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Investigating beads from Chalcolithic funerary cremation contexts of Perdigões, Portugal

M.I. Dias[a,*], Zs. Kasztovszky[b], M.I. Prudêncio[a], I. Harsányi[b], I. Kovács[c], Z. Szőkefalvi-Nagy[c], J. Mihály[d], G. Káli[e], A.C. Valera[f,g], A.L. Rodrigues[a]

[a] Centro de Ciências e Tecnologias Nucleares — C2TN, Campus Tecnológico e Nuclear, Instituto Superior Técnico, Polo de Loures, Univ. Lisboa, Estrada Nacional 10 (km 139.7), 2695-066 Bobadela, Loures, Portugal
[b] Centre for Energy Research, Hungarian Academy of Sciences, Budapest, Hungary
[c] Institute for Particle and Nuclear Physics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary
[d] Research Centre for Natural Sciences, Hungarian Academy of Sciences, H-1117 Budapest, Magyar tudósok körútja 2, Hungary
[e] Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary
[f] Era Arqueologia, Núcleo de Investigação Arqueológica — NIA, Cç. de Santa Catarina, 9C, 1495-705 Cruz Quebrada-Dafundo, Portugal
[g] Interdisciplinary Center for Archaeology and Evolution of Human Behavior (ICArHEB), Universidade do Algarve, Campo de Gambelas, Faro, Portugal

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ABSTRACT

A set of beads was studied to investigate their nature. They come from a funerary feature used for the secondary deposition of cremated remains of more than a hundred individuals. The pit is located in the centre of Perdigões (Évora, Portugal) ditched enclosures (Valera et al., 2014a) and is dated from the third quarter of the 3rd millennium BC. The beads were also burned and were part of the funerary votive assemblages, also composed by arrowheads ivory figurines, marble idols and pots, phalanx idols, copper awls, Pecten shells and pottery sherds. These beads have a diameter between 5 and 10.5 mm, with a central perforation up to 5 mm and maximum thickness of 3 mm, they are dark grey or black and were of unknown nature.

This study shows that these beads were made from shells and submitted to heating processes. The study demonstrates the ability of neutron and X-ray methods to determine the nature of the material even being very calcium rich.

Chemical results show that they have high contents of calcium, and that the surface is more contaminated with soil particles due to high Si, Fe and K contents, and phosphorous was found in higher proportion, certainly originated from the bones. FTIR patterns show that the major part of the beads is calcium carbonate crystallized in calcite form, contaminated with silicates and calcium phosphate, pointing to shells as raw materials. The ToF-ND results also indicate the crystal lattice structure of calcite, and aragonite, a polymorph formed in the biomineralisation process of shells, was not detected, indicating a total phase transformation to calcite probably due to heating processes during funerary practices. The SEM-EDS results confirm the shell nature of beads. The results were of wider significance for the archaeological discussion, especially deciphering the nature of the beads, contributing to the debate of interaction in the Chalcolithic of Southern Iberia.

1. Introduction

The site of Perdigões occupies an area between 16 and 20 ha, comprising a set of ditched enclosures located in the municipality of Reguengos de Monsaraz, Évora district, in the Alentejo hinterland (South Portugal) (Fig. 1). Several enclosures were defined at the site comprising 15 ditches. Inside, several hundred circular pits were identified (Valera et al., 2017) but only about fifty of them have been excavated to date.

The archaeological record and absolute chronology show that Perdigões was a site of long duration, beginning in the late Middle Neolithic (middle of the 4th millennium BCE) and reaching the transition Chalcolithic/Bronze Age (last quarter of the 3rd millennium BCE). By the middle of the 3rd millennium BCE the use of tholoi type tombs for secondary depositions, the depositions of scattered human bones in ditches and the deposition of cremated remains in pits and in open air occurred, together with a large set of diverse types of artefacts (Valera, 2012a, 2012b; Valera et al., 2014a, 2014b).

The Chalcolithic period witnessed a few major socials, economic, and cultural developments in comparison to preceding Neolithic

* Corresponding author.
E-mail address: isadias@ctn.tecnico.ulisboa.pt (M.I. Dias).

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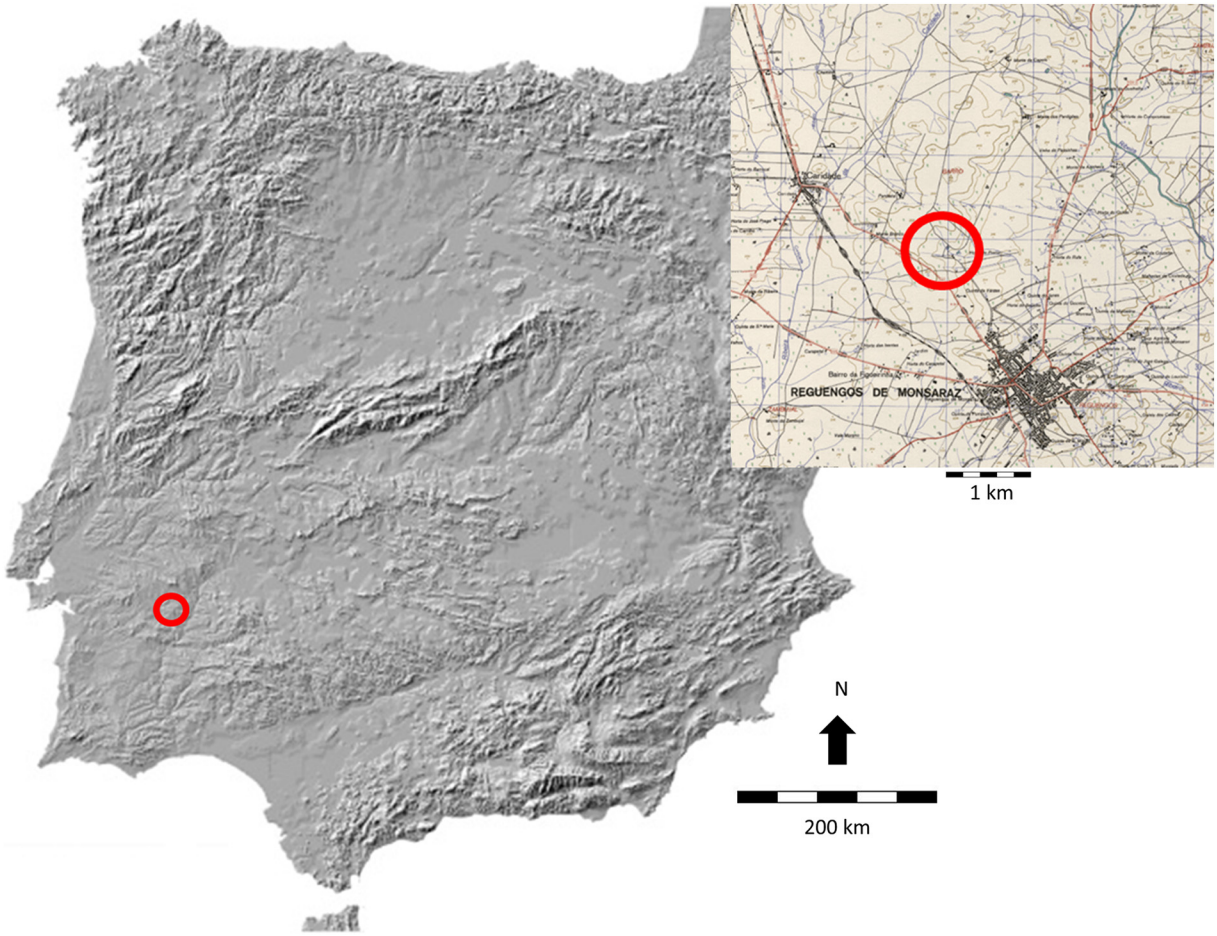

Fig. 1. Location of Perdigões in Iberian Peninsula.

phases. The 3rd millennium BCE in the Iberian Peninsula is known by its relevance in a wide field of scientific discussions comprising social changes. In this context, an increase of interaction and of specialization is attested in pottery and lithic production, stone working, ivory carving, shell carving, etc. Innovation is observed in a large variety of material spheres and in artistic representations (Gilman, 2013; Garcia Sanjuán, 2017; Valera, 2017).

At Perdigões, another relevant matter concerns the management of the dead, that seems to become a central, but diversified, issue during the middle of the 3rd millennium BCE, and, associated with it, the presence of a diversified set of exogenous materials pointing to a large interregional circulation network. This network attesting the circulation of material, people and of the "ideas" was already established for the stone idols (Dias et al., 2017a; Dias, 2015; Dias and Valera, 2017) and the ceramics (Dias et al., 2005), particularly the bell beakers (Dias et al., 2017b), ivory items (Valera et al., 2015), long blades (Valera, 2017), variscite beads (Odriozola et al., 2010a), and shells (Valera and André, 2017). The typological study and compositional analysis of objects and their implications for understanding social interaction, played an important role for the definition of exchange and mobility patterns.

Despite the comprehensive research surrounding the site, little is known about some artefact categories found in funerary contexts, which are of utmost significance, especially those reflecting socio-cultural and economic processes, such as personal bead ornaments.

Hundreds of different beads were collected from Perdigões funerary contexts so far, pointing to different raw materials, such as bones, ivory, amber, schist, variscite, and malachite, but several tens were only macroscopically described as "black stone" beads, constituting a large set of artefacts of unknown nature to be studied. In this work, we intend to characterize a set of blackish grey beads of unknown nature belonging to pit 40, one of the funerary context of Perdigões where remains of cremations were deposited, with the main purpose of establish the raw materials and to contribute to the characterization of interaction and mobility of people and objects in Perdigões, and of the nature of the site, that has been interpreted as an aggregation center (Valera, 2006).

At a first stage, the identification of the raw material of the beads is a priority, followed by the possible identification of origins. At a regional scale, there are few works regarding compositional characterization of pre-historic beads, and they are especially voted to variscite beads, like the work from Pico Centeno pre-historic site (Spanish site on the opposite border; Odriozola et al., 2010b) and Perdigões site (Odriozola et al., 2010a), as well as from Estremadura (west Portuguese coast; Odriozola et al., 2013). Regarding the importance of these artefacts only non-invasive analysis was considered.

2. Materials and methods

The analysed beads come from Pit 40 (Fig. 2), a funerary feature used for the secondary deposition of cremated remains of more than a hundred individuals. The pit is located in the centre of Perdigões (Évora, Portugal) ditched enclosures (Valera et al., 2014a) and is dated from the third quarter of the 3rd millennium BCE. The beads were part of the funerary votive assemblages, composed by arrowheads ivory figurines, marble idols and pots, phalanx idols, copper awls, Pecten shells and pottery sherds. A set of 20 beads of unknown nature were selected for this study. The beads are all micro-perforated, which have a

Fig. 2. Pit 40 — a funerary feature used for the secondary deposition of cremated remains of more than a hundred individuals. The pit is located in the centre of Perdigões ditched enclosures and is dated from the third quarter of the 3rd millennium BCE.

maximum perforation diameter of 5 mm, between 5 and 10.5 mm in diameter, a maximum thickness of 3 mm, and they are mostly grey/black and in a few cases, part of the surface is whitish (Fig. 3). They have straight perforation walls indicating a highly advanced drilling technique using composite tools. Initial morphological examination reveals three main types based on bead dimension. They are all flat. Apart from the characteristics already mention, they also show diameter and perforation standardization. All evidence gathered from earlier analysis suggests that these dark beads production sequence is a highly organized undertaking wherein a particular type of drilling tool was preferred and there had been efforts towards intensive production.

The beads were not submitted to any preparation or cleaning process prior to analyses.

The non-destructive techniques chosen to study all the beads include prompt-gamma activation analysis (PGAA), external milli-beam particle induced X-ray emission spectroscopy (PIXE) and high-resolution time-of-flight diffractometer (ToF-ND). Infrared spectroscopic (FTIR) measurements were also performed on 9 beads, and micro-destructive-Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometry (SEM/EDX) analysis was done in one broken bead.

The prompt-gamma activation analysis experiments have been performed at the PGAA instrument installed on a guided cold-neutron beam of the Budapest Research Reactor. The PGAA instrument operates with a $9.6 \cdot 10^7$ $cm^{-2} \cdot s^{-1}$ intensity guided horizontal cold neutron beam (Szentmiklósi et al., 2010). Because of the high penetrability of the neutrons throughout the analysed material, the PGAA method can determine the bulk concentration of the analysed artefact. The method is applicable to quantify almost all the major and minor components (H, Na, K, Mg, Al, Si, Ti, Mn, Fe and Cl) and some trace elements (B is an important one, occasionally also Cr, Sc, V, Nd, Sm and Gd) in various materials of geological origin, including silica-based and also calcium-based rocks. One of the most successful provenance study is the identification of different obsidian sources. In case of obsidian, B and Cl are discriminative geochemical components (Kasztovszky et al., 2008; Kasztovszky et al., 2017). The importance of trace elements, including B, in the provenance of calcium-based rocks is still the subject of recent research (Dias et al., 2017a). The energies of the prompt- and delayed gamma photons, emitted in the (n,γ) reactions, are characteristic for the emitting identified element and the photon intensity is proportional to the amount of the given element. The γ-photons are detected with a HPGe detector, surrounded with a BGO annulus. The collected spectra have been evaluated with the Hypermet PC software (Fazekas et al., 1997; Révay et al., 2005); the element identification based on BNC PGAA library (Révay et al., 2004) and calculation of concentrations are performed using the prompt k_0-method (Révay, 2009). Because of the low intensity of external neutron beams, PGAA can be considered non-destructive, i.e. no visible or invisible modification on the irradiated objects can be observed following the PGAA investigation. Furthermore, the method does not require sample preparation, since the intact object is positioned directly in the neutron beam, and no significant long-lived radioisotopes are produced during the analysis. The most frequent induced radioactive isotopes in various rocks are Na-24, Al-28 and Mn-56, which fortunately occur in low concentrations in the carbonate samples, and – thanks to their short half-lives – practically vanish within 2 or 3 days.

The PIXE measurements were performed at the 5 MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre for Physics, Hungarian Academy of Sciences. Proton beam of 2.5 MeV energy was extracted from the evacuated beam pipe to air through a 7.5-μm thick Kapton foil. External beam currents in the range of 1–5 nA were used. Characteristic X-ray spectra were taken by an AMPTEK X-123 X-ray spectrometer. The net X-ray peak intensities and the concentration calculations were made by the offline GUPIX program package (Campbell et al., 2000). This technique is useful in analysing the surface composition of the artefacts.

The ToF-ND (Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences) uses neutron pulses (as short as 10 μs) produced by a fast double-disc chopper. The total flight path of the neutrons to the detectors is 25 m, the detector position fixed at 175° (backscattering geometry). Neutron diffraction provides information on structural properties.

For detailed IR spectroscopic investigation (FTIR - Research Centre

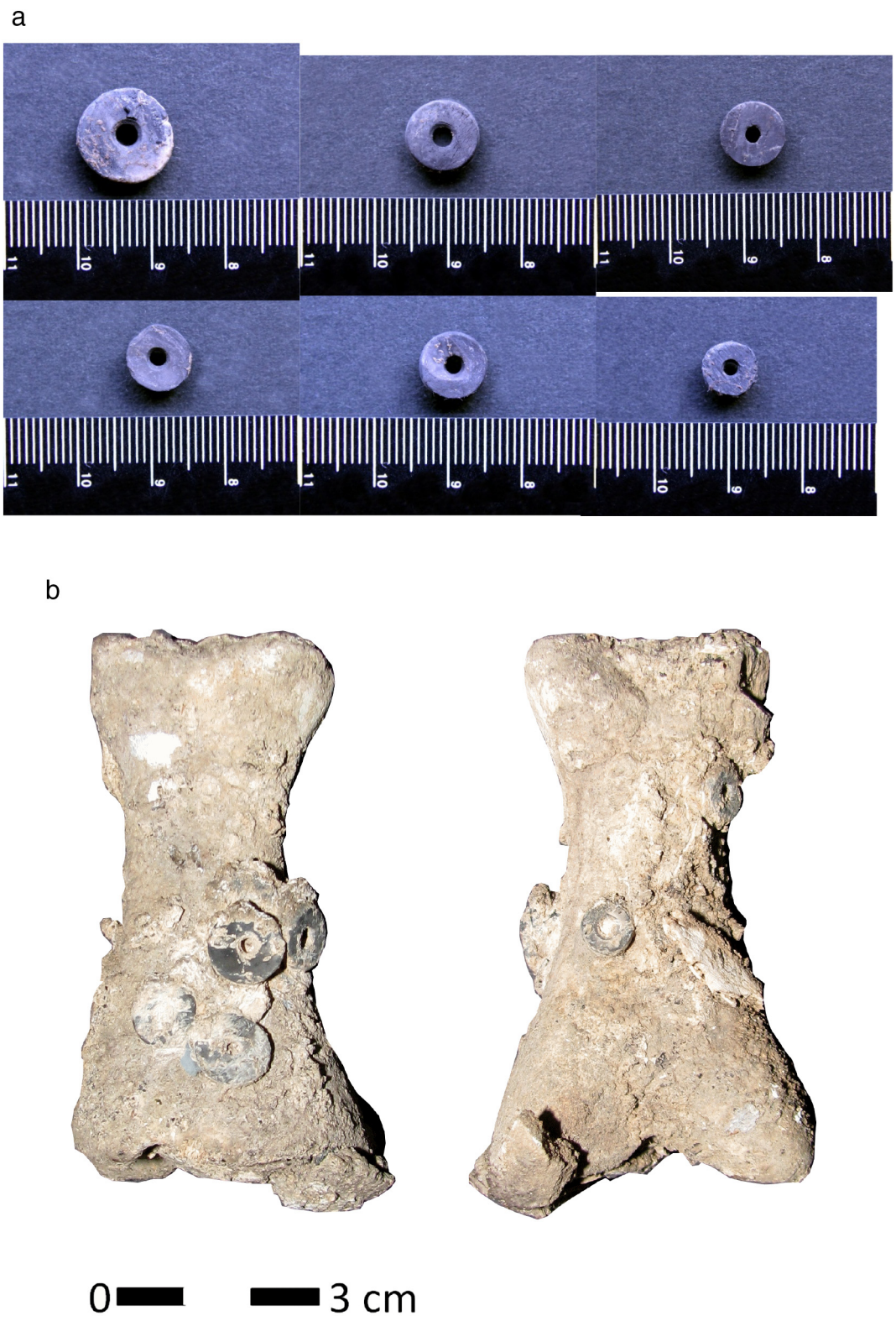

Fig. 3. Short cylindrical beads of unknown nature, with 5–10.5 mm diameter, a central perforation up to 5 mm maximum thickness of 3 mm, colour grey or black (a). Beads attached or adhering to bones (b).

for Natural Sciences, Hungarian Academy of Sciences) the attenuated total reflection (ATR) technique was applied. To study the chemical composition FTIR spectroscopy was also employed (Research Centre for Natural Sciences, Hungarian Academy of Sciences). The outer surface of the beads was monitored using a Varian Scimitar 7000 FTIR spectrometer connected to an UMA 600 microscope system. For detailed IR spectroscopic analysis, the attenuated total reflection (ATR) technique was used. ATR-FTIR spectra were collected by the means of a Varian Scimitar 2000 FTIR spectrometer equipped with a MCT (Mercury-Cadmium-Telluride) detector and with a single reflection 'Golden Gate' ATR accessory (with diamond ATR element). By a needle-point a small grain (~50 μg) was removed from the lateral part of the beads. The

small grain was carefully transported onto the surface of the diamond ATR element and pressed by a sapphire anvil to ensure the perfect contact between the ATR optical element and the sample necessary for suitable signal-to-noise ratio spectra.

SEM (MicroLab-Electron Microscopy Laboratory of IST — Instituto Superior Técnico) was done by using a JEOL 7001F with Oxford light elements EDS detector and EBSD detector. Sputter coating of the bead fragment was done by applying an ultra-thin film of electrically-conducting metal Au/Pd (thickness range of 15–25 nm) using a Quorum Technologies Q150T ES equipment. This technique is especially useful for textural studies of the artefacts, providing three-dimensional images with higher magnification, and coupled with an EDXRS (energy dispersive X-ray spectrometry) system yield chemical composition.

3. Results and discussion

First macroscopic examines of the studied beads have classified them as “black stone” beads, probably schists. Remarkably, the results obtained by PGAA pointed probably for a calcite rich raw material, considering the very high calcium oxide content. Among the chemical elements obtained by PGAA, calcium is the element with major concentrations (53 wt% < CaO < 74 wt%), and in addition, Sr, Si and Fe are also present in the majority of the samples (Fig. 4). The Fe_2O_3 contents were found to be between 0.018 wt% and 0.606 wt%, while the SiO_2 contents were found to be 0.12 wt% and 0.55 wt%. SrO contents were found to be between 0.12 wt% and 0.32 wt% that can be explained by the calcium substitution within the calcite lattice. On the other hand, the Si and Fe contents can be related with the soils particles that are still present in the beads. Therefore, the first analytical approach clears question the schist nature of the beads.

Elemental analysis by PIXE also highlights the high calcium content as can be seen in Fig. 5 where a representative PIXE spectrum is shown. In addition to the dominating Ca K-X-ray peaks the presence of Si, P, S, Cl, K, Ti and Fe is also clearly demonstrated. (The Ar peak is coming from the natural Ar content of the air layer between the exit foil and the sample.) The generally low values and high variability of the concentration values for these elements support the assumption that the presence of these elements can be attributed to contamination of soils particles and bone residues still present in the beads surface and in the original burial context, as well.

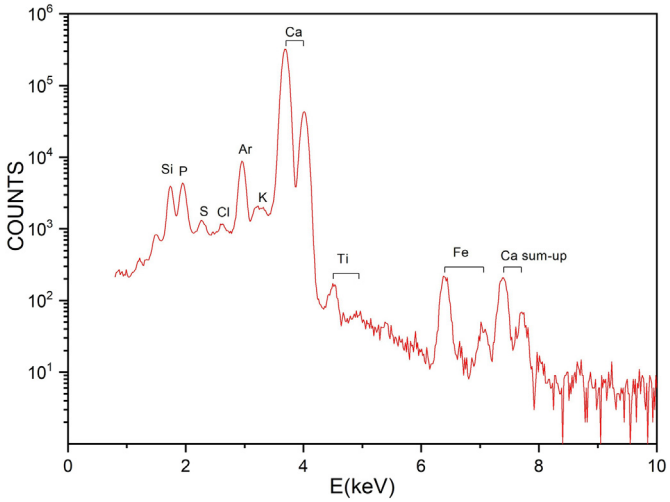

Fig. 5. A representative external milli-beam PIXE spectrum.

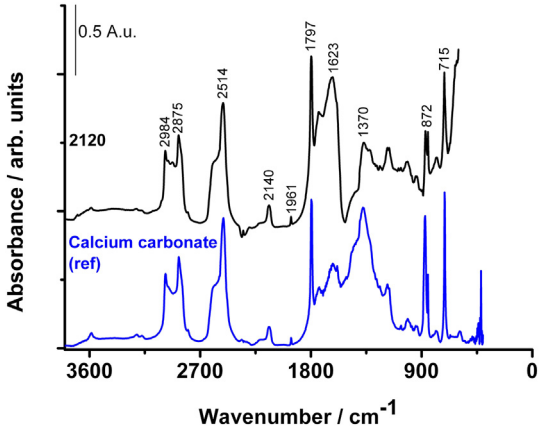

Fig. 6. Typical DRIFT (diffuse reflection infrared Fourier transform) spectrum of one bead (2120) from Perdigões recorded by FTIR microscope, compared with a reference spectrum of calcium carbonate.

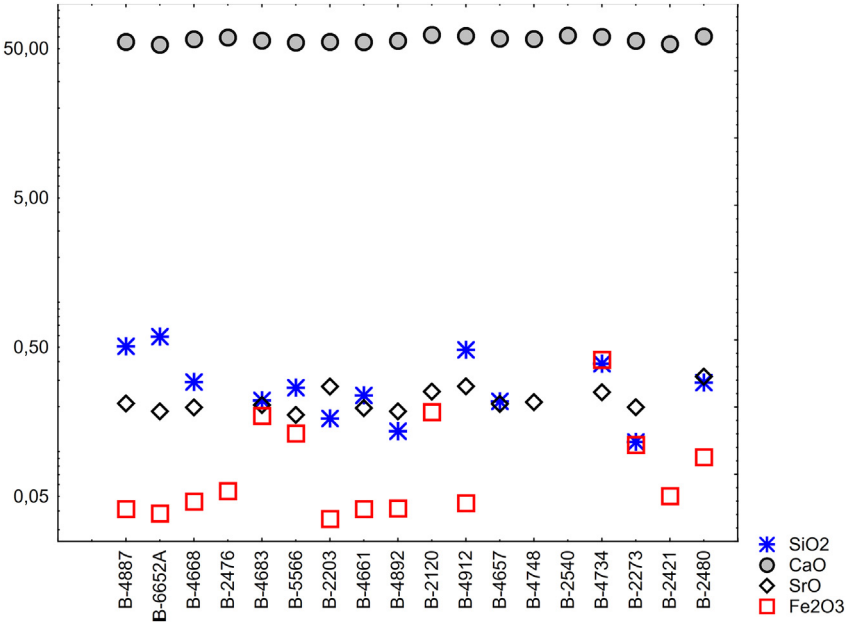

Fig. 4. SiO_2, Fe_2O_3, CaO and SrO contents (in %) obtained by PGAA for the analysed beads from funerary contexts of Perdigões site (concentrations of chemical elements in logarithmic scale).

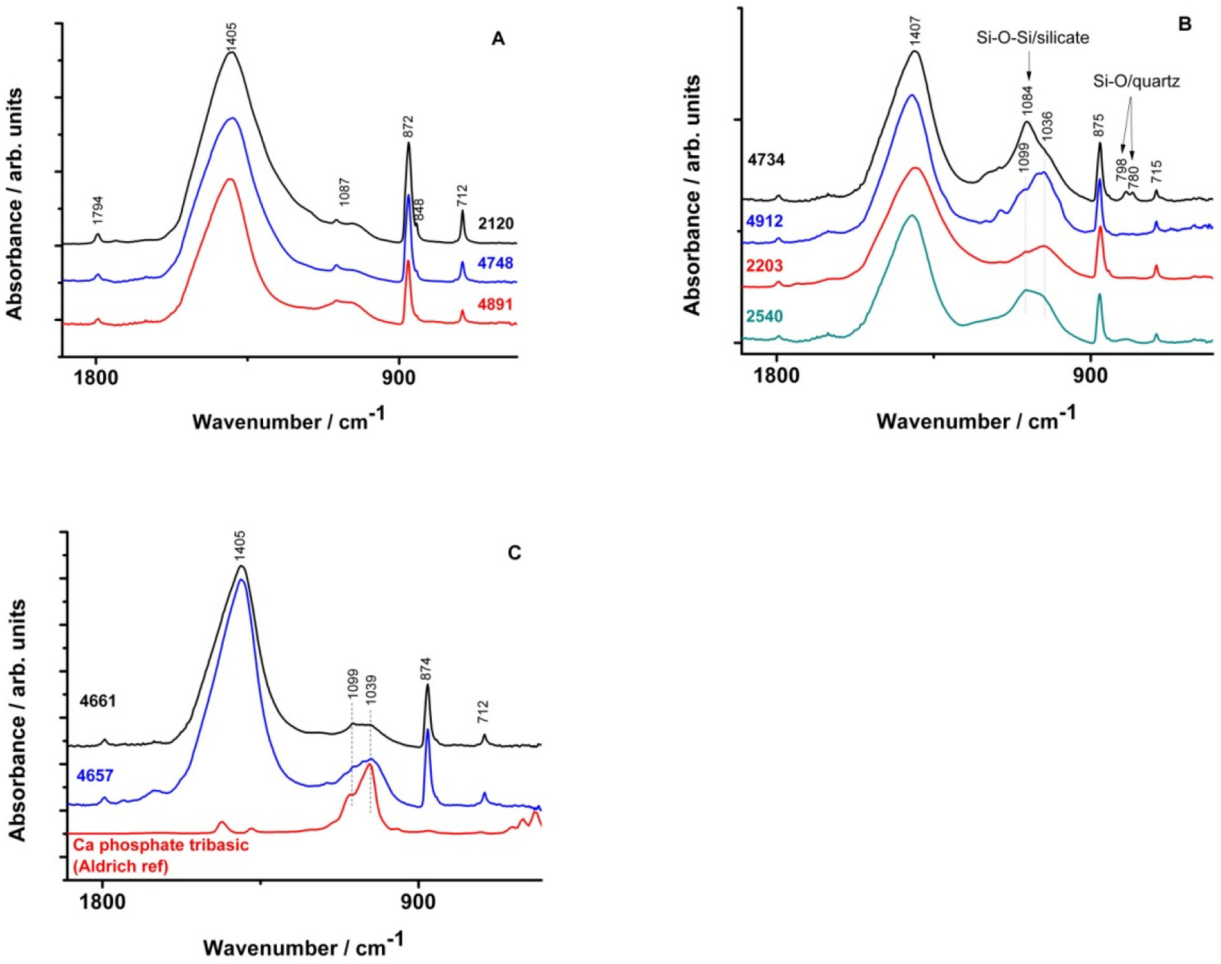

Fig. 7. ATR-FTIR spectra of nine beads from Perdigões.

FTIR patterns also point to the same composition, showing that the major part of the beads is calcium carbonate crystallized in calcite form (Fig. 6).

ATR-FTIR spectra obtained for beads are presented in Fig. 7 and the wavenumber of the main IR bands (cm^{-1}) and their assignment in Table 1. For all analysed cases, the spectral feature of calcium carbonate was identified. As to the bead 4734 (Fig. 7A), same traces of clays were also detected in the spectrum, supported by the presence of the Si—O doublet at 798 and 780 cm^{-1}, typical for quartz and by the broad feature around 1100 cm^{-1} of Si—O—Si stretching of silicates. Moreover, in some beads traces of calcium phosphate were also identified; beads with higher amount of phosphate are 4912 and 4657, respectively (Fig. 7C). These results are in accordance with the previous ones obtained by both PGAA and PIXE techniques, highlighting the soils and bones particles contamination on the beads surface.

To go deeper in the raw material identification, further FTIR studies were applied, particularly to identify the crystal phase of possible carbonate polymorphs. In this way, the so called fingerprint region of the spectra (1000–550 cm^{-1}) was examined and compared with different reference spectra: (i) modern sea coral (*Porites* sp.) with pure aragonite structure; (ii) modern sea shell (*Philippine venus*) with aragonite structure mixed with small amount of calcite; and (iii) marble with calcite structure (Fig. 8) (Zakaria et al., 2008).

Table 1
The wavenumber of the main IR bands (cm^{-1}) and their assignment.

2120, 4748, 4891	4734	4912	2203, 2540	4661, 4657	Assignment
1405	1407	1407	1407	1405	CO_3; carbonate
	1099	1099	1099	1099	PO_4^{3-}, phosphate
	1064	1064			Si—O—Si, silicate
	1036	1036	1036	1039	Si—O—Si/PO_4^{3-} silicate/ phosphate
872	872	872	872	872	CO_3; carbonat$_e$
	798				Si—O; quartz
	780				Si—O; quartz
712	715	712	712	712	CO_3; carbonate

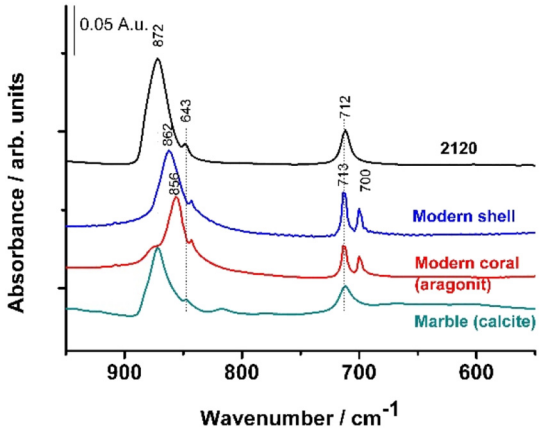

Fig. 8. Fingerprint spectral region of one bead (2120) of Perdigões compared with reference spectra of different carbonate polymorphs.

To identify the crystal phase of possible carbonate polymorphs, we consider that the characteristic carbonate $\nu 2$ band of aragonite is around 860 cm^{-1}, while that of calcite is at 871 cm^{-1} (Nia and Ratnera, 2008). Aragonite shows a doublet of $\nu 4$ band at 713 and 700 cm^{-1}, whereas calcite is at 713 cm^{-1}, and vaterite, another carbonate polymorph, at 744 cm^{-1}. Therefore, taking into consideration the results obtained for the studied beads, obviously we can state that the analysed beads are calcium carbonate crystallized in calcite form.

It is worth to note that recent shells (usually of aragonite structure) transform to calcite during diagenesis; no traces of aragonite polymorph were detected. The position and shape of the $\nu 3$ antisymmetric CO_3^{2-} band might be also indicative in respect with the crystallization degree and the size of crystallites. Among the beads investigated, the beads number 4661 and 4657 show $\nu 3$ bands with asymmetric shape. Spectral deconvolution of this band suggests that the crystallites sizes or crystallization degree of these beads (4661 and 4657) may be different compared to the rest of investigated beads. This may be a future clue for provenancing discussion.

In this stage of the research, the most probable raw materials for the beads manufacture were shells. Mollusk shells, whatever their taxonomic origin, are always made of the superimposition of few calcified layers, generally two to five, and one organic layer and several composite microstructures (Marin et al., 2012; Filho et al., 2014). Shells are almost always composed of polymorphs of calcium carbonate - either calcite or aragonite, and they can occur at the same time (Filho et al., 2014). Aragonite and calcite are more thermodynamically stable structures, and they most commonly occur in nature. The calcium carbonate layers in a shell are generally of two types: an outer prismatic layer and an inner pearly, lamellar or nacreous layer. Shells can have numerous ultrastructural motifs, the most common being crossed-lamellar (aragonite), prismatic (aragonite or calcite), homogeneous (aragonite), foliated (aragonite) and nacre (aragonite); although not the most common, nacre, also known as mother-of-pearl is the most studied type of layer (Marin et al., 2012; Melzner et al., 2011; Fricke and Volkmer, 2007). There are different types of mantle-shell association, resulting in distinct calcified fabric or range of fabrics: complex crossed lamellar fabric of the inner shell layer; irregular prismatic shell fabric; crossed-lamellar fabric and, in the case of some species, proximal and distal radial fabrics (Waller, 1980).

The ToF-ND results also indicate that studied beads have crystal lattice structure of non-dolomitic calcite or pure calcite. The structure is highly anisotropic, but definitely not single crystalline. The c-axis is preferred in the direction perpendicular to the plane of the specimens. This texture most likely originated from the original anisotropy of the aragonite. Thus, aragonite, a polymorph formed in the bio-mineralisation process of shells, was not detected, and like the FTIR results, also pointing to a total phase transformation to calcite due to heating processes. When heated to a temperature of about 400 °C or 500 °C, the structure of the shells changes from aragonite to calcite. This transformation occurs because aragonite is a thermodynamically unstable phase of calcium carbonate (Yang et al., 2011).

The SEM-EDS results show the shell nature of the archaeological beads, but no crossed and/or crossed-lamellar structure was markedly observed most probably due to fusion processes by heating processes. Only calcite was clear observed in a morphological and chemical point of view. Fig. 9 shows the morphology of one broken bead obtained by SEM. Some vestiges of crossed lamellar structure were observed (Fig. 9a; b), like for other studies of heat treated bulk shells (Li, 2013), in the 500 °C-heated sample, the crossed-lamellar structure might be still maintained despite the phase transformation from aragonite to calcite. Nevertheless, detailed examination of lamellae displays grain coarsening and nanoscale holes of calcite particles (Fig. 9c). Here, the formation of nano-holes results from the burning-out stuffing and lattice rearrangement during phase transformation.

Another interesting feature of the set of beads analysed in this work, is that they are all black. The mineral phase transition from aragonite to calcite does not explain in itself the blackening of the shell. Previous studies (Lange et al., 2008) indicate that the black coloration can only be achieved by heating under limited conditions, and probably due to a relatively high amount of amorphous carbon adhering to the surface of the shell, under reducing conditions. Amorphous carbon is a carbonised product released when organic material is burned (Basilia et al., 2006). Only reducing conditions would allow the formation of a black carbonised product staining the shells. Like already noticed for heat-induced modification of marine shells used as ornaments at the pre-historic site of Franchthi Cave, Greece (Lange et al., 2008), we may consider that the studied black shells might have been intentionally heated with a special heat-treatment, prior to the funerary practices. Particularly because of the high blackened homogeneity of the beads, or they were

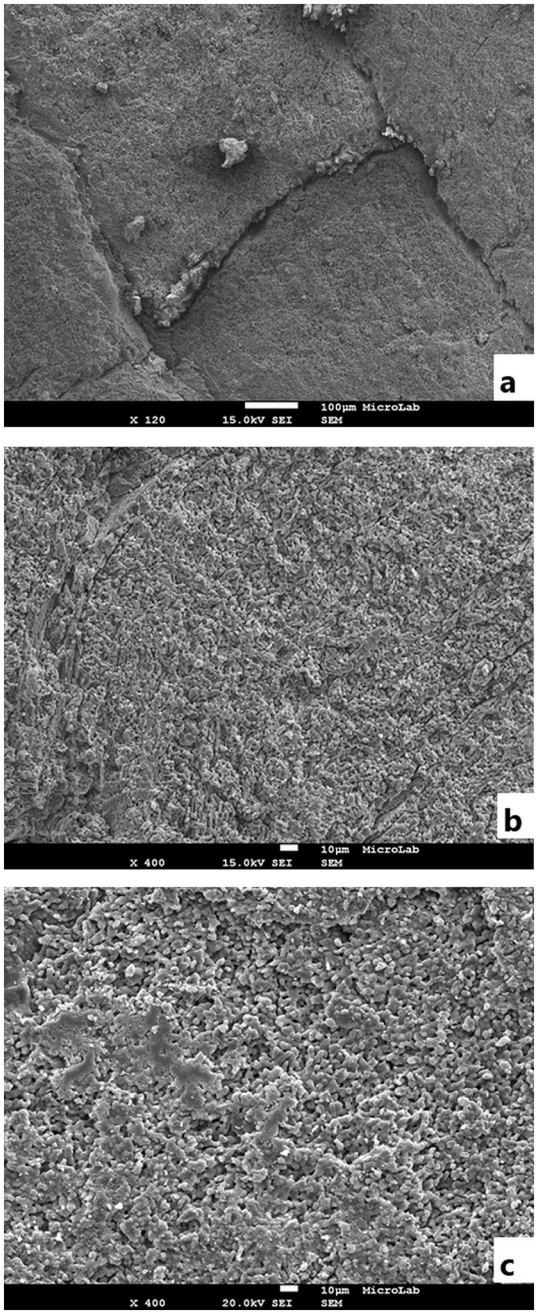

Fig. 9. SEM images of broken bead; a and b displays detailed morphology of shell bead showing some vestiges of crossed lamellar structure and a total phase transformation to calcite; c displays the calcite particles and nanoscale holes in between.

submitted to a heating pre-treatment, or a careful atmosphere control was performed during the heating processes of both bones and ornaments during the funerary practices. This last hypothesis, thought, is contradicted by the burned bones, that show submission to different levels of heating, suggesting heterogeneous burning conditions.

4. Conclusions

All analytical approaches showed that shells were the raw materials used for the production of the dark beads found in funerary contexts of Perdigões archaeological site, pointing to the occurrence of transformation of aragonite to calcite during firing, as a result in restructuring of the crystal structure. As showed by previous studies (Carlson, 1983; Li, 2013) heating the shell nears ~130 °C the crystal structure undergoes a slight change, resulting in expansion, at ~150°, the removal of organic matter will begin, near ~350 °C aragonite will start to convert to calcite, with complete conversion happening around 500 °C. The Si, Fe, K and phosphorous contents observed associated to the high calcium amounts, reflects the contamination of soils particles and bone residues still present in the beads surface. One potential problem is related with diagenesis of the shell beads and their chemical constituents arising from firing and other post-depositional changes caused by possible leaching and ground water fluctuations within the archaeological deposits. Collins (2012) has studied the changes in trace element concentrations between unfired and fired shell at 500 °C, showing that certain trace elements, especially strontium, aluminium, barium and manganese, maintained their concentrations, suggesting that they might be particularly useful for provenance studies.

Another interesting feature is related with the homogenous dark colour of the beads that might have been intentionally heated with a special heat-treatment, prior to the funerary practices. The black coloration can only be achieved by heating under reducing conditions that would allow the formation of a black carbonised product staining the shells. Further studies need to be done, especially including other shells found at the same pit, and at other funerary contexts of Perdigões, in order to better establish if it was pre-treatment or burnt together with bones during funerary practices.

As to the origin, further studies are foreseen, but a first approach at the thickness of the beans indicate marine and estuarine species of mollusks shell, several of them been present at Perdigões (Valera and André, 2017), reinforcing the idea of a strong interaction between Perdigões and the Atlantic coastal areas.

Acknowledgments

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