

A stone bead from a SW Bronze Age burial: analysis by EDXRF and X-Ray Diffraction

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ABSTRACT

A stone bead, a grave good from a SW Bronze Age burial located at Santa Vitória (Beja), and now belonging to the collections of the Museu Nacional de Arqueologia, was analyzed using non-destructive techniques (EDXRF and X-ray Diffraction) in order to identify the rock used for its manufacture. The analysis allowed to classify the material as talc. Two more beads from archaeological contexts, located at north of Lisbon, are known to be made from talc. These only three specimens are in contrast with the most part of the analyzed pre-historic beads, which were made from phosphates of the variscite group.

Key-words: Stone bead – EDXRF – X-ray Diffraction – Talc

RESUMO

Uma conta de pedra proveniente de um enterramento da região de Santa Vitória (Beja) atribuível ao Bronze do Sudoeste e, actualmente, fazendo parte das colecções do Museu Nacional de Arqueologia, foi objecto de análises não destrutivas, designadamente

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por Fluorescência de Raios-X, Dispersiva de Energias, e por Difracção de Raios-X. Estas análises tiveram por objectivo identificar o material de que a conta é feita, tendo-se chegado à conclusão de que se trata do mineral talco. Esta conta, conjuntamente com outras duas provenientes de contextos pré-históricos situados um pouco a norte de Lisboa, constituem os únicos exemplares feitos deste material analisados até hoje no nosso país, enquanto que a maior parte das contas de pedra pré-históricas parecem ter sido manufacturadas em variscite.

Palavras-chave: Contas de pedra – Fluorescência de Raios-X, Dispersiva de Energias – Difracção de Raios-X – Talco

1. INTRODUCTION

The study of the nature and origin of Portuguese pre and proto-historic stone beads is extremely incomplete: only two preliminary systematic works have been reported up to now (Canelhas, 1973; Gonçalves, 1980). As the use of collars in pre-historic times can also be considered as a symbolic expression of status, the identification of the beads material and distribution can give some information about the importance of different communities and eventual routes of commerce.

A stone bead belonging to the collections of the Museu Nacional de Arqueologia (Lisbon) was analyzed using non-destructive techniques (EDXRF and XRD) in order not only to identify the lithological nature of the material used for its manufacture and, if possible, the source of its provenance, but also to demonstrate the potential of these non invasive techniques in this kind of studies.



Fig. 1 – The stone bead from Santa Vitória (Beja).

The analyzed stone bead (Fig. 1) is complete, well polished and exhibits a surface with a bright brown patina that coats green and brown zones of the bead. The artifact presents a spherical form of *ca.* 20 mm diameter, with a central cylindrical hole of 5 mm diameter. The bead seems to be found associated to a pottery vessel (a bowl of Atalaia type) shown in Fig. 2. Both artifacts must be grave goods from a Bronze Age burial located at Santa Vitória (Beja). From the museum reference numbers (10243 and 10244) of these artifacts can be inferred that they enter the museum collections before 1906. Nothing else is known about how these artifacts enter to the museum collections or about the burial itself. Nevertheless, the vessel typology points to the Period I of the SW Bronze Age (Schubart, 1975).



Fig. 2 – The pottery bowl associated as grave good to the stone bead from Santa Vitória.

2. EXPERIMENTAL

2.1. EDXRF

The Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry is widely used in the study of archaeological samples due to its non invasive characteristics. The EDXRF spectrometry is also multi-elemental, fast and allows the detection of chemical elements with an atomic number larger than 12 with high accuracy.

The chemical analyses of the geological sample were performed using a commercial Energy Dispersive X-Ray Fluorescence spectrometer, Kevex – 771EDX. The system is equipped with a rhodium X-ray tube (200 W) and several secondary

targets and filters (Ti, Fe, Ge, Zr, Ag and Gd) to optimize the excitation conditions. The direct excitation mode uses the beam directly from the tube to excite the sample. The secondary excitation mode uses the characteristic X-rays emitted by the selected secondary target to excite the sample. The X-rays emitted by the sample are collimated at 114° or 90° , respectively, and measured in a cryogenically cooled Si(Li) detector with an active area of 30 mm^2 and a resolution of 175 eV at 6.4 keV.

The direct excitation mode was used to measure the Mg, Si and S in the sample by applying a voltage of 4 kV and a current of 0.2 mA to the X-ray tube. The monochromatic beam from the germanium secondary target was used to measure the K, Ca, Mn, Fe, Cu and Zn, using 20 kV and 1.5 mA. The sample was measured in two different areas, A and B (green area), under vacuum through 300 s of live time for each excitation condition. The quantitative determinations included the calibration with a geologic reference standard, Green River Shale – SGR1 from the U.S. Geological Survey.

The elemental concentrations were calculated using the EXACT program (KEVEX, 1990), which is based on the fundamental parameter method (TERTIAN & CLAISSE, 1982). Since the sample is smaller than the excitation beam (which is about 3 cm in diameter) the determined elements were normalized to 100 %. The spherical shape of the studied sample also introduces some additional uncertainties (ARAÚJO *et al.*, 2003), which however do not affect the overall objective of the analysis.

2.2. X-Ray Diffraction

The samples were characterized by X-ray powder diffraction in a reflection mode using an X'Pert Panalytical diffractometer with CuK_α radiation (1.54056 \AA), under set conditions of 45 kV and 40 mA. The data were measured with a 2θ -step size of 0.02° in a 2θ -range of 5.00° - 65.00° and a counting time of 3 s per step. In a first stage, the X-ray patterns were compared against the ICDD PDF X-ray diffraction data book sets. After the identification of the constituent minerals the experimental X-ray powder diffraction patterns were compared with simulated diffractograms from structure refinement data using the program Powder Cell (Nolze and Kraus, 2000).

3. RESULTS

The semi-quantitative results obtained by EDXRF for the stone bead of Santa Vitória indicate that both analyzed areas, despite their different colour, exhibit a similar elemental pattern (Table I), which point out to the uniform lithological composition of the bead.

Table I – Semi-quantitative EDXRF analysis of two areas in the Santa Vitória bead – MNA 10244

	MgO	SiO ₂	S	K ₂ O	CaO	MnO	Fe ₂ O ₃	Cu*	Zn*
	%	%	%	%	%	%	%	mg/kg	mg/kg
a	39	55	~0,2	~0,2	3	~0,03	4	~90	~90
b	36	53	~0,3	~0,4	6	~0,06	5	~120	~220

(a – green area; b – brown area; * - indicative results only).

On the other hand, X-ray diffraction patterns performed on different parts of the surface of the bead (a – green and b – brown zones) show an identical shape, only slightly changing the peaks intensity (Fig. 3), pointing to the same mineral constitution despite the different colours. The comparison with the ICDD PDF X-ray diffraction data book sets indicates that the main mineral of the bead is talc.

The structure of minerals classified as talc is formed by $2\text{SiO}_{2.5}(\text{OH})_{0.5}:1\text{Mg}$ layers. The first structural studies described talc with a monoclinic symmetry (Gruner, 1934; Rayner and Brown, 1966; Perdikatsis, 1972), and later indicated a triclinic structure (Rayner and Brown, 1973; Perdiktasis and Burzlaff, 1981; Lindemann et al., priv. comm.). However, as structural distortions have been reported in layer silicates, due to accommodations between the sheets (Radoslovich and Norrish, 1962), the possibility of such behavior for talc cannot be excluded. More recent studies indicated that the structure of naturally occurring talc is disordered to varying degrees by random layer translations (Wiewióra *et al.*, 1997). Moreover, the existence of different mineral compositions for talc (due

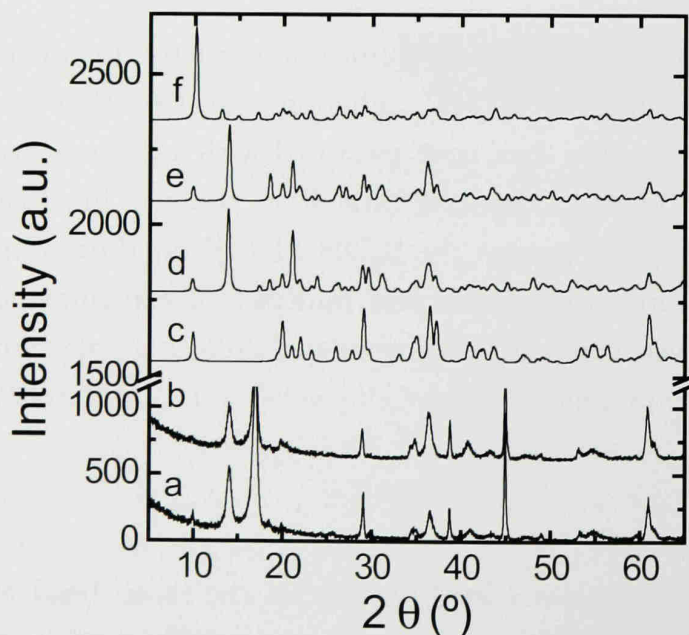


Fig. 3 – X-ray diffraction patterns of: (a) green zone of the bead; (b) brown zone of the bead; (c), (d), (e) and (f) calculated using the structural data from Perdikatsis e Burzlaff (1981), Rayner e Brown (1973), Perdikatsis (1972) and Lindemann *et al.* (private communication), respectively.

to dissimilar impurities) can favor such distortions and can explain the dispersion of the structural refinement results.

In Fig. 3 are shown the experimental X-ray diffraction patterns (a and b for the green and brown zones, respectively), together with the spectra calculated using the reported talc structures: c (Perdikatsis and Burzlaff, 1981); d (Rayner and Brown, 1973); e (Perdikatsis, 1972) and f (Lindemann *et al.*, priv.

comm.). It is interesting to notice that significant differences can be seen between the calculated spectra, reinforcing the possibility of existence of different polymorphs for talc.

Comparison between the experimental and simulated X-ray diffraction patterns confirms that the bead is mainly formed by talc, with a crystal structure probably close to the one reported in Perdikatsis e Burzlaff (1981). However, the experimental patterns differ from the calculated ones in several aspects:

- The most intense peak is located at $2\theta = 16.81^\circ$ and is almost inexistent in the calculated patterns (it exists only a small peak in the d and f simulations);
- Two other intense and sharp peaks can be observed at $2\theta = 38.63^\circ$ and 44.85° and are negligible in the simulated patterns;
- The intensity of most peaks at lower angles ($2\theta < 30^\circ$) are less intense than the expected.

An analysis of the simulated patterns shows that the most intense peak corresponds to diffraction from the 1 0 0 reflection, its increasing being most probably due to texture effects. Concerning the two intense and sharp peaks observed experimentally and almost inexistent in the simulated patterns, a detailed analysis indicates that they belong to aluminum and came from the sample holder. Finally, the decrease of the peaks intensity can be explained by the small size of the analyzed bead surface: at low Bragg angles the sample is illuminated by only a fraction of the incident X-ray beam, underestimating the intensities when compared with the high Bragg angles.

4. CONCLUDING REMARKS

Using absolute non invasive techniques it was possible to identify the stone used to manufacture the bead from Santa Vitória: talc. The talc is the first member of the Mohs scale of hardness and, consequently, can be easily worked. In spite of this, the material mostly used in the Portuguese territory during the Chalcolithic and the Bronze Age to the manufacture of beads were phosphates of the variscite group (Gonçalves, 1980).

Some dozens of stone beads from Portuguese Pre and Proto-Historic contexts were already analyzed, but only two more specimens are made from talc – one from the cave of Furadouro de Rocha Forte (Pragança) and other from another cave: Casa da Moura (Peniche) (Canelhas, 1973).

As the talc has a wide geological distribution and also because some lack of data it is not possible to determine the source or sources of provenance of this stone used to manufacture the bead of Santa Vitória or the other two referred to above.

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