

Use of Monte Carlo Simulation as a Tool for the Nondestructive Energy Dispersive X-ray Fluorescence (ED-XRF) Spectroscopy Analysis of Archaeological Copper-Based Artifacts from the Chalcolithic Site of Perdigões, Southern Portugal

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Abstract

This work is part of a broader research line that aims to develop and implement a nondestructive methodology for the chemical characterization of archaeological metals based on a protocol that combines energy dispersive X-ray fluorescence spectrometry (ED-XRF) with a Monte Carlo (MC) simulation algorithm. In this paper, the ED-XRF/MC protocol has been applied to estimate the chemical composition of a selected group of 26 copper-based artifacts and fragments recovered at Perdigões, one of the larger Chalcolithic sites of Southwest Iberia. All the analyzed artifacts have a multilayered structure composed by the alloy substrate and by a superficial layer common in each metal buried for hundreds of years and consisting of the patina mixed with soil. Due to the difficulty in determining the quantitative composition of these alloys in the presence of this complex patina/encrustation layer, the spectrometric

protocol applied in this paper allows to simulate and to determine the composition of the bulk alloy without any prior removal of the overlying corrosion patina layer and soil-derived crust, even in the presence of rough and irregular surfaces, thus preserving the physical integrity of the artifacts. The overall results obtained with the ED-XRF/MC protocol indicates that the artifacts from Perdigões are almost pure coppers with a low amount of arsenic (<3.0 wt%) and reduced concentration of elements such as Pb, Bi, and Sb, in agreement with the third millennium metallurgy known in Southwestern Iberia. Also based on previously theoretical-experimental studies, the data presented in this paper show how the applied analytical methodology can be a fast and completely nondestructive analytical tool reliable for routine and large-scale chemical analysis of archaeological metals, thus representing a major advance to be broadly applied within the field of Cultural Heritage studies.

Keywords: Energy dispersive X-ray fluorescence spectrometry, ED-XRF, Monte Carlo simulation, MC, Chalcolithic, early metallurgy, Southern Portugal.

Introduction

The study of ancient metallurgical technologies is a very complex and challenging research area requiring a multi-perspective approach able to integrate analytical and archaeological data with anthropological considerations. Indeed, a metallic artifact may be investigated through modern analytical techniques but it cannot simply be considered as the result of a technological process. Indeed, in an anthropological perspective, an object may be also considered as the materialization of humankind's choices and decisions and, as a result, its production, consumption, trade and deposition could be deeply influenced by and embedded in socio-cultural strategies, rituals beliefs and economic constraints whose original logic can only be adequately understood through a holistic and emic approach.¹⁻⁶

Although not sufficient by itself to provide all the required information, material sciences methodologies are a crucial step for the understanding of these ancient technologies and they must be able to provide significant clues for the identification of the chemical and phase composition, raw material sources, and manufacturing processes, thus informing about skills and know-how disseminated among the ancient metalworkers and shedding light on social behaviors, economic options and cultural processes.

The most common type of information about ancient metal artifacts concerns the identification of major and minor elements of the alloy. Although several analytical techniques are available for this purpose, when choosing the most appropriate procedure one should give priority to a technique that is: (a) nondestructive, so that the physical integrity of the object is ensured, avoiding any kind of damage to the artifacts; (b) fast, so that a large amount of material could be analyzed in the shortest possible time; (c) universal, so that the technique could be applicable to materials with different shapes and dimensions; (d) versatile, so that the same technique could be applied at different analytical scales and obtain information from the average composition of heterogeneous materials up to **data on microscopic areas**; (e) sensitive, and (f) multi-elemental, so that the maximum of information could be simultaneously extrapolated for major, minor, and trace elements.⁷

Energy dispersive X-ray fluorescence spectrometry is a well-established elemental technique that meets these requirements, as demonstrated by previously reported studies for both major and minor elemental compounds in several archaeological artifacts, such as ceramic, metal, glass and obsidian.⁸⁻⁹ Since no prior preparation is required for the sample to be analyzed, ED-XRF is generally considered as a nondestructive technique. However, one of the main limitations of ED-XRF lies in the fact that it performs surface analysis and this is quite problematic when one is dealing with archaeological metals buried for hundreds or thousands of years, thus subjected to prolonged alteration and corrosion processes mainly affecting the more superficial layers of the objects. In fact, archaeological metals are generally covered by an outer layer with a variable thickness and a non-homogeneous chemical composition consisting of a mixture of soil encrustations and corrosion patina, whose chemical composition does not reflect the effective composition of the bulk metal. Accordingly, in order to characterize the bulk metal composition of an object, the commonly used analytical protocol in archaeometallurgical studies involves the removal of samples or the mechanical cleaning of small areas of the metal surface. This procedure leads to an alteration of the physical integrity of the artifacts, making copper-based artifacts unsuitable candidates for a complete nondestructive approach.

The analytical protocol used in this work was precisely designed and is being improved in response to a specific constraint: the necessity of developing and implementing a nondestructive methodology to be applied in the chemical analysis of artifacts for which the removal of samples or the cleaning of the superficial area is not admissible. The theoretical description of the ED-XRF/MC protocol applied here were published elsewhere.¹⁰⁻¹¹ In this

paper, we used this methodology for the elemental characterization of a selected group of Chalcolithic metals from Perdigões, a very important site from Southern Portugal (Fig. 1a), under excavation since 1997 by the Archaeological Research Group (NIA) of ERA Arqueologia S.A.

The site covers an area of about 16 hectares and consists of an assemblage of thirteen roughly concentric ditched enclosures, several hundred pits, including different funerary areas with megalithic tombs or pits with cremated human remains and a cromlech (Fig. 1b). From a chronological point of view, the Perdigões area is characterized by a long diachronic occupation spanning the archaeological sequence from the Final Neolithic (3500 BC) to the Late Chalcolithic–Early Bronze Age (end of the third millennium BC).¹²

A great number of archaeological artifacts has been recovered during the excavations, including pottery, ivory objects, and lithic tools. As for metallurgy, evidence for all the phases of the production process, i.e., ores, crucibles, slags, molds, finished objects, and scraps, are documented as well. The available data indicates an increase of metal objects since the middle of the third millennium BC, especially in the central area of the site, where evidence of metal production has been found together with stone and funerary structures with cremated human remains. Besides the artifacts found during the archaeological works, around three hundred objects related to copper metallurgy were found during surveys carried out in the excavation area, thus some lacking reliable contextual provenance.

The overall available data suggests that Perdigões probably was a meeting place able to congregate people and materials from a large transregional area, including the Portuguese coast (Estremadura and Alentejo Litoral), the Spanish Central Meseta, the Western and Central Andalusia and the Northwestern Africa.¹³

The unique morphology of the site where Perdigões is located, a natural theatre opened to the east and with visibility over more than one hundred megalithic monuments located in the surrounding areas and the orientation of the gates of the enclosures, e.g., aligned to both solstices at sunrise and at sunset, suggest that Perdigões was symbolically placed within a cosmological scenario recreated through the interaction between architecture and landscape.¹⁴ Based on the archaeological findings, there is a certain consensus in considering Perdigões as a central site for the understanding of the dynamics which led to the emergence and development of social complexity in Western Iberia over the third millennium BC.

This paper has two main objectives: (a) to investigate the chemical composition of the selected artifacts and to place the data in the context of the Chalcolithic metalworking

tradition from Southwest Iberia; (b) to confirm the reliability and the accuracy of the ED-XRF/MC protocol in establishing itself as a conventional and routine analytical methodology with a far-reaching applicability and suitable for the analysis of large groups of archaeological metals without any previous removal of both soil and patina layers, that would be necessary to clear away if standard quantitative methods, such as fundamental parameters or empirical calibration,¹⁵ were used.

Materials and Methods

Twenty-six finished objects and fragments were selected for analysis using the ED-XRF/MC protocol. From a typological point of view, the artifacts reveal rudimentary morphologies, including both tools (awls, chisels, a fragment of an axe) and weapons (daggers, one arrowhead, and spearheads) (Fig. 1c). The selected metals have been recovered at different excavated areas with a chronology of the middle/third quarter of the third millennium BC, namely at occupation layers, pits 7, 16 and 40, tombs 1 and 2.

ED-XRF of these artifacts was performed with a Bruker TRACER III-SD handheld spectrometer equipped with a rhodium anode tube and a Silicon Drift Detector. The operating conditions were 40 kV and 12.5 μ A current with an Al/Ti filter (304.8 μ m aluminum/25.4 μ m titanium) and 60 seconds acquisition time. Spectral acquisition was performed without any pre-analysis cleaning treatment aimed at removing the corrosion patina and/or soil encrustations present on the artifacts. The visualization and the accurate positioning of the measurement spot was provided by the integrated camera of the equipment (Fig. 2a).

The methodology adopted in this paper was based on the application of a MC simulation, i.e., a probabilistic algorithm simulating the interaction of virtual photons with the sample. An XRF Monte Carlo simulation requires an accurate description of both the experimental setup and the sample composition and structure. In our case, the spectrum acquired from the Bruker system has been corrected within the MC simulation process for the air attenuation as well as for the attenuation introduced by other parts of the detection system, such as entrance window.

In order to obtain a fast simulation, the so-called variance reduction technique has been introduced.¹⁶ This approach allows to speed up the number of photons detected producing a realistic simulation of the measured spectrum in a couple of minutes. Among the available MC codes,¹⁷⁻²⁴ XMI-SIMS and XRMC are two fast MC algorithms developed with the aim to predict the spectral response of ED-XRF spectrometers using MC simulations.²⁵⁻²⁶ In this paper we use the XRMC software package. This code allows to consider the effects of

rough surface, which are typical of Cultural Heritage objects where soil encrustations and patina layers are often found,²⁷ like in the artifacts under investigation.

Furthermore, the application of XRMC software enabled to overcome the restraints caused by the superficial nature of the XRF analysis, thus determining not only the real elemental composition of the underlying layer corresponding to the bulk alloy, as well as the composition and the thickness of the corrosion/encrusted layer (Fig. 2b).²⁸⁻²⁹ For this purpose, all the measured spectra were modeled as two-layered structures formed by: (a) the inner bulk layer; and (b) the outer superficial layer composed by the green oxidized corrosion patina and the brownish carbonate soil-derived encrustation.

In this respect, it is also important to stress that the protocol only works when the XRF photons from the bulk are able to cross the patina/encrustation layer and to reach the detector. In fact, after the definition of the experimental setup and of the sample in terms of MC code language a spectrum is simulated and compared with the experimental one: if differences are found, the model is corrected until the two spectra, the simulated and the measured one, appear to be perfectly superimposed. The comparison is initially visually achieved but a finer difference estimation is performed with a chi-squared test.

In addition, quantitative XRF spectrum analyses were also carried out without the MC simulation method by mean of an empirical approach, following Smith.³⁰ In this case, the quantitative analysis was made through Bruker S1CalProcess v.2.2.33 software using experimental calibration factors that were calculated with five standards from certified reference materials BCR-691.³¹ Since the results obtained do not consider the multilayered structure of the objects, the effects of corrosion processes were not eliminated. These data have been used as comparison test to define the reliability of the quantitative results obtained through the MC approach.

Finally, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was also used with the aim to obtain complementary data able to identify the presence of micro-inclusions in the metal and to observe the differences in composition between the outer layers and the bulk alloys in small corrosion-free areas. The analysis was carried out with an Hitachi S3700N interfaced with a Quantax EDS microanalysis system. The Quantax system was equipped with a Bruker AXS 5010 XFlash Silicon Drift Detector (129eV Spectral Resolution at FWHM/Mn K α). The operating conditions for EDS analysis were as follows: backscattered electron mode (BSEM), 20 kV accelerating voltage, ~10 mm working distance and 90 μ A emission current.

Results and Discussion

Results

The elemental composition of the metals from Perdigões obtained both with the XRMC software package and the Empirical Calibration approach are depicted in Table 1. The uncertainty in the estimation of the concentration for data obtained by the XRMC algorithm is between 2–5% for major elements and can reach 20–30% for minor elements. Instead, as regards the EC data, the margin of error for the measurements may reach values of <2% for major elements, <5% for elements between 1 and 5 wt%, <10% for elements between 0.5 e 1.0 wt%, and <50% for elements lower than 0.1 wt%.

At a first glance, the results obtained through the empirical calibration approach, thus without removing the surface alteration effects (i.e., patina and soil encrustations), show a lower amount of Cu when compared with the data of the bulk alloy obtained by MC simulation. Other elements, such as Si, Ca, Al, Ti, Mn, Fe, and Sr, have also been identified in the XRF spectra and have been mapped with SEM-EDS analysis as well (Fig. 3). The distribution of these elements is not representative of the alloy and is related with the oxygenated corrosive environment in which the metals were buried.

The occurrence of calcium, for instance, could be related with both environmental conditioning and technological features: in fact, calcium could have been incorporated due to the fact that most of these metals were found in association with bones or as consequence of the presence of calcium into the ground where objects were buried. Also, it has been proved that since the Paleolithic, calcium was used as fuel together with wood being able to improve the duration of the combustion process.³² Therefore, it might be also assumed that the presence of Ca could result from the incorporation of bones used as mass fuel within the pyro-metallurgical operations.

It is also important to note that the application of the ED-XRF/MC protocol gives information not only on the chemical composition of the bulk as well as also on the composition and on the thickness of the corrosion layers. In Fig. 4, for instance, the spectra obtained from the simulation of the artifacts PER-1223, PER-4346 and PER-4672 are displayed superimposed to the experimental spectra. In all these cases, the MC simulation suggests that Cu oxides appear to be present in the patina that covers the bulk metal. Although elements lighter than sodium may not be directly detected, the fit of the background accomplished within the MC simulation process is very sensible to the composition, density and thickness of the corrosion layer. Thus, the exact determination of the patina contents both in terms of chemical composition and density is critical for a good fit of the background,

since the lighter elements also gives a contribution to the scattered radiation forming the background.

Furthermore, previous studies proved that ED-XRF/MC protocol is well working regardless the type of corrosion layer, whose chemical nature appears to be irrelevant for the purpose of the simulation process. Indeed, ED-XRF/MC protocol has already been applied in the analysis of metals covered by different corrosion products, such as oxides (cuprite, Cu_2O and tenorite, CuO), carbonates (malachite, $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$ and cerussite PbCO_3), sulfates (brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$) and chlorides (paratacamite, $\text{Cu}_2\text{Cl}(\text{OH})_3$ and atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$).^{27,33–34}

The composition of the bulk metal shows that the selected objects from Perdigões were produced with almost pure Cu (higher than 96.6 wt%). Arsenic was not detected or was below the detection limit in three objects (PER-543, PER-4900 and PER-20261), whilst it appears to be present in quite narrow contents in the rest of the materials, with percentages ranging up to 3.0 wt%. Other minor elements, namely lead, bismuth and antimony, were also detected in form of impurities, with amounts varying from 0.1 wt% Sb (PER-2603) to 0.7 wt% Sb (PER-1221). Others usual impurities in the Chalcolithic copper-based metals from Iberian Peninsula, such as Ni, Ag, Bi and Fe, appear to be absent or below the detection limit of the applied measurement system. Indeed, SEM-EDS analysis allowed to identify Ag, Bi, and Sn rich inclusions in small patina-free areas of a group of metals (Fig. 5).

Discussion and Data Contextualization

In addition to the data published in this paper, SEM-EDS analysis have recently been performed on three more artifacts from Perdigões, i.e., a fragment of metal, a blade, and an awl. The X-ray microanalysis data showed that artifacts were made of arsenical copper with a variation in the As content ranging from 2.8 wt% and 7.7 wt%.³⁵

Even if the discussion about the role of As in copper-based artifacts is beyond the aims of this paper, it is worth remembering that this topic has widely attracted a considerable interest of researchers dealing with Chalcolithic metallurgy.^{36–38} In fact, the improved properties of arsenical copper over pure copper have been frequently emphasized leading to a long-time debate aimed to define a specific compositional threshold (in terms of As content) to be adopted to distinguish between metals in which the arsenic was deliberately added from others in which As would occur in a natural or random way. Indeed, according with a linear vision of the metallurgical progress, the mechanical advantages of Cu/As with respect to pure Cu led many researchers to consider arsenical copper artifacts as a relevant advance in

alloying technology.

Whatever the value taken into account to consider the presence of arsenic as the result of a conscious act, i.e., 0.5 wt%,³⁹ 1.0 wt%,^{40–41} 2.0 wt%,³⁷ or 5.0 wt%,⁴³ it is important to stress that the intentionality of arsenic alloying is not just a mere matter of technology. In fact, the production of an alloy, by voluntary mixing two or more different minerals and/or metals, means that ancient smiths achieved a more advanced know-how and a better control over the production processes when compared with the abilities needed for the production of a pure metal. Furthermore, new forms of work organization and resources management had to be involved in this technological improvement process, both in mining activities and metallurgical manufacturing, thus also having significant social and economic repercussions. The empirical data from Perdigões show that pure Cu and Cu/As have been yielded from the same archaeological contexts not being admissible, at the moment, a linear chronological evolution from pure to arsenical copper. Indeed, if this had happened, one should admit that the more efficient technology, i.e., Cu/As alloys, would gradually have replaced the less effective one in the archaeological record or, for example, pure Cu. After all, the mixing of pure Cu and Cu/As alloys in archaeological contexts with evidences of early Chalcolithic metallurgy has also been observed in other Iberian sites, such Zambujal,^{44–45} Leceia,⁴⁶ and Vila Nova de São Pedro,^{47–48} Central Portugal; São Pedro, Três Moinhos, Atalaia do Peixoto, Castro dos Ratinhos, Tholos de Caladinho⁴⁹, Moinho de Valadares 1, Mercador, Monte Tosco¹⁵⁰, Outeiro de São Bernardo⁵¹, Southern Portugal⁵²; Cerro Virtud⁵³, Almizaraque⁵⁴, Carmona⁵⁵, Los Millares⁵⁶, Cabezo Juré⁵⁷, Southern Spain; and Western Andalusia.^{58–59} Furthermore, there is general consensus over the fact that the metallurgical improvements of As addition to a Cu alloy start to take effect at values around 4.0 wt% As, when a noticeable increase of strength and toughness occur and the Cu/As alloy achieves very similar mechanical properties of a tin bronze metal.⁶⁰ Accordingly, none of the artifacts analyzed in this paper and very few of those found at other Chalcolithic settlements from Portuguese territory, appear to contain As in sufficient amounts to be able to benefit from an appreciable increase of mechanical properties (Fig. 6). From this, one can deduce that ancient metalworkers would not control the amount of arsenic retained in the finished artifacts, and consequently the presence of As could be most likely related with the availability of scrap materials or with the use of ores naturally containing As, rather than a technological choice. As for as the first option, some researchers claim that remelting or hot working copper–arsenic alloys under oxidizing conditions can result in a remarkable loss of arsenic depending on the evaporation of As₂O₃.^{61–62} This circumstance might also explain the fragmentation of

most of the analyzed artifacts from Perdigões, that could have been deliberately broken to be remelted. Alternately, the As variability could be explained with the natural distribution of this element in the minerals used, suggesting that As could result from the smelting of polymetallic ores.⁵⁵ Indeed, it is important to note that smelting experiments have showed that Cu/As alloys may also be produced with Cu ores with low amounts of As.^{63–64} Whatever the reason behind the As variability, the use of both scrap metals and polymetallic ores results in an alloy in which the final As concentration is hard to predict and to control.

Finally, the data reported in this paper also provide a preliminary appreciation of the role that metals had to have at Perdigões. Despite the monumentality and the significance of the site, probably used as meeting point between communities from distinct regions and with clear connections with cosmology and astronomy, and also considering the wealth and variability of the materials recovered in the excavation, in most cases imported from elsewhere¹³, metals from Perdigões appear to confirm a clear trend that also occurs in other Iberian Chalcolithic sites. Artifacts are composed of copper-based alloys with variable amounts of As and appear to be produced domestically, on a small scale and with a simple technology whose knowledge is disseminated all over the Iberian Peninsula, persisting with few innovations up to the last quarter of the II millennium BC.^{65–67} Further investigations including microscopic and isotopic studies are currently underway, with the aim to gather new data for understanding the role that the production and the consumption of metals played at Perdigões.

Conclusion

The spectrometric protocol combining ED-XRF with MC simulations has confirmed to be a fast and reliable methodology to evaluate the elemental composition of archaeological unrestored Cu-based metals. The analysis performed on the artifacts from Perdigões were carried out without any pre-treatment of the metals surface, thus not affecting the physical integrity and not altering the morphology of the objects.

The chemical results achieved with the ED-XRF/MC protocol match with the data already known for the early metallurgy from Southwestern Iberia and obtained with traditional quantitative approaches needing sampling or mechanical cleaning of the metal. The analyzed metals are pure copper with a variable concentration of arsenic, lead, bismuth and antimony. The fluctuating distribution of As is a recurrent feature in the Chalcolithic metallurgy from the Iberian Peninsula and could be related with the use of recycling practices or with the employ of polymetallic ores, thus not resulting from an intentional addition. The

random distribution of this chemical element also suggests that the ancient metalworkers from Perdigões did not select consciously the alloy to use in the production of a certain object, such as the apparent lack of correlations between the As variability and the types of metal suggests.

Taking into account these considerations, the implementation of the ED-XRF/MC protocol represents a major advance in routine elemental analysis of metals covered by a corroded/encrusted stratum, being able to establish itself as a solid alternative to more conventional quantitative methods and proving to be a useful, in situ and nondestructive quantification tool, reliable in reproducing the bulk alloy composition of archaeological artifacts with no need of removing or cleaning the surface of the artifacts. Moreover, the protocol used in this work has a far-reaching applicability, since it is based on the use of a commercial instrumentation such as a handheld XRF spectrometer for spectral acquisition and a free available MC software package for processing the data. Therefore, the ED-XRF/MC protocol can be considered as a powerful analytical technique suitable for archaeologists and conservation science laboratories, with potential to become an accessible tool for mass use in the Cultural Heritage field.

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Table 1

Artifacts nr.	Context	Type	XRMC software package data					Empirical calibration data					
			Cu	As	Pb	Bi	Sb	Cu	As	Pb	Bi	Sb	Others (*)
PER-1218	Surface	Undef. (fr.)	99.5	0.5	n.d.	n.d.	n.d.	98.8	1.2	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-7267	Tomb 2	Awl	99.5	0.5	n.d.	n.d.	n.d.	99.1	0.9	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-7733	Tomb 2	Awl	99.8	0.2	n.d.	n.d.	n.d.	99.1	0.9	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-2603	Surface	Arrowhead	99.2	0.7	n.d.	n.d.	0.1	99.0	1.0	n.d.	n.d.	n.d.	Ca, Ti, Fe, Bi
PER-4900	Layer 267	Awl	100.0	n.d.	n.d.	n.d.	n.d.	100.0	n.d.	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-1219	Surface	Awl	99.9	0.1	n.d.	n.d.	n.d.	99.8	0.2	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-1221	Surface	Dagger (fr.)	99.2	0.1	n.d.	n.d.	0.7	99.2	0.1	n.d.	n.d.	0.7	Ca, Ti, Mn, Fe, Bi
PER-1223	Surface	Blade (fr.)	98.0	2.0	n.d.	n.d.	n.d.	94.0	6.0	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-1708	Surface	Blade (fr.)	98.0	2.0	n.d.	n.d.	n.d.	93.8	6.2	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-2720	Surface	Blade (fr.)	98.6	1.0	0.4	n.d.	n.d.	97.3	2.1	0.6	n.d.	n.d.	Ca, Ti, Fe
PER-4976	Surface	Dagger	99.9	0.1	n.d.	n.d.	n.d.	99.6	0.4	n.d.	n.d.	n.d.	Ca, Ti, Fe
PER-2	Fosso 7	Spearhead	98.9	1.1	n.d.	n.d.	n.d.	92.3	7.7	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-3678	Pit 16	Awl	99.0	1.0	n.d.	n.d.	n.d.	98.6	1.4	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-4672	Pit 40	Awl	98.5	1.5	n.d.	n.d.	n.d.	98.1	1.9	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-4949	Pit 40	Awl	99.5	0.5	n.d.	n.d.	n.d.	99.4	0.6	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-543	Pit 7	Undef. (fr.)	100.0	n.d.	n.d.	n.d.	n.d.	100.0	n.d.	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-10165	Tomb 2	Chisel	99.8	0.2	n.d.	n.d.	n.d.	98.7	1.3	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-11008	Tomb 2	Scrap	99.2	0.2	n.d.	0.6	n.d.	97.9	1.2	n.d.	0.9	n.d.	Ca, Ti, Mn, Fe, Sr
PER-4346	Tomb 1	Awl	97.5	2.5	n.d.	n.d.	n.d.	96.5	3.5	n.d.	n.d.	n.d.	Ca, Ti, Fe, Sr
PER-A483	Fosso 3	Undef.	97.9	2.1	n.d.	n.d.	n.d.	96.3	3.7	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe
PER-A318	Fosso 3	Undef.	97.8	2.2	n.d.	n.d.	n.d.	96.2	3.8	n.d.	n.d.	n.d.	Ca, Ti, Fe
PER-20261	Surface	Undef.	100.0	n.d.	n.d.	n.d.	n.d.	100.0	n.d.	n.d.	n.d.	n.d.	Ca, Ti, Fe
PER-9627	Tomb 1	Awl	99.8	0.2	n.d.	n.d.	n.d.	99.4	0.6	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-4983	Struct 67	Undef.	99.0	1.0	n.d.	n.d.	n.d.	98.0	2.0	n.d.	n.d.	n.d.	Ca, Ti, Fe
PR-1224	Surface	Awl	97.0	3.0	n.d.	n.d.	n.d.	94.7	5.3	n.d.	n.d.	n.d.	Ca, Ti, Mn, Fe, Sr
PER-1220	Surface	Blade (fr.)	97.3	2.7	n.d.	n.d.	n.d.	94.2	5.8	n.d.	n.d.	n.d.	Ca, Ti, Fe, Sr

Figure 1

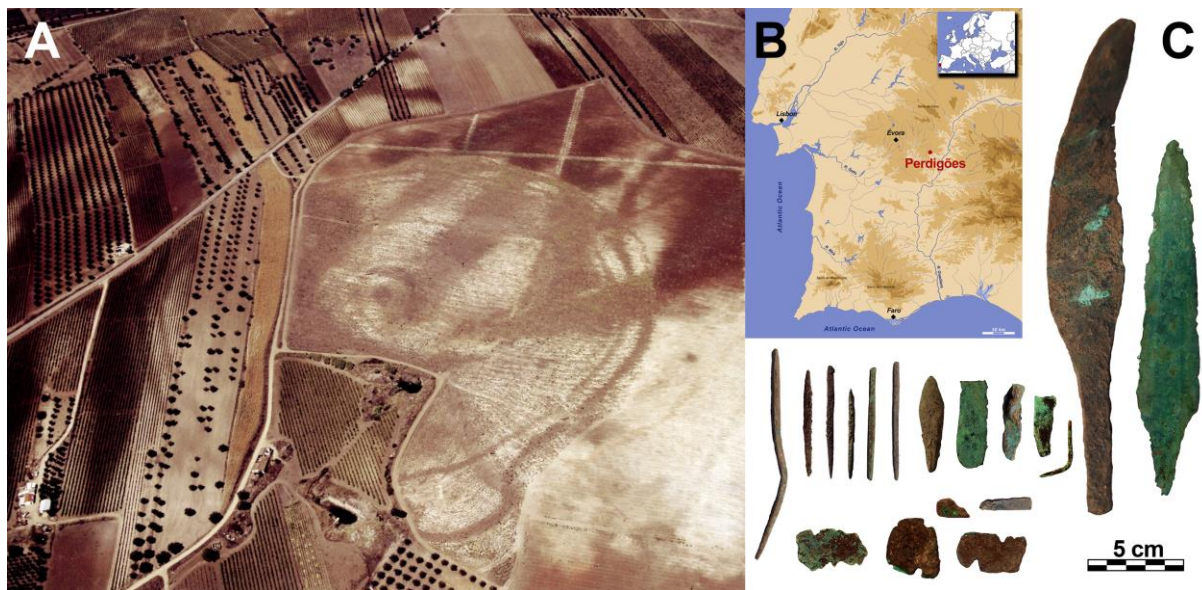


Figure 2

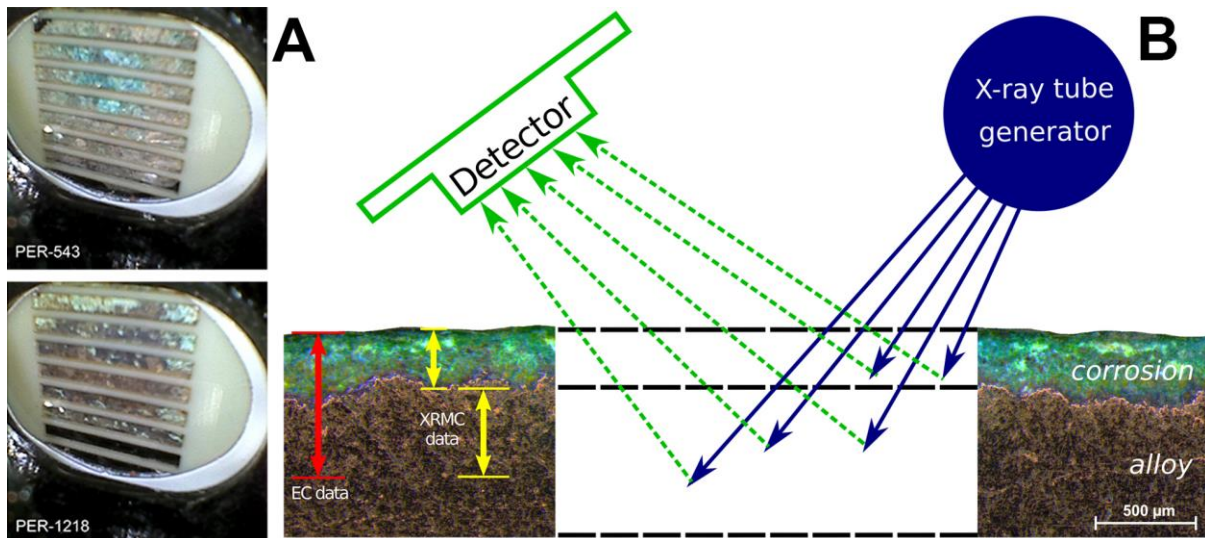


Figure 3

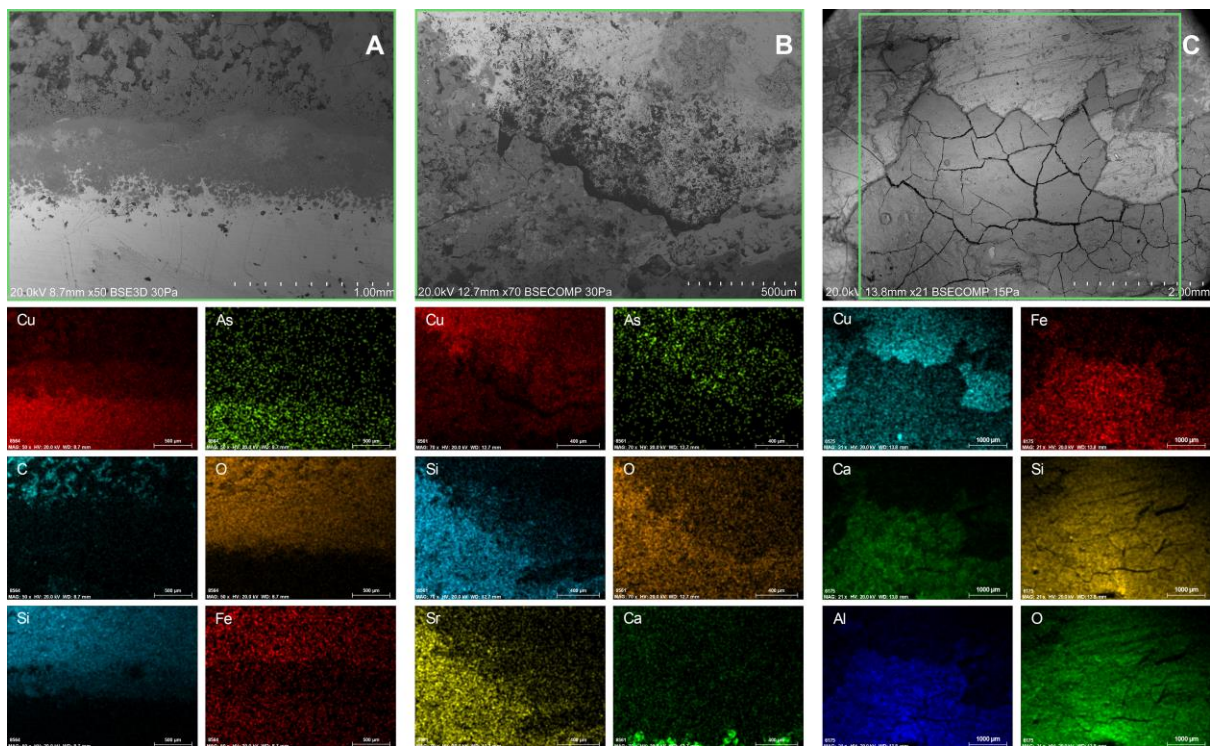


Figure 4

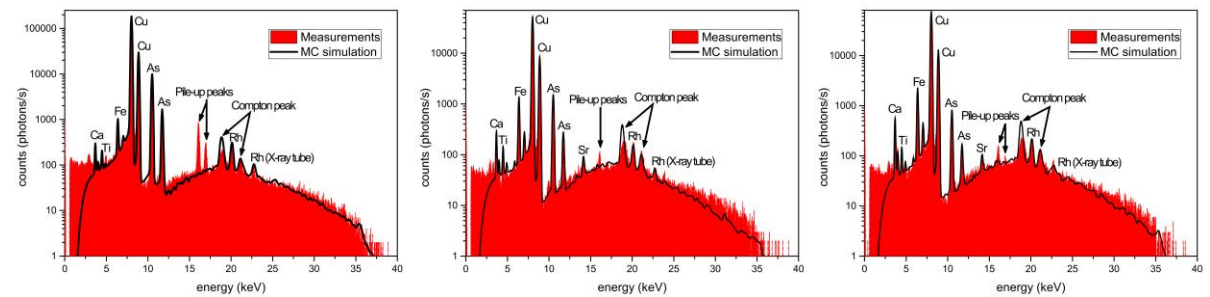


Figure 5

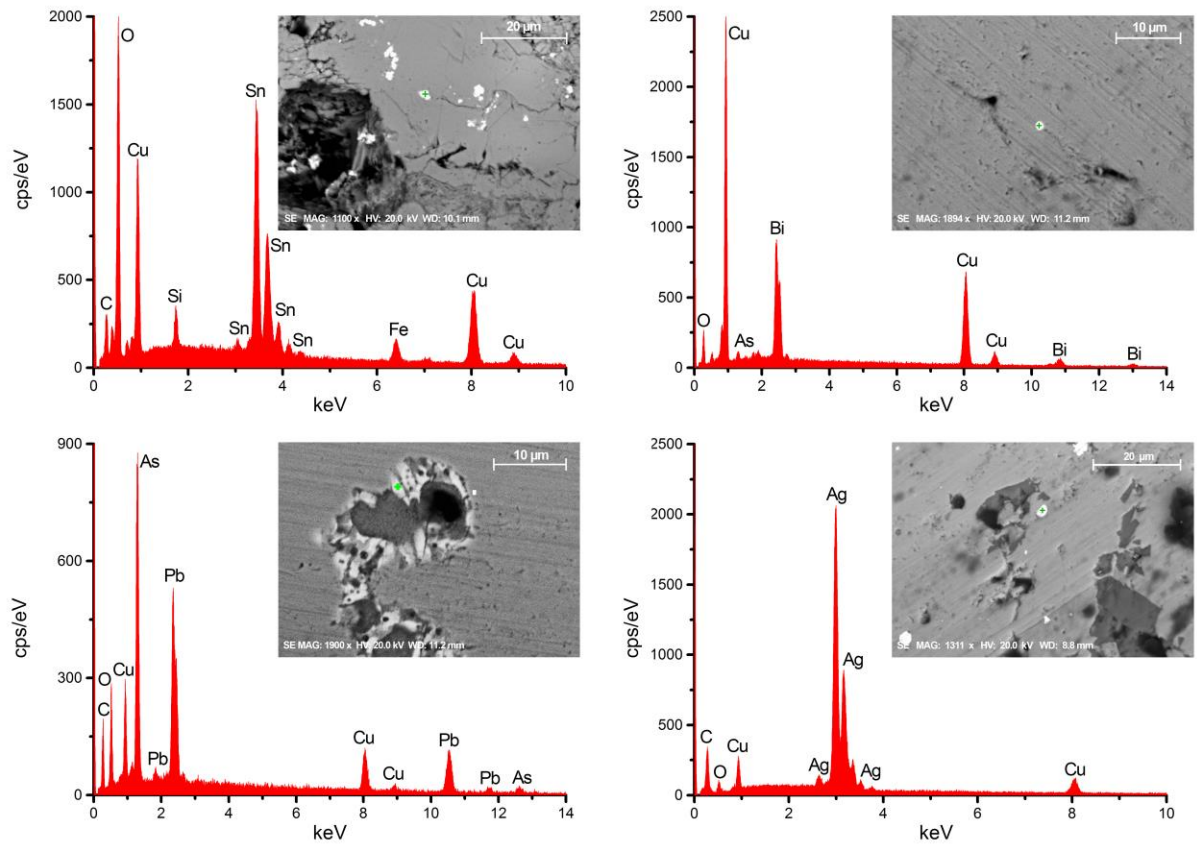


Figure 6

