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Mineralogical and petrographic characterization of the Cerrillo Blanco Iberian sculptures

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Abstract

The archaeological heritage at Cerrillo Blanco (Porcuna, Spain) is made up of 27 sculptural ensembles and hundreds of fragments dated between the seventh and second centuries BC. They represent a fundamental milestone in Iberian art and culture. Despite their relevance, no scientific studies have been carried out to date in order to fully understand the materials, intentions and techniques that led to their creation. This is a study carried out on original pieces from the Archaeological Museum of Jaén using stereoscopic optical microscopy (SOM), polarised optical microscopy (POM), X-ray diffraction analysis (XRD), Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy with energy dispersive x-ray analysis (FESEM-EDX) and spectrophotometry (SF). The results obtained provide new information on the material composition of this important legacy of the Iberian civilization as well as its main alteration factors.

Keywords Cerrillo Blanco, Sculptures, Iberian, Materials, Stone, Analysis

Introduction

The archaeological site of Cerrillo Blanco is located in today's municipality of Porcuna (Jaén, Spain), with the coordinates: latitude 37.88775° and longitude − 4.481556°. This settlement was known in Iberian times as *Ipolka*, the capital of the Turduli, occupying much of the middle and upper Guadalquivir River. It was discovered in 1975 and the excavations were carried out between that year and 1979 [1] (Fig. 1).

The set of sculptures became the property of the Spanish Ministry of Culture and was transferred to the Archaeological Museum of Jaén, where it is now displayed. It is made up of 27 sculptures and hundreds of fragments (Fig. 2), dated between seventh-second centuries BC [2]. Its iconography is based on the history of an aristocratic lineage from Ipolca and boasts of its heroic past, representing the feats of the Iberian prince in various fights with men, animals, mythological beings and ceremonial figures [3, 4].

The Cerrillo Blanco complex is at the same technical level as the best ancient sculpture in the Mediterranean [5]; it may be considered one of the best in the pre-Roman West and a fundamental milestone in Iberian art. The sculptures' extraordinary carving and homogeneity initially led them to be attributed to a Greek sculptor, but recent research indicates that they are the work of a high-level sculpture workshop set up in the area [6].

The pieces studied denote a complex production process that gives many clues as to the work involved in

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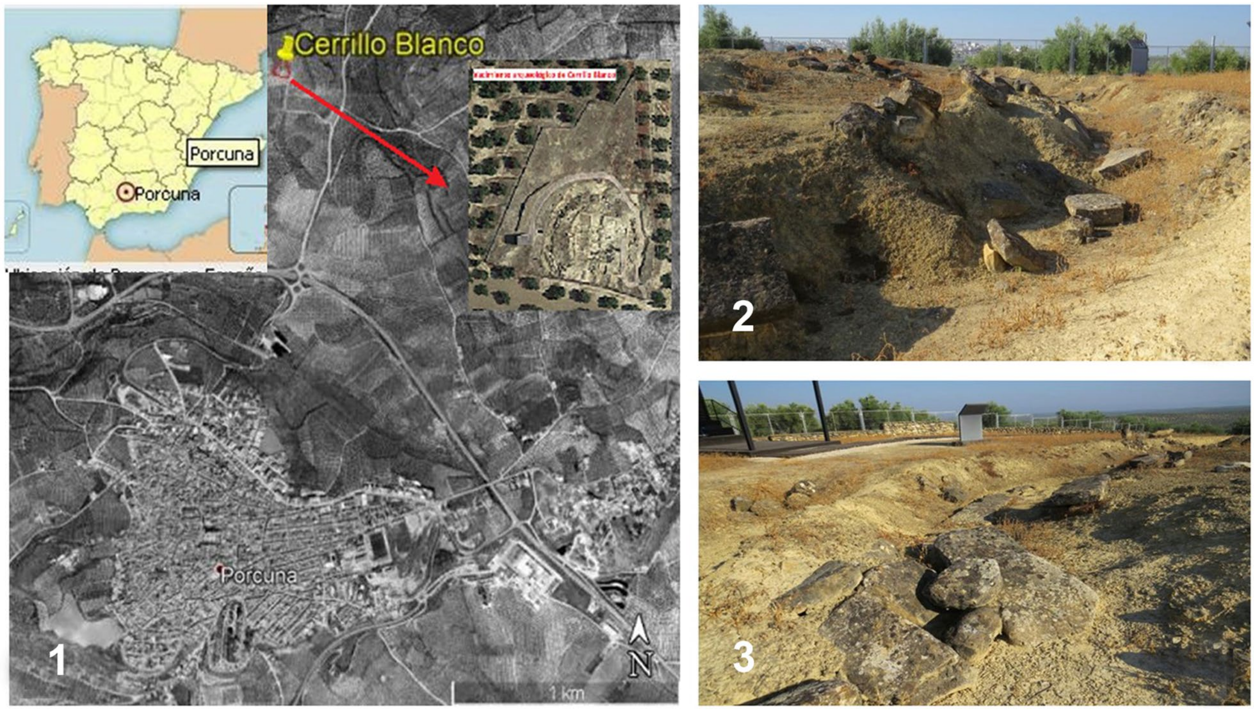

Fig. 1 The archaeological site and its location (1). Southwest and northwest views of the ditches where the sculptures were found (2,3)

Fig. 2 Sculptures belonging to the Cerrillo Blanco complex. Double-armoured warrior (1), offerer with caprids (2), bovine calf (3)

creating them. It took a meticulous manufacturing job to define the contours, minor anatomical details, clothing, weapons, boxes for metal elements and masonry mountings and marks [7]. Most of the sculptures have been made in one piece and their raw material is large limestone, in some cases measuring over 150 cm in width or length. Everything indicates that it comes from the environs of the Porcuna geological unit, in the middle of the Guadalquivir depression, which is rich in sedimentary rocks from the Upper Miocene and Quaternary, less than ten million years old [8]. Stone has been used in the area as a civilising element for more than fifteen thousand years in order to manufacture everything from defensive and hunting tools to ashlars for defensive or residential use [9].

Although such cultural heritage is highly relevant, a complete study of its materials has not been carried out to help understand and preserve it. These pieces have been previously studied for the purpose of a past restoration [10]. This work indicates that the rock corresponds a "calcarenite very rich in globigerinas composed mainly of calcite, quartz and of phyllosilicates traces. The present article aims to help improve knowledge of this outstanding legacy of Iberian culture. The materials that make up the sculptures of Cerrillo Blanco have been studied, concentrating the investigation on the characterization of the stone and its alteration factors.

Material and methods

Sampling

The choice of the archaeological material under study comes from the Museo Provincial de Jaén (Jaén Provincial Museum, Spain). The homogeneity of the materials and alterations in the sculptures have made it possible to carry out a sampling plan concentrating mainly on the pieces conserved in the museum's storage, so as not to cause alterations to the pieces that have already been restored.

Each piece's reference number is described in the museum's Domus collections and the sampling was carried out following the UNE-EN 16085 standards [11]. Samples were taken to study the stone and its possible alterations (Table 1). For the mineralogical and petrographic study, three representative samples of the set were chosen: 0365, 0353 and 1368. Coloured stains can be seen on piece 0365; there is a polished surface on piece 0353; and a slightly polished surface on piece 1368 altered with a whitish appearance and orange spots, probably produced by the migration of salts and terrigenous components when it lay buried. Two samples were taken per piece, identified by the inventory number, and a number in parentheses to differentiate the type of sample: (1) superficial scraping and (2) fragment (Fig. 3).

Orange stains were frequently observed on the pieces' surface in the field study. To study their composition, samples 0530 and 0632 were chosen, which belong to the inner side of the sculpture. The samples were obtained by scratching the surface of the coloured area. Occasional

Table 1 Materials and analytical techniques used in each study of the archaeological site at Cerrillo Blanco

Archaeological material	Reg no	Description	Analytical techniques					
			OM	POM	FTIR	RXD	FESEM-EDX	SF
Stone	0365	Indeterminate fragment						
	0353	Fragment of human thigh						
	1368	Fragment of amorphous sculpture						
Orange chromatic stains	0530 0632	Amorphous fragment with orange stains						
Brown inclusions	0641 1273	Amorphous fragment						

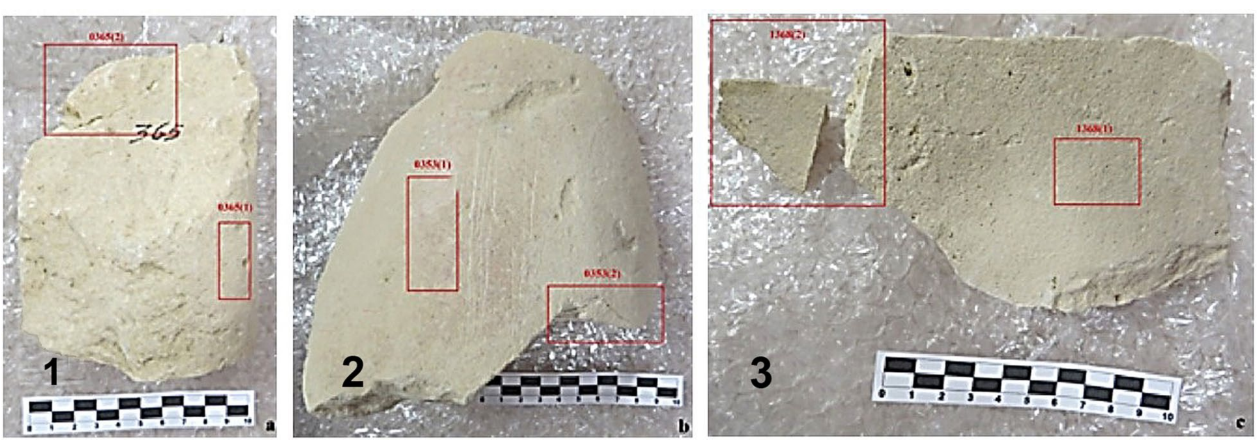

Fig. 3 Pieces studied from the sculptural ensemble from Cerrillo Blanco. 0365 (1), 0353 (2) and 1368 (3). Sampling: (1) surface dust and (2) fragment. Scale in cm

brown inclusions, common in the group, were also studied in two sculpture fragments: 0641 and 1273 (Fig. 4). As in the previous case, special attention was paid to obtaining samples of the coloured deposit with a scalpel, without reaching the substrate, so as not to contaminate them with components from the stone. Remains of materials from previous restoration work carried out on the pieces were also studied.

Methods

The stone's mineralogical, textural and structural composition was studied using the following analysis techniques (Table 1): stereoscopic optical microscopy (SOM), polarized optical microscopy (POM), X-ray diffraction (XRD) to make a quantitative estimate of the mineral phases of the samples, Fourier-transform infrared spectroscopy (FTIR) to determine the inorganic and organic compounds present by identifying their functional groups, field emission scanning electron microscopy with energy dispersive x-ray analysis (FESEM-EDX), which provides information on the elements in the sample and topographical images of the inorganic material; and finally spectrophotometry (SF) to quantitatively determine the materials' colour and chromatic variation [12–14]. The samples and the analytical conditions in each technique were prepared as follows:

Samples 0635 and 1273 were studied by SOM. A Leica S8AP0 (X10-X80) optical microscope equipped with an incident/transmitted illumination system and light polarisation system was used, as well as a Leica Digital FireWire Camera (DFC). Leica Application Suite (LAS) was the software used.

The fragments extracted from the stone samples 0365, 0632 and 1368 were observed under a Carl Zeiss Jena Pol-U polarized light optical microscope equipped with a Nikon D7000 digital microphotography unit, for mineralogical and textural identification.

To study them, thin slices were prepared, and half of the slices were stained red with alizarin to discover the nature of the carbonate present (calcite or dolomite).

In order to know the mineralogical composition of the stone, a small amount of material was extracted from the inner side of the sample fragments 0365, 0632 and 1368 so as to avoid contamination from a possible surface treatment on the sculptures. The samples were ground in an agate mortar until a powder size of less than 0.053 mm was obtained. The analysis was carried out using an X'Pert PRO PANalytical diffractometer with CuKα radiation = 1.545 Å. The working conditions were: 40 kV, 30 mA and interval 2θ studied from 3° to 70°. The data acquired was interpreted with HighScore software (Malvern Panalytical, UK).

The stone samples 0365, 0632 and 1368 were ground in an agate mortar until a powder size of less than 0.053 mm was obtained. A potassium bromide (KBr) tablet was prepared, pressed at 10 tons for 10 s in a Perkin Elmer hydraulic press. The analysis by FTIR was carried out with a Bruker ALPHA portable spectroscope equipped with reflectance, diamond ATR and transmittance accessories. The software used was Opus with the following operating parameters: 4 cm^{-1} resolution, 256 scans, 7500–400 cm^{-1} range and reflectance mode in a gold mirror.

The coloured inclusion sample 1273 was analysed using a Vertex 70 FTIR spectroscope (Bruker Optics) with a detector with temperature stabilised by FRDGTS (fast recovery deuterated triglycine sulphate) Bruker Óptica®, with an MKII Golden Gate attenuated total reflectance mode (ATR) accessory. The working conditions were: number of scans: 32, with a resolution of 4 cm^{-1}. The data was processed with OPUS/IR software, version 5.0.

Fig. 4 Orange deposits in fragment 0632 (1). Oxide inclusions in piece 1273 (2)

The samples 0632 and 1273 were studied on a pin-stub holder, a metallic disc that conducts electricity on which a double-sided adhesive with carbon is placed to make it conductive, too.

A Jeol JSM 6300 scanning electron microscope was used, running with a Link-Oxford-Isis X-ray field emission microanalysis system. The analytical conditions were 20 kV voltage, 2×10 9A filament current, and a working distance of 15 mm. The analysis was performed with a Jeol JSM 6300 scanning electron microscope operating with a Link-Oxford-Isis X-ray microanalysis system. The analytical conditions were: 20 kV accelerating voltage, 2×10-9A beam current and 15 mm as the working distance. Quantification was carried out using the ZAF method for correction of interelement effects [an average of 20 individual analyses based on three factors: atomic number (Z), absorption (A) and fluorescence (F)]. Meanwhile, specific measurements were made on individual grains and aggregates to obtain an estimate of their stoichiometric composition.

A Konica-Minolta CM-700d spectrophotometer (SF) was used following the UNE-EN 15,886 standard [15]. To study the colour, the CIEL*a*b* system was chosen, where L* (luminosity) varies from black (with a value of 0) to white (with a value of 100) and the chromaticity parameters vary from -60 to 60, where a* corresponds to red (+a*) and green (–a*), and b* to yellow (+b*) and blue (–b*). The measurement conditions were as follows: measurement area 3 mm^2, standard illuminant D65 and 10° observer with SCI mode and wavelength range between 400 and 700 nm [16–18]. Two measurements were taken per sample. The values of L*, a* and b* were obtained on a fresh cut of the fragments extracted from the stone samples 0365, 0632 and 1368, making use of the surface cut to prepare the thin slices, so as to avoid possible contamination due to the sculptures being buried [19].

Results and discussion

Characterization of the stone

Polarised optical microscopy (POM)

The petrographic study of the sculpture samples 0365(2), 0353(2) and 1368(2) coincides in their mineralogical composition and in their texture, so it is the same type of stone.

The three samples have given similar results, so only the results obtained for the fragment from archaeological piece 0365(2) are shown (Fig. 5). The sculptures' raw material is mainly composed of a planktonic foraminifera mud and to a lesser extent of benthic foraminifera homogeneously spread throughout the carbonate matrix, and a negligible terrigenous component. The latter is exclusively composed of metamorphic quartz with subrounded grains. The rock can be classified as a bioclastic limestone [20].

Some reddish-brown iron oxide-hydroxides with a single polariser were observed. Plagioclases with albite-type twinning and some sparitic calcite crystals with high-interference colours were also identified. The porosity is predominantly of the intraclastic type, though larger pores of an irregular morphology (interclastic porosity) were occasionally observed. The matrix is micritic,

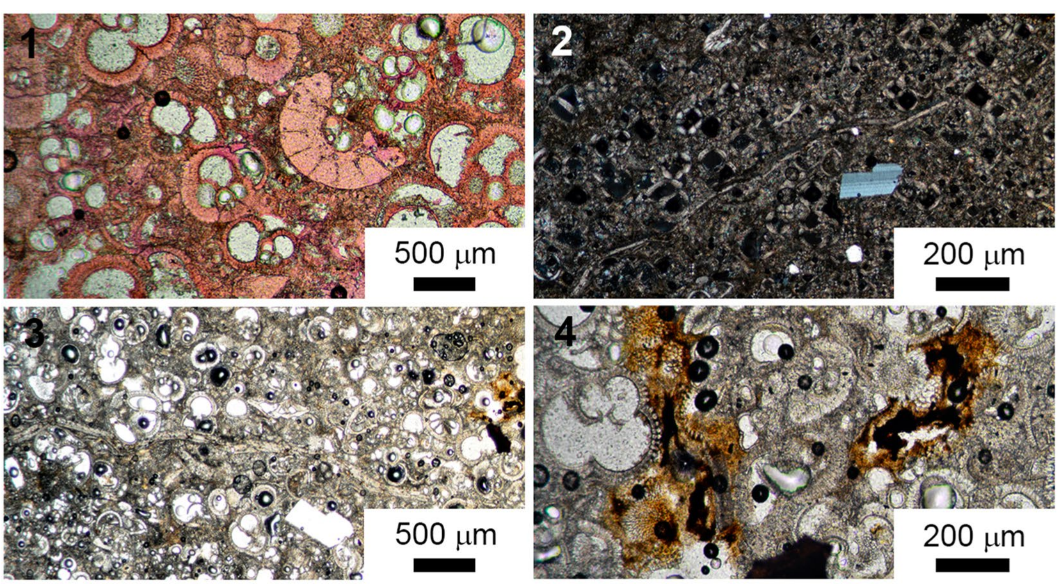

Fig. 5 Sample 0365 Micritic calcarenite rock with a predominance of microfossils. 1: 3.2×field ≈ 4.2 mm (1); detail at 10×field ≈ 1.45 mm (2), 3.2×field ≈ 4.2 mm (3); and 10×field ≈ 1.45 mm (4)

and dolomite was not detected in the part of the sample stained with alizarin (Fig. 5).

XRD analysis

In the samples from the sculptures (0365, 0353 and 1368, from both the surface of the fragment and from the inner side), the average phase content indicates that there is 93.88% calcite and 5.64% quartz. Exceptionally, traces of feldspars are also observed in 0.82% in sample 0353(2), specifically orthoclase (Table 2).

The comparison of the mineral phases of the stone material from the surface and from the piece's inner side is intended to search for minerals in low quantity, mainly on the surface, caused by contamination from the terrain, since they are archaeological pieces that have been buried for approximately 2,500 years. No traces of other minerals have been detected, but it was observed that the amount of compounds present on the surface is homogeneous—unlike inside the piece—which could be caused by a surface polishing treatment on the sculptures.

Table 2 Composition of the mineral phases (%)

Sample	Cal %	Qtz %	Or %
0365(1)[a]	95.84	4.16	
0353(1)	95.86	4.14	
1365(1)	94.55	5.45	
0365(2)	97.67	2.33	
0353(2)	83.50	13.67	0.82
1365(2)	95.88	4.12	

Sculpture samples: 0365, 0353 and 1368

Mineral phases: *Cal* calcite; *Qtz* quartz; *Or* orthoclase

[a] Different sampling of the same piece: (1) surface dust and (2) fragment

FTIR

In the sculpture samples' IR spectrum, the same organic and inorganic compounds have been identified on both the surface of the pieces (Fig. 6) and the inner side. Bands of mineral compounds predominate: characteristic bands of calcite were identified at 1433 cm^{-1}, 875 cm^{-1} and 713 cm^{-1}; and silicates at 1000 cm^{-1} and 1100 cm^{-1}; as well as low intensity bands of organic compounds.

The designations of bands associated with the organic compounds were made in accordance with the interpretations suggested by Morrison [21]. The ester C=O band is found at 1735 cm^{-1}, the amide CH band at 1640 cm^{-1} and the C–O tension band of polysaccharides at 1030 cm^{-1}. The functional groups, associated with the sculpture's bands of organic compounds, could indicate the application of a protective, polishing or pictorial treatment on the sculptures' surface.

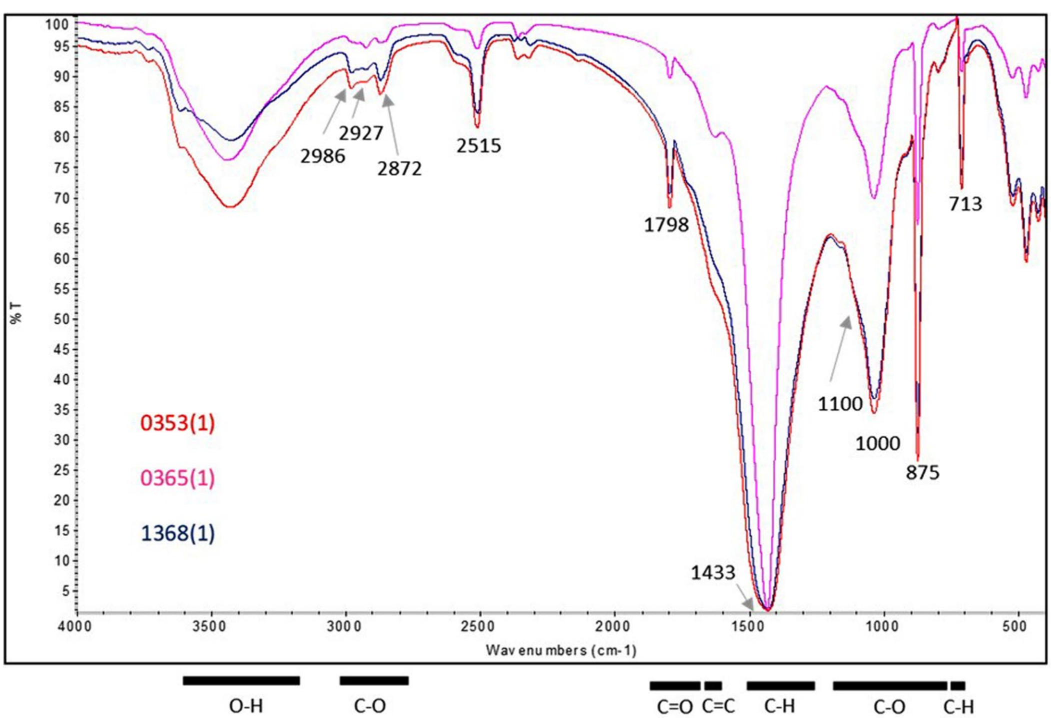

Fig. 6 Infrared absorption spectrum of inorganic and organic matter from samples 0365(1), 0353(1) and 1368(1). Characteristic bands of calcite were identified at 2515 and 1798 cm^{-1} as well as low intensity bands of nonspecific organic compounds at 2872, 2927 and 2986 cm^{-1}

Spectrophotometry
The chromatic and luminosity difference between the stone fragments studied (1368, 0363 and 0365) is very low and not detectable with the naked eye (Fig. 7).

Coloured deposits
This section studies the composition and origin of the alterations due to orange stains that can frequently be found in fragments of sculpture, and which may come from the remains of polychromy, the migration of ferrous minerals in the site's soil or from dyeing substances produced by microorganisms. SOM, FESEM-EDX and FTIR analysis was carried out to identify the morphology of the coloured stains and characterise their elemental composition in samples 0530 and 0632. The results for piece 0632 are shown.

Stereoscopic optical microscopy (SOM)
The images obtained by SOM with episcopic illumination (Fig. 8) show this sample's micromorphology. There are irregular microcrystalline aggregates of biocalcarenite rock (size approx. 200 μm) and brown-black and ochre aggregates associated with clay minerals and iron oxides [22].

FESEM-EDX
In the FESEM analysis, small crystals (< 1 μm) with a laminar habit were identified [23] that are associated with clay minerals and/or hematite. The presence of clay minerals was confirmed by the presence of Si, Al, Mg and K, and the presence partially hydrated calcium sulphate by the S signal (Fig. 9). The percentage higher than 28.37% of Fe found in some specific analyses indicates the presence of hematite.

Coloured inclusions
In the archaeological site, metallic elements have been found close to the sculptures' burial area, so it is thought that the brown inclusions could be due to corrosion phenomena owing to the stone surface being in contact with them [24]. The composition and structure of these inclusions were studied in samples 0641 and 1273 by SOM, FESEM-EDX and FTIR spectroscopy. Both have given

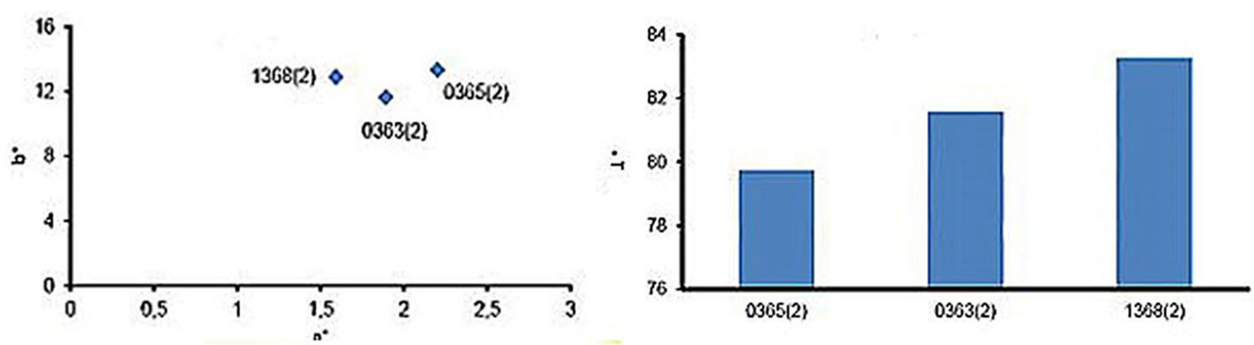

Fig. 7 Variation of chromaticity (left) and luminosity (right) for the fragments from the Iberian pieces from Cerrillo Blanco (1368, 0363, 0365)

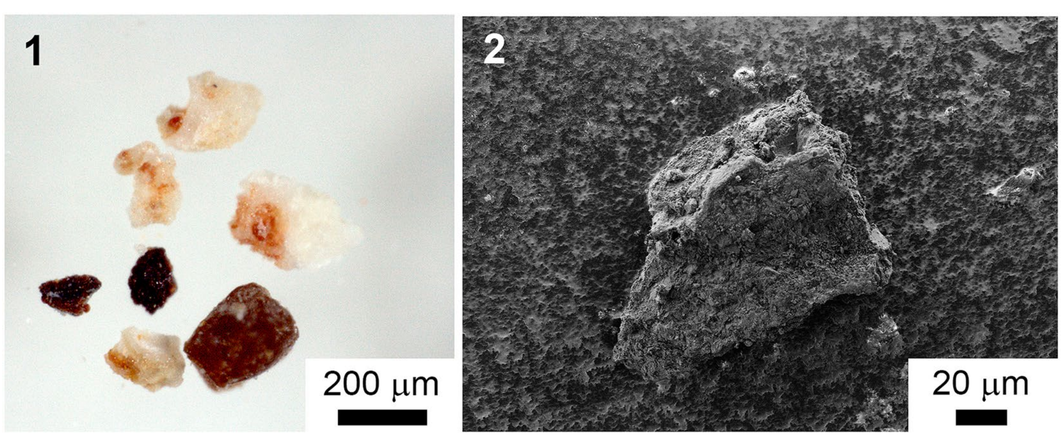

Fig. 8 Episcopic illumination shows 0632 (1). FESEM Image in secondary electrons acquired at 3 kV. Sample 0632 (2)

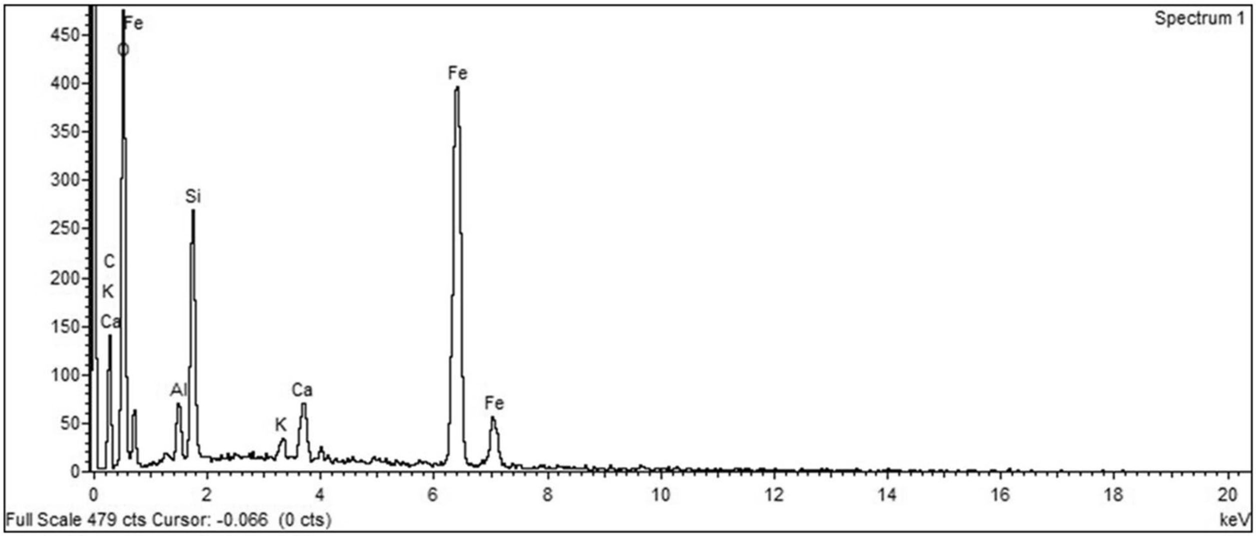

Fig. 9 X-ray spectra obtained from an area of the sample 0632 (100 × 100)

very similar results, so only the results obtained in sample 1273 are shown.

Stereoscopic optical microscopy (SOM)

The images obtained by SOM with episcopic illumination show this sample's micromorphology. There are irregular microcrystalline aggregates with an orange hue (maximum dimension approx. 800 µm).

FESEM-EDX

The images obtained by secondary electrons with FESEM show these same aggregates, mainly made up of particles smaller than 1 µm. Acicular habit crystals with a length in the range of 200–400 µm were identified, that are associated with clay minerals and crystals of irregular and laminar morphology, which in turn are associated with whewellite/weddellite, goethite and hematite (Fig. 10).

Structures of a microbiological nature or coccoliths have also been identified in the sample. These form the external mineralised structure (calcite) or cocosphere of coccolithophore-type marine algae, probably *Calcidiscus leptoporus,* which are also part of the biocalcarenite rock that makes up the structures.

The X-ray spectrum obtained from one of these aggregates gives the average elemental composition of the sample. The percentage higher than 25% of Fe in the sample confirms the majority presence of iron oxides. The presence of aluminosilicate-type minerals is also confirmed by the presence of Si, Al, Mg and K in low proportions. The Ca content is associated with calcite or calcareous materials (Table 3).

FTIR

The IR spectrum obtained from the sample (Fig. 11) is dominated by the characteristic absorption bands of whewellite/weddellite, calcite and clay/plagioclase and quartz/amorphous silica-type minerals, which are mainly associated with the sculpture's stone base, given the similarity of the corresponding IR spectra [25–27]. Goethite and hematite have also been identified. Table 4 shows the characteristic bands of the minerals identified.

Restoration work

Previous reports about restoration of the Cerrillo Blanco sculptures indicate that the most eroded areas of the sculptures were consolidated with Paraloid B72 [10]. Using FTIR spectroscopy, the study describes the presence of an organic compound compatible with an acrylic resin such as Paraloid [28, 29] in most of the surface samples taken from the entire complex, its use not being concentrated on specific areas.

The application of Paraloid B72 on the sculptures from Cerrillo Blanco does not imply a deterioration of the original material in the short-term, due to the low quantity applied [30]. No relevant chromatic difference has been observed between the untreated samples and the consolidated samples. Even so, it is considered to be an unnecessary treatment due to the good state of conservation of the pieces since their discovery. That treatment has meant a setback in the scientific characterisation of the sculptures' materials and technologies due to the fact that the consolidant has hindered the analyses carried out on most of the samples, and has even concealed the presence of a possible organic binder [31].

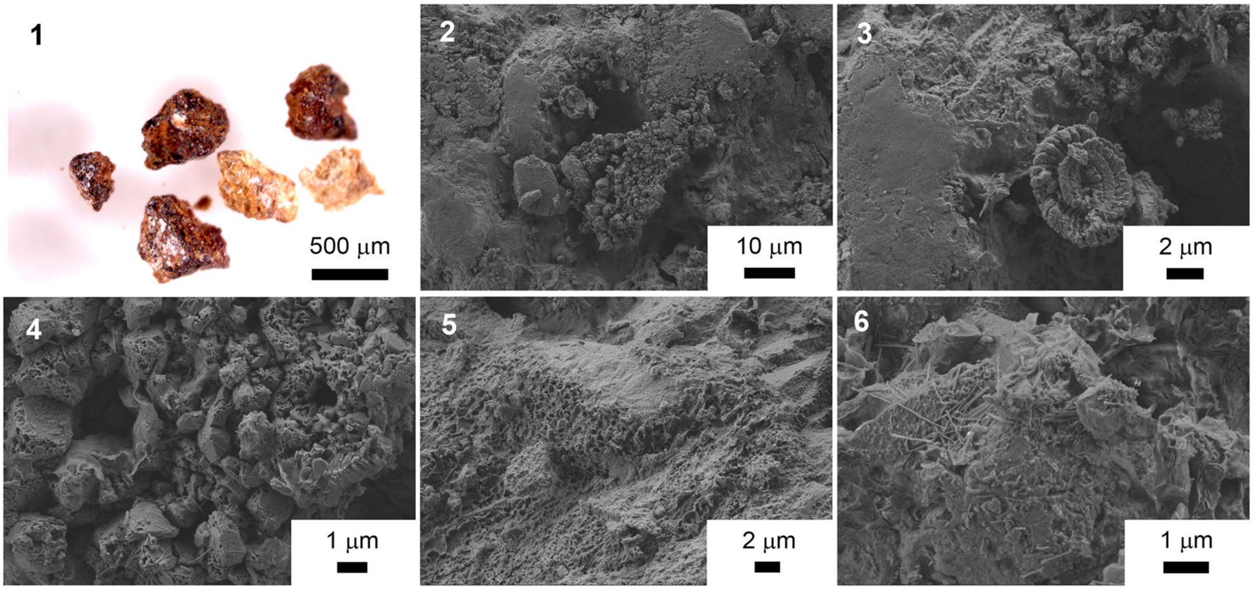

Fig. 10 Episcopic illumination of sample 1273 (1). Images in secondary electrons acquired at 3 kV: General image of the sample (2), Detail of a microorganism (3), Equidimensional carbonate crystals (4), Lamellar aggregates in the form of a honeycomb (5), Acicular crystals of clay (6)

Table 3 Elemental composition (expressed as % of elements) obtained by FESEM-EDX from sample 1273

Element	Elemental composition (% mass)
C	15.88
O	50.14
Mg	0.59
Al	0.41
Si	5.77
Ca	1.73
Fe	25.47
Total	100

Conclusions

From the study carried out on the Cerrillo Blanco Iberian sculptures (Porcuna, Jaen, Spain) is concluded:

1. For the elaboration of the sculptures has been used a bioclastic limestone, composed mainly of a planktonic foraminifera mud, and to a lesser extent of benthic foraminifera, homogeneously spread out in the carbonate matrix, and of quartz in a tiny proportion. There are also traces of phyllosilicates and some reddish-brown iron oxide-hydroxides. It is known as white rock due to its homogeneous light beige colour in all of the sculptures, as shown by the spectrophotometric analysis. All Iberian stone art uses similar

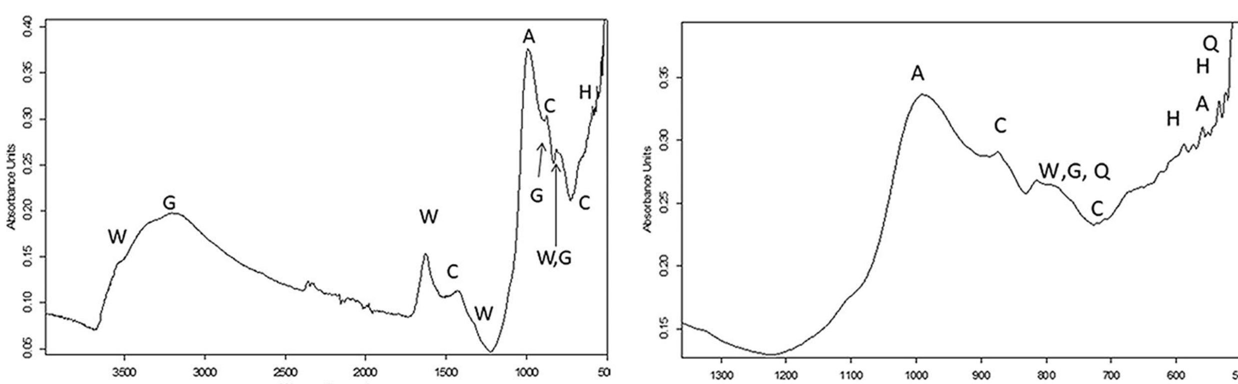

Fig. 11 IR analysis from of sample 1273. General IR spectrum and detail in the 900–500 cm^{-1} region. *A* clays/plagioclase, *C* calcite, *H* hematite, *W* whewellite/weddellite, *Q* quartz, *G* goethite

Table 4 Wavelength ratio at 1600 cm^{-1} for the minerals identified in samples 0641 and 1273

Minerals identified	IR bands (cm^{-1})
Calcite	2873 (vibration $2v_3$ carbonate group) 2515 (vibration $2v_2 + v_4$ carbonate group) 1798 (vibration $2v_1 + v_4$ carbonate group) 1425, 1397 (v_3, symmetric stretching vibration of the carbonate group) 878 (v_2, out-of-plane bending vibration of the carbonate group) 710 (v_4, out-of-plane stretching vibration of the carbonate group)
Whewellite/Weddellite (calcium oxalate mono- and dihydrate)	3541, 3400 (stretching vibration of hydroxyl groups) 1627 (COO group asymmetric stretching vibration) 1324 (COO group asymmetric stretching vibration) 789 (-COO group vibration)
Clay/plagioclase minerals	3380 (stretching vibrations of water) 994 (stetching vibration of Si–O silicate bonds) 910 (internal hydroxyl deformation vibration) 542 (OH bending vibration)
Quartz	1089 (stetching vibration of Si–O silicate bonds with E symmetry) 798, 778 (Qtz double) 512 (Si–O bond deformation vibration)
Goethite	3185 (stretching vibration of hydroxyl group) 892 (shoulder) (OH bending vibration) 790 (shoulder) (OH bending vibration)
Hematite	524 (an-isodimensional Fe–O bond stretching vibration) 557 (isodimensional Fe–O bonds' stretching vibration)

types of this sedimentary rock, which are abundant in the geological area of the Mediterranean and close to this culture's settlement sites. It has optimal characteristics for workability due to its low hardness (3 on the Mohs scale), which allows it to be carved relatively easily, and it is still an artistic material in great demand today.

2. The Porcuna area, where Cerrillo Blanco is located, is formed by alternating sandstone and marl. Specifically, the southwest of the town sits on an outcrop of tertiary formations from the Upper Miocene (Andalusian), where calcareous sandstones rich in organic fragments are characteristic [IGME 2023]. It is therefore very probable that materials that makes up the sculptures comes from this area, where there are still quarries in operation, such as those of Porcuna, Santiago de Calatrava or Mercadillo, close to the Iberian city of Ipolca and the archaeological site.
3. The analyses carried out show the presence of oxides deposited on the samples' inner surfaces, which rules out the possibility that they belong to a polychrome layer, and implies that the orange oxides form part of the stone's composition due to contact with the soil where the sculptures were deposited, owing to the influence of climatic conditions.

Occasional inclusions of approximately 0.5 to 1 mm thick can also be seen, which is an exceptional form of alteration, albeit representative of the general state of conservation of the complex. The presence of clay minerals and crystals of irregular and laminar morphology, associated with whewellite/weddellite, goethite and hematite in contact with the stone for a long time, would explain the high percentage of iron content in the sample. It could also be associated with some type of clay from the ground that has crystallized on the surface.

There are still matters to be studied regarding the possible existence of polychromy, metallic elements added to the sculptures or used to carve them, deterioration of anthropic origin (marks and incisions), origin of stone materials and biodeterioration factors, which will be the subject of further investigation.

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Author contributions
Conceptualization and work design, MBR-R, and JR-N; methodology and analyses, TD-C, G.C. and MBR-R; writing—original draft preparation review and editing, JR-N; project administration, funding acquisition, FB-G. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analysed during this study are included in this published article [and its supplementary information files].

Declarations

Competing interests
The authors declare that they have no competing interests.

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References

1. González Navarrete J, Witte P. (1987). Escultura ibérica de Cerrillo Blanco, Porcuna, Jaén (Iberian sculpture of Cerrillo Blanco, Porcuna, Jaén. In Spanish). Jaén: Diputación provincial de Jaén, Instituto de Cultura; 1987. ISBN: 84–505–5150–1
2. Negueruela Martínez, I. Los monumentos escultóricos ibéricos del Cerrillo Blanco de Porcuna (Jaén) (The Iberian sculptural monuments of Cerrillo Blanco at Porcuna (Jaén). In Spanish). Madrid: Ministerio de Educación Cultura y Deporte; 1990: 447p. ISBN: 84–7483–668–9
3. Olmos, R. Los grupos escultóricos del Cerrillo Blanco de Porcuna (Jaén). Un ensayo de lectura iconográfica convergente (The sculptural groups of Cerrillo Blanco at Porcuna (Jaén). A convergent iconographic reading essay. In Spanish). Madrid: Instituto de Historia; 2002: 107–122. https://doi.org/10.3989/aespa.2002.v75.130
4. Blanco A. Las esculturas de porcuna I, Estatuas de guerreros (The sculptures of porcuna I, Statues of warriors. In Spanish). BRAH 1987; 184/3: 405–445.
5. Blázquez Martínez JM, García Gelabert MP. Relaciones entre la Meseta y Oretania (Relations between the Meseta and Oretania. In Spanish). Complutum. 1992;2–3:45–55.
6. Vallejo Delgado LE. Los conjuntos escultóricos de Cerrillo Blanco de Porcuna (Jaén): procesos, técnicas y grafismos. Un ensayo perceptivo y experimental sobre la mirada de los escultores (The sculptural ensembles of Cerrillo Blanco at Porcuna (Jaén): processes, techniques and graphics. In Spanish). A perceptive and experimental essay on the gaze of sculptors. Granada: Universidad de Granada; 2012: 60–61.
7. Chapa Brunet T, Vallejo I, Belén B, Martínez-Navarrete MI, Ceprián B, Rodero A, Pereira J. El trabajo de los escultores ibéricos: un ejemplo de Porcuna (Jaén) (The work of Iberian sculptors: an example from Porcuna (Jaén). In Spanish). Trab. de Prehist. 2009; 66(1): 161–173. https://doi.org/10.3989/tp.2009.09018
8. IGME. Mapa geológico de España 1:50.000. Magna 50, hoja 925 (Porcuna). Madrid: Ministerio de Industria; 2023. https://info.igme.es/cartografiadigital/geologica/Magna50Hoja.aspx?Id=925&language=es
9. Vallejo Delgado LE. Paisajes de la piedra. Técnicas de la cantería y la escultura íbera. Porcuna (Jaén) (Stone landscapes. Stonemasonry techniques and Iberian sculpture. Porcuna (Jaen). In Spanish). Madrid: Playa de Ákaba; 2017: 23–49.
10. Espinosa Gaitán J, Sameño Puerto M, Gutiérrez Montero F (2001). Esculturas ibéricas del Museo de Jaén. Caracterización de materiales y evaluación de productos de tratamiento (Iberian sculptures from the Museum of Jaén. Characterization of materials and evaluation of treatment products. In Spanish). 3rd Congreso de Arqueometría. Sevilla, 1999: 369–378. http://hdl.handle.net/11532/307027
11. UNE-EN 16085. Conservation of Cultural property - Methodology for sampling from materials of cultural property - General rules. Madrid: AENOR. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0053258
12. Betancourth D, Gómez JF, Mosquera JC, Mejía LT. Análisis por difracción de rayos X de rocas provenientes de región esmeraldífera (X-ray diffraction analysis of rocks from the emerald región. In Spanish). Sci Tech. 2010;1(44):409–13. https://doi.org/10.22517/23447214.1871.
13. Brunetti B, Sgamellotti A, Clark AJ. Advanced techniques in art conservation. Acc Chem Res. 2010;43:693–4. https://doi.org/10.1021/ar100072f.
14. Matteini M, Mazzeo R, Moles A. Chemistry for restoration. Painting and restoration materials. 1st ed. Firenze: Nardini Editore; 2016. p. 25–137.
15. UNE-EN 15886. Conservation of cultural property—Test methods—Colour measurement of surfaces. Madrid: AENOR; 2011. https://www.une.org/encuentra-tu-norma/busca-tu-norma/norma?c=N0046629
16. Wyszecki G, Stiles WS. Color Science. Concepts and methods. Quantitative data and formulae. 2nd ed. Hoboken: John Wiley and Sons; 2006. p. 976.
17. Fraser B, Murphy C, Bunting F. Color Management: Industrial-Strength Production Techniques. 2nd ed. San Francisco: Peachpit; 2005. p. 582.
18. Völz HG. Industrial Color Testing Fundamentals and Techniques. 2nd ed. Hoboken: John Wiley and Sons; 2003. p. 388.
19. May-Crespo J, Martínez-Torres P, Quintana P, Alvarado-Gil J, Vilca-Quispe L, Camacho N. Study of the effects of heating on organic matter and mineral phases in limestones. J Spectrosc. 2021. https://doi.org/10.1155/2021/9082863.
20. Folk RL. Petrology of sedimentary rocks. 2nd ed. Austin: Hemphill Publishing Company; 1980.
21. Morrison RT, Boyd RN. Organic chemistry. 6th ed. Hoboken: Prentice all; 1992. p. 978–0136436690.
22. Madejová J, Kečkéš J, Pálková H, Komadel P. Identification of components in smectite/kaolinite mixtures. Clay Miner. 2002;37:377–88. https://doi.org/10.1180/0009855023720042.
23. Feller RL, Bayard. Examination of pigment particles with polarizing microscope. In: Feller RL, editor. Artists'pigment. A handbook of their history and characteristics, (1). Washington: National Gallery of Art; 1986. p. 285–98.
24. Doménech A, Lastras M, Rodriguez F, Osete L. Mapping of corrosion products of highly altered archaeological iron using voltammetry of microparticles. Microchem J. 2013;106:41–50. https://doi.org/10.1016/j.microc.2012.05.002.
25. Farmer VC. The infrared spectra of mineral. 1st ed. London: Mineralogical Society of Great Britain and Ireland; 1974. p. 539. https://doi.org/10.1180/mono-4.
26. Gunasekaran S, Anbalagan G, Pandi S. Raman and infrared spectra of carbonates of calcite structure. J Raman Spectrosc. 2006;37(9):892–9. https://doi.org/10.1002/jrs.1518.
27. Silva CE, Silva LP, Edward HGM, de Oliveira LF. Diffuse reflection FTIR spectral database of dyes and pigments. Anal Bioanal Chem. 2006;2006(368):2183–91. https://doi.org/10.1007/s00216-006-0865-8.
28. Shelton SY, Chaney DS. An evaluation of adhesives and consolidants recommended for fossil vertebrates. In: Leiggi P, May P, editors. Vertebrate paleontological techniques, 1. Cambridge: Cambridge University Press; 1993. p. 35–45.
29. Pinto AF, Rodrigues JD. Stone consolidation: the role of treatment procedures. J Cult Herit. 2008;9(1):38–53. https://doi.org/10.1016/j.culher.2007.06.004.
30. Lazzari M, Chiantore O. Thermal-age in paraloid acrylic protective polymers. Polymer. 2000;41:6447–55. https://doi.org/10.1016/S0032-3861(99)00877-0.
31. Elder A, Madsen S, Brown G, Herbel C, Collins C, Whelan S, Wenz C, Alderson S, Kronthal L. Adhesives and consolidants in geological and paleontological conservation. A wall chart. Washington: SPNHC Leaflets 1997: 1(2).

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