis. An analysis of Pearson correlations indicate that a first subgroup of elements {Ca, P, Y} can be attributed to bone materials in the form of hydroxyapatite, while {Fe, Al, Si, K, Na}, and Ti to a lesser extent, form a coherent set of mineral-forming elements.

The iron concentrations on the skull vary between 2 and 6% in both coloured and uncoloured zones. This raises the possibility that the sediment surrounding the skeleton may also be rich in iron.

The SEM-EDX data indicates that iron proportions within the sediment are relatively high, oscillating between 11.5% and 16%. X-ray diffraction confirms the presence of quartz, albite, hornblende and biotite within the sediment. The latter two are responsible, at least

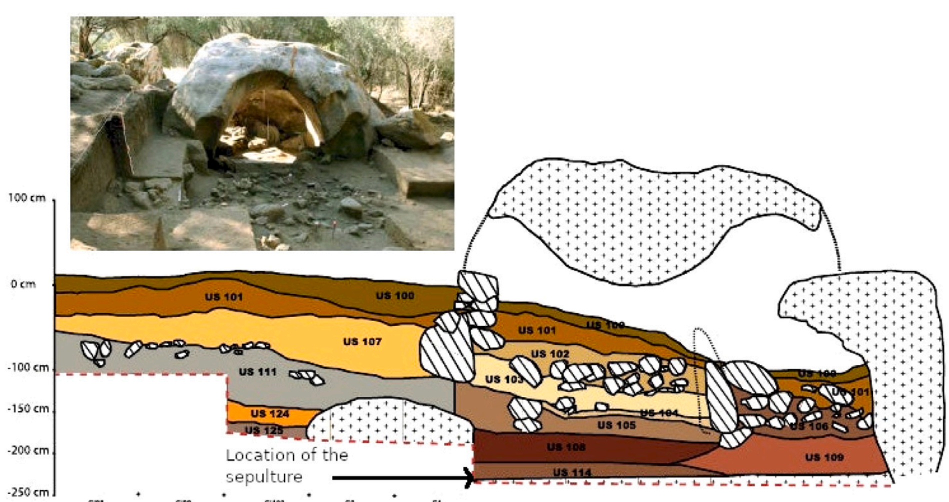

Fig. 2. Stratigraphy of the taffonu hosting the Mesolithic sepulture at Campu Stefanu. After [2].

Fig. 3. Cranium from the Mesolithic sepulture at Campu Stefanu. Photo ML.

in part, for the observed iron concentrations. This composition is consistent with the granitoidic nature of the geological environment of the site, which is dominated by granodiorites. These observations indicate that it is not sufficient to rely solely on iron concentrations to distinguish a potential pigment.

Since a red colouration could be attributable to an haematite content coming from the alteration of ferromagnesian minerals [13], it is necessary to assess the contribution of the sediment on the skull. To mitigate the effect of having variable amounts of sediment and colouring powder, the concentrations of major elements from both analyses were converted using an additive-log-ratio transform [14] and expressed as a ratio to the iron concentrations. In this setting, a strong correlation is seen for the Al and Si log ratios across all sediment measurements (Fig. 4), while the measurements taken from the coloured zones deviate from this regression line. This suggests that the sediment alone is not sufficient to explain the mineral composition in the coloured areas.

Referring again to Fig. 4, the measurements taken in cleaned areas of the block (no 17) provide a close match to those within the coloured zones. This correspondence is further evidenced using the isometric logarithmic ratio (ILR) transform. For a D-dimensional composition $\mathbf{x} = (x_1, \ldots, x_D)$, which is not necessarily closed, the centre-logarithmic ratio (CLR) transform is defined as [14]

$$\mathrm{clr}(\mathbf{x}) = \left[\log \frac{x_1}{g(\mathbf{x})}, \ldots, \log \frac{x_D}{g(\mathbf{x})}\right],$$

where $g(\mathbf{x}) = \sqrt[D]{x_1 \cdot \ldots \cdot x_D}$ is the geometric mean. This transformation amounts to subtracting the mean of the composition, after taking the logarithm. Since each CLR-transformed composition sums up to 0, this enables the representation of the data in a $D-1$ dimensional subspace, for which a suitable orthogonal basis can be constructed [15]. The resulting mapping is called the isometric logarithmic ratio (ILR) transform. Focusing on the $\{\mathrm{Fe}, \mathrm{Al}, \mathrm{Si}, \mathrm{K}\}$ sub-composition, the ILR allows to represent the data in a three-dimensional space (Fig. 5), highlighting the similarity between block 17 and the colouring matter on the skull. The k-means algorithm was subsequently used to separate the data into clusters, with a confidence interval of 95%. In view of this match, it seems likely that the colouration concerned all studied zones of the skull to a variable degree.

The difference and variability in compositions on this block are illustrated in Fig. 6. It shows that this block contains moderate concentrations of iron, between 6 and 10%, and that the internal relative variability is low for each element.

4. Discussion

While the presence of ochre in Mesolithic burials has been reported in many European contexts, a precise assessment permitting the confirmation of the nature of the pigment is often lacking. The possibility that the sediment and its alteration over time may be responsible for a red colouration deserves special attention to draw an accurate portrait of the nature and scale of the phenomenon. This is especially true in granitic environments where the weathering of ferromagnesian minerals can lead to the formation of haematite. The presence of iron oxides is not, then, generally sufficient to assess the presence of a pigment. At Campu Stefanu, the discovery of worn iron-oxide-rich blocks has enabled us to provide evidence for a match with the pigment on the skull. The strong correlation in the SEM-EDX data for the sediment

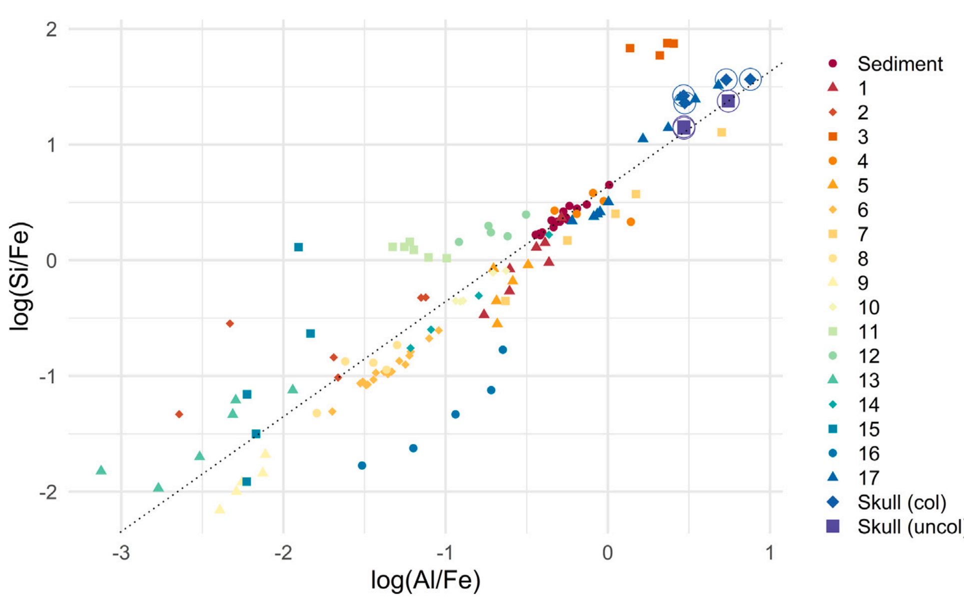

Fig. 4. Logarithmic plot of Si and Al as ratios to Fe concentrations for the sediment, the lithic blocks (1–17) and the skull measurements (circled). The dotted line corresponds to the regression line for the sediment only ($r = 0.968$).

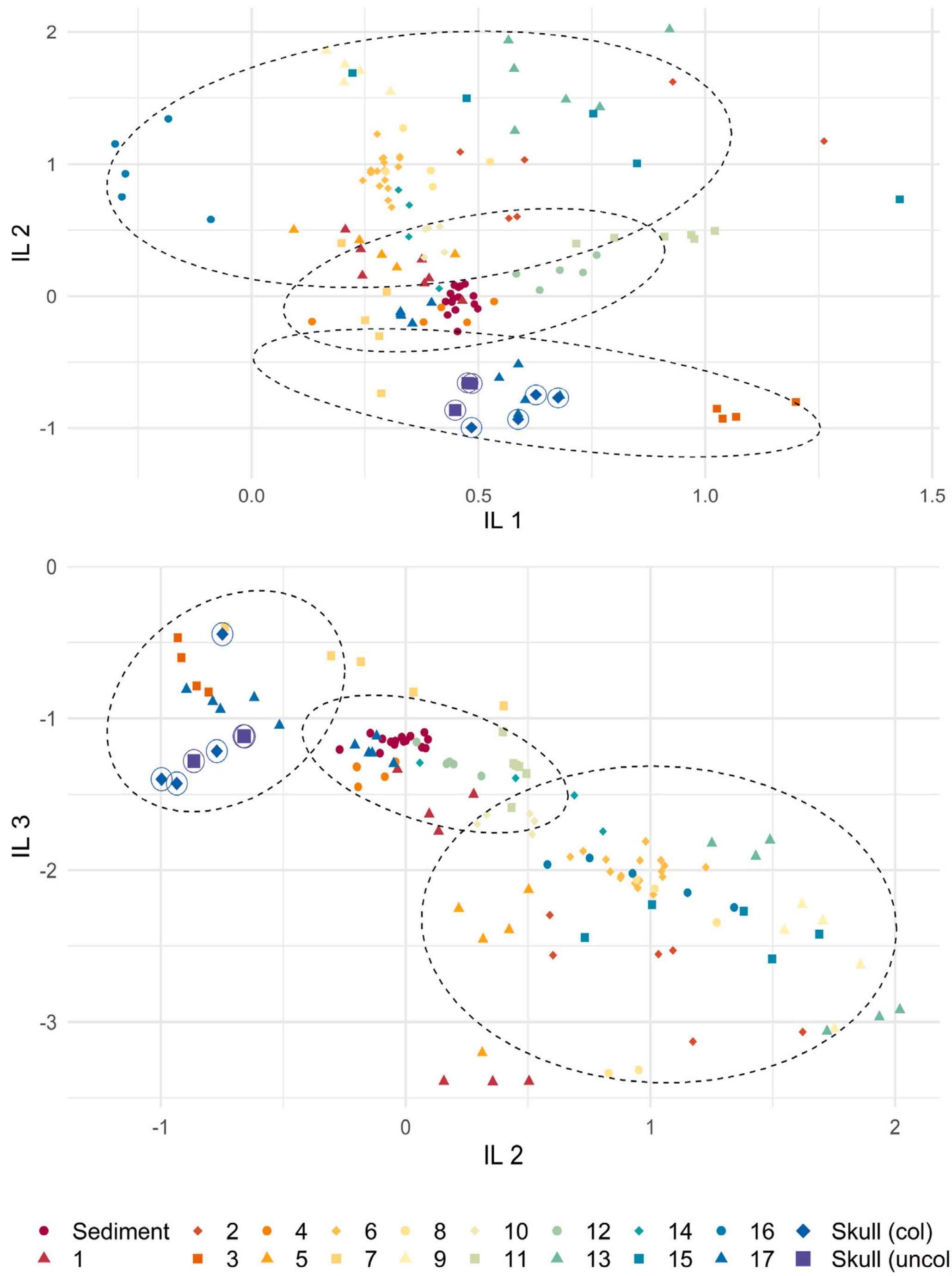

Fig. 5. The compositional data expressed in ILR coordinates for the sediment, blocks 1 to 17 and the coloured and non-coloured zones of the skull. Ellipses at 95% confidence interval around cluster means computed using the *k*-means algorithm.

collected in three distinct spots within the burial provides a means to evaluate its contribution on the skull. It is seen that one of the nodules, after cleaning, provides a better match for the skull pigment than the sediment itself.

Campu Stefanu represents the first and earliest collective burial to be discovered in Corsica and our analysis indicates that ochre played a role in the funerary ritual. It therefore appears that, similarly to other contexts on the Continent (e.g. [7]), this practice is now confirmed at two Mesolithic sites in Corsica. Although it is not currently possible to distinguish at which stage of the burial process the pigment powder was deposited, it appears that only the skull bears evidence of this ritual practice.

Such a selective treatment was also noted at the Mesolithic burial of S'Omu e S'Orku in Sardinia [16] where only the skull, the upper thorax and the knees bore pigment traces. While two zones may have been subjected to treatment, this may also suggest the deceased was originally buried in a crouched position [16].

In Corsica, no pigment was reported by the finders of the bones found within the Mesolithic sepulture at Torre d'Aquila, although a number of ochre blocks were uncovered [3]. Similarly to several late prehistoric archaeological sites from South Corsica [17], the blocks from Campu Stefanu are of a granitic composition (quartz, ferromagnesians, feldspars, iron oxides). Although the question of their precise origin is difficult to assess, it had been noted by R. Grosjean [18] that iron-oxide crusts form within ochred sands on granitic hills near

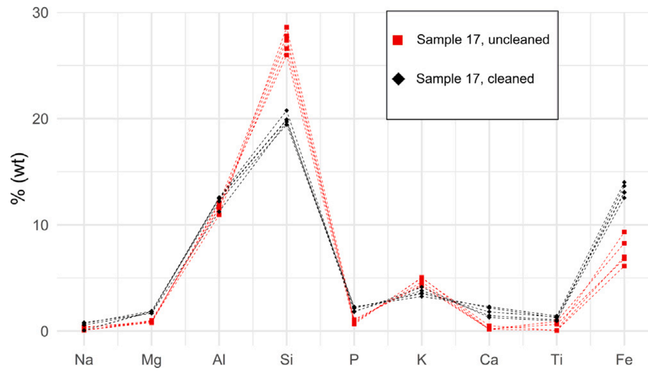

Fig. 6. SEM-EDX measurements on 5 cleaned and 5 uncleaned areas of block no 17.

the entrance of the Taravu valley, around 2 km away from the site as the crow flies. An ongoing programme of characterisation of iron-oxide-rich deposits in Corsica aims to provide further insights into the procurement of these materials throughout prehistory.

CRediT authorship contribution statement

M. Lambert: Study design, Analyses, Archaeological interpretations, Proof reading. **P. Courtaud:** Study design, Archaeological interpretations, Proof reading. **F.-X. Le Bourdonnec:** Study design, Analyses, Proof reading. **Q. Lemasson:** Analyses, Proof reading. **L. Pichon:** Analyses, Proof reading. **F. Leandri:** Archaeological interpretations, Proof reading. **J. Cesari:** Study design, Proof reading. **C. Bressy-Leandri:** Archaeological interpretations, Proof reading. **R. Skeates:** Archaeological interpretations, Proof reading.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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