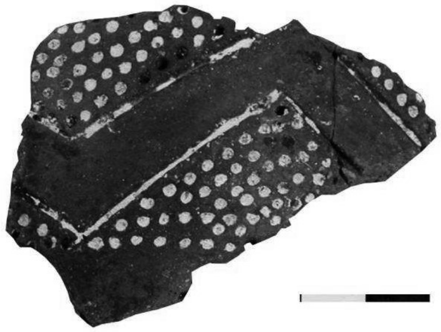
SCIENTIFIC ANALYSES OF THE WHITE INLAYED MATERIAL OF THE SYMBOLIC POTTERY FROM POVOADO DOS PERDIGÕES.



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1. Introduction

The aim of this work is to characterize and determine the nature of the so-typical white inlayed decoration that are present in incised/impressed pottery within a large number of Recent Prehistory ceramics from all over Europe. We have study particularly symbolic pottery (inverted triangles filled with dots) coming from the Portuguese Guadiana River Bank (Reguengos de Monsaraz, Portugal), focusing in one of the most important Cooper Age sites of this region: Povoado dos Perdigões (Lago et al. 1997).

Pottery inlays are of common use in the decoration of incised/impressed pottery from the Neolithic to the Iron Age all over Europe, from the Iberian Peninsula to the Balkans. The raw materials and techniques used in the production results in the diversity of these inlays which can take many different colours, *i.e.* red, yellow, white, when the colour depends mainly on the technological choice of raw material and firing behaviour made upon the decoration stage of the *Chaîne Opératoire*.

In the Iberian Neolithic, Copper and Bronze Ages many pots are decorated with a white inlayed paste, which has been characterized as calcium carbonate in France (Salanova 2000), NE Spain (Martín et al. 1989) and the Spanish Meseta (Blasco et al. 1994), whereas the scientific analysis developed in the Iberian Peninsula, over inlayed Copper Age pottery coming from Pajares de Adaja and Fuente Olmedo (Valladolid, Spain) (Martín et al. 1989), and Ciempozuelos necropolis (Madrid, Spain) (Blasco et al. 1994) has give rise to calcium carbonate inlays.

Figure 1 – Povoado dos Perdigões location whithin the Iberian Peninsula

Other kind of inlays have been characterized in other chronological contexts, *i.e.* French Bronze-Iron Ages, or Hungarian Neolithic-Bronze Ages where the use of bone as an inlay have been pointed out (Constantin 2003, Gherdán 2005, Sziki et al. 2003), although it has not been certainly assessed.

Determining the nature of the inlays from Guadiana River is a complex issue due to the multiple interactions and transformations suffered from production to deposition by the inlays over its live. These interactions have yielded structural transformations on the original material making difficult to assess its nature.

The difficulty is due to several possible origins and interactions of the inlayed material, calcium carbonate, biological apatite -bone-, burned biological apatite -burnt bone- (Surovell and Stiner 2001), or non-biological apatite -rock forming mineral. This uncertainty in its origin makes essential the use of several analytical techniques for assessing the raw material used in the manufacture of these white inlayed pots.

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Recently Odriozola and Hurtado (2007) have demonstrate throughout a compared study of these inlays with archaeological bone materials and geological apatites, that it is possible to differentiate between these origins using XRD and FTIR, and thus solving a important clue on the choices of raw material. Furthermore Odriozola and Martínez-Blanes (2007) had demonstrated, based on the previous work, that is even possible to estimate the firing temperature of the pots throughout the comparison of the XRD FWHM of experimentally calcined archaeological bones and the ones of the inlayed material.

Methodology

This work has been carried out over 4 sherds of inlayed symbolic decorated pots coming from Povoado dos Perdigões archaeological site (samples A6/790, A6/791, A6/793 and A6/794).

Bone's apatite (hydroxyl-deficient and carbonate-rich hydroxyapatite) suffers a transformation with temperature: hydroxyapatite to β-tricalcium phosphate - remaining the same crystallographic structure (apatitical). This transformation occurs at *c.* 700-900ºC and results in a stretching of the XRD peaks with the increase of temperature and/or firing time, and the occurrence of a band at 630 cm^{-1} (OH translational mode) in the FTIR spectra (see Odriozola and Hurtado 2007). Thus we will perform XRD and FTIR analysis of the 4 samples as follows to test the biological vs. geological nature of the inlayed material.

The inlays where carefully sampled by mechanical extraction and especial attention was placed during sampling in order avoid the pollution of the sample with the ceramic matrix. Afterwards the samples were submitted to X-ray diffraction, developed over the powdered samples of the inlays in a Philips X'Pert Pro diffractometer with a theta-theta goniometer, using the following measurement conditions: 1/8º for divergence slit and 1/4º for antiscattering slit, with a copper anode at 40 kV and 40 mA (λ= 1.5406 *Å*) equipped with a X'Celerator detector and a $K\beta$ filter (Ni). The diffractograms were recorded in the scanning ranges 2θ from 29.5 to 35.5º with a step size of 0.033º and a counting time of 200 *s* per step. The powdered white paste was suspended in ethanol and poured into a Zero background holder (silicon single crystal) upon the evaporation of the solvent.

Infrared spectra of the powdered sampled white inlays 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} resolutions. The system was N_2 purged to reduce atmospheric CO_2 and H_2O 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 400ºC. A 13mm pellet was made using a Perkin-Elmer holder and a hand press working at 11Ton.

Results

The XRD pattern of the 4 analysed samples fits with the hydroxyapatite pattern (ICDD card 9-432), showing sharp peaks for the major planes [211], [112] and [300] (figure 2a). Hydroxyapatite is the mineral, of which bones are constituted, but the shape of these peaks are to sharp to be biological apatite which normally results in a pattern with much broader peaks where the plane [300] appears as a shoulder of the plane [112] (figure 2b). At this point the inlayed material could be a geological apatite, *i.e.* phosphorite, or thermally altered bone (figure 2b).

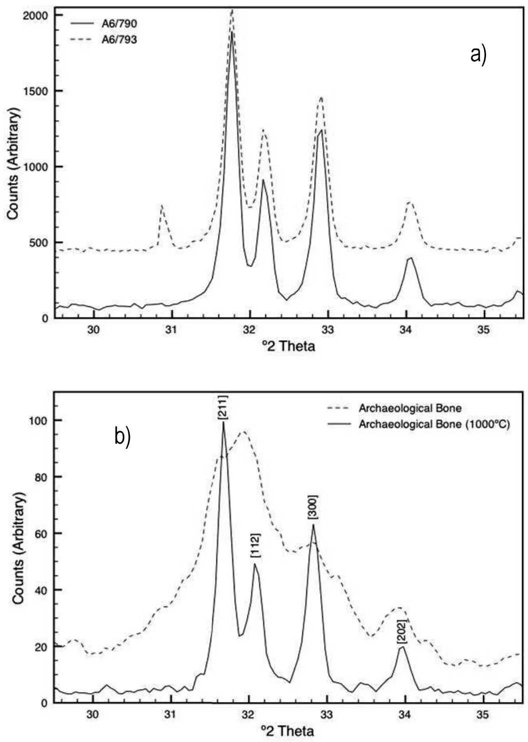

Figure 2 – a) shows the powder diagrams recorded from samples and b) biological and experimentally calcined biological materials (adapted from Odriozola and Hurtado 2007). It is possible to observe clear differences in the pattern shape between the major planes of Hydroxyapatite [211], [112] and [300] for biological and experimentally calcined bone, which indeed appears to match the samples pattern shape.

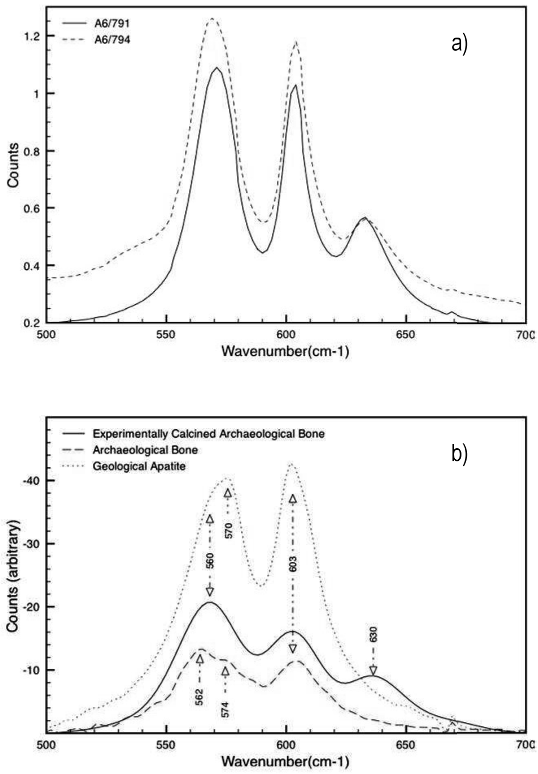

Figure 3 – a) FTIR spectra recorded from samples in the region of interest and b) biological and experimentally calcined biological materials and geological apatite (adapted from Odriozola and Hurtado 2007). It is possible to observe clearly the presence of the band at 630 cm^{-1} in the samples and in the experimentally calcined archaeological bone, which indeed points to a thermally altered biological apatite.

As seen in previous works (Odriozola and Hurtado 2007) FTIR throws differential spectra for geological, biological and experimentally calcined apatites.

The absorption bands 1458, 1418, 1388 & 870 cm^{-1} that are observed in the samples spectra are typical of biological apatites and are completely absence in the geological ones (Fowler 1974), this is a key point to consider the material as biological, but further on the bands at *c.* 603 & 570 cm^{-1} (combination of two overlapping bands at 562 & 574 cm^{-1}), do not appear in the geological apatites that shows a intense band at 574 cm^{-1}, appearing the band at 560 cm^{-1} as a shoulder. Contrary to the biological apatites situation where the main band peaks at 560 cm^{-1}. But there is still a difference between the biological apatites and our samples, the presence of a band at 630 cm^{-1} assigned to the translational mode of the hydroxyl group in hydroxyapatite that appears upon air calcination at high temperature (figure 3). And that doubtlessly points out a biological apatite origin of the inlay that has been thermally altered raising temperatures above 700ºC.

Remarks

The analytical procedure demonstrates the nature of the white inlayed paste is burned bone, on the basis of the combined use of these analytical techniques.

From our point of view a crushed bone paste has been incrusted before firing the pot; and as the exclusive result of the interactions that took place upon the firing, the bone suffers a transformation process to β-tricalcium phosphate that happens *c.* 700-900ºC, this transformation is the responsible for the materialization of the FTIR band at 630 cm^{-1} as well as the different intensities that depends on the transformation stage. This stage is also responsible in the XRD diagram of the sharpening of the peaks [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 process of these pots (figure 2a, 3a).

It has pointed out recently (Hurtado and Odriozola 2008) that the use of bone inlays in the Guadiana River prestige pottery (mainly Bell Beaker style pottery) is a technical facet that typifies Tierra de Barros technical identity; till today no evidence of this technological choice was found outside its boundaries in the Guadiana River.

Technical style distribution within a territory is undoubtedly the result of social interactions. On the one hand interaction may cause exchange of goods; and in the other hand the mod of different facets of the chainê opératoire as a function of the intensity and contexts of the interaction.

Can the distribution of this technological choice delineate the social interaction border between Alta Alentejo and Tierra de Barros on the basis of social interactions between individuals, or the result of an exchange interaction between individuals or elites? Today we cannot give an answer to these questions. We need more clues to render a picture of how could social interactions boundaries be in the Iberian Southwest puzzle.

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Resumo

Análise científica da pasta branca incrustada na "Cerâmica Simbólica" proveniente dos Perdigões

O objectivo deste trabalhos foi caracterizar a natureza do material utilizado no preenchimento da "decoração simbólica" persente em cerâmicas provenientes dos Perdigões (Reguengos de Monsaraz).

Através da análise de difrecção de raio-x, foi possível demonstrar que a pasta branca das amostras estudadas é constituída por osso queimado. Uma pasta de osso esmagado seria utilizada no preenchimento das decorações incisas e impressas antes da cozedura, ocorrendo a transformação mineralógica do osso durante o processo de cozedura.

Esta técnica foi igualmente atestada na bacia do médio Guadiana na Tierra de Barros (Badajoz), surgindo a sua presença nos Perdigões como mais um indicador de interacção transregional.