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## ***Analysis of a Celtiberian protective paste and its possible use by Arevaci warriors***

Jesús Martín-Gil\*, Gonzalo Palacios-Leblé, Pablo Martín Ramos and Francisco J. Martín-Gil

### **Abstract**

This article presents an infrared spectroscopy and X-ray diffraction analysis of residue adhering to a Celtiberian pottery sherd of late Iron Age date from the Arevacian site of *Cerro del Castillo*, in Ayllón (Segovia, Spain). This residue may be a paste used since antiquity for protective aims. Orange-sepia in colour, made from crushed bones and glue, the paste was used by Greeks and Romans and later in the construction of the cathedrals and monasteries of Europe to confer a warm colour to the stone and to protect it against environmental deterioration. In this article we also suggest a possible ritual use of this paste in the protection of the skin of the Arevaci and Edetani warriors, and the previously unreported pleasant aroma of this material is highlighted. The possible nutritional use of this paste is also considered.

### **Keywords**

Protective paste; Celtiberian Age; Arevacian warriors; pottery; X-ray diffraction

### **Introduction**

"Arevaci" is the name given to a pre-Roman Iberian tribe that together with the Belli, Titti and Lusones constituted the most influential ethnic group in pre-Roman Iberia, the Celtiberians. The cultural stronghold of the Celtiberians was the area that encompasses the Central Iberian Mountain Range and the limits of the sedimentary basins of the Ebro, Duero, and Tajo Rivers. When Greek and Roman geographers and historians encountered them, the Celtiberians were controlled by a military aristocracy who had become a hereditary elite. The Arevaci, who inhabited the area near Numantia and Uxama, excelled at horsemanship, fighting, and metalworking. They wore sewn garments made of woven and dyed cloth. They dominated their neighbors from powerful strongholds at Okilis (Medinaceli) and rallied the powerful

alliance of peoples composed of Vaccaei and Celtiberians who confronted Rome. The Arevaci were not completely under Roman domination until 133 BC, when Publius Cornelius Scipio Aemilianus destroyed Numantia.

*Cerro del Castillo*, in Ayllón (Segovia, Spain), is a late Iron Age Arevacian site that was first documented more than a decade ago (Zamora 1993). Of particular interest are certain decorated Celtiberian sherds, preserved in the soft and slightly alkaline soil. The remains of the contents of one of the vessels aroused our curiosity, in particular when, after cleaning the sherd with a 20% hydrochloric acid solution and putting it out to dry, a pleasant aroma could be detected.

In this paper we report our results of the characterization of the sample using both more traditional methods (chemical analysis and X-ray diffraction) and a non-destructive method, attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). Other main aims of this paper are to determine the origin and applications of this paste in Celtiberian and Iberian cultures, and to analyze the survival of such applications in later periods.

## Material and Methods

### Description of the site and the pottery sherd

The Arevacian archaeological site of *Cerro del Castillo* is located in the northeast of the province of Segovia, within the Ayllón municipal area. The high plateau where the settlement is located is on the southern edge of the Castilian plateau, in a strategic and defensive position that takes advantage of the precipitous topography of the area along the right bank of the Ayllón River. The modern town is situated on the southern slope of the same plateau.

The ceramic sherd that is the focus of this study is typical of Celtiberian pottery with geometric drawings in spiral shape (Figure 1) found within the occupation area of the Arevacian town. It does not appear to present any



Figure 1. Ceramic sherd on whose inner wall (below) the paste analyzed here was found.

unusual features, but is composed of several layers of the typical argillaceous deposits found in the zone where the town is located, which usually disintegrate when treated with a diluted acid treatment. Nevertheless, when treated with this solution, a cinnamon coloured (d2/b4/86 in the RGB chart) solid residue remained embedded on the inside of the sherd. Even after several treatments with the acid solution, this residue proved impossible to remove. During the drying process, the residue gave off a perfume aroma.

### Physicochemical study of the sherd's paste

The results of the infrared spectroscopy and X-ray diffraction analysis of the sample were compared to the spectra and patterns obtained from natural products found in published databases. The infrared spectra were systematically checked first for major and then for minor components found in the four main groups of natural products: sugars, lipids, proteins and resins.

The infrared spectra of the samples were registered with a Golden Gate ATR Mk II system (lenses KRS 5, superior plate and motherboard that covers interval 300 to 5000  $\text{cm}^{-1}$ ) based on attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), a fast analytical technique that has the advantage over other methods of being non-destructive. X-ray diffraction patterns were registered using an automatic diffractometer Philips PW1710 equipped with a graphite monochromator, automatic aperture and copper anticathode tube. The diffractograms were obtained at 40 kV voltages and 30 mA current, angular interval  $2\theta$  from  $5^\circ$  to  $70^\circ$ ; and continuous scanning. Both types of analyses (ATR scans and diffraction patterns) were carried out in the Laboratory of Instrumental Techniques of the Faculty of Sciences of the University of Valladolid.

### Attenuated total reflection (ATR) method

Over the past few years, attenuated total reflection (ATR), also called multiple internal reflectance, has become one of the most powerful and versatile improvements in infrared absorption spectrometry. The use of accessories of this application in FTIR instruments has two main advantages: it produces scans with a greater sensitivity than dispersive infrared instruments and is non-destructive character in relation to the samples, a characteristic not exhibited by the traditional technology, which involves immersion in a Nujol or KBr pellet solution.

Infrared spectra are obtained by putting the samples in contact with an internal reflection element (IRE), e.g., zinc selenide (ZnSe) or germanium (Ge). IR radiation is focused on the end of the IRE. Light enters the IRE and reflects down the length of the crystal. At each internal reflection, the IR radiation actually penetrates a short distance ( $\sim 1 \mu\text{m}$ ) from the surface of the IRE into the sample (Figure 2). Thus, the obtained spectra are similar to those obtained from a very thin layer of the sample.

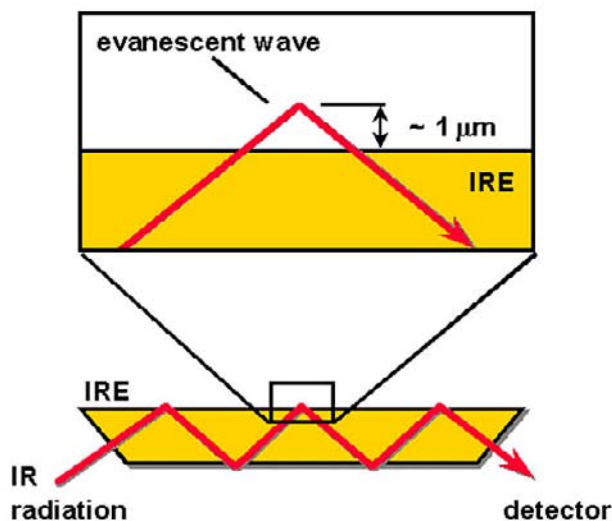


Figure 2. Total internal reflection at the interface of an internal reflection element. Depth of penetration of the evanescent wave is approximately  $1 \mu\text{m}$ .

Two requirements of the ATR method are: 1) the sample must be in close contact with the surface of the prism and 2) the prism must have a greater refracting index than the sample. The infrared light can penetrate to a depth expressed by the equation:

$$dp = \lambda / 2\pi (\text{sen}^2\theta - n_{21}^2)^{1/2}$$

where  $\theta$ : incident angle

$n_{21}$ : refracting index of the sample / refracting index of the prism

$\lambda$ : wavelength

The ATR method provides spectra for superficial layers of a few micrometers without, in fact, cutting into them. The instruments have software programs designed to adjust the required penetration depth.

## Results

The infrared spectroscopic (ATR-FTIR) analysis identified the characteristic absorption bands of the residue as partially carbonated bone hydroxyapatite and calcium oxalate (whewellite) (Figure 3). These bands are also present in ATR-FTIR spectra of ancient patinas made with crushed bone and glue that were used by the Greeks and Romans and later by the builders of cathedrals and monasteries across Europe and southern England to confer a warm colour to the stone and to protect it from environmental deterioration (Martín-Gil et al. 1999).

The ATR-FTIR bands of the paste identified on this sherd are the same as the patinas from the Monastery of Silos and Salisbury Cathedral (Martín-Gil et al. 2005) (Figure 4), which is why the identification presented here can be considered definitive. A small portion of the sample was made available for destructive analysis by X-ray diffraction. The presence of bone hydroxyapatite was verified by comparing the X-ray diffraction peaks of the Celtiberian paste (Figure 5) with the ones obtained from the patina at Salisbury Cathedral (Figure 6), which matched cards 9-432 (carbonated hydroxyapatite) and 03-727 (apatite) [JCPDS].

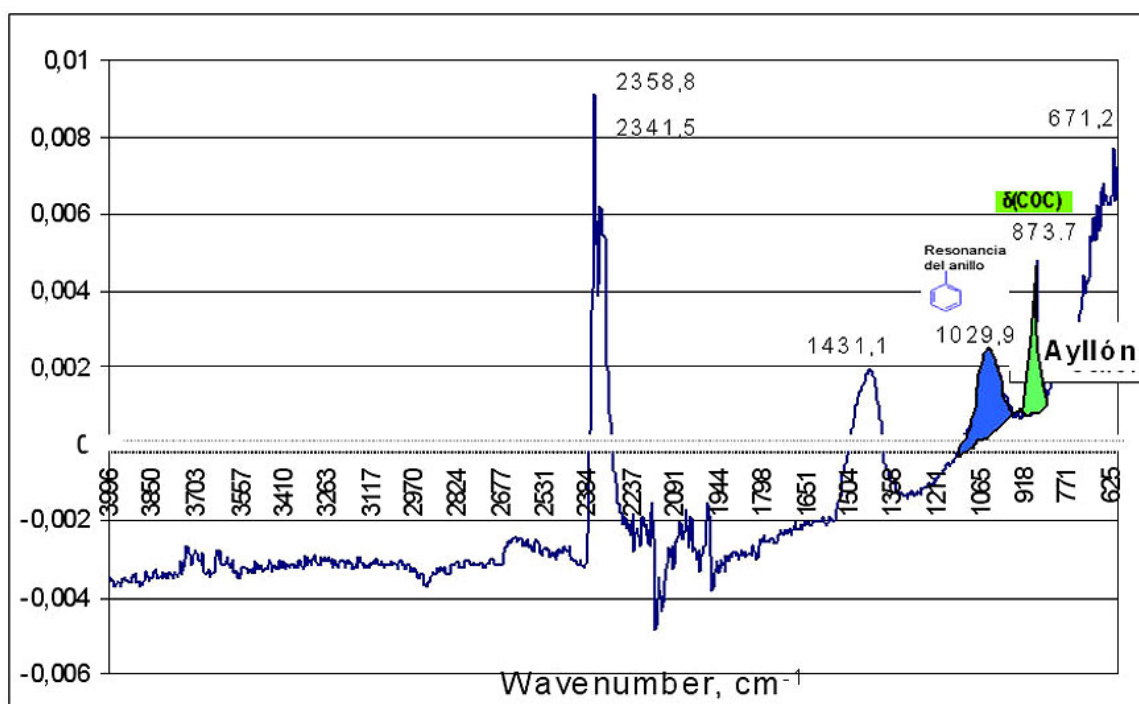


Figure 3. ATR-FTIR spectra of a paste found in a ceramic vessel of Celtiberian date.

In order to understand the nature of the matrix component of the aromatic remainder we followed an elimination procedure, discarding two of the substance-types possibly responsible for the aroma (resins, oils, proteins and polysaccharides). In the FTIR spectra no absorption band consistent with resins was observed (Figure 7) (Mills and White 1989; Vandenabeele and Moens 2004) and only one absorption band could possibly be assigned to oils, corresponding to the deformation mode - CH<sub>2</sub> at 1031 cm<sup>-1</sup>. Due to the absence of the rancid scent expected when oils are present, we do not believe that this absorption band represents an oil.

The two remaining types of possible glues or additives, protein or polysaccharide, cannot both be present, because their coexistence would generate melanoidines as a reaction product that in turn would have given the mixture a dark instead of an orange colour.

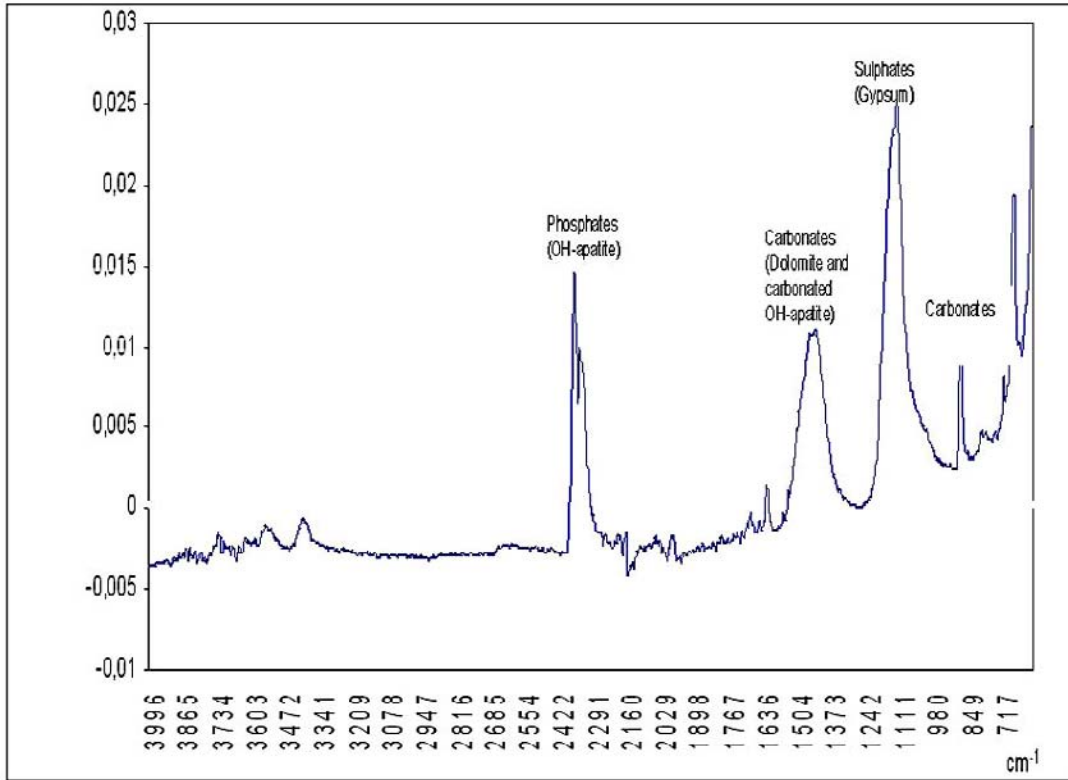


Figure 4. ATR-FTIR spectra of the patina of the Salisbury Cathedral.

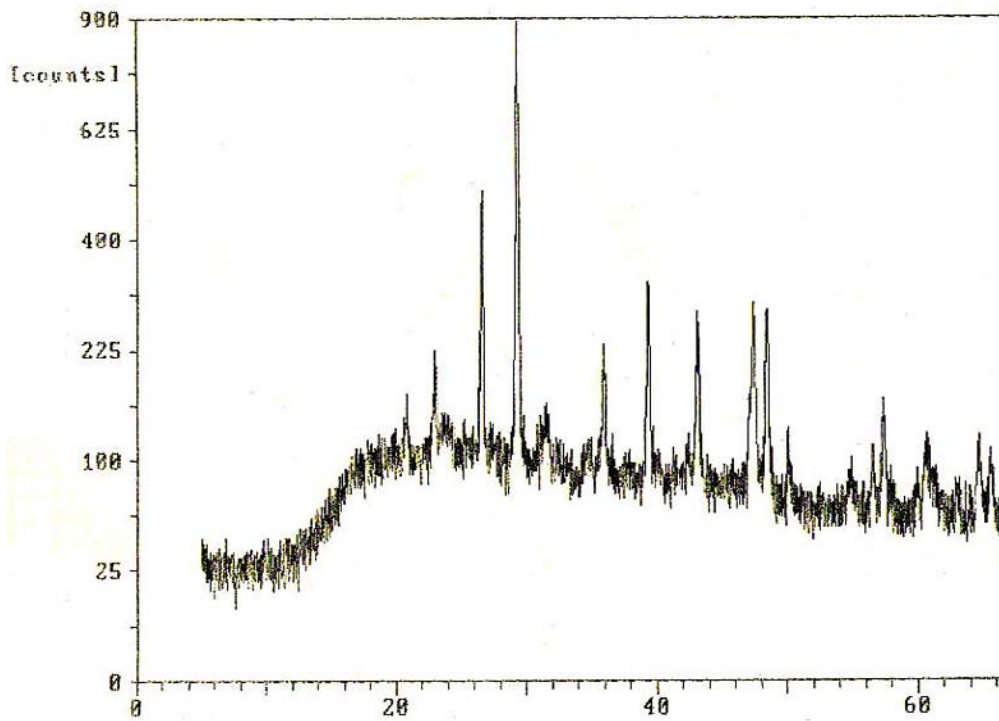


Figure 5. X-ray diffraction pattern of the Celtiberian paste found on the Ayllon sherd ( $2\theta = 26.60; 29.34; 31.49; 39.36; 43.11; 47.43$ ).

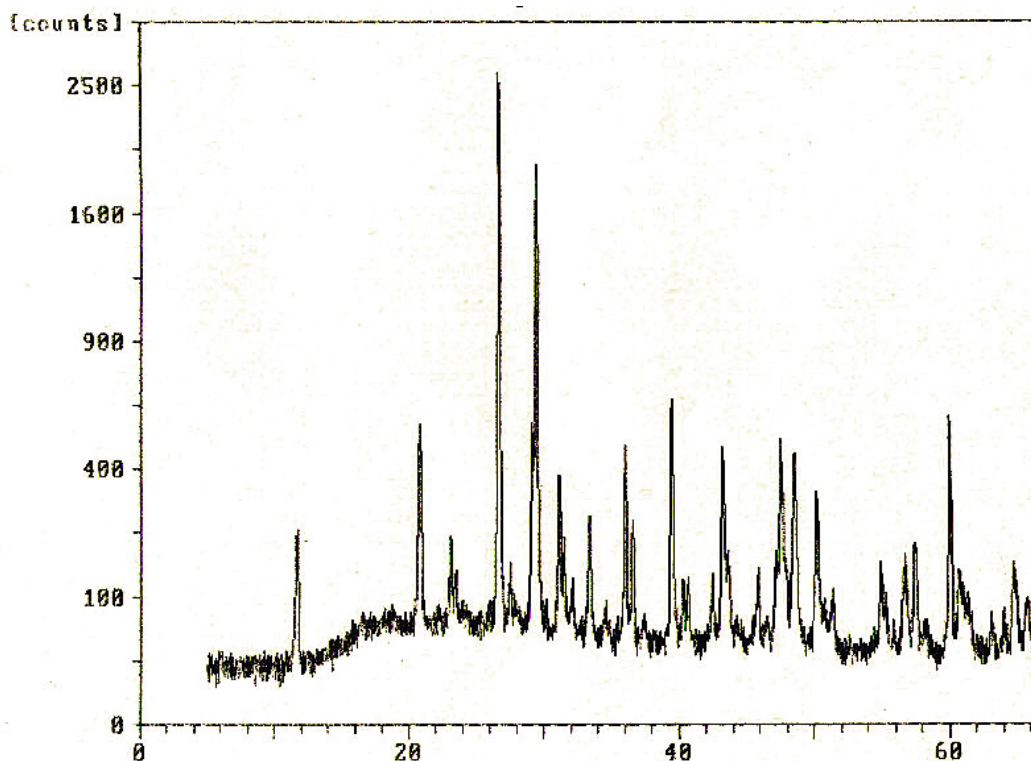


Figure 6. X-ray diffraction pattern of the Salisbury Cathedral patina ( $2\theta = 26.67; 29.44; 31.47; 39.46; 43.19; 47.53$ ).

Supporting evidence for the presence of a protein product is the possible attribution of the band around  $1000\text{ cm}^{-1}$  to the resonance movement, or breathing, of the aromatic ring of the phenylalanine (typical of animal glue spectra) and the existence of the absorption bands of the calcium oxalate (from metabolization of the components of egg yolk along the pathway serin  $\rightarrow$  glycin  $\rightarrow$  glyoxilic acid  $\rightarrow$  oxalic acid).

Supporting evidence for the presence of polysaccharides is the possible attribution of the band at  $874\text{ cm}^{-1}$  to the deformation vibrations of the COC group of the saccharide ring, (typically found in the spectra of potato starch, Arabic gum or cherry-tree gum). This interpretation is also supported by the generally pleasant scent of vegetal mucilage (a characteristic rarely exhibited by protein products).

An alternative to these identifications is that the residue represents the remains of *Rubia tinctorum*, used for staining purposes by the Phoenicians, the Greeks and the Carthaginians (Huq et al. 2005; Zohary and Hopf 1994) and possibly by the Arevaci and Edetani as well. The band at  $1030\text{ cm}^{-1}$  may correspond to the benzene ring of alizarin, a colorant based on anthrachinone, while the band at  $874\text{ cm}^{-1}$  may correspond to the saccharidic ring of the most usual components



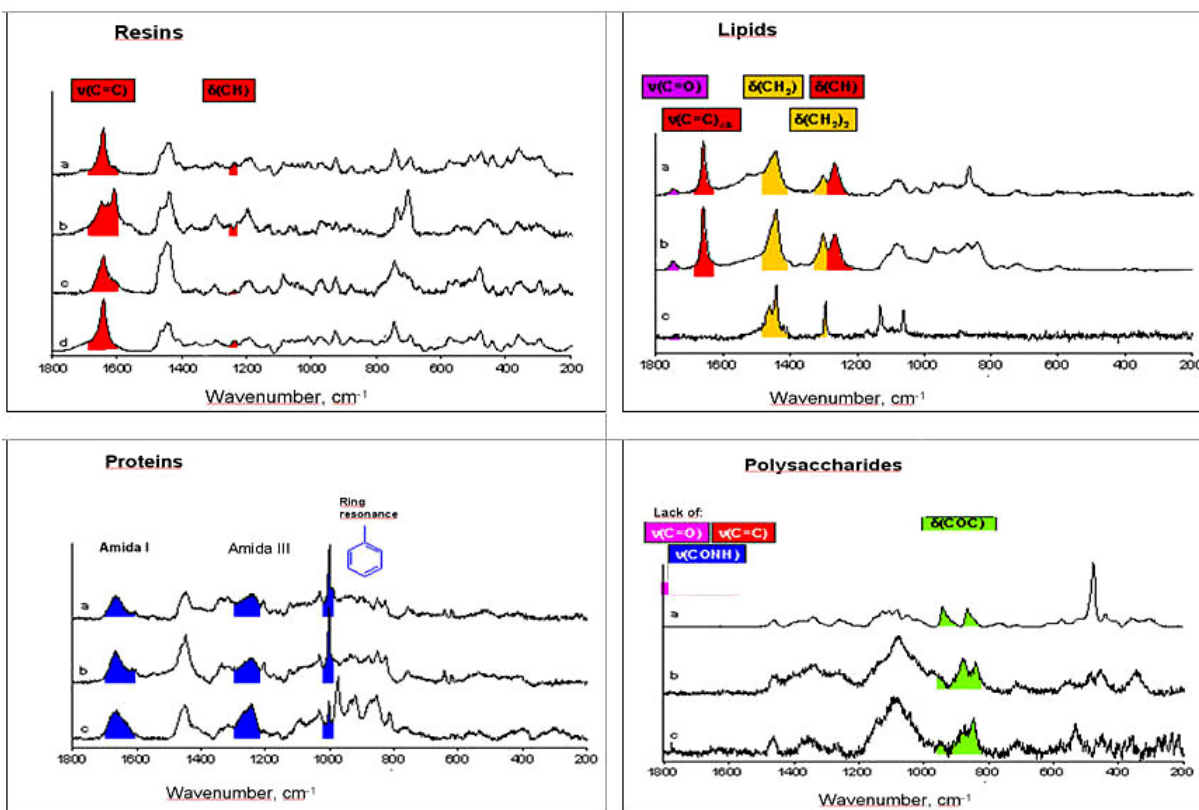


Figure 7. Spectra of resin-based glues: (a) shellac, (b) mastic, (c) colophony and (d) sandarac; spectra of lipid-based glues: (a) linseed oil; (b) poppy-seed oil; (c) beeswax; spectra of protein-based glues: (a) egg white; (b) casein; (c) gelatine; spectra of polysaccharide-based glues: (a) potato starch; (b) Arabic gum; (c) cherry-tree gum.

of the plant. Mixing *Rubia* with crushed bones, which would act as particulates, would result in a composite material of similar appearance to that observed in the residue from the Celtiberian sherd. Freshly prepared and applied to the skin, on the other hand, such a mixture would produce an aged leather color and a cracked aspect that could be easily confused with a reduction product of permanganate (manganese dioxide). Qualitative chemical analyses conducted to test for the presence of coloured inorganic ions (such as permanganate) in our sample were negative.

## Discussion

The paste found adhering to the ceramic sherd from the Arevacian *oppidum* of Ayllon could have had three different uses: skin protection or decoration of warriors in religious ceremonies and/or warlike circumstances; ornamentation and/or conservation of materials (stone or ceramic); and/or as a nutrient.

The use of pastes or body paint by warriors is a cultural phenomenon through space and

time that is shared by many cultures. In some situations, such pastes were applied for prophylactic purposes and in others to camouflage the warrior. A paste made of *Lepidium sativum* L. seed-flour and water was rubbed onto the skin by Ethiopian warriors for warmth on cold nights, for example (Getahun 1976). Pictish warriors in Scotland were reported to ritually apply a blue coloured war pigment known as woad to their bodies, a practice incompatible with wearing clothing or armor, which presumably was thought to protect the user. Chichimec warriors in North America were easily identifiable because they went into combat completely naked, wearing only war paint (Coopwood 1900). Likewise, it has recently been reported that Edetani warriors (neighbours of the Arevaci) went naked (or, at least, barefoot) for ritual reasons, and that they protected themselves with a paste tentatively identified as a manganese compound. Sarriugarte (2003: 1) literally states: "They (the Edetani) went totally barefoot, applying to themselves a product (permanganate) that made the skin wizened when it dried out, and allowed them to walk as if they were wearing some sort of footwear". Eslava-Galán (2004: 166) makes a similar assertion: "It is possible that some naked parts, arms and legs, were smeared with permanganate, which would give them a stiff texture".

The most probable application for the paste residue analysed here by the Arevaci of Ayllón is the areas of religion and/or war. Its use to stiffen the skin of the feet in religious ceremonies and/or battles could correspond to a ritual exigency reported for other Iberian tribes, as has been documented elsewhere (Aranegui Gasco 1983; Ruíz Bremón 1989). Our identification of the perfumed character of the paste supports this interpretation of a ritual use as well (Erard-Cerceau 1990; Faure 1987; Shelmerdine 1985).

On the other hand, applications of such pastes on stone or ceramic materials are also well known in the literature. The investigation of ancient protective pastes on stone has received great attention for over twenty years, both in the area of the conservation of artistic historical heritage and in environmental chemistry. For example, protective pastes on sculptures and monuments include the orange-brown patina of the Venus of Willendorf, the surfaces of marbles from the Parthenon now conserved in the British Museum (particularly the Oinochoai and Dionne groups), and in monuments such as the Propyleos (Acropolis, Athens) or the Olympieion (Polikreti and Maniatis 2003). Brown coloured patinas also cover the Pentelic marble in the base of the Arc of Titus in Rome, where analyses have identified very high amounts of phosphates mixed with a silicate compound (Franzini et al. 1984). The relationship between the ubiquitous

presence of phosphates in the patina and the nature of *scialbatura* was reported by Lazzarini and Salvadori (1989). On the basis of previous data (Del Monte 1987; Franzini et al. 1984; Guidobaldi et al. 1984) and their original findings, the last mentioned authors established that the patinas of monuments in Rome and Verona have an artificial origin and that they should be attributed to the application of protective treatments (Lazzarini and Salvadori 1989). These patinas generally contain amino acids, which are the final stable degradation products of collagen glue from animal skins or other protein glues (Halpine 1992).

The correspondence of composition between the main component of the paste analysed here and the patina on the monuments of the Athenian Acropolis (Polikreti and Maniatis 2003) allows us to trace its origins to the fifth century BC in the Mediterranean under Greek influence. The Arevaci may have had access to knowledge of this paste as a result of their proximity to the Edetani or some other Iberian tribe with known contacts to Greece located between the right bank of the Ebro River and the sea. Nevertheless, to date, no evidence of the use of the paste analysed here has been found on Celtiberian sculptures.

Finally, we cannot entirely discount the alternative use of the Arevacian paste as a nutrient. In this connection two relevant ethnographic references may be cited. The first is that a paste made of *Heeria reticulata*, bark boiled and mixed with milk, was used by ancient Kenyan warriors as medicine to increase strength (AFLORA 1998). The second is that until very recently, in Sardinia, acorns were crushed, peeled, boiled, ground in a mortar and boiled again in order to produce a sort of purée to which was added powdered bone ash and red clay. Once it had cooled, this paste was modelled and eaten (Mason 1995; Zapata 2000). We know that dried acorns were an important component of the diet of the Arevaci (Juan-Tresseras 2000; Tarancón et al. 2003), but we do not know whether they cooked acorns, as is documented in Sardinia, or whether they only roasted them between ashes, as reported by Pliny. The reproduction of this paste and its analysis by ATR-FTIR will, we hope, allow us to test whether the nutritional hypothesis can be supported.

In conclusion, it is appropriate to state that the paste in question has been identified as containing calcium phosphate particles, probably crushed bone ash, in an organic matrix originally comprised either of proteins and related products, or of polysaccharides, indicating vegetal matter. At present, the latter interpretation appears more likely to us, mostly because of the pleasant aroma that the paste gives off when treated with acid.

We have identified the potential uses of this paste, as body ornament and protection, in architectural surface protection, and as a nutrient. Of these, the first is the most likely based on historical sources related to the Arevaci. No evidence exists so far for its use as a surface coating in architecture or sculpture in pre-Roman Iberia, despite much research in this particular field elsewhere. The third interpretation is the least well documented in an archaeological context, and requires further research to be tested.

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