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Characterisation of a Proto-historic bronze collection by micro-EDXRF

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ABSTRACT

Studies concerning European Proto-historic metallic artefacts can provide important clues about technological transfers during a period of time characterised by diverse cultural interactions. A collection of Proto-historic metallic artefacts from Medronhal (western Iberian Peninsula) composed by rings, bracelets and a fibula related to different cultural affiliations were investigated by micro-EDXRF to provide a major and a minor elemental characterisation. Results show that the Medronhal collection was manufactured in a Cu–Sn alloy (binary bronze) with similar Sn contents among the various types of artefacts and a low impurity pattern. Results of the type and quality of metal were compared to other artefact collections to infer about metallurgical parallels. Strong parallels with indigenous Late Bronze Age Iberian metallurgical productions were found.

1. Introduction

Analytical studies involving elemental analysis, including major and minor elemental characterisations, can be very important in the study of ancient metallurgy to identify the type and quality of metal employed. These studies can provide important information about the adoption of new metals and alloys, details regarding ancient technological particularities related to different chronological periods or specific regions, and also give important clues about the skills of the ancient metallurgists.

Energy dispersive X-ray spectrometry (EDXRF) has established itself as an important and frequently employed analytical technique for the study of cultural materials, due to its non-destructive character (i.e. respecting the physical integrity of the material/object), its multi-elemental and relatively fast results [1,2].

Given the crescent interest for elemental studies on various cultural objects and materials, during the last decades EDXRF equipments specially designed for cultural studies were developed, and among those, portable micro-EDXRF has become an important and frequently applied analytical tool (e.g. [3–5]). Besides allowing the possibility of working outside the laboratory in the case of objects that cannot be moved, the versatility of these equipments allows the study of various shaped and sized artefacts, the selection of different surface spots to be analysed, with no need of sampling. Also, regarding the study of ancient metals, given the specificities of some alloys that develop superficial corrosion layers with altered elemental compositions, only small size areas have to be superficially cleaned to allow the analysis of the unaltered metal, minimizing physical interventions to the objects [5].

The study of ancient metallic artefacts can be very important to help tracing ancient contacts among different cultures or regions, by allowing the identification of technological developments of local communities, particularly among the illiterate, Pre- and Proto-historic societies.

Since the early introduction of metal for artefact production in the European territory, that manufacturing techniques improved, and by Proto-historic times, artefacts with diverse typologies and complex shapes were produced.

In western Iberian Peninsula, namely in the Portuguese territory, by Late Bronze Age and Early Iron Age the significant diversification in artefacts typologies can frequently be related to Atlantic or Mediterranean influences [6–8]. Among those, are artefacts with a strong decorative or symbolic function, such as rings, bracelets and fibulae.

Generally, rings and bracelets can be found in various Late Bronze Age archaeological contexts. Rings could have had diverse functions, as to be worn in the body/fingers, or to be part of more complex objects. Bracelets were worn in the body/arms for embellishment purposes. Among the Atlantic cultural sphere, as in central and northern Portuguese regions, bracelets can be found particularly in burial contexts [9,10].

The fibulae are generally related to a Mediterranean cultural sphere, and begin to appear in various archaeological contexts by

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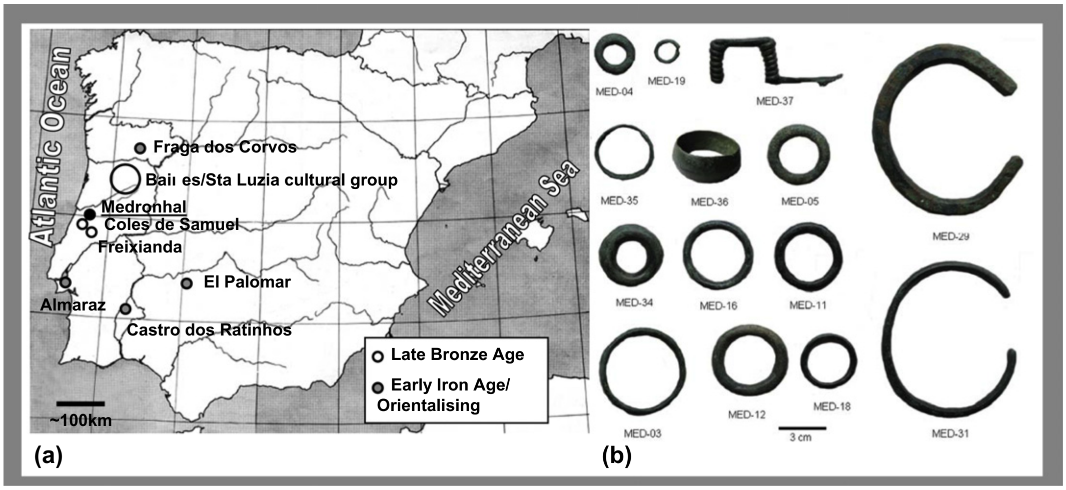

Fig. 1. (a) Map of the Iberian Peninsula with the location of Medronhal cave annotated, as well as various Late Bronze Age and Early Iron Age/Orientalising hoards and sites mentioned in the study. (b) Part of the artefact collection found in Medronhal cave (Portugal).

a late period of Late Bronze Age/beginning of Early Iron Age. These items, which served to hold clothes/textiles over the body, had a significant decorative function besides the utilitarian one. Frequently, these items are considered as an indication of increasing contacts of the Iberian communities with Eastern ones, as with those from the Italic or Sicilian territories.

In the 1940's, an interesting set of 37 metallic artefacts was found together with human and various animals bones in Medronhal cave (Condeixa-a-Nova, Portugal), suggesting the discovery of a Proto-historic burial. The metallic collection is composed by 31 rings, 5 bracelets and 1 double-spring fibula, bearing artefacts related both to the Atlantic as to the Mediterranean cultural spheres. Part of the collection is shown in Fig. 1.

Taking into consideration the typologies of the artefacts, the collection can be attributed to around the VIII century B.C., and can thus be considered as an important testimony for a period that comprises the transition from Late Bronze Age to Early Iron Age.

For the present work, an analytical study was performed on the Medronhal collection, to provide archaeometallurgical relevant information. All the artefacts were analysed by energy dispersive micro X-ray fluorescence spectrometry (micro-EDXRF) in a small prepared area to determine major and minor elements and thus provide a characterisation of the Proto-historic alloy. The results were compared to the compositions of other metal artefacts from Late Bronze Age sites and Early Iron Age/Orientalising sites to infer about metallurgical parallels.

2. Experimental

The elemental composition of the artefacts was obtained thought micro-EDXRF analyses performed in an ArtTAX Pro spectrometer. This spectrometer has been developed especially for applications in the archaeometric field, combining the advantages of non-destructive and sensitive multi-elemental analysis at a sub-mm lateral resolution, with the possibility of working outside the laboratory in the case of objects that cannot be transported to the laboratory. The system consists of an air-cooled, low-power molybdenium tube, a set of polycapillary lenses that generates a spot of about 70 μm in diameter of primary radiation, a silicon drift detector, a CCD camera and three light diodes for sample positioning. Further details on the equipment can be found elsewhere [11].

For the present study the micro-EDXRF analysis were performed on small cleaned areas (<25 mm^2) of the artefacts. The preparation involved the removal of the superficial corrosion layers followed by a metallographic preparation. The metallographic preparation consisted of a manual polishing with several diamond suspensions in a cotton swab until 1 μm diamond size. In each area, three analyses were made on different spots to account for heterogeneities at the microstructural level, being considered the average values. Each analysis was performed using 40 kV of tube voltage, 0.5 mA of current intensity, and 100 s of live time.

Table 1
Micro-EDXRF analysis of Phosphor Bronze 553 from BCS (average ± one standard deviation for 3 spot analyses).

wt.%	Cu	Sn	Pb	Zn	Fe	Ni
Certified	87.0	10.8	0.47	0.49	0.06	0.44
Obtained	87.7 ± 0.1	10.5 ± 0.1	0.56 ± 0.07	0.58 ± 0.01	0.05 ± 0.01	0.51 ± 0.01
Accuracy	0.8	2.5	19.1	18.4	10.2	15.9

Table 2
Quantification limits for micro-EDXRF analysis (calculated as 10 × (background)$^{1/2}$/sensitivity [12]).

Cu	Sn	Pb	As	Fe	Ni
0.04%	0.5%	0.10%	0.10%	0.05%	0.07%

The quantitative analysis was made through WinAxil software using fundamental parameter method and experimental calibration factors that were calculated with the certified reference material Bronze 551 from British Chemical Standards (BCS).

The accuracy of the analytical technique was determined with the analysis of another certified reference material, Phosphor Bronze 553 from BCS, and the results are shown in Table 1.

Quantification limits were also calculated and are shown in Table 2. Due to the frequent presence of Pb and As in ancient metals and due to the interference between the lines of Pb (Lα) and As (Kα), the quantification limit of As was (under)estimated as being the quantification limit calculated for Pb.

3. Results and discussion

The results of the micro-EDXRF analysis are presented in Table 3. These show that all the artefacts are made of Cu–Sn alloy (bronze) with a low impurity pattern (sum is generally <0.5 wt.%).

Table 3
Results of micro-EDXRF analysis (results normalised; average of three analysis ± standard deviation; nd = not detected).

No.	Item	Composition (wt.%)					
		Cu	Sn	Pb	As	Fe	Ni
MED-01	Ring	88.6 ± 2.3	11.3 ± 2.3	n.d.	0.12 ± 0.0	<0.05	n.d.
MED-02	Ring	85.5 ± 0.2	14.4 ± 0.2	n.d.	0.13 ± 0.0	<0.05	n.d.
MED-03	Ring	88.1 ± 0.9	11.9 ± 0.9	n.d.	n.d.	<0.05	n.d.
MED-04	Ring	84.4 ± 2.9	15.4 ± 2.9	n.d.	0.23 ± 0.0	<0.05	n.d.
MED-05	Ring	86.9 ± 1.0	12.9 ± 0.9	0.14 ± 0.0	n.d.	<0.05	n.d.
MED-06	Ring	86.2 ± 2.3	13.6 ± 2.3	0.17 ± 0.0	n.d.	<0.05	n.d.
MED-07	Ring	86.9 ± 2.9	12.9 ± 3.0	0.21 ± 0.0	n.d.	<0.05	n.d.
MED-08	Ring	84.9 ± 0.3	14.8 ± 0.3	0.19 ± 0.0	n.d.	<0.05	n.d.
MED-09	Ring	86.6 ± 2.5	12.9 ± 2.5	0.49 ± 0.2	n.d.	<0.05	n.d.
MED-10	Ring	88.3 ± 1.5	11.4 ± 1.5	0.13 ± 0.0	n.d.	<0.05	n.d.
MED-11	Ring	85.8 ± 2.9	14.0 ± 2.8	n.d.	0.18 ± 0.0	<0.05	n.d.
MED-12	Ring	85.2 ± 0.9	14.7 ± 0.9	n.d.	0.12 ± 0.0	<0.05	n.d.
MED-13	Ring	87.4 ± 0.6	12.3 ± 0.6	0.17 ± 0.0	n.d.	<0.05	n.d.
MED-14	Ring	87.1 ± 4.2	12.7 ± 4.2	n.d.	0.16 ± 0.0	<0.05	n.d.
MED-15	Ring	86.6 ± 0.6	12.1 ± 0.5	0.61 ± 0.1	0.54 ± 0.0	<0.05	0.21
MED-16	Ring	85.2 ± 0.4	14.8 ± 0.4	n.d.	n.d.	<0.05	n.d.
MED-17	Ring	87.3 ± 0.9	12.6 ± 0.9	n.d.	0.15 ± 0.0	<0.05	n.d.
MED-18	Ring	84.8 ± 0.2	15.1 ± 0.2	n.d.	0.15 ± 0.0	<0.05	n.d.
MED-19	Open ring	87.9 ± 1.3	12.1 ± 1.3	n.d.	n.d.	<0.05	n.d.
MED-20	Ring	88.5 ± 0.6	11.1 ± 0.6	0.30 ± 0.0	n.d.	<0.05	n.d.
MED-21	Ring	86.6 ± 1.1	13.2 ± 1.1	n.d.	0.17 ± 0.0	<0.05	n.d.
MED-22	Ring	85.1 ± 1.2	14.8 ± 1.1	n.d.	0.15 ± 0.0	<0.05	n.d.
MED-23	Ring	86.9 ± 0.1	12.9 ± 0.0	n.d.	0.16 ± 0.0	<0.05	n.d.
MED-24	Ring	85.0 ± 2.9	14.8 ± 2.9	0.16 ± 0.0	n.d.	<0.05	n.d.
MED-25	Ring	87.5 ± 0.8	12.5 ± 0.9	n.d.	n.d.	<0.05	n.d.
MED-26	Ring	84.4 ± 1.9	15.6 ± 1.9	n.d.	n.d.	<0.05	n.d.
MED-27	Ring	84.6 ± 0.5	15.3 ± 0.6	n.d.	n.d.	<0.05	n.d.
MED-28	Ring	85.1 ± 5.5	14.6 ± 5.0	n.d.	0.21 ± 0.0	<0.05	n.d.
MED-29	Bracelet	89.8 ± 2.2	10.1 ± 2.1	0.19 ± 0.0	n.d.	<0.05	n.d.
MED-30	Bracelet	88.0 ± 0.3	11.7 ± 0.3	0.24 ± 0.0	n.d.	<0.05	n.d.
MED-31	Bracelet	87.3 ± 0.1	12.7 ± 0.0	n.d.	n.d.	<0.05	n.d.
MED-32	Bracelet	86.7 ± 1.5	13.1 ± 1.5	n.d.	n.d.	<0.05	n.d.
MED-33	Bracelet	89.8 ± 0.2	10.1 ± 0.2	n.d.	n.d.	<0.05	n.d.
MED-34	Open ring	85.9 ± 0.0	13.9 ± 0.0	0.17	n.d.	<0.05	n.d.
MED-35	Ring	88.3 ± 1.2	11.3 ± 1.2	0.18 ± 0.1	0.17 ± 0.0	<0.05	n.d.
MED-36	Ring[a]	87.1	12.9	n.d.	n.d.	<0.05	n.d.
MED-37	Fíbula	88.2 ± 1.4	11.6 ± 1.4	n.d.	0.12 ± 0.0	<0.05	n.d.

[a] Only one micro-EDXRF analysis was considered due to the small size of the cleaned area (constrained by the shape of the artefact).

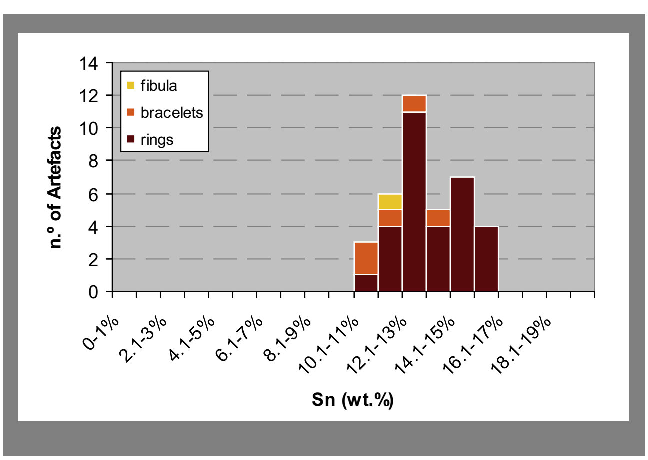

Fig. 2. Histogram with the Sn contents in the studied artefacts from Medronhal collection.

The Sn content is in the range of 10–15 wt.% (average of 13.1 ± 1.5%Sn), without significant differences among the different typologies (Fig. 2). Probably, the ancient metallurgists have interest in the properties that this range of Sn contents could present, as regarding hue/colour and mechanical properties.

The addition of up to 15%Sn to copper modifies the colour of copper by decreasing its redness, so that the alloy approaches a golden hue [13]. In the case of higher Sn contents (>18%Sn, high tin bronzes) the increase of tin does not only reduces the redness but does also reduces the yellowness of the alloy, making it to approach a silvery colour. Besides showing a gold-like colour, a 10–15 wt.%Sn bronze has the properties of being substantially harder than pure copper or low tin bronzes [14], but does still have adequate mechanical properties when compared to high tin bronzes to be worked through deformation processes. As a consequence, the manufacture of all the items in an alloy with 10–15%Sn could have been a deliberate choice of the ancient metallurgists to attend both to colour preference as well as to adequate mechanical properties.

Comparing the Sn contents of the Medronhal collection with the Sn contents in bronze collections from both Late Bronze Age and Early Iron Age/Orientalising sites similarities and differences can be found (Fig. 3). Bronzes from neighbouring Late Bronze Age hoards and sites show clear parallels to the Medronhal collection, despite different numbers of artefacts studied from each site or hoard and the use of different analytical techniques for the elemental analysis. An incidence in bronzes with 10–15%Sn can be observed not only for the Medronhal collection but also for the Baiões/Santa Luzia cultural group analysed by micro-EDXRF [15–18], Freixianda hoard analysed by PIXE [19] and Coles de Samuel hoard analysed by optical emission spectroscopy (atomic emission spectrometry) [6]. In contrast, when compared to bronzes from Early Iron Age/Orientalising sites from western Iberian Peninsula, such as Fraga dos Corvos shelter in northern Portugal [20], Almaraz in central Portugal [21], Castro dos Ratinhos in southern

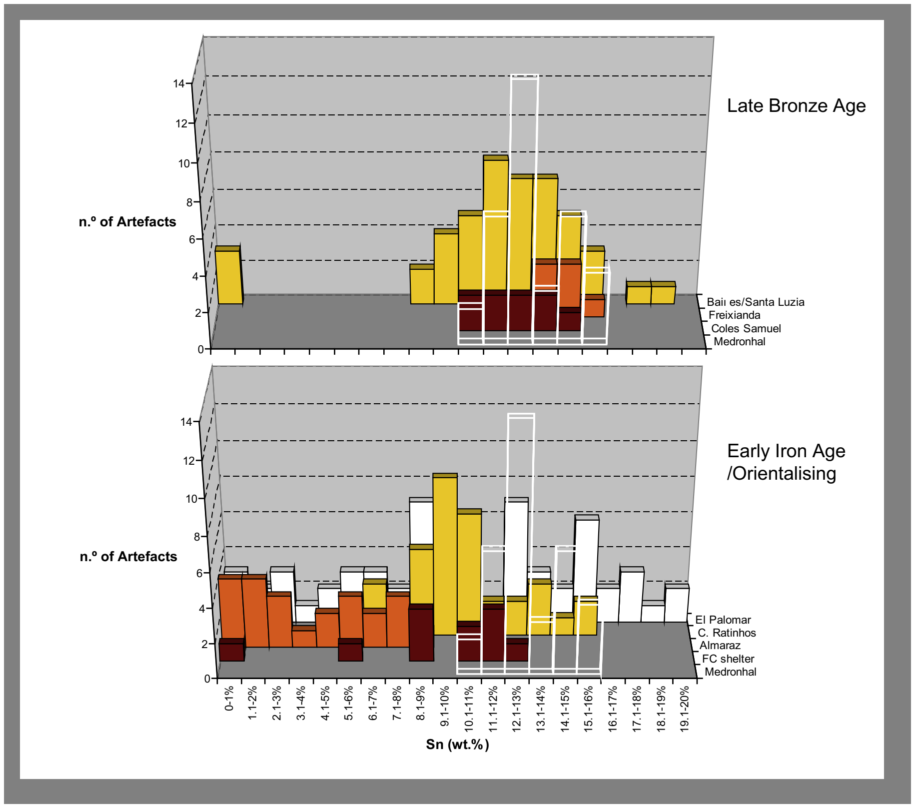

Fig. 3. Comparison of Sn contents in the Medronhal collection and (top) Late Bronze Age bronze artefacts from neighbouring sites and hoards, and (bottom) Early Iron Age/Orientalising bronze artefacts from western Iberian Peninsula.

Portugal [22] and El Palomar in south-western Spain [23], clear differences are observed, showing more dispersed Sn contents, combining the presence of bronzes with low Sn contents with those with 10–15%Sn.

When comparing the contents of minor elements in the alloy, such as Pb, As and Fe, relationships among collections of artefacts can be observed despite different sensitivities of the analytical techniques used in the studies (Fig. 4).

The presence of Pb occurs in the Medronhal collection in low concentrations, namely <0.1%Pb in about 60% of the artefacts, having the remaining ones <0.5%Pb, except for one artefact, the ring MED-15 with 0.61%. This low Pb pattern is also found among the Late Bronze Age artefacts from the Baiões/Sta Luzia cultural group, Freixianda and Coles de Samuel hoards, where more than 60% of the artefacts have <0.1%Pb, and the rest <0.5%Pb. The Early Iron Age site of Castro dos Ratinhos does also show a high number of artefacts with low Pb content (about 60% have <0.1%Pb), a few with <0.5%Pb similarly to the Medronhal collection, however, it has some bronzes with 1–2%Pb, which are absent in Medronhal and the Late Bronze Age sites and hoards. The remaining sites with Orientalising influences do show clear differences from the Medronhal collection and those of Late Bronze Age, with the presence of artefacts with higher Pb contents, namely artefacts with 2–10% Pb, which can already be considered as intentionally leaded bronzes. Such alloy has different properties when compared to a binary Cu–Sn alloy, as a lower liquidus temperature which can facilitate the casting of larger sized objects, and can also confer different mechanical properties to the objects.

The As content in the Medronhal collection is rather low, generally <0.5%As, similarly to bronzes from both Late Bronze Age and Early Iron Age/Orientalising hoards and sites, where more than 90% of the artefacts show this low As content. Medronhal, Castro dos Ratinhos, Almaraz and El Palomar have a small amount of artefacts with higher As contents (0.5–1.0%As) and only the Orientalising site of El Palomar have artefacts with an even higher content (1–2%As). Relatively low and dispersed As contents can be expected in bronzes from both Late Bronze Age and Early Iron Age/Orientalising sites as a result of impurities in copper ores, namely when ores from the Iberian Peninsula have been used since these can be rich in this element [24], explaining the absence of differences among the two cultural stages.

The Fe content in the Medronhal collection is very low, below the quantification limit of 0.05%. Late Bronze Age bronzes do also show these rather low contents, as those from Baiões/Santa Luzia cultural group, Freixianda and Coles de Samuel hoards. On the other hand, the Fe content in bronze artefacts from Early Iron Age/Orientalising sites can be higher, reaching 0.5%Fe in some artefacts from Castro dos Ratinhos and Fraga dos Corvos Shelter, 1% in El Palomar and even higher contents in Almaraz (1.1–2.0%Fe), which is also the only site which has absence of bronzes with <0.05%Fe. Craddock [25] has previously pointed out to Fe content differences among indigenous bronzes of Spanish interior regions when compared to bronzes from Phoenician/Orientalising settlements dating to the beginning of the 1st millennium B.C., and explained it as a result of the smelting processes used to obtain metal, with those smelted by more primitive processes resulting in very low Fe contents and those smelted by more sophisticated techniques (more reducing conditions) resulting in higher Fe contents.

Regarding the Medronhal collection, its low Fe content clearly points out to parallels with the indigenous Late Bronze Age metallurgy. Taking into account its Pb and As contents, close affinities can be found with the Late Bronze Age bronzes, however, the Early Iron Age site of Castro dos Ratinhos does also find close

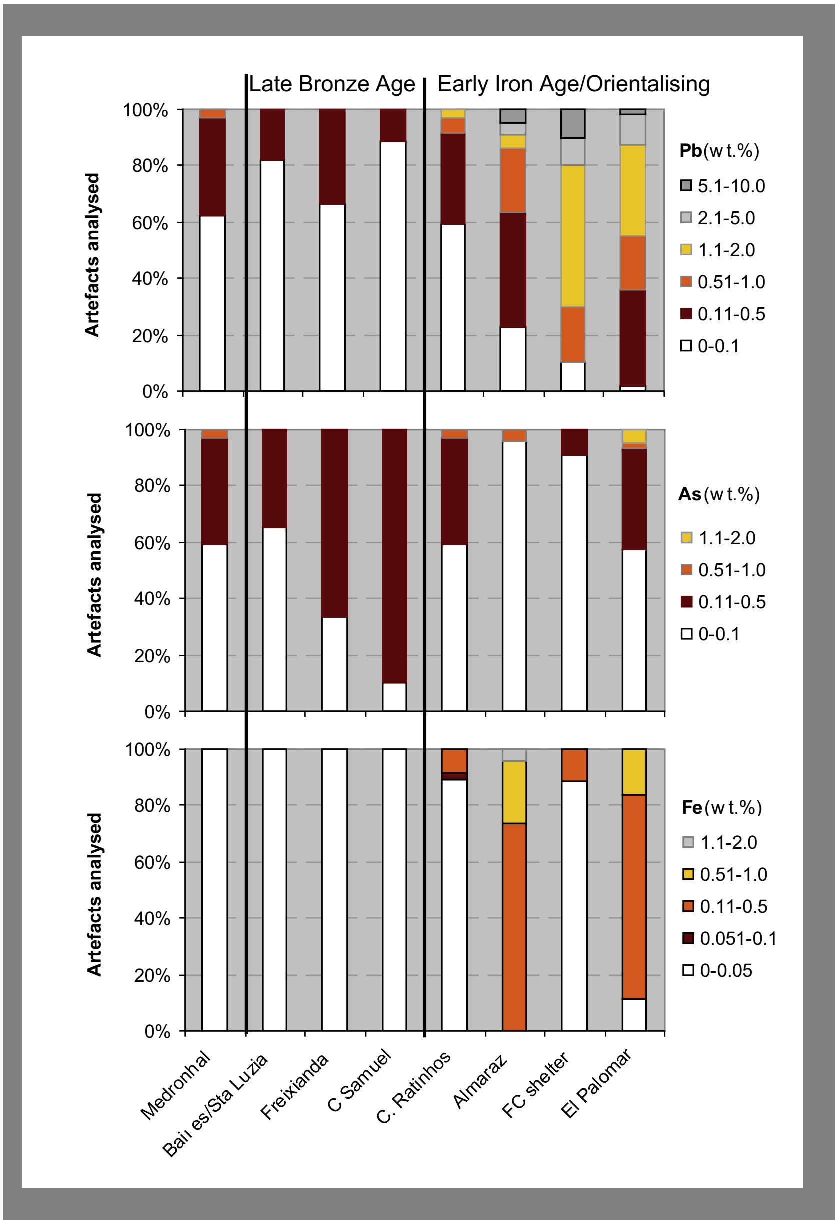

Fig. 4. Comparison of Pb, As and Fe contents in the Medronhal collection and Late Bronze Age and Early Iron Age/Orientalising bronze artefacts.

resemblances, namely in the presence of some artefacts with 0.51–1.0% of Pb and As, which are absent in the Late Bronze Age artefacts. Since Castro dos Ratinhos has previously been described as a site where Early Iron Age bronzes retain many characteristics from earlier Late Bronze Age bronzes [22], further support to parallels of the Medronhal collection with a Late Bronze Age metallurgical tradition from western Iberian Peninsula can be considered.

4. Conclusions

The present study shows that elemental micro-EDXRF analysis made on ancient metallic bronzes can deliver very important information regarding the composition of the alloy, namely the contents of the alloying and relevant minor elements. This, in turn, can be very important to consign a collection to a specific metallurgical tradition, giving important clues about its manufacturers.

In the present case, the Medronhal collection shows a composition with a rather high and narrow Sn range and a low impurity pattern if compared to bronzes from Early Iron Age/Orientalising sites, finding closer affinities to metallic collections from sites and hoards attributed to Late Bronze Age from neighbouring areas. Despite the presence of an artefact in the collection with a clear Mediterranean typological affiliation – the fibula – the composition of this particular item is not distinct from the composition of the remaining artefacts with an Atlantic typological affiliation, which could point out towards a collection composed by artefacts from different workshops/cultural traditions. Instead, the results point out to the production of the Medronhal collection following an indigenous metallurgical bronze tradition, from the western Iberian Late Bronze Age communities.

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References

[1] L. Musílek, T. Čechák, T. Trojek, X-ray fluorescence in investigations of cultural relics and archaeological finds, Appl. Radiat. Isot. 70 (2012) 1193–1202.

[2] K. Janssens, G. Vittiglio, I. Deraedt, A. Aerts, B. Vekmans, L. Vincze, F. Wei, I. De Ryck, O. Schalm, F. Adams, A. Rindby, A. Knöchel, A. Simionovici, A. Snigirev, Use of microscopic XRF for non-destructive analyses in art and archaeometry, X-Ray Spectrom. 29 (2000) 73–91.

[3] V. Desnica, M. Schreiner, A LabVIEW-controlled portable X-ray fluorescence spectrometer for the analysis of art objects, X-Ray Spectrom. 35 (2006) 280–286.

[4] G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, S. Bamford, A portable micro-X-ray fluorescence spectrometer with polycapillary optics and vacuum chamber for archaeometric and other applications, Spectrochim. Acta B 62 (2007) 1252–1256.

[5] G. Vittiglio, K. Janssens, B. Vekemans, F. Adams, A. Oost, A compact small-beam XRF instrument for in-situ analysis of objects of historical and/or artistic value, Spectrochim. Acta B 54 (1999) 1697–1710.

[6] A. Coffyn, Le Bronze Final Atlantique dans la Péninsule Ibérique, Centre Pierre Paris, Bordeaux, 1985.

[7] C. Giardino, The western Mediterranean Between the 14th and the 8th Centuries B.C., BAR International Series, 612, Oxford, 1995.

[8] R. Vilaça, Reflexões em torno da presença mediterrânea no Centro do território português, na charneira do Bronze para o Ferro, in: S. Celestino Pérez, N. Rafel, X.-L. Armada (Eds.), Contacto cultural entre el Mediterráneo y el Atlántico (siglos XII–VIII ANE): La Precolonización a debate, Escuela Española de Historia y Arqueologia de Roma del CSIC, Madrid, 2008, pp. 371–400.

[9] R. Vilaça, D. Cruz, Práticas funerárias e culturais dos finais da Idade do Bronze na Beira Alta, Arqueologia 24 (1999) 73–99.

[10] R. Vilaça, D. Cruz, A.H.B. Gonçalves, A Necrópole de Tanchoal dos Patudos (Alpiarça, Santarém), Conimbriga XXXVII (1999) 5–29.

[11] H. Bronk, S. Rohrs, A. Bjeoumikhov, N. Langhoff, J. Schmalz, R. Wedell, H.E. Gorny, A. Herold, U. Waldschlager, ArtTAX – a new mobile spectrometer for energy-dispersive micro X-ray fluorescence spectrometry on art and archaeological objects Fresenius', J. Anal. Chem. 371 (2001) 307–316.

[12] IUPAC, Nomenclature, symbols, units and their usage in spectrochemical analysis – II. Data interpretation, Spectrochim. Acta B 33 (1978) 242–245.

[13] J.-L. Fang, G. McDonnell, The colour of copper alloys, Hist. Metall. 45 (2011) 52–61.

[14] H. Lechtman, Bronze: dirty copper or chosen alloy? A view from the Americas, J. Field Archaeol. 23 (1996) 477–514.

[15] E. Figueiredo, A study on metallurgy and corrosion of ancient copper-based artefacts from the Portuguese territory, Ph.D. Thesis, Universidade Nova de Lisboa, Lisboa, 2012 (unpublished).

[16] E. Figueiredo, R.J.C. Silva, J.C. Senna-Martinez, M.F. Araújo, F.M.B. Fernandes, J.L. Inês Vaz, Smelting and recycling evidences from the Late Bronze Age habitat site of Baiões (Viseu, Portugal), J. Archaeol. Sci. 37 (2010) 1623–1634.

[17] E. Figueiredo, R.J.C. Silva, M.F. Araújo, J.C. Senna-Martinez, Identification of ancient gilding technology and Late Bronze Age metallurgy by EDXRF, micro-EDXRF, SEM-EDS and metallographic techniques, Microchim. Acta 168 (2010) 283–291.

[18] E. Figueiredo, M.F. Araújo, R.J.C. Silva, J.C. Senna-Martinez, J.L. Inês Vaz, Characterisation of Late Bronze Age large size shield nails by EDXRF, micro-EDXRF and X-ray digital radiography, Appl. Radiat. Isot. 69 (2011) 1025–1211.

[19] P.C. Gutiérrez Neira, A. Zucchiatti, I. Montero-Ruiz, R. Vilaça, C. Bottanini, M. Gener, A. Climent-Font, Late Bronze Age hoard studied by PIXE, Nucl. Instrum. Methods Phys. Res. Sect. B 269 (2011) 3082–3086.

[20] E. Figueiredo, J.C. Senna-Martinez, R.J.C. Silva, M.F. Araújo, Orientalizing artifacts from fraga dos corvos rock shelter in north Portugal, Mater. Manuf. Processes 24 (2009) 949–954.

[21] P. Valério, R.J.C. Silva, M.F. Araújo, A.M.M. Soares, L. Barros, A multianalytical approach to the study of the Phoenician bronze technology in the Iberian Peninsula – a view from Quinta do Almaraz, Mater. Charact. 67 (2012) 74–82.

[22] P. Valério, R.J.C. Silva, A.M. Monge Soares, M.F. Araújo, F.B. Braz Fernandes, A. Silva, L. Berrocal-Rangel, Technological continuity in Early Iron Age bronze metallurgy at the south-western Iberian Península – a sight from Castro dos Ratinhos, J. Archaeol. Sci. 37 (2010) 1811–1819.

[23] S. Rovira, I. Montero, J. Ortega, J.J. Ávila, Bronce y trabajo del bronce en el poblado orientalizante de "El Palomar" (Oliva de Mérida, Badajoz), Anejos de AEspA XXXV (2005) 1231–1240.

[24] O. Veiga Ferreira, Acerca da presença de arsénio em instrumentos primitivos, encontrados em Portugal, Boletim de Minas 12 (1961) 1–8.

[25] P.T. Craddock, Early Metal Mining and Production, Smithsonian Institution Press, Washington, DC, 1995.