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ISOTOPIC LEAD CHARACTERIZATION OF ARCHAEOLOGICAL BRONZES FROM FRAGA DOS CORVOS (N PORTUGAL)

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Abstract

A set of bronzes recovered from Fraga dos Corvos (Macedo de Cavaleiros) archaeological site, located in Northern Portugal, was analyzed to investigate their lead isotope ratios. The studied metallic artefacts have diverse typologies and include two bar fragments, four fibulae, a pendant and fragments of a possible cauldron. Besides these, two metallurgical remains (nodule and droplet) were also analyzed. Elemental analysis by μ-EDXRF showed that bronzes have a Sn content varying between 5.1 and 13.9% and a Pb content from 1.4 to 6.1%, which allowed to select a suitable methodology for lead separation, prior to isotope ratio determinations. In these alloys the Pb isotope determinations (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) are influenced by matrix effects that decrease the sensitivity and the reproducibility of the measurements. Analytical procedure consisted in electrochemical Pb separation by anodic oxidation. The determination of Pb isotope ratios was made by ICP-MS with a quadrupole mass filter and provided the first results of Pb isotopic composition of bronze alloys from the Northern Portuguese territory. Isotope ratios determinations were obtained with a relative standard deviation below 0.5%. Pb isotope ratio distributions allowed the identification of different composition patterns indicating probable distinct provenances, although the similar isotopic ratios among some artefacts and the metallurgical remains pointed out to local metallurgical activities.

Keywords: *Archaeological bronzes; Fraga dos Corvos; μ-EDXRF; Pb isotope ratio; Q-ICPMS*

Introduction

The compositions of bronzes that characterize archaeological artefacts from Iberian Peninsula, during pre and proto history, have variable contents of Sn. These alloys also present some other elements (e.g. Ni, As, Pb) usually as traces (below 0.1%) although in the case of Pb, sometimes it is present with higher concentrations, as a minor element.

Studies on the elemental composition of archaeological copper-based artefacts from the Portuguese territory have been developed during a large research project SAM (*Studien zu den Anfängen der Metallurgie*), by Junghans and co-workers [1-3], during which were analysed about 22,000 metal objects originating the first large scale study on the metallurgy during

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Chalcolithic and Bronze Age in Europe. The study aimed to investigate the technological aspects of “workshop-recipes” and “metal provinces” which might have corresponded to the smelting processes and ore deposits. However, and in spite of the high number of analysed artefacts, results demonstrate that it was not possible to establish a direct relation between a particular ore deposit and the artefacts by means of elemental composition. Most probably, the geochemical variability of ore deposits and the fractioning of some trace elements during metallurgical processes from ore to metal would be the main reason.

More recently, various studies have been carried out in archaeological bronzes from the Portuguese territory, mainly focused on the alloy composition determination and microstructural characterization, to investigate the metallurgical technological evolution during pre and proto historic times including manufacturing processes [4-6]. In a study on artefacts from Quinta do Almaraz (Almada, Western Coast of Portugal), concerning bronze artefacts with diverse typologies, chronologies and lead contents, it could be established the exogeneous influence of Phoenicians [7]. Another study focused on bronze artefacts recovered from Fraga dos Corvos archaeological site presenting orientalizing features showed that they exhibited variable Pb concentrations (0.4 – 4.8%) [8].

The lead content in a bronze artefact can be important in order to understand if lead was intentionally added to the alloy to improve its casting properties, a relevant development of metallurgical technology [9], or if it is present as an impurity resulting from the ores used. Some authors have considered lead as being intentionally added to the alloy when present in contents higher than 2% [10, 11].

Although elemental composition is important in the understanding of the evolution of the early metallurgy, to infer about the origin of the ores used in the fabrication of artefacts it is necessary the determination of lead isotope composition of artefacts and ores, since they are not altered during metallurgical processes [12].

Lead (Pb) is naturally occurring as four main isotopes: ^{204}Pb (1.4%), ^{206} Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.4%). While radiogenic isotopes ^{206} Pb, ^{207}Pb and ^{208}Pb are products of radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively, ^{204}Pb is the only primordial stable isotope with a constant abundance on Earth along time. The relative ratios of Pb isotopes are not constant amongst terrestrial materials, and depend on the concentrations of primordial Pb, U and Th and the lengths of the decay processes and the half-lives ($t_{1/2}$) of the parent isotopes (Table 1).

Table 1. The formation of the three radiogenic lead isotopes and half-life of the decay processes of uranium and thorium [13].

Decay	Half-life (years)	Decay constant (years^{-1})
^{238}U ...... ^{206}Pb	4.468×10^{9}	$\lambda^{238}U = 1.552 \times 10^{-10}$
^{235}U ...... ^{207}Pb	0.704×10^{9}	$\lambda^{235}U = 9.850 \times 10^{-10}$
^{232}Th ...... ^{208}Pb	1.401×10^{10}	$\lambda^{232}Th = 4.948 \times 10^{-11}$

The interpretation of Pb isotopic composition is a very important tool for studies on provenance and trade routes of archaeological metal artefacts. These studies are based on the different distributions of the four stable lead isotopes (^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb) present in the materials and/or ores that were used in the manufacturing process of the artefacts. This can be explained by the fact that most metal artefacts and many metal ores have traces of Pb, with specific isotope ratios that do not change during metallurgical processes remaining identical on the produced artefacts. Lead isotopic composition can be directly associated to particular/distinct mineral deposits, being similar whenever submitted to identical geological processes [12, 14]. Even when the ore deposits are geographically far apart, the isotopic composition can be identical or overlapping [12]. However, it should be stressed that a manufactured metal alloy can be a result of a mixture of ores from different sources providing a mean isotopic composition of lead, different from each ore itself. Also, considering recycling of scrap metal artefacts to produce new ones, the lead isotope composition does not reflect those of the ores used for manufacturing the primary metal artefacts. These processes have to be interpreted using archaeological evidences such as metallurgical, typological and distributional data [14, 15].

Although in Europe many publications on archaeometallurgical issues use lead isotope ratios, in Portugal such studies are rather scarce. To our knowledge, the first work published in Portugal about lead isotopes was during the sixties, and focused on the lead isotope signature of four lead pipes from Conimbriga hydraulic system [16]. The goal of this work was to establish the origin of lead used in the manufacturing of the pipes. More recently, it was published another work on the lead isotope composition of archaeological copper artefacts found in Estremadura, south-central Portugal, for a possible reconstruction of trade routes and interregional contacts [17].

The present work is a preliminary study for the determination of lead isotope ratio by Q-ICPMS (Quadrupole Inductively Coupled Plasma Mass Spectrometry) in archaeological bronze artefacts and metallurgical remains having a lead content above 1%. Ten selected artefacts were recovered in Fraga dos Corvos archaeological site, located at Macedo dos Cavaleiros in Northern Portugal (Fig. 1). Bulk elemental composition was carried out by micro-Energy-Dispersive X-Ray Fluorescence spectrometry (μ-EDXRF).

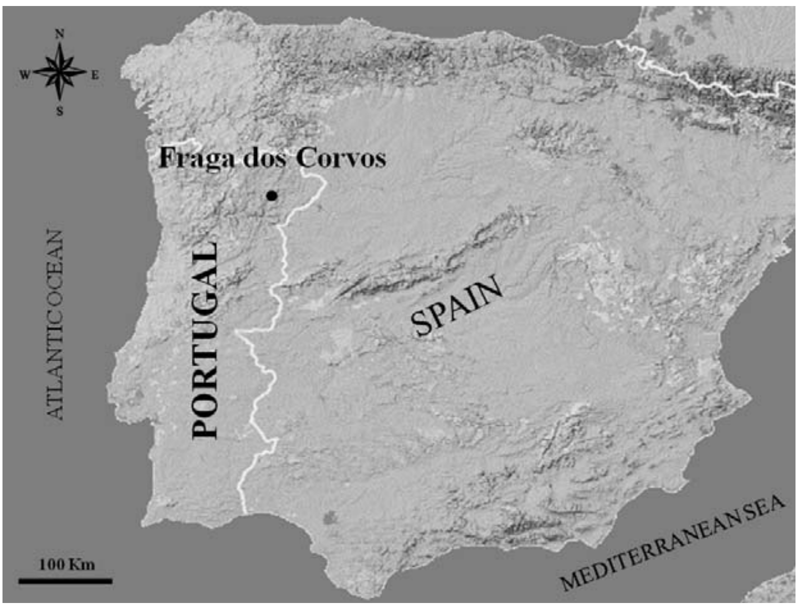

Fig. 1. The location of the archaeological site of Fraga dos Corvos in Northern Portugal.

Experimental

Sampling

The set of bronze artefacts selected for the present study has been recovered during excavations carried out in the archaeological site of Fraga dos Corvos, in Northern Portugal. Ten artefacts were selected with different typologies and chronologies [18, 19]. They include two bar fragments, four fibulae fragments, a pendant and a caldron fragment, and also two metallurgical remains, a nodule and a droplet (Fig. 2).

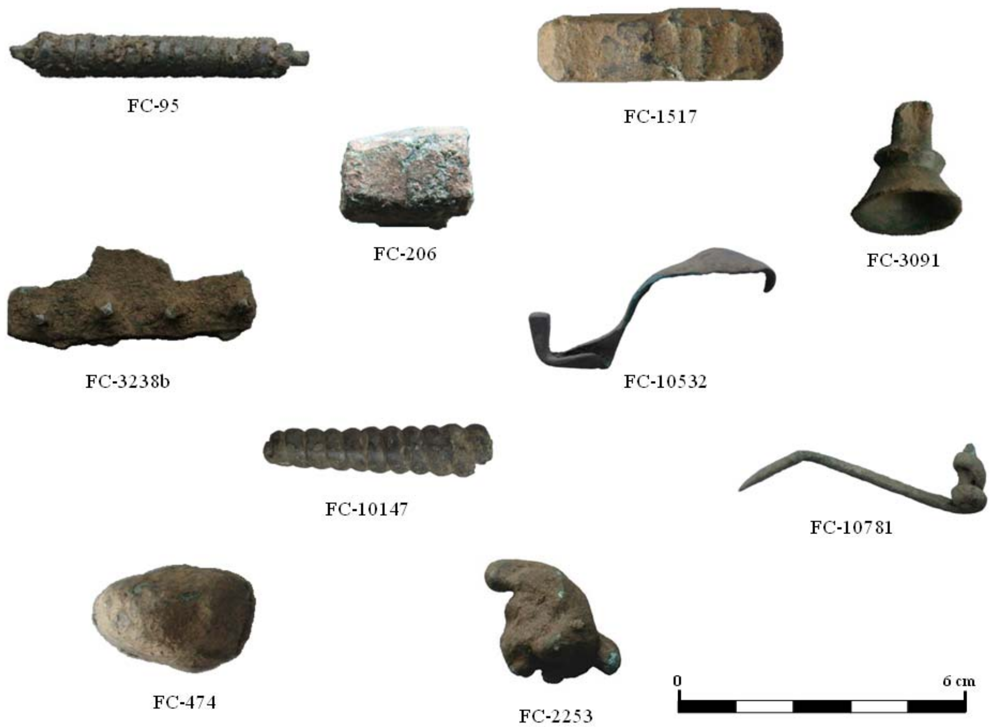

Fig. 2. Photographs of the archaeological bronze artefacts (Fibulae FC-95, FC-10147, FC-10532 and FC-10781; bar fragments FC-206 and FC-1517; pendant FC-3091; caldron FC-3238b) and metallurgical remains (nodule FC-474 and droplet FC-2253).

Sample preparation

The μ-EDXRF analyses performed for the elemental determination of the alloy composition were conducted on cleaned and polished areas since Sn and Pb content in corrosion surface can be up to four times higher than in metal surface [20].

For lead isotope ratio determinations by Q-ICPMS a small amount (~3mg) was taken by drilling on the polished areas with HSS DIN 338 bits with 1 and 1.5mm in diameter. Each sample was transferred to a polypropylene tube, where it was dissolved with 10mL HNO_3 20% and heated for 90min at 35ºC, in an ultrasonic bath. The reagents used were acid bi-distilled and ultra-pure water (18.2MΩ.cm).

Elemental analysis

μ-EDXRF analyses were performed using an ArtTAX Pro spectrometer which comprises: a low-power X-ray tube with a molybdenum anode; a set of polycapillary lens that generate a microspot of ~70μm in diameter of primary radiation; an integrated CCD camera and three beam-crossing diodes that provide the control over the exact position on the sample to be analysed; and a silicon drift electro-thermally cooled detector with a resolution of 160eV at Mn-Kα [21]. Artefacts were analysed using 40kV, 0.5mA and 100s of tube voltage, current intensity and live time respectively, and three analyses were made on each artefact in order to have the average value.

Quantitative analysis was made with the WinAxil software that uses the fundamental parameter method and experimental calibration factors that were calculated with the certified reference material Phosphor Bronze 551 Spectrographic Standard from BCS. Details of the accuracy of the analytical technique and quantification limits have been previously published [22].

Lead separation by anodic electrodeposition

After acid dissolution, each sample was submitted to an anodic electrochemical Pb separation following a previously described procedure [23]. In bronze alloys, besides the major elements (copper and tin) the Pb may be present in variable concentrations with some other minor or trace elements. The electrochemical reaction requires a reduced amount of the sample, essential when investigating cultural artefacts. It was performed in a polypropylene tube in a water bath at 80ºC, for 60min. with platinum electrodes. During the electrochemical reaction Cu^{2+} and Sn^{2+} are the major interferences. As a consequence of the standard electrode potentials (Fig. 3), Cu^{2+} is reduced on cathode and Pb^{2+} is oxidized on the anode to PbO_2. Additionally, due to the Sn^{2+} standard electrode potential (-0.14V), during electrochemical reaction Sn^{2+} salts deposit may form. Figure 3 illustrates the electrochemical reaction and the dark layer coloration on platinum electrode.

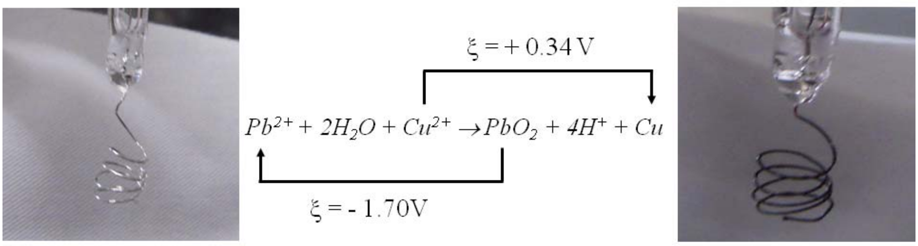

Fig. 3. The platinum electrode before and after anodic oxidation of Pb from SRM BCS 183.

The PbO_2 precipitate was stripped using a mixing solution with HNO_3/H_2O_2. For anodic electrodeposition time optimization, the standard reference material BCS 183 (Leaded Gunmetal) with a certified chemical composition of 84.5% Cu, 6.69% Sn, 3.25% Zn and 3.40% Pb was used. The adequate reaction time has been investigated during the study, performing reactions during 120, 60, 45 and 30min.

Lead isotope ratio

After lead electrochemical separation, the PbO_2 is diluted with ultra-pure water (18.2MΩ.cm) from MilliQ system (Millipore) up to 100μg/L. Lead isotope measurements were carried out with a quadrupole mass filter ICP-MS, the ELAN DRC-e from PerkinElmer Sciex (*Axial Field Technology*). NIST 981 (Common Lead Isotopic Standard) from National Institute of Standards and Technology was used as a mass bias correction solution for isotope ratio analysis. The abundance of Pb isotope ratio from standard NIST 981 certified is: $^{206}Pb/^{204}Pb$ = 16.973; $^{207}Pb/^{206}Pb$ = 0.9146; $^{208}Pb/^{206}Pb$ = 2.1681. The accuracy of the analytical determinations was < 0.2%.

Results and Discussions

Alloy Composition Analysis

The elemental composition obtained by μ-EDXRF analyses of the archaeological artefacts and metallurgical remains from Fraga dos Corvos is displayed in Table 2.

Table 2. Elemental composition by μ-EDXRF of the metallurgical remains and artefacts (in wt%, average value of three measurements and standard deviation)

Archaeological Bronzes Alloy			Cu	Sn	Pb	As	Fe
Metallurgical remains	Nodule	FC-474	88.3 ± 0.8	5.5 ± 0.4	6.1 ± 0.7	n.d.	<0.05
	Droplet	FC-2253	90.7 ± 0.9	5.1 ± 0.3	4.2 ± 0.7	<0.1	<0.05
Artefacts	Fibulae fragments	FC-95	88.2 ± 0.2	9.2 ± 0.1	2.5 ± 0.2	<0.1	<0.05
		FC-10147	92.3 ± 0.4	6.2 ± 0.3	1.4 ± 0.5	<0.1	0.05
		FC-10532	90.0 ± 0.3	5.6 ± 0.3	4.3 ± 0.4	n.d.	0.05
		FC-10781	91.9 ± 0.3	5.7 ± 0.2	2.2 ± 0.2	<0.1	<0.05
	Bar fragments	FC-206	89.2 ± 0.5	8.6 ± 0.5	2.0 ± 0.3	n.d.	<0.05
		FC-1517	84.4 ± 2.7	13.9 ± 2.4	1.6 ± 0.6	n.d.	<0.05
	Pendant	FC-3091	86.0 ± 0.2	11.6 ± 0.3	2.3 ± 0.3	n.d.	<0.05
	Cauldron	FC-3238b	85.0 ± 3.0	10.9 ± 0.9	2.0 ± 0.5	<0.1	<0.05

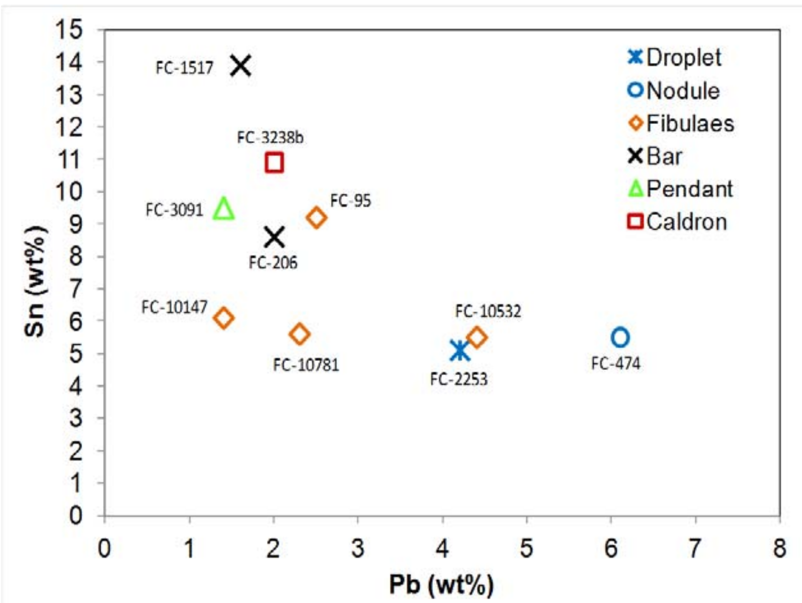

Fig. 4. Sn and Pb average contents in the bronze artefacts determined by μ-EDXRF analyses.

The results show that all the artefacts are made of bronze with variable Sn and Pb concentration values: from ~5 to 14% Sn and from ~1 to 6% Pb. Fig. 4 shows the distribution of the artefacts regarding their Sn and Pb concentrations.

Generally, the objects with the highest tin contents present the lowest lead contents, and on the opposite, those with low tin contents exhibit higher lead values.

The artefacts with the higher Pb contents (> 4%) are a fibula fragment (FC-10532) and the two metallurgical remains (a nodule and a droplet). The latest may be related to metallurgical processes that were performed at the site, as smelting and/or melting operations. All the other objects have Pb contents < 3%.

Lead Isotopic Ratio Analysis

The data processing obtained by Q-ICPMS results was based on comparison of the three lead isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$) in two "mirror" plots, where the two vertical axes are $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ and the horizontal axis is always $^{207}Pb/^{206}Pb$ [24].

Standard Reference Material BCS 183

Table 3 shows the variation of isotope ratios $^{206/204}Pb$, $^{207/206}Pb$ and $^{208/206}Pb$ obtained for BCS 183 in Pb^{2+} solution without anodic electrodeposition (after acid dissolution) and PbO_2 solution obtained for different electrochemical reaction times.

Table 3. Comparison between the isotope ratios $^{206/204}Pb$, $^{207/206}Pb$ and $^{208/206}Pb$ in the Pb^{2+} obtained without lead separation and the PbO_2, obtained at different electrodeposition time for SRM BCS183. The Pb isotope ratios are given as average values with standard deviation, respectively.

Reaction product solution	Reaction time (min)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
Pb^{2+}	-	17.582±0.084	0.891±0.002	2.153±0.004
PbO_2	120	17.424±0.024	0.891±0.001	2.124±0.002
PbO_2	60	17.471±0.026	0.888±0.002	2.126±0.003
PbO_2	45	17.410±0.047	0.891±0.001	2.136±0.008
PbO_2	30	17.469±0.036	0.890±0.002	2.138±0.005

Results indicate that isotope ratio $^{206/204}Pb$ (17.582±0.084) for the Pb^{2+} solution, without anodic electrodeposition, is higher than in PbO_2 solutions. This difference can be explained by ^{204}Pb being the less abundant isotope (1.4255%) on Earth and not a product of radioactive decay, so as a consequence it is stable and has a constant abundance. In the bronze alloy matrix, the sensitivity and reproducibility for Pb isotope determinations decrease. To overcome such limitation anodic electrodeposition is the fastest method to separate the Pb.

The PbO_2 solutions had a smaller standard deviation with a high homogeneity among replicates. The reaction time choice was between 120 or 60min. To optimize the bronze alloy preparation and to attain a larger laboratory profitability an anodic electrodeposition time of 60 min for samples with Pb content around 3.40% was chosen.

The precision of method for SRM BCS 183 is given by standard deviation: $^{206}Pb/^{204}Pb$ = 0.046%, $^{207}Pb/^{206}Pb$ = 0.001% and $^{208}Pb/^{206}Pb$ = 0.015%.

Fraga dos Corvos Bronze Alloys

The Pb isotope ratios of the archaeological artefacts and metallurgical remains (ten bronze alloys) are displayed in figure 5. The standard deviation of the measurements is represented by error bars.

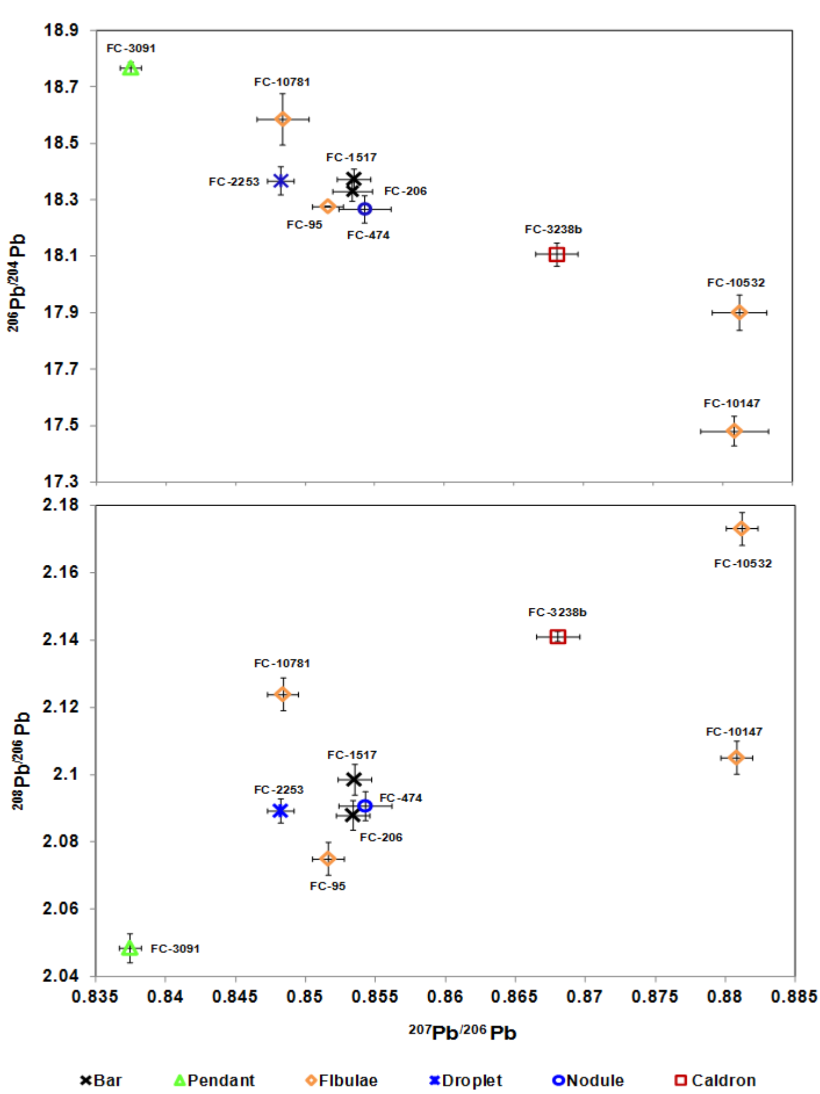

Fig. 5. Lead isotope ratios determined by Q-ICPMS of the archaeological artefacts and metallurgical remains from Fraga dos Corvos.

The four fibulae fragments show very different isotope ratios, which are also different from the caldron and the pendant fragments. Only one of the fibulae fragments, the FC-95, shows values closer to other objects, namely to those obtained for the two bar fragments (FC-1517 and FC-206) and the two metallurgical remains. Among the latest, the values obtained for the nodule FC-474 and the two bar fragments are very close, suggesting the same origin of ores/metal, and possibly some metallurgical relationship. Interestingly, these three artefacts have very different elemental compositions, with low Pb but variable Sn contents among the bars and high Pb and low Sn content in the nodule. One explanation for the similarity in the isotopic ratios despite the different elemental compositions could be that the nodule could have been an intermediate metal product, as resulting from a smelting operation where nodules of different compositions could have been produced [25], which were lately melted together to produce metallic objects, whose composition would result from the average composition of the nodules used.

On the other hand, two objects which have a very similar elemental composition, the droplet FC-2253 and the fibula FC-10532 (with about ~5%Sn and ~4%Pb) show very different Pb isotopic compositions. Such different isotopic compositions clearly distinguishing them from what could initially seem to have been a relationship among a metallurgical remain and an artefact, bonded together by some kind of metallurgical process.

The dispersion of $^{206/204}$Pb ratios (17.901 to 18.767) suggests the use of ores of very different geological age deposits. ^{204}Pb is not the product of radioactive decay and its concentration is constant. Therefore, the radioactive decay is irreversible, and the terrestrial rocks have Pb isotope ratios ($^{208/204}$Pb, $^{207/204}$Pb and $^{206/204}$Pb) that increase with time [26]. Given the results of the samples studied it can be proposed that the pendant (FC-3091) was produced from the oldest deposit and the fibula fragment (FC-10532) from the most recent deposit.

Conclusion

The lead separation by anodic electrodeposition demonstrated to be an efficient process for lead isotopic ratios determination by Q-ICPMS in archaeological bronzes having Pb contents above 1%.

Generally, the present results indicate some degree of complexity on the site related both to the origin of artefacts/metals or ores used for producing the artefacts, as well as on the composition of the metal/artefacts that could have been produced or used on the site.

The dispersion identified between artefacts and metallurgical remains seems to indicate a dynamic and differentiated metallurgical production, as has been suggested for other Iberian sites [27]. Although the great dispersion of alloy compositions and lead isotopic ratios determined for the artefacts studied, the similarity between lead isotope ratios among one metallurgical remain (a nodule) and two bar fragments can point out to local metallurgical activities.

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