Corrosion of bronze alloy with some lead content: implications in the archaeometallurgical study of Late Bronze Age metal artefacts from Fraga dos Corvos (northern Portugal)

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Abstract

Distinguishing bronzes with low lead content from those with high lead content through non-destructive surface techniques, such as energy dispersive X-ray spectrometry (EDXRF) performed over corrosion layers, can be very dubious. Three artefacts and four metal fragments dated to the Late Bronze Age, found in a rock shelter at the Fraga dos Corvos archaeological site in northern Portugal, have been analyszed through non-invasive EDXRF surface analyses. Those results were compared with m-EDXRF analysis performed over small areas where the metal core was exposed. The metal fragments have also been subjected to metallographic studies by optical (OM) and electron scanning microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) for corrosion assessment. A relationship between the EDXRF results, corrosion thickness and metal bulk composition was established for this group of artefacts, showing that the Pb content determined through EDXRF analyses can reach values eight times higher than the content in metal alloy.

Keywords: Late Bronze Age; Bronze alloys; lead content; decuprification; surface analyses

Introduction

During the archaeological fieldwork carried out in 2005 in a rock shelter at the Fraga dos Corvos archaeological site, in Macedo de Cavaleiros, northern Portugal, a pendant, a needle and a fibula were found, together with three bar fragments and a ring fragment. The artefacts show oriental typological influences, and have been attributed to a late period of the Late Bronze Age (LBA) (Senna-Martinez et al. 2006). The set of artefacts can be described as uncommon, since LBA metal artefacts with oriental features are uncommon in the northwestern areas of the Iberian Peninsula. The LBA artefacts from these areas are normally related with Atlantic typological features.

Current data regarding the kind of metal/alloys used during LBA in the Iberian Peninsula shows that most of the artefacts were manufactured in Cu-Sn alloys. Leaded bronzes (Pb>2 wt%, with no specific lead content), although common in the Atlantic areas (Craddock 1977, Rey 1999), have only been associated to double-looped palstaves in the Iberian Peninsula areas (Montero et al. 2003).

Due to the particular characteristics of artefacts with a historical and artistic value, analyses leading to partial physical destruction or chemical change are frequently not allowed. The use of the non-invasive analytical technique, energy dispersive X-ray fluorescence spectrometry (EDXRF), has been one of the most common methods applied to access the kind of metal or alloy employed. Since EDXRF is a surface analysis, variable contributions from the corrosion layer and the metal core are to be expected. Distinguishing copper from bronze through analyses of this kind is not difficult, but distinguishing intentional leaded bronzes from bronzes in which lead is present as an impurity (in small amounts due to ore impurities) can become difficult. Non-invasive analyses are frequently the only chemical characterization of archaeological artefacts. So, data regarding relationships between elemental content observed by these methods and the true element content in the metal core would be of great importance. In principle, these relationships should only be valid for a set of artefacts buried under the same environmental conditions, let us say at the same archaeological site. In the present study, a relationship between the Pb content measured by surface EDXRF and the Pb content in the metal core is considered for the LBA artefacts from the Fraga dos Corvos archaeological site.

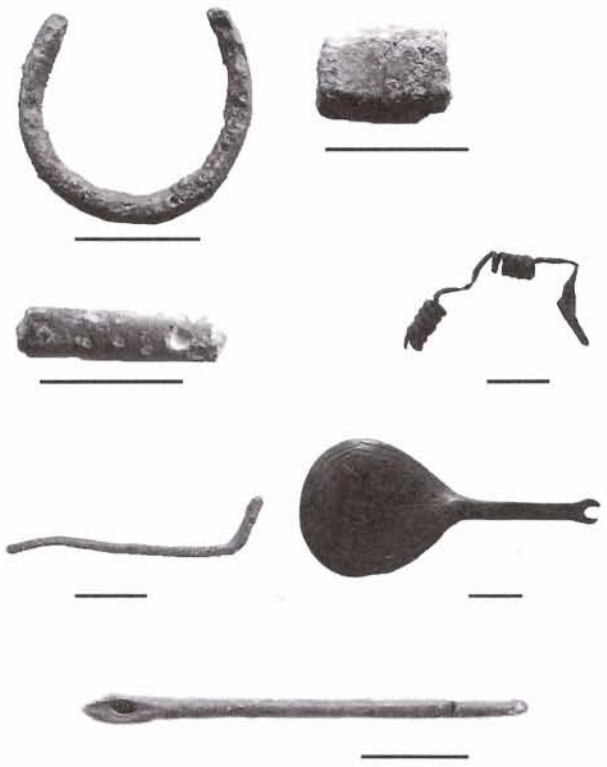


Figure 1. Image of the artefacts and fragments analyzed in this work. From left to right and top to bottom: 120/05 ring fragment; 206/05 bar fragment; 208/05 bar fragment; 181/05 fibula; 215/05 bar fragment; 252/05 pendant; and 188/05 needle. Black lines represent one centimetre for each metal artefact/fragment

Experimental details

Artefacts and fragments

The artefacts and fragments (see figure 1) found in the natural rock cavity of Fraga dos Corvos are listed and described in table 1.

Sample preparation and analytical techniques

Metal artefacts and fragments were first analyzed in a conventional energy dispersive X-ray fluorescence spectrometer (EDXRF) in order to get an initial approach to the kind of metal alloy present. Those results concern to the corrosion surface and are therefore considered as semi-quantitative for the archaeometallurgical studies. More than two analyses were performed for each artefact whenever possible. For these cases the average values were considered. The EDXRF equipment used was a Kevex 771 with an incident X-ray beam that permits analyses of a circular area up to 3 cm in diameter. Quantification was made using calibration lines calculated by using a standard phosphor bronze (SS551) certificated by Burial of Analyzed Samples LTD. Detailed descriptions of the equipment as well as quantification procedures were previously described in Araújo et al. (1993).

Samples from the four fragments (bar fragments 208/05, 206/05, 215/05 and ring fragment 120/05) were mounted for metallographic observation. The samples were positioned in such a way that their cross-section could be analyzed by optical microscopy (OM). Samples were examined in unetched and etched conditions. The etching was made using an aqueous ferric chloride solution.

Micro-EDXRF analyses (m-EDXRF) were made over the metal core of the cross-section of all the mounted samples and in recent fractures of the needle and fibula in order to obtain the metal alloy composition. In the pendant, since no metallic surface was exposed, analyses were performed on an internal cor-

Table 1. Description of the artefacts studied

		Description	Weight (g)	Surface color and pattern	Presence of fractures
252/05	Pendant	Artefact complete	3.8	Even green with localized outer corrosion loss	No, but the area from which the pendant was suspended is worn out
188/05	Needle	Artefact complete	0.6	Green and dark with some pits	Recent fracture with metal exposed
181/05	Fibula	Almost complete. Missing the pin.	0.7	Dark with some pits	Recent fracture with metal exposed
208/05	Bar frag	Fragment of a larger object. Function not recognized.	0.3	Uneven dark and green with some pits	Ancient fracture covered with corrosion
206/05	Bar frag	Fragment of a larger object. Function not recognized.	1.0	Uneven dark and green with some pits	Ancient fracture covered with corrosion
215/05	Bar frag	Fragment of a larger object. Function not recognized.	0.9	Uneven dark and green with some pits	Ancient fracture covered with corrosion
120/05	Ring frag	Fragment of a larger object (?). Function not recognized.	0.9	Uneven dark and green with some pits	Not conclusive

Table 2. Analyses performed in each artefact studied

		EDXRF	μ-EDXRF			SEM-EDS	OM
		Superficial corrosion layer	Metal core		Internal corrosion layer	Sample cross-section	Sample cross-section
			Sample cross-section	Surface fracture			
252/05	Pendant	x			x		
188/05	Needle	x		x			
181/05	Fibula	x		x			
208/05	Bar frag	x	x				x
206/05	Bar frag	x	x			x	x
215/05	Bar frag	x	x				x
120/05	Ring frag	x	x				x

rosion layer. Whenever possible, more than two analyses were carried out for each artefact. The m-EDXRF equipment used was an ArtTAX Pro spectrometer that comprises a low-power X-ray tube with a molybdenum anode. The system includes a set of polycapillary lenses that generate a micro spot, smaller than 100 μm in diameter, of primary radiation (Bronk et al. 2001).
The cross-section of bar fragment 206/05 was analyzed under the scanning electron microscope (EDS-SEM). The sample was previously sputtered with a thin layer of gold. The scanning electron microscopy (SEM) was performed with a Zeiss DSM 962, equipped with a secondary electrons detector (SE), back-scattered electrons detector (BSE) and an energy dispersive spectrometer (EDS) from Oxford Instruments INCAx-sight.
Details of the analyses performed on each artefact can be found in table 2.

Results and discussion

The results of elemental analyses performed on all the artefacts are shown in table 3, which lists the elemental compositions determined through EDXRF analyses performed on the corrosion layers and m-EDXRF analyses of the metal bulks. The EDXRF results show Sn values >20 wt%. The expected content for a typical LBA bronze composition is around 10 wt% (Montero et al. 2003, Pare 2000). Higher values can be explained as a result of the decuprification phenomena (Robbiola et al. 1998). Regarding the Pb contents, the artefacts could be separated into two groups: those that show Pb values in the range of 1.7-4.0 wt% (pendant 252/05, fibula 181/05, ring fragment 120/05); and those that show higher Pb values, >10 wt% (bar fragments 206/05, 208/05 and 215/05, and needle 188/05). If only EDXRF analyses had been performed, this last group

Table 3. EDXRF and μ-EDXRF analyses performed on artefacts and metal fragments. Due to analytical constraints, antimony (Sb) is only detected in conventional EDXRF analyses (n.d. = not detected)

				% wt, normalized						
				Cu	Sn	Pb	As	Sb	Fe	Ni
252/05	Pendant	EDXRF	corr1	65.7	30.5	3.3	n.d.	0.1	0.4	n.d.
		μ-EDXRF	corr1,2	72.2	26.6	1.2	n.d.	-	<0.04	n.d.
188/05	Needle	EDXRF	corr1	48.8	38.1	10.9	n.d.	0.1	2.0	0.14
		μ-EDXRF	metal1	86.8	11.8	1.5	n.d.	-	<0.04	n.d.
181/05	Fibula	EDXRF	corr1	71.7	22.3	1.7	n.d.	n.d.	4.3	n.d.
		μ-EDXRF	metal1,3	87.4	11.9	0.6	n.d.	-	<0.04	n.d.
208/05	Bar frag	EDXRF	corr1	33.0	51.9	10.8	n.d.	0.1	4.3	n.d.
		μ-EDXRF	metal	88.6	9.8	1.3	<0.1	-	<0.04	n.d.
206/05	Bar frag	EDXRF	corr	60.1	26.1	11.6	n.d.	0.1	2.0	n.d.
		μ-EDXRF	metal	89.2	8.6	2.0	n.d.	-	<0.04	n.d.
215/05	Bar frag	EDXRF	corr	42.4	39.2	15.4	n.d.	0.3	2.5	0.18
		μ-EDXRF	metal	89.7	8.1	1.8	<0.1	-	<0.04	n.d.
120/05	Ring frag	EDXRF	corr1	60.6	33.5	4.0	n.d.	0.1	2.0	n.d.
		μ-EDXRF	metal	86.8	12.2	0.8	<0.1	-	<0.04	n.d.

1 Average of two or three analyses
2 Analyses that refer to an internal corrosion layer that was uncovered by the loss of a superficial corrosion layer
3 Analyses of metal in fracture zones with no surface preparation

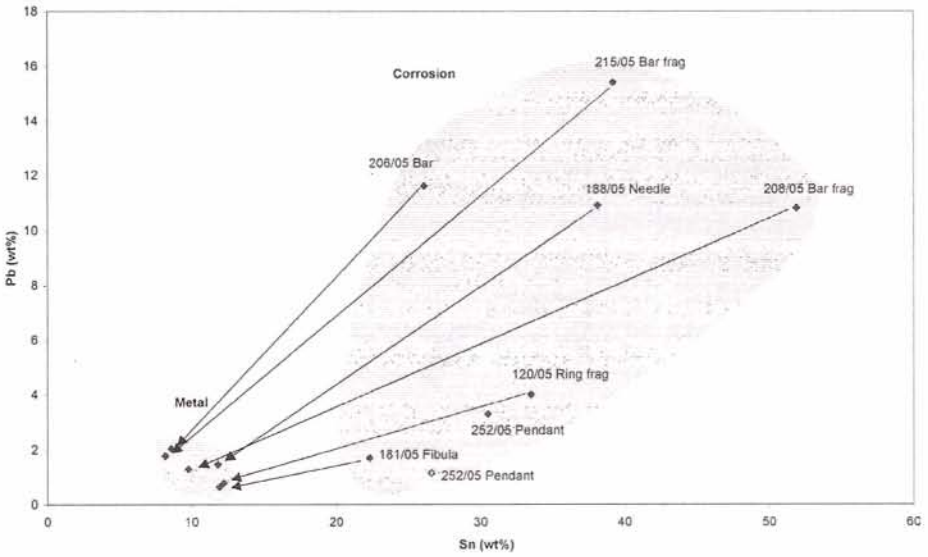


Figure 2. Results of μ-EDXRF analyses performed on the metal core of artefacts (area named "Metal") and on an internal corrosion layer of the pendant (marker without black center), and EDXRF results performed over corrosion layers (area named "Corrosion")

could have been considered as having a higher Pb content in the metal bulk. The presence of such high Pb content would suggest that the artefacts could have been manufactured with a leaded bronze. This, in turn, would be unexpected for LBA artefacts with these typological features (see Introduction). The analyses performed by m-EDXRF on different points of the metal core surface of the artefacts (exception made for the pendant 252/05) shows that the alloy composition of the artefacts and fragments is very similar, 8.1-12.2 wt% Sn and <2.0 wt% Pb (see figure 2). So no major differences in lead content between the analyzed artefacts are observed. Furthermore, the lead content of the alloys, <2 wt%, suggests that this element was probably transferred to the metal alloy as an ore impurity. Additionally, the tin content of around 10 wt% reveals a bronze alloy with good thermo-mechanical properties, which suggests good manufacturing skills, making the artefacts consistent with LBA metallic alloys from the Iberian Peninsula.

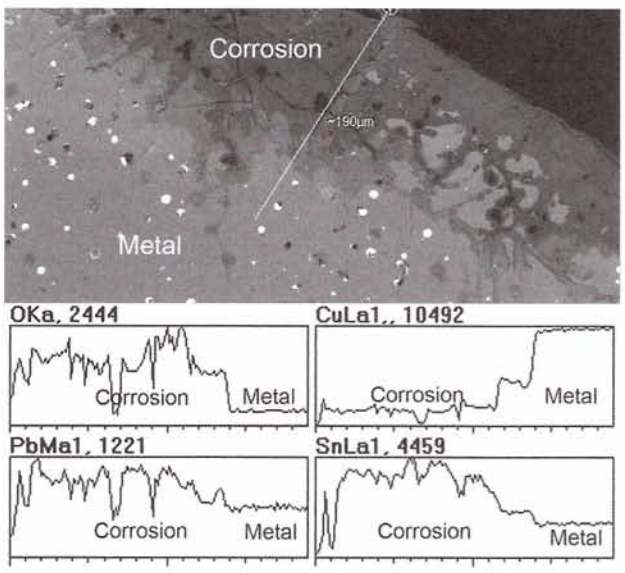


Figure 3. Line scan analysis (~190 μm) made along the cross-section of the 206/05 bar fragment with SEM-EDS. Top: image obtained by BSE, the white dots are lead globules in the metal. Bottom, from left to right and top to bottom: oxygen (O) elemental line scan; copper (Cu) elemental line scan; lead (Pb) elemental line scan; tin (Sn) elemental line scan

The observation under the OM of the fragments cross-sections showed 1): an outermost external corrosion layer characterized by green color under polarized light, and 2): a more internal corrosion development, characterized by red color under polarized light, composed of intergranular corrosion and corrosion following the slip bands, for those artefacts that had been cold-worked as the final thermo-mechanical operation.

The decuprification phenomena in the outermost external corrosion layer was confirmed by a line scan made with the SEM-EDS equipment on the bar fragment 206/05 cross-section. Results evidenced Sn and Pb enrichments in corrosion due to the Cu depletion (see figure 3). This elemental distribution is in agreement with the EDXRF observations.

According to Robbiola et al. (1998), copper dissolution factor (f_{Cu}) is expected to be around 0.96±0.04 for monophasic (α-Cu) bronze alloys. An f_{Cu}=1 means total dissolution of Cu in the corrosion layer, and f_{Cu} =0 means no loss of Cu. Since only α-Cu phase and lead globules were identified in the OM and SEM-EDS observations of the fragment cross-sections, the copper dissolution factor (f_{Cu}) was calculated for the fibula, needle and ring and bar fragments based on the data given in table 2. Cu and Sn were normalized (Cu+Sn=100 at%), ignoring the effect of the other elements present. The equation used was published elsewhere (Robbiola et al. 1998). Results are plotted in figure 4.

The results show that only bar fragments 208/05 and 215/05 have f_{Cu} near the expected values (0.96±0.04) and that all the other artefacts show much lower f_{Cu}.

The low f_{Cu} values can be explained through the EDXRF analyses made over the corrosion layers: for those fragments that have thinner corrosion layers the EDXRF analyses not only concern corrosion composition but also suffer a significant influence from the metal core composition. This could be confirmed through a correspondence between calculated f_{Cu} and

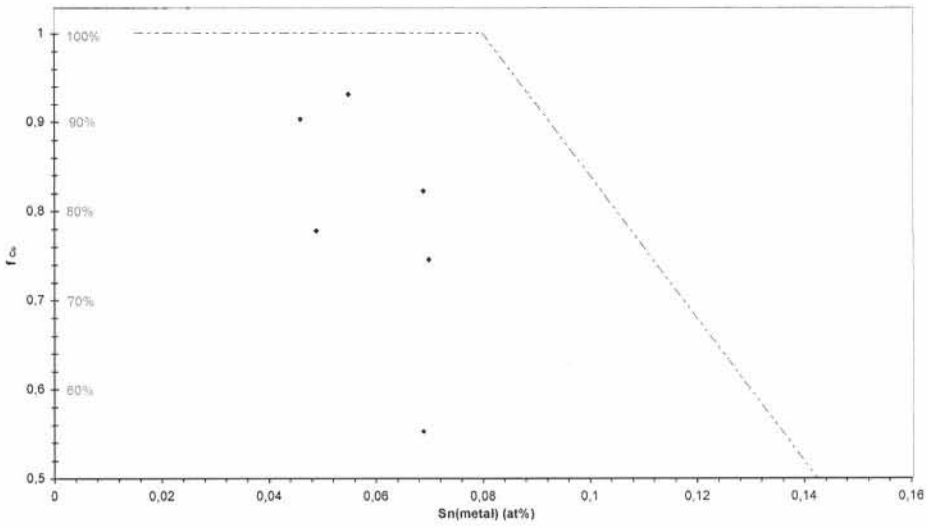


Figure 4. Plot of the copper dissolution factors (f_{Cu}) calculated for metal artefacts and fragments based on the results shown in table 2. Results lower than 0.9 are due to a combination of corrosion and metal compositions in the EDXRF results (graph design based on Robbiola et al. 1998)

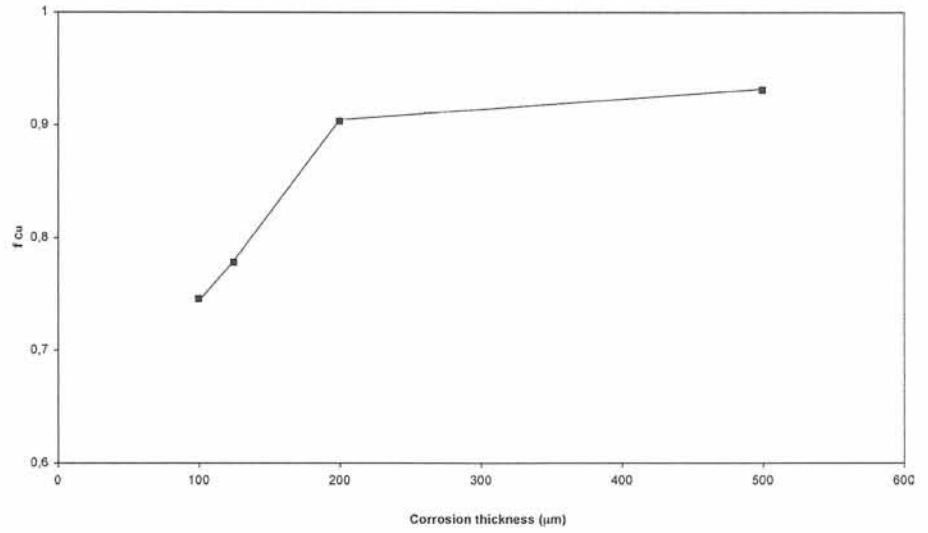
corrosion layer thickness (determined through OM observations in all cross-sections made) (see figure 5). Those fragments that showed thinner corrosion layers were also those that exhibited smaller f_{Cu}.

A near-linear correlation was drawn between Pb(corrosion)/Pb(metal) versus Sn(corrosion)/Sn(metal), as demonstrated in figure 6. This means that the tin enrichment in corrosion layers during burial is followed by a analogous Pb enrichment. Since all artefacts are from the same archaeological site, they are likely to have been subjected to the same environmental conditions during burial. So, the higher Pb and Sn ratios should be related to thicker corrosion layers. This relationship can be used to estimate the thickness of the corrosion layers in the artefacts that have not been sampled, namely, the needle and fibula, 125-200 µm and <100 µm, respectively.

Since the Fraga dos Corvos archaeological site is still under excavation, this data may be useful for artefacts found in the near future. For artefacts where only surface EDXRF analyses are permitted, the true Pb content (at. %) in metal can be expected to be about 7 times lower than the EDXRF results for the artefacts that have a corrosion layer of 100-125 µm, and around 12 times lower for a thicker corrosion layer, >200 µm (in weight percent, the Pb content in the metal corresponds to around 5 times and 8 times lower, respectively).

Conclusion

The results showed that the artefacts buried in the shelter at the Fraga dos Corvos archaeological site where made with a similar bronze metal alloy, 8.1-12.2 wt% Sn and <2.0 wt% Pb. Nevertheless, EDXRF results made directly over corrosion layers shows very dispersed Pb contents: lower than 4 wt% to higher than 10 wt%. By itself, the EDXRF results could lead to an initial idea that the artefacts were made with significantly different alloys, and, in certain cases, that some of the artefacts were made of a leaded bronze that was not expected from their typological features. The relationship observed between calculated decuprification factors (using the EDXRF data regarding to corrosion composition) and the corrosion thickness measured by OM observations proved that the dispersed EDXRF results were mostly a consequence of different corrosion layer thicknesses,



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leading to different contributions of the metal alloy under the corrosion layer. A relationship between the Pb content determined by surface EDXRF and the Pb content in the metal alloy could therefore be established for the site: Pb content (wt. %) is about 5 times higher than in metal bulk for those artefact with corrosion layers of 100-125 µm and around 8 higher for artefacts that have corrosion layers >200 µm. Artefacts from this site are therefore expected to show Pb values up to 8 times higher in the surface EDXRF analyses than the Pb content in the metal bulk (in wt%).

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References

- Araújo M.F., L.C. Alves and J.M.P. Cabral 1993. Comparison of EDXRF and PIXE in the analysis of ancient gold coins, Nuclear Instruments and Methods, B 75, 450-453
- Bronk H., S. Rohrs, A. Bjeoumikhov, N. Langhoff, J. Schmalz, R. Wedell, H.E. Gorny, A. Herold and U. Waldschlager. 2001. ArtTAX – A new mobile spectrometer for Energy-Dispersive Micro X-Ray Fluorescence spectrometry on art and archaeological objects, Journal Analytical Chemistry, 371(3), 307-316
- Craddock P.T. 1977. The composition of the copper alloys used by the Greek, Etruscan and Roman civilizations: 2. The Archaic, Classical and Helenistic Greeks, Journal of Archaeological Science, 4(2), 103-123
- Montero I., S. Rovira, G. Delibes, J. Férnandez-Manzano, M.D. Fernández-Posse, J.I. Herran, C. Martín and R. Maicas. 2003. High leaded bronze in the Late Bronze Age metallurgy in the Iberian Península, in Archaeometallurgy in Europe, Associazione Italiana di Metallurgia: Milan, Italy, 39-46
- Pare C.F.E. 2000. Bronze and the Bronze Age, In Pare, C.F.E. (ed.), Metals make the world go round. Exeter: Oxbow books, 1-38
- Rey B.C. 1999. Cambios en la escala de producción metalúrgica durante las fases finales de la Edad del Bronze en el Noroeste Peninsular. Revista de Guimarães, Vol Especial II, 515-537
- Robbiola L., J-M. Blengino and C. Fiaud. 1998. Morphology and mechanisms of formation of natural patinas on archaeological Cu-Sn alloys, Corrosion Science, 40(12), 2083-2111
- Senna-Martinez J.C., J.M.Q. Ventura, H.A. Carvalho and E. Figueiredo. 2006. A Fraga dos Corvos [Macedo de Cavaleiros]: Um sítio de Habitat da Primeira Idade do Bronze em Trás-os-Montes Oriental. A Campanha 3 [2005]. Caderno Terras Quentes, 3, 61-85