The manufacturing process of 3rd millennium BC bone based incrusted pottery decoration from the Middle Guadiana river basin (Badajoz, Spain)

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Abstract

The aim of this study is to present the manufacturing process developed on 3rd millennium BC white incrusted pottery from the middle Guadiana River basin (Badajoz, Spain), alongside the analytical procedure developed to determine the nature of these incrustations. The analytical procedure developed in this paper will assess the nature of these incrustations as burnt bone and in fewer cases as calcium carbonate, turning upside down the usual tendency for the Iberian Peninsula, where calcium carbonate has been the only kind of incrustation identified up until now. The analytical facilities used are: SEM-EDX, XRF microprobe, XRD and FTIR. The assessment of the nature of the incrustations as burnt bone has been a hazardous task and it has been necessary to develop a procedure using several analytical techniques and reference materials.

Keywords: 3rd millennium BC; Bell Beaker pottery; Incrusted pottery; Bone; SEM-EDX; XRF microprobe; XRD; FTIR

1. Introduction

Two of the largest 3rd millennium BC settlements throughout all of Iberia are found within the Spanish middle Guadiana River basin (Badajoz, Spain): La Pijotilla (80 ha) (Hurtado, 1984) and San Blas (30 ha) (Hurtado, 2004). These two large settlements together with some other smaller and fortified settlements (Fig. 1), politically organized around La Pijotilla, shape the Tierra de Barros landscape as a Copper Age organized territory (Hurtado, 1995). San Blas is one of the most outstanding settlements in the periphery. As usual, many of the Bell Beaker pots are decorated with a white incrusted paste, which has been characterized as calcium carbonate in France (Salanova, 2000), NE Spain (Martín and Delibes, 1989) and the Spanish Meseta (Blasco, 1994), whereas the Beaker pots from the middle Guadiana River basin have not been studied before. This kind of decoration is not as typical of the decorated pottery of the second half of the 3rd millennium BC as it is of the Bell Beaker pots.

Up until now, the analysis developed in the Iberian Peninsula of 3rd millennium BC incrusted Bell Beaker pottery from Pajares de Adaja and Fuente Olmedo (Valladolid, Spain) (Martín and Delibes, 1989) and Cieza de los Molinos necropolis (Madrid, Spain) (Blasco, 1994) has exclusively evidenced calcium carbonate incrustations.

It has been complex to work out the nature of the incrustations belonging to the 3rd millennium BC middle Guadiana River basin decorated pottery due to the multiple interactions and transformations undergone from production to deposition by the original material over its behavioural chain (Schiffer, 1976). These interactions have caused structural transformations of the original material, making it extremely difficult to assess the nature of the incrusted material. This difficulty is discussed in (Gherdán et al., 2005; Sziki et al., 2003) in which the bone nature of the white incrustations has been...
suggested for Hungarian prehistoric pottery, although this has not been securely determined.

The aim of this paper is to characterize these incrustations and assess their uncertain nature. The uncertainty over their nature makes essential the use of several analytical techniques in order to assess the raw materials used in the manufacture of these white incrusted pots.

2. Materials and methods

2.1. Materials

The 32 samples of white incrusted pots studied in this work (Table 1) were selected from the 3rd millennium BC decorated pottery (continental style Bell Beaker, incised and impressed pots) recovered from the middle Guadiana River basin territory (Hurtado, 1995). Within this territory, pottery sherds from three sites were sampled (La Pijotilla, San Blas and Molino Perdido). The sampled materials from La Pijotilla, as well as those from Molino Perdido, were recovered in field surveys. The pottery from San Blas on the other hand was recovered in archaeological excavations.

The samples labelled H22, H23, J27, R7 and U7 correspond to domestic structures of c. 8 m in diameter, while the sample labelled IIII022 corresponds to a tholos type burial of the San Blas site (Hurtado, 2004). The stratigraphic unit and the pottery record number separated by hyphens are also indicated in the label. For samples from La Pijotilla and Molino Perdido, the initial P or MP indicates the site, SUP indicates that the samples were recovered in field surveys, and the digits correspond to the pottery record numbers.

The decorative technique briefly described in Table 1 must be born in mind: all of the incised Bell Beaker sherds correspond to continental style Beakers, for which the thickness

Table 1
Brief description and labels of the sampled incrusted white pastes

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>Label</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>H22-11-457</td>
<td>Incised beaker</td>
<td>P-SUP-26</td>
<td>Incised/Impressed beaker</td>
</tr>
<tr>
<td>H22-8-607</td>
<td>Incised beaker</td>
<td>P-SUP-31</td>
<td>Incised beaker</td>
</tr>
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<td>H23-10-154</td>
<td>Incised beaker</td>
<td>P-SUP-32</td>
<td>Incised beaker</td>
</tr>
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<td>Incised</td>
<td>P-SUP-34</td>
<td>Incised beaker</td>
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<td>Incised</td>
<td>P-SUP-35</td>
<td>Incised beaker</td>
</tr>
<tr>
<td>H23-19-295</td>
<td>Incised</td>
<td>P-SUP-43</td>
<td>Impressed/Incised</td>
</tr>
<tr>
<td>H23-6-28</td>
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<td>Impressed</td>
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<td>P-SUP-48</td>
<td>Impressed/Incised</td>
</tr>
<tr>
<td>J27-28-717</td>
<td>Incised beaker</td>
<td>P-SUP-50</td>
<td>Impressed/Incised</td>
</tr>
<tr>
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<td>P-SUP-51</td>
<td>Impressed/Incised</td>
</tr>
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<td>P-SUP-69</td>
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<td>MP-SUP-5</td>
<td>Incised beaker</td>
<td>R7-6-205</td>
<td>Impressed</td>
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<td>P-SUP-22</td>
<td>Incised beaker</td>
<td>R7-6-225</td>
<td>Impressed</td>
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<tr>
<td>P-SUP-23</td>
<td>Incised/Impressed beaker</td>
<td>R7-8-372</td>
<td>Impressed</td>
</tr>
<tr>
<td>P-SUP-24</td>
<td>Incised beaker</td>
<td>U7-7-179</td>
<td>Impressed</td>
</tr>
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</table>

Fig. 1. The middle Guadiana River basin landscape. La Pijotilla, San Blas and Molino Perdido sites are marked on the zoomed part of the map.
and depth of the incisions range from 0.4 to 1.0 mm. In the case of non-Bell Beaker decoration, the technique can be either incised, impressed or a mixture of both, in which case the impressions are generally dots and in few cases genuine impressions.

Some bone artefacts (recovered from the San Blas site) and non-biogenic apatites (sampled from Spanish and French mines) were studied as reference material (Table 2) in order to compare their physicochemical characteristics with those of the incrusted white pastes.

The fossil bone remains (Table 2) correspond to an unidentified faunal bone found in trench E9, near a wall bastion at San Blas; J27-18-248 is a perforated and polished bone plaque and H22-4-218 is a small continental style decorated bone Beaker bowl.

The incrusted white pastes were carefully separated from the ceramic body prior to any physicochemical analysis and powdered using an agate mortar. This homogeneous powder was prepared for all physicochemical analyses through this process, except in the case of scanning electron microscopy (SEM-EDX) and X-ray fluorescence (XRF) in which the analyses were performed on the original material without further manipulation.

3. Methods

The samples shown in Tables 1 and 2 were studied by scanning electron microscopy (SEM-EDX), X-ray fluorescence microprobe (μ-XRF), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) in order to determine the nature of the incrusted white pastes.

SEM-EDX analysis of the ceramic sherds was carried out on gold-coated fresh sections of the original pottery, taking care that both the ceramic body and the incrustation were present in the section. Gold coating was carried out in a Balzers SCD 040 metallizer. A Jeol JSM-5400 microscope coupled to an Oxford Link Pentaflex energy dispersive analyzer was used for obtaining the morphology. The EDX analyzer was operated in mapping mode in order to identify compositional regions in the analyzed samples.

The chemical analysis of the white incrustation was obtained with an EDAX Eagle III μ-XRF. After focusing with an optical microscope, a 40 μm area was analyzed using 40 kV Kα radiation produced by an Rh tube. Quantification was performed in the standardless mode provided in the software of the instrument in order to avoid misleading results caused by the non-homogeneous nature of the samples. Quantitative data were reported after averaging five measurements.

X-ray diffraction patterns were obtained with a Siemens D501 diffractometer, using a copper tube (λ = 1.5406 Å). The diffractograms were recorded in the scanning ranges 2θ from 25 to 55° with a step size of 0.02° and a counting time of 10 s per step. The powdered white paste was suspended in ethanol and poured into a glass holder upon the evaporation of the solvent.

The specimens of fossil bone were submitted to an in situ calcination process in a Phillips X’pert Pro spectrometer using Cu Kα radiation and an Xcellerator detector equipped with a high temperature chamber. After measuring the XRD pattern at room temperature, a linear heating schedule with β = 10 °C/min was applied and a diagram was collected every 50 °C.

Infrared spectra of the original powdered white incrustations as well as the reference materials were obtained using a Nicolet 510P Fourier transform infrared spectrometer with a DTGS detector. Data was collected by co-adding 32 scans at 4 cm−1 resolution. The system was N2 purged to reduce atmospheric CO2 and H2O absorption.

FTIR spectra were acquired using the transmission mode upon pellets of the studied powdered samples dispersed in KBr. The samples were uniformly ground in an agate mortar with KBr (IR grade) previously degasified at 400 °C. A 13 mm pellet was made using a Perkin–Elmer holder and a hand press working at 11 Ton.

The non-biogenic reference materials were submitted to heating schedules similar to those used for the XRD analysis. They were placed in a ceramic crucible and heated isothermally for 24 h at the chosen temperature, ensuring this way that the recorded spectra correspond to equilibrium phases. The calcined powders were converted into pellets as described above for the other samples.

The XRF microprobe compositional data of the studied samples were statistically evaluated using the Kernel Density Estimate (KDE) formula (Baxter, 2003). A subroutine implemented in Microsoft Excel was used (Ellison, 2002). The archaeological inferences drawn from the statistical analysis depend on the interval width (h). In this case, the density estimate has been evaluated for h values in the range 0.075–0.125, obtaining the optimum value for h = 0.100.

4. Results

Among all of the decorated pottery found in San Blas, La Pijotilla and Molino Perdido, the 32 sherds described in Table 1 are the only ones with white incrusted decoration. These sherds represent c. 17% of the total of all the Chalcolithic decorated pottery found at these three sites.

Microscopically, the incrustations can be described as a uniform and homogenous white material that fills the gap left by the incisions or impressions. This can be observed in the fresh section of P-SUP-69 (Fig. 2), representative of the whole set under study. Microstructurally, the specimen shows two distinguished regions, separated by an empty area (illustrated by two lines in Fig. 2). On the right hand side, a fine-grained
microstructure is observed while, on the left hand side, grains of different size and shape coexist. X-ray emission maps corresponding to silicon and aluminium, together with oxygen, are dominant in the left hand side of the image (Fig. 2b and c). In contrast, on the right hand side of the image, the signals corresponding to phosphorus and calcium are almost exclusively present in addition to oxygen (Fig. 2d and e). The left-hand side corresponds to the ceramic body, in which Si and Al dominate the composition, and the right-hand side (the white decoration) should be assigned to a calcium phosphate phase. This is a general result for most of the 32 sherds, although in 4 samples (not shown in the figure) the incrusted white paste only shows the presence of calcium and oxygen as major components which, in turn, may be associated to a calcium carbonate phase.

The μ-XRF analyses of the white pastes are summarized in Table 3. In most samples, the amount of Ca and P accounts for more than 90% of the total elemental composition, thus indicating that the white pastes correspond to a pure calcium phosphate phase.

Only samples H22-11-457, P-SUP-32, P-SUP-43 and P-SUP-48 mislead the consideration of a calcium phosphate
phase since the amount of phosphorus accounts for as much as 3%. The presence of calcium carbonate should thus be considered, as has been previously reported for Beaker pots from Pajares de Adaja and Fuente Olmedo (Valladolid, Spain) (Martín and Delibes, 1989), Ciempozuelos necropolis (Madrid, Spain) (Blasco, 1994) and France (Salanova, 2000).

The calcium phosphate Ca-to-P ratios vary from 1.73 to 2.88 weight percentages, thus covering the variability described for either biogenic or non-biogenic apatites (Table 4). This range can be explained by differences in provenance or thermal treatment of the calcium phosphate raw material and in some cases by the existence of carbonation processes that might result in the formation of calcite crystallites as seen in some XRD traces (Fig. 3). Only sample P-SUP-52 falls outside of any tendency with a Ca/P ratio equal to 3.60. This result has been attributed to the presence of a carbonate-rich contamination layer.

Kernel Density Estimate of the whole set of samples leads to the presence of a maximum Ca-to-P ratio of 2.01 and a well-defined shoulder at 2.55. These atomic ratios are indicative of apatite phases pointing undoubtedly to the use of either biogenic or non-biogenic apatites \([\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2]\), where X is a monovalent anion\) in the production process of these incrusted white decorations from the middle Guadiana River basin.

The easy access of non-biogenic hydroxylapatites mines in the studied area -actually exploited as a mining resource- lead us to perform a more detailed study, thus the samples were studied by XRD in order to distinguish between the use of mineral or biological apatite as a raw material for the incrustations. The XRD patterns of the white decoration correspond to hydroxylapatite phases according to the Inorganic index of the powder diffraction file (2000), card number 9-432. As an example, Fig. 3 shows the XRD diagrams of samples H23-19-291 (Ca/P = 2.01) and MP-SUP-4 (Ca/P = 2.55) as representative of the whole set of samples the main differences may be associated to the presence of calcite in the samples with the higher Ca/P ratio.

Hydroxylapatite is the major inorganic constituent of bone, accounting for 40% of the total weight of bone. The remaining

### Table 3

Weight percentage of P and Ca in the white pastes of the studied sherds, as obtained from μ-XRF analysis

<table>
<thead>
<tr>
<th>ID #</th>
<th>Ca</th>
<th>P</th>
<th>Ca/P</th>
<th>ID #</th>
<th>Ca</th>
<th>P</th>
<th>Ca/P</th>
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<td>H22-11-457</td>
<td>67.94</td>
<td>0.00</td>
<td></td>
<td>P-SUP-26</td>
<td>54.95</td>
<td>30.14</td>
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<td>60.21</td>
<td>30.92</td>
<td>1.95</td>
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<td>47.76</td>
<td>23.19</td>
<td>2.06</td>
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<td>26.85</td>
<td>1.89</td>
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<td>87.11</td>
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<td>58.25</td>
<td>28.91</td>
<td>2.01</td>
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<td>38.43</td>
<td>19.57</td>
<td>1.96</td>
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<td>58.25</td>
<td>28.91</td>
<td>2.01</td>
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<td>44.70</td>
<td>22.61</td>
<td>1.98</td>
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<td>28.91</td>
<td>2.01</td>
<td>P-SUP-43</td>
<td>58.22</td>
<td>2.32</td>
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<td>36.31</td>
<td>19.40</td>
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### Table 4

Ca/P ratio weight percentages

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<th>Sample</th>
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<tr>
<td>Non-biogenic apatite*</td>
<td>1.53–1.98</td>
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<tr>
<td>Burnt bone*</td>
<td>1.83</td>
</tr>
<tr>
<td>Burnt bone*</td>
<td>1.97</td>
</tr>
<tr>
<td>Burnt bone*</td>
<td>1.95</td>
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<tr>
<td>Fresh cow bone*</td>
<td>2.14</td>
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<tr>
<td>Fossil antler bone*</td>
<td>2.51</td>
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<tr>
<td>Fossil antler bone*</td>
<td>2.51</td>
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<tr>
<td>Fresh human femoral neck bone**</td>
<td>1.86–2.48</td>
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</table>

*For fossil and burnt bones, after Shiegl et al. (2003). **For human (healthy female and male between 15 and 55 years old) fresh femoral neck bone, after Zaichicka and Tzaphlidou (2002).
60% corresponds to water and organic constituents. The X-ray diagrams of biogenic and non-biogenic apatite reference materials are shown in Fig. 4, together with the X-ray diagram of sample P-SUP-22. Hydroxylapatite is the mineral phase of all of the samples (biogenic apatites, non-biogenic apatites and the studied samples).

The XRD diagrams show sharper peaks for the studied samples and for the geological reference materials. In contrast, it is possible to observe how the biogenic reference materials have broader and less well defined peaks, particularly those corresponding to the planes [211], [112] and [300] of the hydroxylapatite structure, thus pointing to a possible non-biogenic origin of the samples.

However, the sharpening of the XRD peaks of the studied samples occurs during the crystallization process at high temperature (Rogers and Daniels, 2002), showing sharper peaks for the geological reference materials and the calcined fossil bone. It is however impossible to distinguish between both possible origins, geological or burnt bone.

The fossil bone and the studied samples have undergone similar post depositional processes [diagenesis-fossilization (Bartsiokas and Middleton, 1992; Lee-Thrope and van der Merwe, 1991) and/or weathering (Shiegl et al., 2003)], thus making it possible to discard them as the cause of the structural transformations shown in the XRD patterns.

The study of the bone calcination process may enable us to understand the structural transformations observed in the XRD pattern as a consequence of temperature. Thermally induced changes of experimentally calcined fossil bone are shown in a 2D plot (Fig. 5). At room temperature, the diffraction lines corresponding to planes [211], [112] and [300] overlap in such a way that the first two lines are indistinguishable and the third one appears only as a shoulder which is in accordance with the small extent of transformations in the splitting factor (SF) for the low temperature transformation of bones (Surovell and Stiner, 2001). Once the temperature exceeds 700–750 °C, the [211] and [112] diffraction lines still overlap but are clearly differentiated from the [300] diffraction line. However, above 850–900 °C, it is possible to differentiate between these three lines. This phenomenon corresponds to the hydroxylapatite to β-tricalcium phosphate transformation process (Grupe and Hummel, 1991).

The FTIR data of both the reference materials and the white paste samples indicate the presence of hydroxylapatite. Bands corresponding to the stretching and bending modes of phosphate groups of hydroxylapatite are clearly identified in the 1700–900 and 750–400 cm$^{-1}$ regions.

The biogenic apatites present more or less well defined peaks in the 1550–1300 region, peaking at 1458, 1418 and 1388 cm$^{-1}$, that correspond to carbonate substitutions of either the hydroxyl or the phosphate groups within the apatite structure (Fowler, 1974; Smith, 1999). These bands are absent in the non-biogenic samples (Fig. 6).

Bands at c. 1090 and 960 cm$^{-1}$ must be ascribed to the stretching modes of phosphate groups of hydroxylapatite (Babet and Apella, 2003; Dauphin, 1993; Fowler, 1974; Koutsopoulos, 1991; Rogers and Daniels, 2002). A band at around 870 cm$^{-1}$ is present in all of the biogenic apatites attributed to the bending mode ($\nu_2$) of carbonate in hydroxylapatite which is characteristic of fossil bones (Dauphin, 1993; Farmer, 1974). Mammal bone and teeth usually have an apatitical structure that frequently contains up to 5% carbonate. In the 750–400 cm$^{-1}$ region, O–P–O bending modes and translational modes of water occur. All of the reference materials show bands at 603 and around 570 cm$^{-1}$. The later band is in fact a combination of two bands at 562 and 574 cm$^{-1}$ that overlap and change in intensity depending on the morphology of the hydroxylapatite crystals. However, in non-biogenic apatites the most intense
band is the one at 574 cm\(^{-1}\), while the band at 560 cm\(^{-1}\) appears as a shoulder. For biogenic apatites the situation is the opposite: the main band peaks at 560 cm\(^{-1}\) and the band at 574 cm\(^{-1}\) appears as a shoulder (Fig. 7). The main difference between all of the measurements consists in the presence of a band at 630 cm\(^{-1}\) in the calcined fossil bone. This band is assigned to the librational mode of the hydroxyl group within the hydroxylapatite, and appears upon air calcination at high temperature, since \textit{in situ} calcination at temperatures up to 650 °C does not allow this band to develop.

The FTIR spectra of the sampled incrustations show hydroxylapatite phases that can be divided into two groups. All samples (except the carbonate white pastes) show the characteristic bands assigned to hydroxylapatite and the bands at 870 cm\(^{-1}\) that indicate the presence of carbonate groups substituting either hydroxyl or phosphate groups. This may allow us to discard the non-biogenic origin of the apatite forming the incrusted white material. The differentiating issue between non-biogenic and burnt bone is hence the presence of the librational mode of hydroxyl groups at 630 cm\(^{-1}\). The presence or absence of this band and its intensity may be associated to different behaviours during the manufacturing procedure and may be envisaged as a consequence of the control of the firing conditions that could have led to the different stages in the apatite to \(\beta\)-tricalcium phosphate transformation process.

5. Discussion

The technology used by the potters of the middle Guadiana River basin in the decoration stage that follows the drawing of the decorative motifs and themes by incisions or impression involves the application over the gap left by the incisions and impressions of a thick, soft, moist paste, produced by mixing dry powdered bone with a liquid, either water or a fatty agent. The incrustation of this bone paste may have been carried out before firing as argued by Salanova (2000), although it could also have been applied afterwards as has been suggested for carbonate pastes by Covertini and Querre´ (1998).

We think that the bone paste could have been prepared with some kind of fatty agent (for instance bone marrow), glue or beeswax instead of water in order to improve its workability and adherence to the clay matrix and that it should have been applied before burnishing and firing. However, no physicochemical evidence is found to support this theory due to the
firing temperatures c. 750–900 °C applied in the manufacturing process that would have burnt the evidence. The empty area observed between the ceramic body and the incrustation (Fig. 2) could be interpreted as evidence of some kind of organic agent used to fix the bone paste to the ceramic body, the physicochemical evidence of which disappeared when the pot was fired. In this case, this empty area seems to be weak evidence of the use of an organic agent in the fixation of the bone paste. Without further evidence, we should thus state that the dry bone paste was simply incrusted without any kind of fixer.

The data obtained in this study suggest that the bone paste was made with fresh bone, or cooking bones which may not have started the hydroxylapatite to β-tricalcium phosphate transformation process (Nielsen-Marsh, 2000; Roberts et al., 2002). Having demonstrated the hypothesis of the biogenic nature of the incrusted paste, we focus the following discussion on the transformation process of the bone paste to β-tricalcium phosphate during either the manufacture or the use of the pot. For this purpose, we must establish whether the pots have suffered use-alteration processes that may have started the hydroxylapatite to β-tricalcium phosphate transformation process.

Decorated pots are assumed to have had a domestic use (in the Beaker case, “drinking cups” as stated by Sherrat, 1987) and decorated wares (such as Bell Beakers) are considered “prestige” wares, thus it is thought that they would not usually have been used as cooking pots or working wares during prehistory and as a consequence may not have interacted with any heating source. Furthermore, even if they were used as cooking pots, they may not have reached a temperature above oil’s boiling temperature (c. 200 °C). But pots are also affected by post-depositional thermal alterations, such as the fire of a kiln used in a stratigraphic level immediately above the sherd and that may have interacted with it, as is argued by Bennet (1999) and Stiner and Kuhn (1995). In any case, this kind of heating source would not have been strong enough to induce the thermal transformations observed in the incrusted bone-based pastes. Consequently, we can discard the possibility of any use-alteration processes of the incrusted bone pastes during their use and burial. The exclusive heating source that could have modified the bone structure is its firing during manufacture.

It is possible to suggest that, throughout the middle Guadiana River basin, two manufacturing behaviours coexisted in the production of white incrusted pots: (i) principally the use of bone paste, and (ii) secondarily the use of calcium carbonate paste. These two procedures would have led to different behavioural activities taking place throughout the manufacturing process: one based around the use of bone as a raw material and one (4 samples) based around the use of calcium carbonate. Both raw materials were reduced to paste before their incrustation on the pot.

Bell Beaker and decorated pottery are assumed to be a low-fired production (Blasco, 1994; Clop, 2000; Covertini, 1996; Morzadec, 1995; Salanova, 2000), meaning that the firing temperatures vary between 750 and 900 °C, depending on the literature consulted. The bone paste was probably applied to the gaps before the firing, given that surface treatment (decoration and burnish) and decorating may often be carried out in stages prior to firing. The different degrees of thermal transformations are the result of differentiated firing procedures in the temperature ranges of low-fired pottery. So far it is possible to think of the thermally altered bone as a by-product of the firing behavioural activities or potter skills (Longacre, 1999) in the control of the firing conditions.

Bone begins its transformation at a temperature near 700–750 °C (Fig. 5), which is in some cases the estimated lower threshold of firing temperatures for low-fired pots. The transformation of the shape—width and intensity—of the XRD peaks with temperature correlates with the intensity of the
FTIR spectra band at 630 cm\(^{-1}\) for samples IIIIF022-2-64 and MP-SUP-4 (Fig. 7).

Low-fired pottery productions are quite monotonous in colour: the only possibilities are red, black and white (white clays are extremely rare), in such a way that the white incrusted paste breaks the monotony of this decorated pottery. This effect is an important part of the decoration design. The Chalcolithic potters were already developing firing technology, as can be understood through the early development of copper metallurgy in southwest Iberia some centuries before the development of this decorated pottery. It can thus be thought that the real difficulty in the manufacturing process lay in the control of the firing conditions. In many cases (Schiffer and Skibo, 1997), this control would have depended upon the potter’s behavioural activities, including the interpretation of the sensorial characteristics of the firing: when is the pot fired, does it need more fuel, is the colour not red or black enough, etc., and would have varied according to the potter’s skill, age and experience (Longacre, 1999). The presence of burnt bone in different degrees based on the FHWM of XRD pattern is probably due to the potter’s behaviour or skill in the control of the firing conditions, contrary to what may be seen as different technological choices in the use and processing of the raw materials. Obviously these different behaviours are thought of as different ways of making pots, and can always be explained in terms of artefact variability as a household production, although it is also possible to think in terms of differentiated workshops.

6. Concluding remarks

The difficulty of assessing the nature of the incrustations has been one of the most highlighted issues in this study, due to the difficulties of the identification of the nature of the paste as burnt bone, in turn due to the interactions and structural transformations suffered during its behavioural chain. In this paper, we have demonstrated that there are two different coexisting manufacturing behaviours surrounding the manufacturing process and specifically the decorative stage of the white incrusted pots from the middle Guadiana River basin territory. Based on their limited number, calcium carbonate incrustations can be considered as a “foreign” material within this territory. Calcium carbonate and white clay incrustations are cited from the Pyrenees to the middle Guadiana basin, through the Ciempozuelos influence area (Blasco, 1994; Martín and Delibes, 1989), and incrusted white clays have also been recorded in Brittany and Provence, as well as at Pajares de Adaja, Spain (Martín and Delibes, 1989).

The bone paste was incrusted before the firing of the pot and, as the exclusive result of the interactions that took place upon firing, the bone suffered a transformation process to β-tricalcium phosphate at around 700–900°C. This transformation is responsible for the materialization of the FTIR band at 630 cm\(^{-1}\). These stages are otherwise responsible for the sharpening of the peaks in the XRD diagram [hkl 211, 112, 300]. In this sense, we are able to see different intensities in the band at 630 cm\(^{-1}\) as well as in the XRD peaks [hkl 211, 112, 300] due to the different conditions that took place in the manufacturing processes of these pots.

The absence of organic bands in the FTIR spectra may allow us to discard the use of organic agents in the bone paste production and incrustation, although the temperature reached during the firing would have burnt the organic components thus making their detection extremely difficult.

The use of bone as a decorative technique has been observed, up until now in Iberia, exclusively in the middle Guadiana River basin. In this context, it is seen as a sign of the technological identity of the Tierra de Barros Copper Age territory, in contrast with other neighbouring territorial identities such as those of the Spanish Meseta in which only calcium carbonate pastes were used. The materialization of such identities in the neighbouring Portuguese regions remains to be studied.

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