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ARCHAEOMETALLURGIGAL STUDIES OF PRE-HISTORICAL ARTEFACTS FROM *QUINTA DO ALMARAZ* (*CACILHAS, PORTUGAL*)

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ABSTRACT

The *Quinta do Almaraz* archaeological site is located in *Cacilhas (Almada),* a sprawling riverside village situated in the Tagus estuary. It lays on Miocenic limestone clay and sandstone formations. This site occupies an elevated platform of about 4ha which provides control over the nearby river and surrounding area and has favoured Human occupation since the Neolithic. The area has been excavated since 1988 and the enormous amount of recovered metal artefacts, slags, crucibles and metal debris constitutes the basis of "*Quinta do Almaraz* Archaeometallurgical Project". Previous investigations have identified bronzes with low and high Pb content, as well as iron artefacts. In the present work, further metallic artefacts, crucible fragments and several slag fragments were analysed in order to understand the evolution of the metalworking activities in *Quinta do Almaraz*. The artefacts elemental compositions were determined using an EDXRF spectrometer (Kevex EDX-771). The majority of the metallic artefacts were composed of copper and tin, although one copper and one arsenical copper were also detected. The identification of silver, lead and bismuth on the internal surface of several crucible fragments was an important evidence of the silver production by cupellation in the Portuguese territory before the Roman period.

KEYWORDS: *Quinta do Almaraz*, archaeometallurgy, Bronze Age, Iron Age and EDXRF.

INTRODUCTION

The *Quinta do Almaraz* archaeological site occupies an area of about 4ha over Miocenic limestone clay and sandstone formations in *Cacilhas (Almada)* (Fig. 1). The site is close to the western Portuguese Coast and is situated on an elevated spur over the left bank of the Tagus estuary and close to a small sheltered cove located downhill to the east (Fig. 2). The platform presents an average altitude of 50m (maximum of 60m and minimum of 35m) conferring the control over the river and surrounding area. Consequently, this geographical position favoured the Human occupation at least since the Neolithic period, as revealed by the excavated archaeological remains.

The *Quinta do Almaraz* was discovered in 1985, but the earliest field works were conducted during 1987 with a systematic survey of the area and the elaboration of a dispersion map to prepare the archaeological excavations. These started in 1988 and recovered a vast amount of archaeological artefacts (lithic, ceramic and metallic) and animal remains (1). The total area of the settlement and its structures were also identified by a geophysical survey which found two lines of walls along with a set of orthogonal structures. Archaeological remains points out to an occupation from the Neolithic/Chalcolithic through to the Roman Republican period. Furthermore there are some indications of preferential occupational areas at different times: the Neolithic/Chalcolithic to Late Bronze Age period occupies the higher areas, the Iron Age settlement is spread out through the whole structure and the Roman settlement takes up a small area situated on the western side.

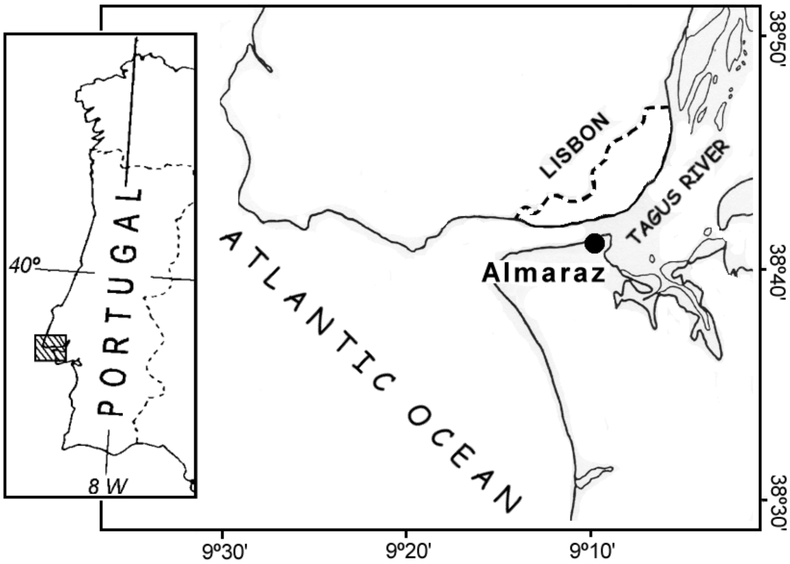


Fig. 1 – Geographical location of *Quinta do Almaraz* archaeological site.

There are also evidences of the presence of a Phoenician settlement in *Almaraz* between the IX and VIII centuries BC. Actually, the elevated location of the site controlling the nearby river is a typical geomorphological characteristic of a Phoenician Iberian settlement. This feature was obviously of great value to their mercantile and maritime activities and several sites with these characteristics are spread throughout the southerly Iberian coast: Rio Antas (Almería, Spain), Cerro del Prado (Cádiz, Spain), Montilla (Córdoba, Spain) and Toscanos (Málaga, Spain) (2).

Using stratigraphy and radiocarbon dates it was possible to establish the chronology of three distinct realities already identified: the moat, the habitation area and the ditch. The moat display three phases (VIII century BC, VII century BC and V century BC). The habitation area dates from around the VII century BC. The ditch was rapidly filled and abandoned around the VII century BC except for a small area dated from the IV century BC.

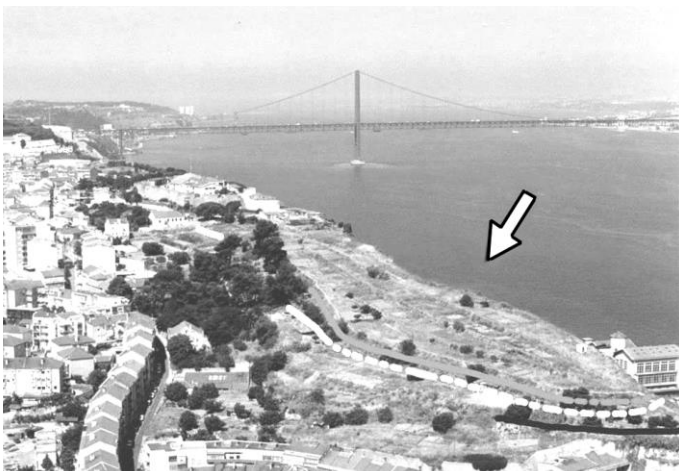


Fig. 2 - Aerial photo of *Quinta do Almaraz* archaeological site showing the dominant position of the area over the Tagus estuary.

In a recently published work, metallic artefacts and ceramic fragments were non-destructively analysed by EDXRF. The obtained results point out to the presence of different types of bronzes and iron made artefacts. The analysis of the surfaces of crucible fragments allowed the identification of different metallurgical operations, specifically the remains of a silver cuppelation process and a gold alloying (3). In the present paper, further metallic artefacts and metalworking debris were studied aiming to enlarge the knowledge about the archaeometallurgy in *Almaraz*, to contribute to the understanding of the technological evolution since the Chalcolithic and, furthermore, to ascertain the Phoenician influence. This will ultimately contribute to the better understanding of the economical and social activities within the *Almaraz* archaeological site.

EXPERIMENTAL

Considering the nature and importance of the "samples" involved in archaeometallurgical studies, it is extremely important that the techniques used in the analysis of the excavated artefacts are completely non-destructive. Due to this particular characteristic, the Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry is widely used in archaeometallurgical studies (4;5;6;7;8;9). Besides the EDXRF spectrometry is also multielemental, fast and allows the detection of elements with an atomic number larger than 12 with high accuracy.

However, this is a "surface" analytical technique and in metallic alloys the analysed layer does not exceed several tens of microns. Consequently, in metallic artefacts, the corroded/patinated surface gives a main contribution to the obtained results (10;11). This problem could be solved by using methods of surface preparation; nevertheless, deviations in the obtained values have a common tendency (namely, As and Sn enhanced concentrations) which do not affect the alloying type characteristic of the studied Periods. In the present work, artefacts were analysed without any surface treatment.

Chemical analyses were performed using an Energy Dispersive X-Ray Fluorescence spectrometer, Kevex model 771. This system is equipped with a power Rh X-ray tube (200W) and several secondary targets and filters (Ti, Fe, Ge, Zr, Ag and Gd) to optimise the excitation conditions. The characteristic X-rays emitted by the analysed sample area (of about 3cm in diameter) are collimated at 90º and measured in a cryogenically cooled Si(Li) detector (30mm^2 of active area and a resolution of 175eV at 6.4keV). The monochromatic beams of the silver and gadolinium secondary targets were used to promote the sample characteristic X-rays, using 35kV and 57kV tube voltage, respectively. Current intensities varying between 0.5mA and 3.0mA were used in order to obtain dead times close to 40%. Each sample was measured with 300s of live time and some of them were measured in more than one region. Quantitative determinations included the calibration with several reference standards: Phosphor Bronze 551, 552, 553, 554, 555 and 556 (from British Chemical Standards) and Leaded Bronze 50.01, 50.03 and 50.04 (from BNF Metals Technology Centre). Elemental concentrations were calculated using the EXACT program (12), based on the fundamental parameter method. The accuracy of the major element determinations was calculated as 1% for copper, 9% for tin and 4% for lead.

METALLIC ARTEFACTS

The collection of studied metal artefacts (27 objects) presents similar typological attributes and is composed mainly by tools (fish-hooks, one pair of tweezers, knifes, needles, one arrowhead and one sickle). Considering the proximity of *Almaraz* to the Tagus river it is of no surprise the large amount of recovered fish-hooks, which can be attributed to a period from the Early Bronze Age through to the Late Bronze. Besides these, other prestige artefacts such as (bracelets, *fibulae* and one buckle) and several weights are also part of the studied collection. The absence of weapons, with the exception of one bronze arrowhead, is in agreement with previous authors which state that, in Portugal, the majority of Bronze Age weapons were recovered from votive or scrap deposits and not from settlements or burials (13). The pair of tweezers and *fibulae* clearly indicate a West Mediterranean late Bronze Age influence. The double spring brooches (*fibulae*) are typologically related with the transition from Late Bronze Age through to the Iron Age in this region.

The group of iron-based artefacts includes knife fragments, one sickle and one knife with bronze rivets. Iron knives are common in Late Bronze Age settlements in Portugal, usually interpreted as prestige goods introduced through the contacts with the Phoenicians (14).

The EDXRF analysis of these metallic artefacts allowed the identification of the different alloys present in the archaeological site as copper, iron and lead based artefacts (Fig. 3).

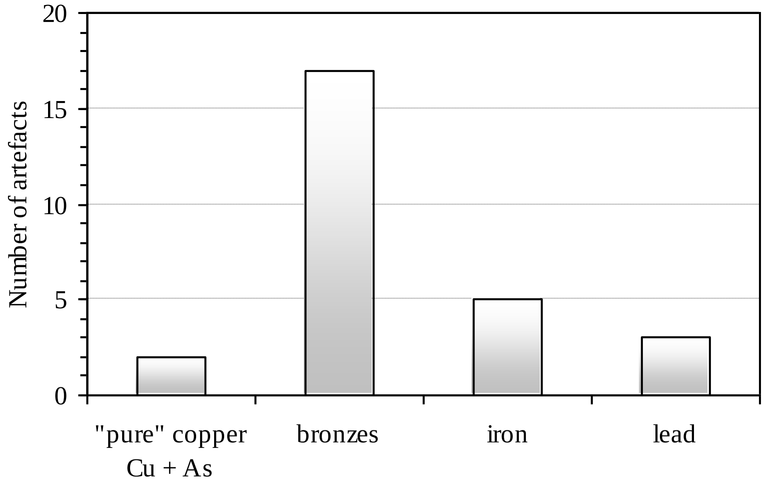


Fig. 3 – Metallic artefacts from *Almaraz* archaeological site.

COPPER-BASED ARTEFACTS

Most of the copper based artefacts were bronze alloys with variable tin content. On the other hand, a single object of “pure” copper (handle) and one arsenical copper (bracelet section containing 1.7% of arsenic) were identified. Results indicate that bronzes from *Almaraz* seem to be of two types, the first with a tin content ranging from 4 to 8 % (Fig. 4) and the second with around 16% Sn, although these values might be enhanced due to the Sn enrichment in the superficial corroded layer

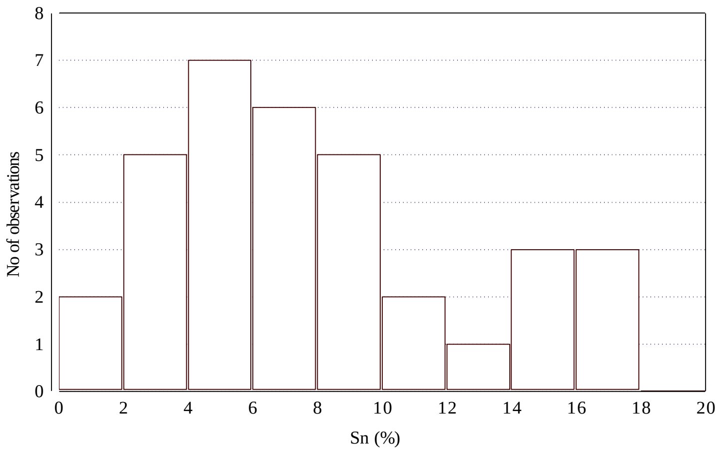


Fig. 4 – Tin content in copper based artefacts from *Almaraz* archaeological site.

The analysed bronzes also present a highly variable lead content (Fig. 5) which allow us to divide them into binary (Cu + Sn) and ternary (Cu + Sn + Pb) alloys. The first group includes both the bronzes without lead or with low lead content (<2%) which present again the lowest Sn concentrations. The small amounts of lead might have been originated from the ore used or from the remelting of artefacts which points to the probability that it is not an intentional addition of lead to the bronze.

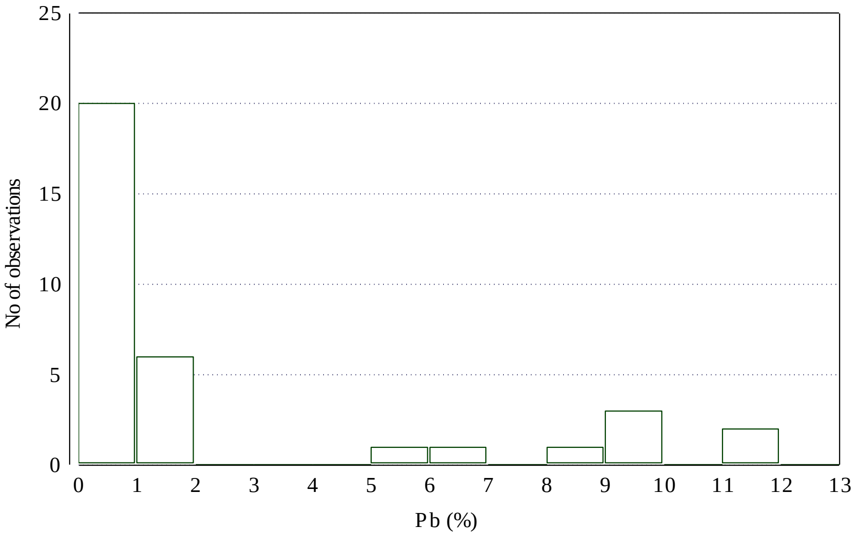
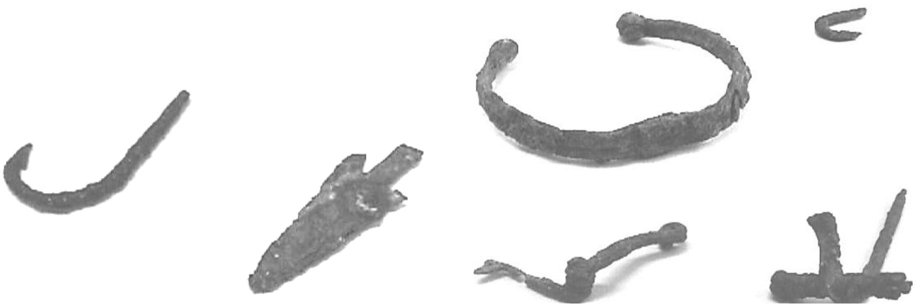


Fig. 5 – Lead content in copper-based artefacts from *Almaraz* archaeological site.

Tab. 1 – Minimum and maximum copper, tin and iron contents in bronzes from *Almaraz*.

	Cu (%)	Sn (%)	Pb (%)
fish-hooks arrow head needles bracelets *fibulae*	80.7 – 98.3	1.24 – 16.3	0.12* - 1.98
			
fish-hooks Tweezers	69.9 – 82.6	7.64 – 16.8	5.85 – 12.0
			

* - detection limit divided by 2.

The second group presents a variable high tin (7.64-16.8%) and lead content (5.85-12.0%) and is constituted mainly by fish-hooks (3) and one pair of tweezers (Tab. 1). The addition of lead to the copper-tin alloys reduces the alloy melting point and improves its fusibility. However, this addition also makes the object fragile and, therefore, it is not suitable for weapons or tools (e.g. axes or palstaves). In this particular case, the addition of lead made the alloy more malleable and adequate to produce the fish-hooks and tweezers, objects that usually are not submitted to high strengths. It is worth noticing that the three other analysed fish-hooks were binary bronzes with an anomalously low Sn content.

During the transition of the Late Bronze Age to the Iron Age there was an increase in the lead content in bronze artefacts from Western Europe, mainly in France and in the British Isles. This is also a characteristic of the "Atlantic Metallurgy". In our case, the fish-hooks and the pair of tweezers with a high lead content can be related to this metallurgy, which can be confirmed either by the alloy elemental composition or according to their typology. In fact, tweezers are a rare object in Portuguese Late Bronze Age archaeological contexts and fish-hooks have a large time span since the Chalcolithic through to the Late Bronze Age and Iron Age (15).

IRON-BASED ARTEFACTS

The analysis of the five iron-based artefacts (knives and one sickle) showed that they were mainly composed by iron with some impurities of As and Cu (Tab. 2). Iron metallurgy was introduced in the region by the Phoenicians during the VIII century BC. The first iron objects found in Portuguese Late Bronze Age settlements were probably imported prestige goods and not locally produced. Actually, iron knives were the first imported iron items found in Portuguese Late Bronze Age settlements (14). Further research will contribute to a better understanding on the question whether those items where locally made or imported.

Tab. 2 – Minimum and maximum iron, copper and arsenic contents in iron-based artefacts from *Quinta do Almaraz* archaeological site.

Fe (%)	Cu (%)	As (%)
98.4 - 99.5	0.29 – 1.45	0.20 – 0.38

LEAD WEIGHTS

Other small metallic artefacts, identified as weights, were also researched. Two of these artefacts possess a cubic format, which is the typology more commonly found in the Phoenician world. Similar weights were also found in the archaeological sites of Cerro del Villar (Málaga, Spain) and Ibiza (Spain) (16). Contrary to the weights from *Almaraz*, which are mainly composed of lead (Fig. 6), the weights from Cerro del Vilar were made of an alloy of lead with a high tin content. Some authors (17) attribute this particular composition to a way of reducing the weight of the object in order to deceive the costumer – the density of tin is 7,310 kg.m^{-3}, while the density of lead is 11,340 kg.m^{-3}.

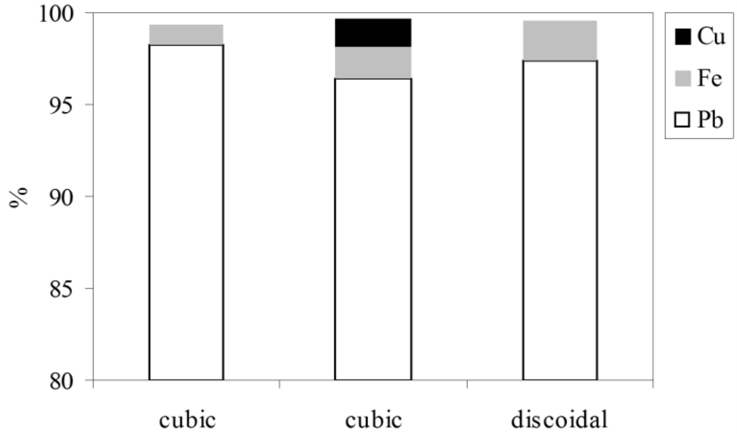


Fig. 6 – Composition of lead weights from *Almaraz* archaeological site.

The third weight from *Almaraz* presents a discoidal form with a small hole in the centre, opened to fit into the *ponderarium*. This weight is also made essentially from lead (97.4% Pb and 2.2% Fe), in accordance with the discoidal weights from Ibiza (Spain). Once again, the typological identical artefacts from the Iberian area, such as the Cancho Roano (Sevilha, Spain), present a lead alloy with a high tin content, contrary to the lead weights from *Almaraz* and Ibiza. In similar artefacts from the Middle East, namely of Phoenician and Greek origin, there was a transition from the lead-tin alloy to the almost pure lead, being the enriched tin artefacts associated to rituals (17).

METALWORKING DEBRIS

Slags, tuyeres and ceramic remains were analysed in order to ascertain the possible local metallurgical processes carried out at *Almaraz*. In a previous work (3), the analysis of ceramic remains (crucible fragments) allowed the identification of some metallurgical operations performed at *Almaraz*, namely the silver cuppelation and the gold alloying. In the present study, further evidence of metallurgical operations were detected by the analysis of two small curved crucible fragments recovered in radiocarbon dated layers from the seventh century BC. These remains are characterised by a glazed inner surface and, in particular, one presents an internal face heavily slagged and vitrified, particularly at the bottom. They also exhibit a red surface, typical of have being utilised under the oxidising atmosphere associated with the cupellation process.

EDXRF analysis of both sides of these artefacts identified the presence of silver, lead, bismuth and copper in the inner surface. Crucible fragment MAH8236.ALZ1351 was also enriched in bromine in the interior surface. The two outer surfaces are enhanced in iron and zirconium due to the presence of ceramic clay materials (Fig. 7).

The finding of silver, lead, bismuth and copper in the inner surface of these crucibles is an evidence of silver production by the cupellation process. The high bismuth content present in the analysed debris also points out to the use of an argentiferous ore rich in this element. Argentiferous lead and jarosite ores constitute the major silver sources to the ancient world and both require the use of the cupellation process to obtain the refined silver. The argentiferous lead ores used were mostly galena (PbS) but also cerussite ($PbCO_3$) and anglesite ($PbSO_4$). Jarosites ores are mixed hydrated sulphates $\{KFe_3[(OH)_6(SO_4)_2]\}$ derived from the oxidation of the primary deposits.

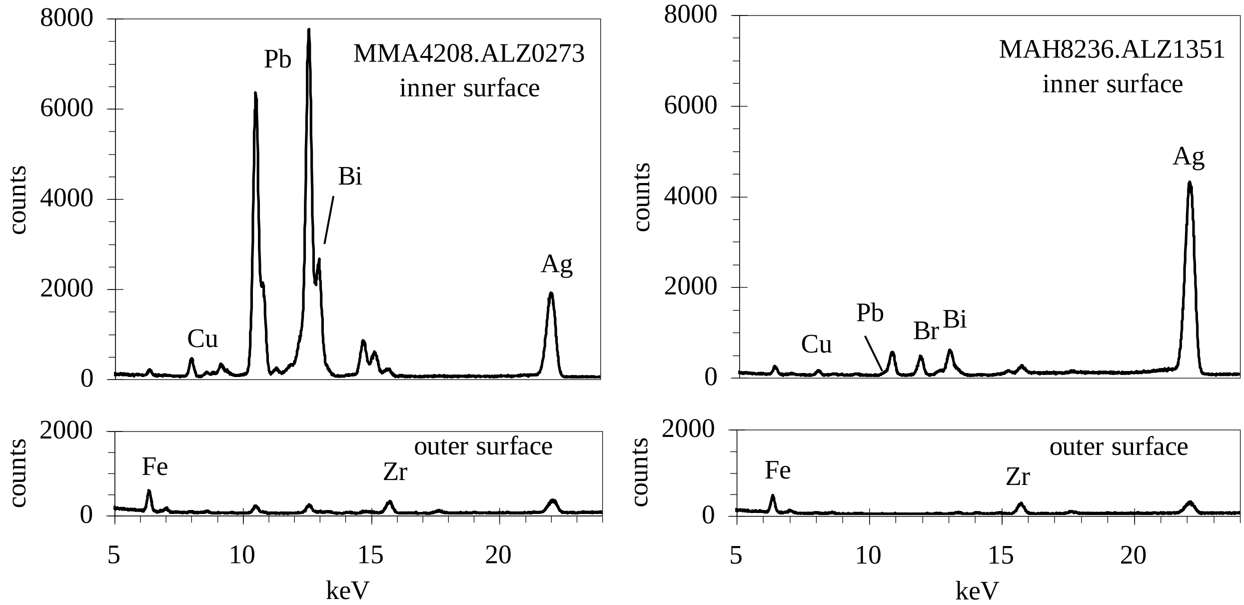


Fig. 7 - EDXRF analysis of the inner and outer surfaces of two crucibles fragments from *Almaraz.*

These ores can be enriched in silver due to the selective removal of other elements and therefore typically show variable compositions. To obtain the refined silver from the jarosite ores, lead was added during the cupellation operations. During the cuppelation process the smelted silver ore is heated at a temperature of about 1000º C and exposed to a flux of air that will oxidise the lead into litharge (PbO). The litharge will coat the hot inner surface of the crucibles, confering the glazed appearance observed in the two analysed ceramic bodies. The glazed aspect is characteristic of this type of archaeometallurgical debris (18).

One of the analysed crucible fragments from *Almaraz* (MMA4208.ALZ0273) is remarkably similar to the typical clay wedges from jarosite smelting at Rio Tinto (Huelva, Spain), belonging to the Iberian Pyrite Belt. Located in the Iberian Peninsula, the Rio Tinto mines are the most famous ancient mines, where jarosites were exploited by the Phoenician followed by the Roman (19). During the Late Bronze Age (900 BC) these mines were worked mainly for galena (20).

Slagged pottery from a 7th century BC silver workshop in Monte Romero (Huelva, Spain) revealed the presence of lead, antimony and copper originated from a metallurgical step to refine the argentiferous lead before the cupellation process (21). In the previously analysed crucible fragment from *Almaraz* (MMA9434.ALZ1750), the elements Cu, Ag, Bi and Pb were also identified and attributed to be a result of silver cupellation process. Those results proved to be rather similar to those of the present artefact MAH8236.ALZ1351.

Copper - and essentially bismuth - are quite difficult to separate from silver (22); consequently, the Ag refinement could include repeated cupellation stages, which involve the addition of lead to the raw silver in each separation. Since other elements present in the ore are promptly removed by the lead in the earliest separation, the “litharge” left in the crucibles will probably contain copper and bismuth, which have been identified in the *Almaraz* crucible debris. The two similar analysed crucible fragments (MAH8236.ALZ1351 and MMA9434.ALZ1750) present a higher silver content. It is worth noticing that both these fragments seem to belong to small crucibles, which might indicate that they could have been used in a later silver purification stage, contrary to the fragment belonging to the bigger crucible (MMA4208.ALZ0273), which displays a higher lead content.

CONCLUSIONS

The *Quinta do Almaraz* archeometallurgical research has developed some interesting questions about the metal production in the period spanning from Copper and Early Bronze Age to the Iron Age. The compositions of the analysed bronze artefacts establish the presence of two different metallurgical practices at *Almaraz*: bronzes with high and low lead content. Bronze artefacts with the same typology (e.g. fish-hooks) present both low and high lead contents. However, the typology of these artefacts is also consistent with the high lead content of this group, i.e. these are artefacts that are not submitted to high strengths. The existence of two distinct types of metallurgy can be related to either the Mediterranean influences (low lead content) or to the Atlantic metallurgy, characterised by bronzes with high lead content. Furthermore, the low lead bronzes present also unusually low tin contents. The bronzes with low tin content seem to be a particular characteristic of the *Almaraz* archaeological site within the context of analysed bronze artefacts from other archaeological Portuguese sites.

The enormous amount of metal artefacts and debris points *Quinta do Almaraz* as a metal production centre since the inception of local metallurgy through the Iron Age. The analysis of metalworking debris, such as crucibles, slags and tuyeres confirmed the silver cupellation and gold alloying in such ancient times. To our knowledge, *Almaraz* is the first Portuguese archaeological site where silver cupellation was detected before the Roman conquest.

In this work some iron based artefacts and slags might indicate a local iron production. Apparently, these are the first analytical evidences of pre-historical iron artefacts recovered in Portuguese territory. Iron smelting activities at *Almaraz* were not clearly detected; therefore, iron artefacts could be locally produced or introduced by the Phoenicians arrival. The Phoenician influence at *Almaraz* seems to be relevant, based on the presence lead weights and the production of silver by the cupellation process.

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