Nuclear Instruments and Methods in Physics Research B 306 (2013) 236–240

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

The earrings of Pancas treasure: Analytical study by X-ray based techniques – A first approach

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ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form 25 October 2012
Accepted 24 November 2012
Available online 18 January 2013

Keywords:
Gold
Earrings
Iberian
PIXE
XRF
SEM–EDS

ABSTRACT

The development of new metallurgical technologies in the Iberian Peninsula during the Iron Age is well represented by the 10 gold earrings from the treasure of Pancas. This work presents a first approach to the analytical study of these earrings and contributes to the construction of a typological evolution of the Iberian earrings. The manufacture techniques and the alloys composition were studied with three complementary X-ray spectroscopy techniques: portable EDXRF, μ-PIXE and SEM–EDS. The results were compared with earrings from the same and previous periods.

1. Introduction – the Iberian earrings

The *Pancas* treasure, conserved nowadays at the National Museum of Archaeology (NMA) in Lisbon, was found in 1979 in *Quinta das Pancas* (Alenquer-Lisbon), and consists on 3 silver necklaces, 1 silver smelting drop, 10 gold earrings and 136 silver denarii from the Roman Republic period, giving a *terminus post quem* of 1st c. BC [1]. The earrings (Fig. 1) are representative of the development of technological traditions in the Iberian Peninsula during the Iron Age: the change from a massive casting, characteristic of the Late Bronze Age, to a *repoussé* work decorated with wires and granulation and the use of hard soldering [2].

Fig. 2 proposes a chronological evolution of the Iberian earrings, which starts with a single casted round ring typical of the Late Atlantic Bronze Age gold work and of the North European traditions. The arrival of new technologies and cultural influences from the Eastern Mediterranean [3] brings the application of granules joined by solder to the main ring (Au171), in different patterns (Au169), and finally the introduction of twisted wire and *repoussé* work (Au833 typologically close to the earrings of Serradilla, Cáceres [4]), typical of the orientalising period and the Etruscan traditions.

Very few studies consider the identification of the goldsmith's technologies and the gold base alloys used in the Iberian Peninsula in the Bronze and Iron Ages [5,6]. This work is the first analytical study by SEM–EDS, EDXRF, μ-PIXE of the Pancas earrings and aims not only to characterise the manufacturing techniques and the gold alloys, but also to compare these results with data published for equivalent objects from southern Spain and 3 earrings (Au169, Au171, Au577), from the NMA collection excavated in Cabeça de Vaiamonte, located at Monforte, a region below the Tagus River. In order to search for a possible chronological continuity of technologies and supplies in one area of production the results were also compared with the analyses of 3 earrings (Au11, Au196, Au571) of earlier productions in the Lisbon region, also belonging to NMA collection.

2. Methods and instrumentation

The earrings were studied using EDXRF, micro PIXE and SEM–EDS.

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http://dx.doi.org/10.1016/j.nimb.2012.11.054

Fig. 1. Earrings from the Pancas Treasure, Santana da Carnota, c. 400–200 BC (1st line and by order Au834; 832; 833; 836; 837; 2nd line: 835; 839; 840; 841 and 838. National Museum of Archaeology, Lisbon).

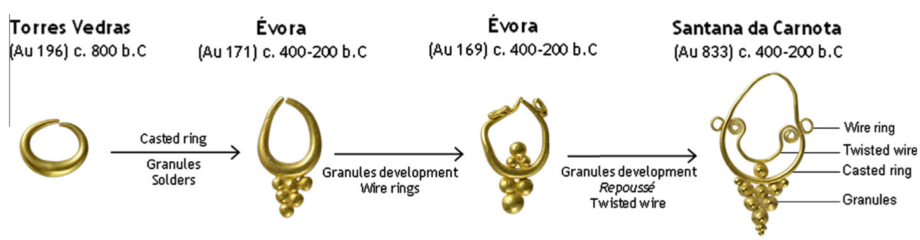

Fig. 2. Typological evolution (hypothesis) of the earrings produced in the Late Bronze Age and the Iron Age in the Iberian Peninsula.

All the earrings were analyzed by portable EDXRF [7]. This system for *in situ* gold alloys identification comprises an Oxford Instruments Eclipse IV (45 kV, 50 μA, 2.25 W max.) X-ray source with an anode of Rh and a 250 μm thick be window coupled to a XR-100SDD Amptek X-ray detector and preamplifier. The accuracy of the quantitative results was validated by analysis of gold standards.

A selected group of earrings was studied by μ-PIXE and SEM–EDS. μ-PIXE analysis was carried out using one of the three beam lines of the 2.5 MV van de Graaff accelerator from IST/ITN in Lisbon, with a 2 MeV proton focused beam ($3 \times 4\ \mu m^2$) using an Oxford Microbeams quadrupole triplet system [8]. For collection of the X-ray signals a link X-ray detector of 145 eV energy resolution with a 50 μm thick mylar foil filter was used. This filter essentially prevents backscattered protons from entering into the detector crystal then improving the detector life time. SEM–EDS was performed at LNEG, with a Philips XL 30 FEG (field emission electron source) and an EDAX spectrometer coupled to the microscope. All compositional data is referred in weight.

3. Results and discussion

3.1. Decoration elements – granulation and wires

Plain granules (Au836 & Au837) and hollow granules, dieformed in two halves (Au832 & Au833), with no compositional differences could be identified. Both types are characteristic of the southern Iberian Peninsula goldwork [6]. The granulation patterns can be achieved by joining the granules in different rows by soldering either directly to the casted ring or after assemblage [9], requiring the use of distinct alloys [10].

Fig. 3 shows the variation of the granules (Gra) compositions for earring Au169, shown in Fig. 2: 1&6 are richer in copper and 2&3 and 4&5 have similar compositions. These differences could correspond to the following mounting scheme: 2 distinct sets of granules – 2&3 and 4&5 – are soldered together and then to these are added granules 1&6, respectively.

The hard soldering technique, characterised by joining two parts by melting a filler alloy with a lower melting point – already reported for objects from the same period [11] – was found in different earrings. SEM reveals the dendritic structure of the Au–Ag–Cu solder (Fig. 4). Moreover, EDS analysis confirmed the use of solders with different compositions (the Ag/Cu ratio ranging from 8 to 18).

Six earrings from the Pancas Treasure are decorated with strip-twisted wire (Fig. 5a). The spiral seams and the solders joints are shown in Fig. 5b. It is possible to observe the fragment of the dendrite structure of the Au–Ag–Cu solder at the lower limit of the gold.

3.2. The casted main ring and the identification of earring pairs

Fig. 6 shows the Au/Ag ratio plotted *vs* Cu content, obtained by EDXRF, for the main casted rings of Pancas and, inside the dotted line, the 3 earrings (Au11, Au196, Au571) from the Lisbon region. The Pancas' alloys are heterogeneous, but different from those of Lisbon, which shows a higher Au/Ag ratio, between 6.5 and 7.4, and a Cu content ranging between 1.5% and 3.1%. This data and

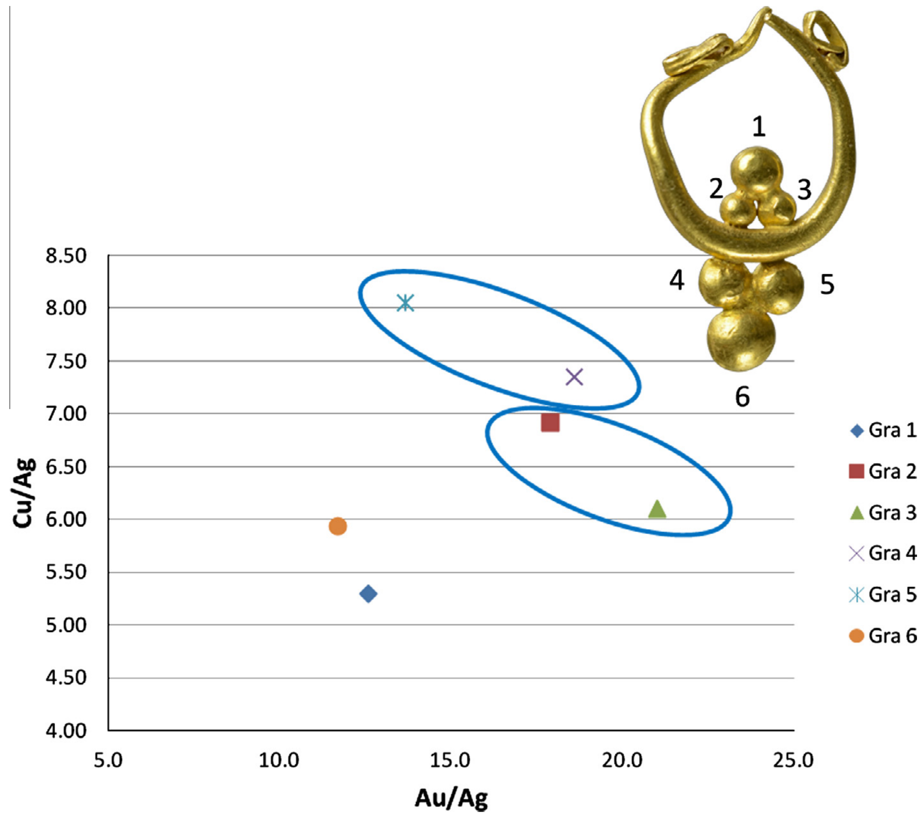

Fig. 3. Plot of Ag/Cu *vs* Au/Ag ratios determined by SEM/EDS for the granules of the earring Au169.

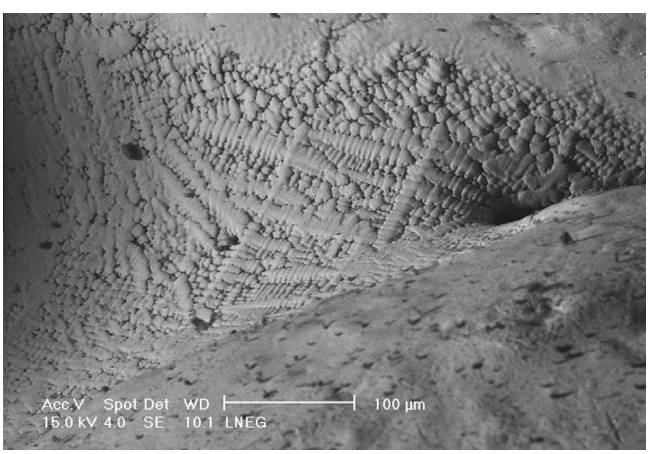

Fig. 4. SEM image (secondary electrons) of the dendritic structure of the solder between the decorative granules of the earring Au840.

the data reported by Soares et al. for earrings from the same period, typology and region [12] match together, but differs from the results published by Perea et al. for southern Spain earrings of the same typology (Au/Ag ratio 21–25 and 0.21–3.84% Cu) [2]. Data also shows a Cu content in the same range but a lower Au/Ag ratio which could correspond to the use of an equivalent technology but a different gold supply.

For Pancas two groups can be established, one with a Au/Ag ratio between 5.5 and 6.5 (Au836 & 837) and another with Au/Ag ratio in the range of 3.5–4.5. Certainly representing two distinct gold supplies. The addition of different amounts of Cu confirms the intentional use of different alloys.

Our results for the casted central rings ascertain the presence of 4 pairs (Au832/Au833; Au836/Au837; Au835/Au839 and Au840/841) in accordance with the Viegas and Parreira's proposal based on the earrings decoration [1]. Although two of the earrings (Au838 & Au834) present a similar alloy they do not form a pair, since they have a distinct decoration.

3.3. The alloys composition

Fig. 7 shows the μ-PIXE results for two earrings (Au833 and Au840) from Pancas and one from Monforte (Au577). The ternary diagram (Au–Ag–Cu) shows that the earrings have similar compositions, although it is possible to distinguish 3 Au/Ag ratios: Au833 with 6.6 (for 2% Cu), Au840 with 4.9 (for 3.4% Cu); and Au577 with 4.5 (for 2.5% Cu).

The Monforte alloys match data published by Montero and Rovira [13] for Late Bronze Age Iberian objects from the Iberian Peninsula: Ag contents between 10% and 20% and Cu contents higher than 1%, characteristic of the use of alluvial gold. In addition to this, results obtained by Respaldiza et al. for jewellery sets from southern Iberian Peninsula, representative of the period of oriental influence, show that gold alloys contain either 70% of Au or more than 90%, with a Cu content around 2.5%, the rest being Ag ranging from 7.5% to 27.5% [14]. The alloy composition of Au832 and Au577 are consistent with this data, but the Cu content of Au840 is higher, in the range of 3.4%. However, data on Iberian gold work reported by Hartmman, particularly for earrings from the same period [15], show an Ag content between 20% and 29% and a Cu content between 3.4% and 7%. Analyses of gold grains from different Spanish deposits [16] show that gold might be very pure or present the following Ag contents: 3.5–4%, 15–17%, and 26–27%. These values match data obtained for the Iberian jewellery. However, the origin of the gold used in the production of the earrings of Pancas is difficult to identify. By using destructive optical emission spectroscopy (OES), Hartmann identified for Bronze and Iron Ages

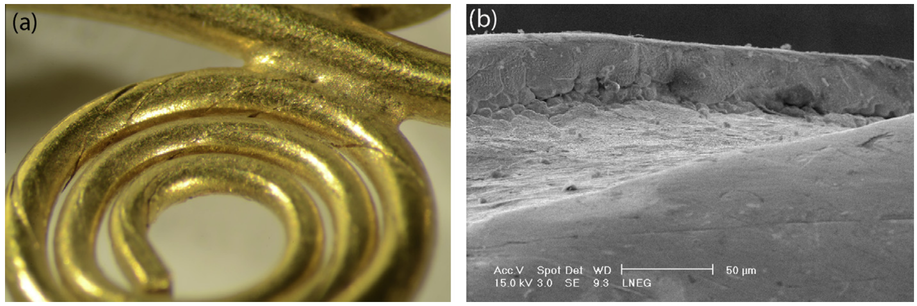

Fig. 5. Strip-twisted wire of earring Au841: (a) macrophotography of the wire and soldering and (b) SEM image (secondary electrons) of the foil.

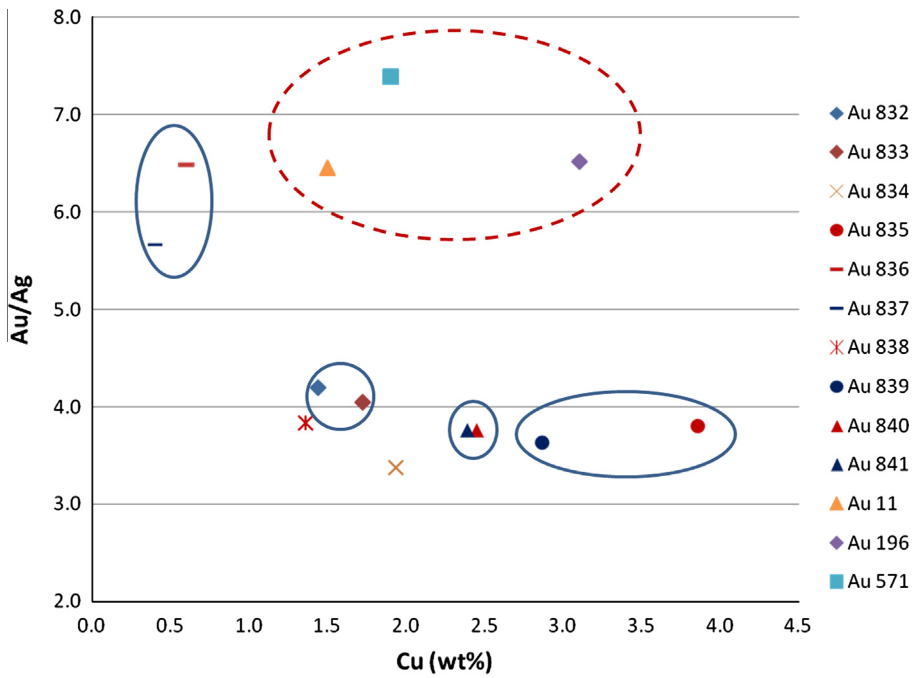

Fig. 6. Plot of Au/Ag ratio *vs* Cu (%) measured by EDXRF for the casted main-rings of the 10 earrings from the Pancas treasure (solid lines) and 3 earrings from an early chronology (dashed lines).

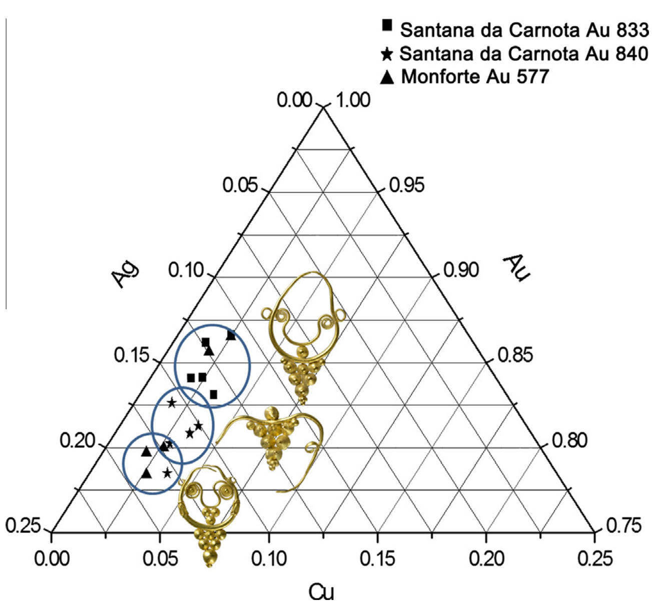

Fig. 7. Ternary diagram of Au–Ag–Cu obtained by PIXE, with the composition data of 2 earrings from the Pancas Treasure (Au833 and Au840) and 1 earring from Monforte (Au577).

Portuguese area jewellery the presence of Sn in the range of 0.014–0.044%; Garcia-Guinea et al. [17] identified for the Aliseda treasure and Extremadura gold nuggets the presence of Bi 0.35%, Sb 0.05% and Te 0.04%; while Ontalba-Salamanca et al. showed the presence of about 0.30% Pd in Punic gold items (400 B.C.), from the Museum of Cádiz [18].

In the present work, PIXE data was obtained with limits of detection ranging from 160 to 500 μg/g. In spite of the fact that published data on Sn, Bi, Sb, Te and Pd for Iberian gold is included in our range of detection, we could not confirm the presence of those elements in the earrings. Further studies will be developed to optimise the detection limits of those elements in order to identify the possible sources of gold.

4. Conclusions

The 10 earrings of the Pancas Treasure, dated to a period between the 5th and the 3rd centuries BC, were analysed by μ-PIXE, EDXRF and SEM–EDS together with 3 contemporary earrings from Monforte in different technological stages and 3 earlier earrings from the Lisbon region. In this first approach to the production techniques and alloys composition of Iron Age earrings from the Portuguese area we could show that: (1) granulation and twisted wire motifs are applied with hard soldering; (2) the granules either plain or hollow, are applied in different mounting schemes patterns; (3) the alloys compositions form pairs of earrings; (4) the alloys are different within the Pancas group and correspond to the compositions of objects from the south of the Iberian Peninsula, representative of the period of oriental influence.

Acknowledgements

The present work was financed by Portuguese National Funds through the FCT (*Fundação para a Ciência e Tecnologia*) in the framework of AuCORRE project (PTDC/HIS-HIS/114698/2009).

M. Manso acknowledges Grant SFRH/BPD/70021/2010 and V. Corregidor FCT program *Ciência 2008*.

References

[1] J.R. Viegas, R. Parreira, Der Schatzund von Santana da Carnota (Alenquer/Portugal), Madrider Mitteilungen 25 (1984) 79–91.
[2] R. Parreira, C. Vaz Pinto, Tesouros da Arqueologia Portuguesa no Museu Nacional de Arqueologia e Etnologia, Secretaria de Estado da Cultura, Instituto Português do Património Cultural, Lisboa, 1980.
[3] C.M. Martins, A Ourivesaria Proto-histórica de Portugal: influências mediterrânicas, Faculdade de Letras, Universidade do Porto, Porto, 1996.
[4] G. Nicollini, Techniques des ors antiques La bijouterie ibérique du VII au IV siècle vol 1, Picard, Paris, 1990.
[5] A. Perea, O. Garcia Vuelta, C.F. Freire, El Proyecto Au, Estudio arqueométrico de la producción de oro en la Península ibérica – Bibliotheca Praeshistorica Hispana, CSIC, 2010.
[6] A. Perea, Estudo del proceso técnico de fabricacíon y significado de la orfebrería de Talavera la Vieja, in: J. Ávila (Ed.), El conjunto Orientalizante de Talavera la Vieja, Museo de Cáceres, Cáceres, 2006, pp. 63–87.
[7] S. Pessanha, A. Guilherme, M.L. Carvalho, Comparison of matrix effects on portable and stationary XRF spectrometers for cultural heritage samples, Appl. Phys. A 97 (2009) 497–505.
[8] L.C. Alves, M.B.H. Breese, E. Alves, A. Paúl, M.R. da Silva, M.F. da Silva, J.C. Soares, Micron-scale analysis of SiC/SiC$_f$ composites using the new Lisbon nuclear microprobe, Nucl. Instr. Meth. B 161–163 (2000) 334–338.
[9] H. Maryon, Metal working in the ancient world, Am. J. Archaeol. 53 (2) (1949) 93–125.
[10] L.G. Troalen, M.F. Guerra, J. Tate, B. Manley, Technological study of gold jewellery pieces dating from the Middle Kingdom to the New Kingdom in Egypt, ArchéoSciences 33 (2009) 111–119.
[11] M.Á. Ontalba Salamanca, F.J. Ager, M.D. Ynsa, B.M. Gómez Túbio, M. Á Respaldiza, F. Fernández-Gómez, M-L. de la Bandera, G.W. Grime, External microbeam set-up at the CNA (Sevilla) and its application to the study of tartesic jewellery, Nucl. Instr. Meth. B 181 (2001) 664–669.
[12] A.M. Soares, P. Valério, R.J.C. Silva, L.C. Alves, M.F. Araújo, Early Iron Age gold buttons from South-Western Iberian Peninsula. Identification of a gold metallurgical workshop, Trabajos de Prehistoria 67 (2010) 501–510.
[13] I. Montero, S. Rovira, El Oro y sus aleaciones en la orfebrería preromana, AEspA 64 (1991) 7–21.
[14] M.Á. Respaldiza, F.J. Ager, A. Carmona, J. Ferrer, M. García-León, J. García-López, I. García-Orellana, B. Gómez-Tubío, Y. Morilla, M.A. Ontalba, I. Ortega-Feliu, Accelerator-based research activities at "Centro Nacional de Aceleradores", Seville (Spain), Nucl. Instr. Meth. B 266 (2008) 2105–2109.
[15] A. Hartmann, Prähistorische Goldfunde aus Europa Studien zu den Anfängen der Metallurgie 3:2, Mann, Berlin, 1982.
[16] L.C. Pérez-García, F.J. Sánchez-Palencia, J. Torres-Ruiz, Tertiary and quartenary alluvial gold deposits of Northwest Spain and Roman Minig (NW of Duero and Bierzo Basins), J. Geochem. Explor. 71 (2000) 225–240.
[17] J. Garcia-Guinea, V. Correcher, R.M. Rojas, J.L.G. Fierro, C. Fernandez-Martin, P. López-Arce, S. Rovira-Llorens, Chemical tracers in archaeological and natural gold: Aliseda Tartessos treasure and new discovered nuggets (SW Spain), Gold Bull. 38 (2005) 23–28.
[18] M.Á. Ontalba Salamanca, B. Gómez-Tubío, I. Ortega-Feliu, M.Á. Respaldiza, M. Luisa de la Bandera, G. Ovejero Zappino, A. Bouzas, A. Gómez-Morón, External-beam PIXE spectrometry for the study of Punic jewellery (SW Spain): the geographical provenance of the palladium-bearing gold, Nucl. Instr. Meth. B 249 (2006) 622–627.