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Lead provenance study in medieval metallic materials from Madinat al-Zahra (Medina Azahara, Córdoba)

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ABSTRACT

The objective of this study is to provide insight into the origin of the lead present in the 10th-century. AD Islamic city of Madinat al-Zahra, both as unalloyed metal and as a component of the copper-based alloys, as well as a first approach to technological details related to the production of these materials. Recycling lead is argued to be a common practice but, nonetheless, the lead isotope analysis suggests a single origin for all the lead at the site. Two main options are discussed as lead sources: mines in the Linares district (100 km east) or in Villanueva del Duque (75 km north). Other interesting features are the use of lead-tin solder and fire gilding on a copper–zinc alloy.

1. Introduction

The aim of this work is to make a first approach to the analysis of metallic materials from the 10th century. AD archaeological site of the Islamic city of Madinat al-Zahra (known nowadays as Medina Azahara, in Córdoba, Spain). The original Muslim city was established ca. 936 four miles west of Córdoba (Fig. 1) by the first Caliph of Al-Andalus, Abd al-Rahman III, following a long tradition with its origins in the Eastern Islamic world that associated the Caliph's status with the creation of large urban nuclei adjacent to the old cities.

For the whole length of its existence, this city was an extraordinary focus of production, import and export of all kind of goods, from the plain and quotidian to the most luxurious and sumptuary. It was in Madinat al-Zahra where the official workshops that produced, consumed and/or distributed all kind of goods in the name of the Caliph were established, in order to supply the Court, the army or to provide presents and elements of political propaganda.

Despite its early destruction, which occurred during the so-called second *fitna*, between the years 1010 and 1013, Madinat al-Zahra is one of the most representative archaeological sites of the Islamic presence in the Mediterranean (For a general overview about the site and the research performed on it see Vallejo, 2007, 2010). Its extension, with a surface of 1500 by 750 m, its historical significance, the urban and architectural solutions used in its construction, and the quality of its decorative programs and artistic productions, all make Madinat al-Zahra a truly unique reference for the study of the history of Islam.

Furthermore, as the city has not undergone any major occupation after its abandonment and destruction, we have in Madinat al-Zahra a site with an extraordinary potential in multiple fields of the research of the Al-Andalus Caliphate and the Mediterranean area in the Middle Ages.

Since the beginning of the archaeological efforts, which started in 1911, the range and significance of the different materials recovered and documented in the excavations have been constantly increasing. This paper focuses on a very specific group: the non-ferrous metallic materials found at the site over a century of fieldwork, and now in custody at the Museum of Madinat al-Zahra. The objective of this study is to provide insight to the origin of the lead present at the site, both as unalloyed metal and as a component of the copper-based alloys, as well as a first approach to technological details related to the production of these materials. This information is used to better understand the historical, cultural and social processes associated to the context that produced these objects.

The technology of metals was one of the staple points of Islamic culture and it influenced the production practises of the areas that came under Muslim control. As such, it became one of the

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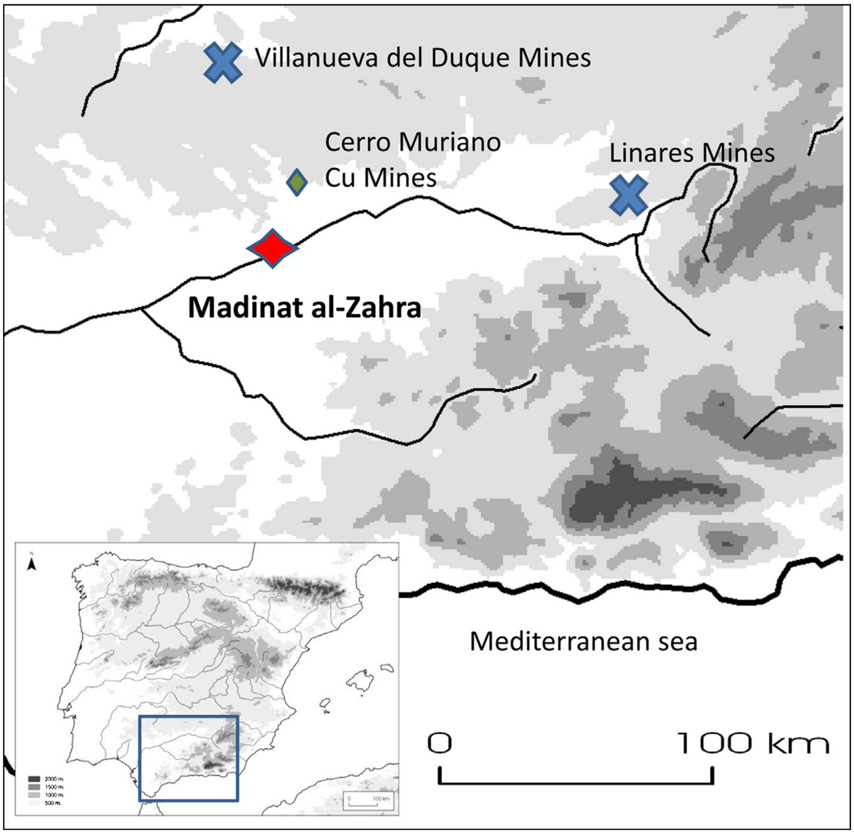

Fig. 1. Map showing the location of the Madinat al-Zahra site and the main mining areas cited in the text.

characteristic traits that allows for the identification of Islamic cultural influence over a given territory (Al-Hassan and Hill, 1986). Hence the importance of characterising the metallic materials of a site like Madinat al-Zahra, given its geographical situation, chronology and particular archaeological features.

2. Materials and methods

The materials used in this study were selected in order to offer a significant range of results to characterise the use and provenance of lead at the site and at the same time provide a broad view of the metals technology. These materials, some of which are illustrated in Fig. 2, are:

- two lead pipe fragments (Ref.: 0.25715 and 0.25745).
- one fragment of lead extracted from a repair in a capital stone (Ref.: 24090).
- one fragment of lead from a sewer grate (Ref.: Caja Y-51a).
- one shapeless and unidentified fragment of lead (Ref.: Caja 2045)
- one fragment of a decorative nail's head made of a copper-based alloy (Ref.: C-13/B-244)
- one fragment of a scabbard's chape made of a copper-based alloy (Ref.: (31) SAL-43).
- one fragment of a decorative embossed metal sheet (*appliqué*) made of a copper-based alloy (Ref.: C62/10446).
- one fragment of an embossed and gilt metal sheet, probably a decorative cover for a door or window (Ref.: LC-1990/HA).

Different analytical techniques were applied to these materials in order to obtain the most meaningful information from them. Electronic microscopy and microanalysis were carried out at the Laboratory of Electronic Microscopy: Microlab, at the *Centro de Ciencias Humanas y Sociales* (CCHS-CSIC, Madrid, Spain), using a variable pressure scanning electron microscope (SEM) HITACHI 3400N-II, with secondary (SE) and backscattered (BSE) electron detectors (SEM resolution: 3 nm-30 KV (HV); 10nm-3 KV(HV), 4 nm-30 KV (LV)) and an energy-dispersive X-ray (EDX) spectrometer for microanalysis, with a Bruker Quantax 200 Xflash 4010 (133eV) silicon drift detector (SDD), and a signal processing unit Bruker SVE III. The results of the analysis of gold and copper-based materials were processed with the Bruker Quantax ESPRIT v. 2.1 software, using P/B-ZAF algorithms. The detection limit for this technique is 0.8–1%, so minor or trace elements cannot be evaluated.

When metallographic analysis was required, samples were extracted from the objects, embedded in resin and then ground and polished following the standard procedures for metallographic analysis (Rovira and Gómez, 2003; Scott, 1991). After that, they were etched with an aqueous ferric chloride solution (H_2O, HCL, $FeCl_3$) and studied by optical microscopy (OM) using a Leica DMLM microscope equipped with a Leica DFC480 digital camera. Some of these samples were also studied by SEM-EDX before etching. All these procedures were carried out at the Laboratory of Archaeometry of Materials (CCHS-CSIC, Madrid, Spain).

For the lead objects, the elemental analysis was performed by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) with a Thermo Scientific ELEMENT XR spectrometer. Sample 1:1000 solutions in 5% HNO_3 were used for the detection of major components, and 1:10 dilutions for trace elements. The study was carried out with a SC-FAST system, a ST 5532 PFA μ-FLOW nebulizer, a Peltier-cooled PFA spray chamber and a 1.8 mm sapphire injector

Fig. 2. Some of the objects sampled for determination of the origin of their metal using lead isotope analysis. a) Lead pipe (ref. 0.25745). b) Lead pipe (ref. 0.25715). c) Capital stone (ref. 24090) with a repair sealed with lead (circle). d) Embossed copper alloy decorative sheet or *appliqué* (ref. C62/10446). e) Copper alloy scabbard chape (ref. (31) SAL-43). f) Copper alloy nail head (ref. C-13/B-244).

tube, using triple detection mode in the three different mass resolutions (m/Δm), depending on the particular element of interest. The measurements were done using standards FER-2 (Canadian Certified Reference Materials Project), GBW 07107 (MC Certified Reference Material), BAM-376 (Bundesanstalt für Materialforschung und –prüfung), Bronze C (British Chemical Standards) and GF-1 (Bergakademie Freiberg BAF). These chemical analyses were performed at the Research Laboratory for Archaeology and Materials Science of the Deutsches Bergbau-Museum, in Bochum, Germany.

Sample preparation and Pb extraction for lead isotope analysis were also carried out in the Research Laboratory for Archaeology and Materials Science, and the measurements were done at the *Institut für Geowissenschaften*, Goethe-Universität Frankfurt am Main, with a high-resolution and multicollection mass spectrometer with an inductively coupled plasma source (MC-ICP-MS *Neptune*). The analytical procedure applied is described in Klein et al. (2009). The internal standard error (2SE precision) was always lower than 0.01%. Each sample has its own standard deviation in each ratio, but in order to help graphic representation, the figures include a 2σ standard deviation calculated as the average of the 9 samples.

3. Elemental analysis results

3.1. Lead objects

The results for the elemental characterisation of the lead objects by ICP-MS are summarized in Table 1.

The sample extracted from the edge of the large pipe 0.25715 (in bold italics in Table 1) was identified as remnants of the soldering process from the assembly of the different conduits that configured

Table 1
Results of the ICP-SFMS elemental analyses on the lead objects, expressed in ppm. The balance is lead.

Signature	Object	Ag	Sn	Sb	Bi	P	Ni	Cu	Zn	Fe	As
0.25715	Large pipe	***100***	***(32%)***	***13***	***8.9***	***2.4***	***3.0***	***1435***	***4.3***	***60***	***3.9***
0.25745	Small pipe	155	2725	690	75	13	1.4	560	1.8	13	75
24090	Capital stone	90	4645	125	32	8.4	7.1	215	3.7	7.5	6.8
Caja Y-51bis	Grate	190	6.5	320	62	385	1.0	670	3.2	41	115
Caja 2045	Shapeless fragment	110	2025	555	78	8.9	1.4	440	1.0	2.1	105

the water supply network. It is a Pb–Sn alloy with 32% Sn, forming what is technically known as a solder. The Romans were already using a Pb–Sn alloy with this proportion of tin (1/3) as a solder to join lead pipes, as Pliny recorded (C. Plinius Secundus, *"Naturalis Historia"*, XXXI, 60 and 61) and Paparazzo (1994) confirmed in a 3rd century. AD Roman pipe.

The recycling of lead objects carrying remnants of tin solder can be the source of the increase of Sn as an impurity in lead. This trait is detected in three out of the other four analysed lead objects, with amounts of Sn above 1000 ppm (0.1%). The amount of tin detected in galena (the main lead mineral in the Iberian Peninsula) depends on each mining area, although it is generally less than 100 ppm (detection limit in ED-XRF analysis used in the Archaeometallurgy of the Iberian Peninsula Project). The highest proportions correspond to the Molar-Bellmunt-Falset mining district (Northeastern Iberia), where some galenas reached 2000–4000 ppm of tin with a mean value (46 samples) in the range of 800 ppm Sn and 230 ppm Ag (Montero et al., 2008). Data obtained with more precise techniques show low tin content in primary lead (ingots). ICP analyses of Hellenistic lead (Asderaki and Rehren, 2006) showed it to contain less than 20 ppm of tin, except one lead sheet (130 ppm Sn), with a range between 30 and 110 ppm Ag. In this case, the lead isotope analysis matches mainly with Laurion, indicating that the lead is clearly a de-silvered metal. Roman lead ingots published by Wyttenbach and Schubiger (1973) contain always less than 10 ppm Sn, while 21 Roman water pipes show higher amounts of tin (>200 ppm) except in three cases, proving the frequency of recycling lead. The proportions of tin are variable, depending on the amount of solder scrap recycled or the addition of pure lead to the mix.

In our study, only the grate, with 6.5 ppm Sn, can be considered to be made of unrecycled lead. The grate also shows higher values for phosphorus (385 ppm) and iron (41 ppm) than the other samples. The amount of phosphorus detected by ICP in galenas from the Iberian Peninsula is usually lower than 100 ppm, and in metallic lead, less than 10 ppm. Given the high volatility of this element (its boiling point is 280 °C, lower than the 327 °C of the melting point of lead), its loss increases with each melting. Under these conditions the amount detected in the grate could be explained as a corrosion process within a soil or an environment rich in phosphorus (Cao et al., 2008), and could be related with its function in a sewer.

The silver content of all five samples is low (between 90 and 190 ppm). The amount of silver is commonly used as criterion to recognise the use of de-silvered lead. However, it is not possible to really tell if lead comes from a previous de-silvering process or from the reduction of silver-poor galena. Typically, concentrations below 300 ppm Ag are taken as indicative of lead that has been obtained after the separation of silver, but there is evidence of the exploitation of silver-poor galena with amounts of less than 200 ppm Ag dating from the Iron Age (Montero et al., 2008: 297; Renzi et al., 2009: 2586).

Table 2
Results of the EDX elemental analyses of the copper alloy objects, in normalised %wt.

Signature	Object	Cu	Zn	Sn	Pb
C-13/B-244	Nail head	77.5	18.5	–	3.8
LC-1990/HA	Gilt sheet	83.6	13.9	2.5	–
C62/10446	Appliqué	81.0	5.7	13.1	–
(31)SAL-43	Chape	82.2	11.9	–	4.8

Taken all together, the impurities in the lead (except for the solder sample from the large pipe which, as already mentioned, is a Pb–Sn alloy, and some of the impurities may be contributed by tin) indicate quite a similarity between the four objects, with the sample from the capital stone being the one with the lowest values in a number of elements (Ag, Sb, Cu, As) but not for Sn. This difference is most distinct in the arsenic content (only 6.8 ppm).

3.2. *Copper-based alloys*

The results for the elemental characterisation of the copper-based objects by EDX are summarised in Table 2.

All of them are ternary alloys, with different proportions of the respective elements. The decorative nail head is technically brass, but with some added lead, as usually done to cast metals in Islamic metallurgy (Craddock, 1979: 74). The scabbard chape is made of a similar alloy, but with less Zn. We classify both of them as leaded brass. The gilt sheet is brass, and the embossed appliqué, with a much higher amount of tin than zinc, would be classified as gunmetal: in these two sheet objects, lead was not added into the alloy. According to Craddock's study (1979), there is no tin-bronze in use in Islamic metallurgy, and the main difference between sheet and cast metals in the Islamic work is the presence of often considerable quantities of lead in the latter (p. 69), with the larger and more intricate castings (like vessels) having a relatively higher lead content (p. 74). In our samples, only the decorative nail head is a cast object, but the amount of lead is not high (3.8%).

The appliqué shows an unusual alloy of unleaded gunmetal, although some similar alloys were reported by Craddock. However, to assess the real use of bronze alloys at this time we must take into account that tin could be more easily available in Al-Andalus than in other parts of the Islamic world, as some tin resources in Iberia were under their political control (Allan, 1979; Craddock et al., 1990). Nonetheless, at the moment, the analytical study of Islamic metal objects found in Spain is limited,[1] and the available results show the same general trend that Craddock (1979) proposed years ago: brass alloy and scarce use of tin.

It is in the framework of this Islamic tradition of a preferential use of brass alloy that the embossed gilt sheet LC-1990/HA (Fig. 3) has to be considered. After taking a sample from a corner, the metallographic study of the cross-section revealed a worked and annealed grain structure with some twinning and strain lines visible due to hammering. Non-metallic flattened and deformed inclusions are also evident (Fig. 4). All this indicates that the brass sheet was obtained by forging the metal. This process was executed

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[1] The number of Islamic objects (9th–13th century) studied in the Archaeometallurgy of the Iberian Peninsula Project (Perea et al., 2008) is around 20, from the Albacete, Cordoba and National Archaeological Museums. The only exception so far is the unpublished study from the Alarcos (Ciudad Real) archaeological research, with near one hundred metallic copper-based objects analysed.

Fig. 3. Embossed gilt metal sheet LC-1990/HA.

on a brass block or pre-form (probably cast) either by hot-working or by alternating cold-hammering with annealing. It is the combination of mechanical deformation and application of heat that results in the structure of fairly regular re-crystallized grains with inner annealing twins that can be observed in Fig. 4. The presence of strain lines, which only occur near the surface (Fig. 4b) and are not present in the core of the section (Fig. 4a) indicates that the last step in the manufacture of the brass sheet involved slight cold work. Probably, this was executed in order to homogenise the surface's appearance, but it could have been also part of the embossing decorative process (although the sample was taken from an undecorated part).

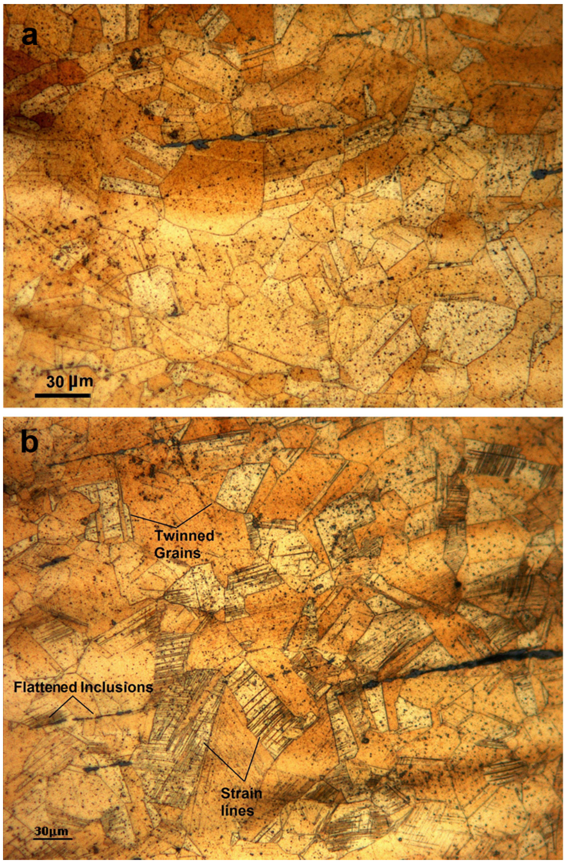

Fig. 4. OM micrographs (×500) from the cross-section of a fragment of the gilt metal sheet LC-1990/HA. a) Microstructure of the core of the sheet showing twinned grains as a result of hammering and annealing. b) Microstructure near the surface of the sheet showing twinned grains with strain lines indicating a last step of cold-working. In both pictures some elongated non-metallic inclusions (in grey) can be noticed, flattened and deformed as a consequence of hammering.

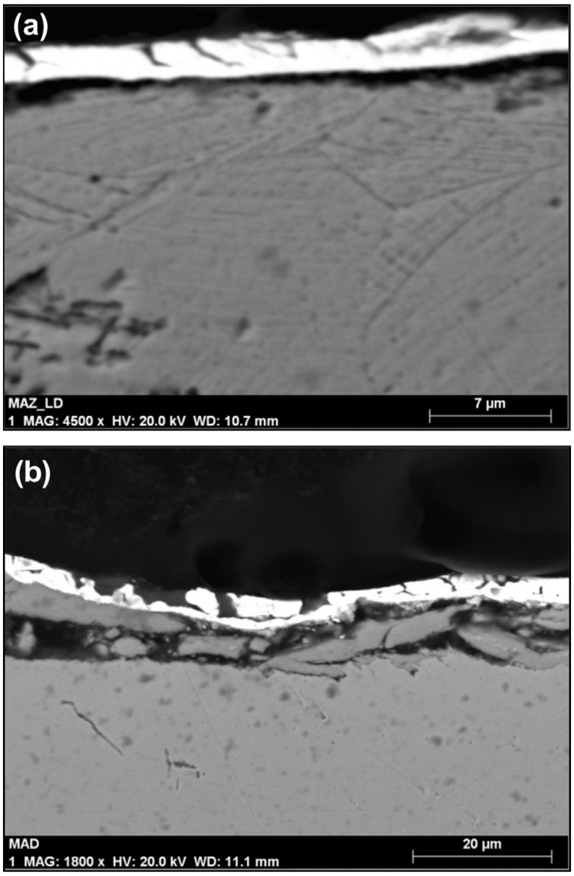

Fig. 5. SEM pictures (BSE) from the cross-section of the sample fragment of LC-1990/HA. The white strip in the upper part on the pictures corresponds to the gold layer. a) Detail of the gold layer on top of the metallic substrate. b) Detail of the gold layer, lying on top of the substrate's corrosion products.

The surface gold coating is very thin and difficult to see under the OM, so it was studied using SEM-EDX (Fig 5). The gold foil (bright white) can be clearly noticed as a thin layer of variable thickness (2–3 μm) resting on the brass substrate (Fig. 5a) as well as on an interface mainly composed of corrosion products (Fig 5b).

The presence of a noticeable amount of Hg (about 10%) in the gold layer (Table 3) indicates that the application of the coating was achieved with techniques involving this component. The presence of copper (7.6%) in the coating might be attributed to impurities in the gold, but more probably it is due to the analytical beam of the EDX reaching the brass substrate, which also explains the presence of Zn (1.1%). This amount of Hg and the thickness of the layer are consistent with the technique of fire gilding (Anheuser, 1996, 1997),

Table 3
Results for the EDX compositional analyses for LC-1990/HA, measured on the cross-section of the sample fragment and expressed in normalised % wt.

	Cu	Zn	Sn	Au	Hg	Al	Cl	Si
Substrate	83.6	13.9	2.5					
Coating	7.6	1.1		79.6	10.1	0.6	0.5	0.3

Table 4
Results of the MC-ICP-MS lead isotope analysis performed on the sampled metals (lead and copper alloys) from Madinat al-Zahra. The 2 Std Dev is based on the average of the standard deviation for all analyses and is used in Figs. 6–9.

Signature	Object	^{206}Pb/^{204} pb	^{207}Pb/^{204} pb	^{208}Pb/^{204} pb	^{207}Pb/^{206} pb	^{208}Pb/^{206} pb
0.25715	Large Pipe	18.252	15.626	38.386	0.8561	2.1031
0.25745	Small Pipe	18.237	15.615	38.361	0.8563	2.1035
24090	Capital Stone	18.289	15.654	38.447	0.8559	2.1022
Caja Y-51bis	Grate	18.237	15.615	38.362	0.8562	2.1034
Caja 2045	Shapeless fragment	18.249	15.618	38.379	0.8558	2.1030
C-13/B-244	Nail head	18.251	15.618	38.375	0.8557	2.1026
LC-1990/HA	Gilt sheet	18.156	15.617	38.363	0.8602	2.1130
C62/10446	Appliqué	18.165	15.618	38.369	0.8598	2.1123
(31)SAL-43	Chape	18.252	15.624	38.389	0.8560	2.1033
2 Std Dev		0.0054	0.0056	0.0137	0.000133	0.000277

where an amalgam of gold and mercury is prepared and then applied on the surface to be gilt. Afterwards, heat is applied so the mercury evaporates, leaving behind a thin layer of metallic gold. Burnishing was the final step.

Fire gilding of brass was not in use in Roman times, when silver or unalloyed-copper were the main metals to be found gilt, due to technical reasons. There are some difficulties encountered in fire gilding copper alloys as opposed to pure copper. The presence of other elements may favour the formation of surface oxides during the heating stage, which may even combine with the amalgam (Anheuser, 1997), compromising in all instances the adherence of the gold layer. In our case, the substrate is brass with a 13.9% Zn and some Sn (2.5%). In order to prevent the problems of adherence of the gold coating, a previous treatment of the surface was recommended by some of the historical sources that describe the fire gilding process (see for example 10th century Yemeni Al-Hamdani in Allan, 1979: 11 or 16th century Italian Benvenuto Cellini in Anheuser, 1997: 59). It involved rubbing it with an acid agent to clean it from oxides and providing more surface area for the amalgam to wet the surface.

One could wonder why a material like brass was gilded, as the alloy has itself a golden aspect. In this sense, it is worth remembering that brass is more yellow the more zinc it contains (with an upper limit of around 30% in that period), and in our case the amount of zinc is not too high, so it probably had a reddish hue.[2] If a truly golden appearance was desired, gilding was the best option. Also, brass develops a patina over time when exposed to the atmosphere, but a gilded surface would prevent this decay. This would be a particularly important factor in our case, as the gilt metal sheet was probably an appliqué or a decorative metal covering for a piece of furniture or for a construction element, such as a door or a window, which would be exposed to the elements.

4. Lead isotope analysis (LIA)

The results of the lead isotope analysis for the 9 analysed samples are shown in Table 4. The interpretation of the results is based on the comparison of the isotopic ratios obtained from our materials with those known for the mines or the mining districts. In this study we focused on the mineralisations of the Iberian Peninsula, especially on those in the South. We have a good isotopic characterisation of the South-Western area, which includes the Pyrite Belt – Aznalcóllar and Río Tinto – (Marcoux, 1998) as well as the Ossa Morena zone (OMZ) and its various belts. Although as a whole, the lead isotope data from OMZ form an irregular cluster (Tornos and Chiaradia, 2004; Tornos et al., 2004), some belts have well defined isotopic fields. The Pb–Ag mineralisations of the Peninsular South-East (Sierra Almagrera, Bedar, Cartagena and Mazarrón, Sierra Alhamilla, Sierra de Gador and Cabo de Gata), and the southern deposits in the Central Iberian Zone (CIZ) such as Linares, Los Pedroches and Alcudia area are also sufficiently well characterised (Hunt, 2003; Klein et al., 2009; Santos Zalduegui et al., 2004; Stos-Gale et al., 1995).

The first impression given by the results obtained is that of proximity between the majority of the nine samples, lead and copper alloys alike. Fig. 6 depicts the grouping, with the exceptions of the gilt sheet and the appliqué. The leaded brasses (decorative nail head and chape) appear grouped with the lead objects. It must be emphasised that, in this latter case, as there is lead in the alloy, the analysis reflects the origin of said added lead, not that of copper or zinc. It is thus interesting to note that the lead alloyed with copper seems to have the same origin as the metal constituting the unalloyed lead objects.

Other relevant information obtained from these results is that lead from the grate, which was considered as non-recycled based on the chemical analyses, presents a similar isotopic signature to that of the recycled lead objects. This indicates that most of the recycled lead has a single origin, that is, that the lead used in the metal objects of Madinat al-Zahra comes from a single main area of exploitation.

The identification of possible places of origin using the geological lead isotope data available needs some detailed analysis due to the overlapping areas in a general view. A discriminative effort is necessary to confirm that archaeological data matches with a group of data from a given mine or area. What we see in a single bivariate scatterplot could change its relative position if other ratios are compared in another graph. All ratios must be considered and a mismatch between archaeological and geological samples in a single ratio is enough to discard a specific provenance. In this study we compare the following ratios: ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb, ^{206}Pb/^{204}Pb versus ^{207}Pb/^{206}Pb, ^{206}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb. To suggest a provenance the samples must match in all 4 graphs. The mirror graphs in Fig. 6 are an appropriate example to convey the complexity of graphic representation. The Pyrite Belt could be suggested as a possible provenance of the unleaded copper-based samples if only the graph 6b is given, however this provenance option is clearly not supported by the position of the data in the graph 6a.

After considering all the options from the OMZ and CIZ, only two areas from the CIZ could be suggested as probable provenance of the lead. They are, on the one hand, the mines in the Linares district

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[2] As mentioned in the "Brass" entry in the 1911 edition of the *Encyclopaedia Britannica*: "(…) When a small percentage of zinc is present, the colour of brass is reddish, as in *tombac* or red brass, which contains about 10%. With about 20% the colour becomes more yellow, and a series of metals is obtained which simulate gold more or less closely; such are *Dutch metal, Mannheim gold, similor* and *pinchbeck*, (…). Ordinary brass contains about 30% of zinc, and when 40% is present, as in *Muntz, yellow* or *patent* metal (invented by G. F. Muntz in 1832), the colour becomes a full yellow (…)".

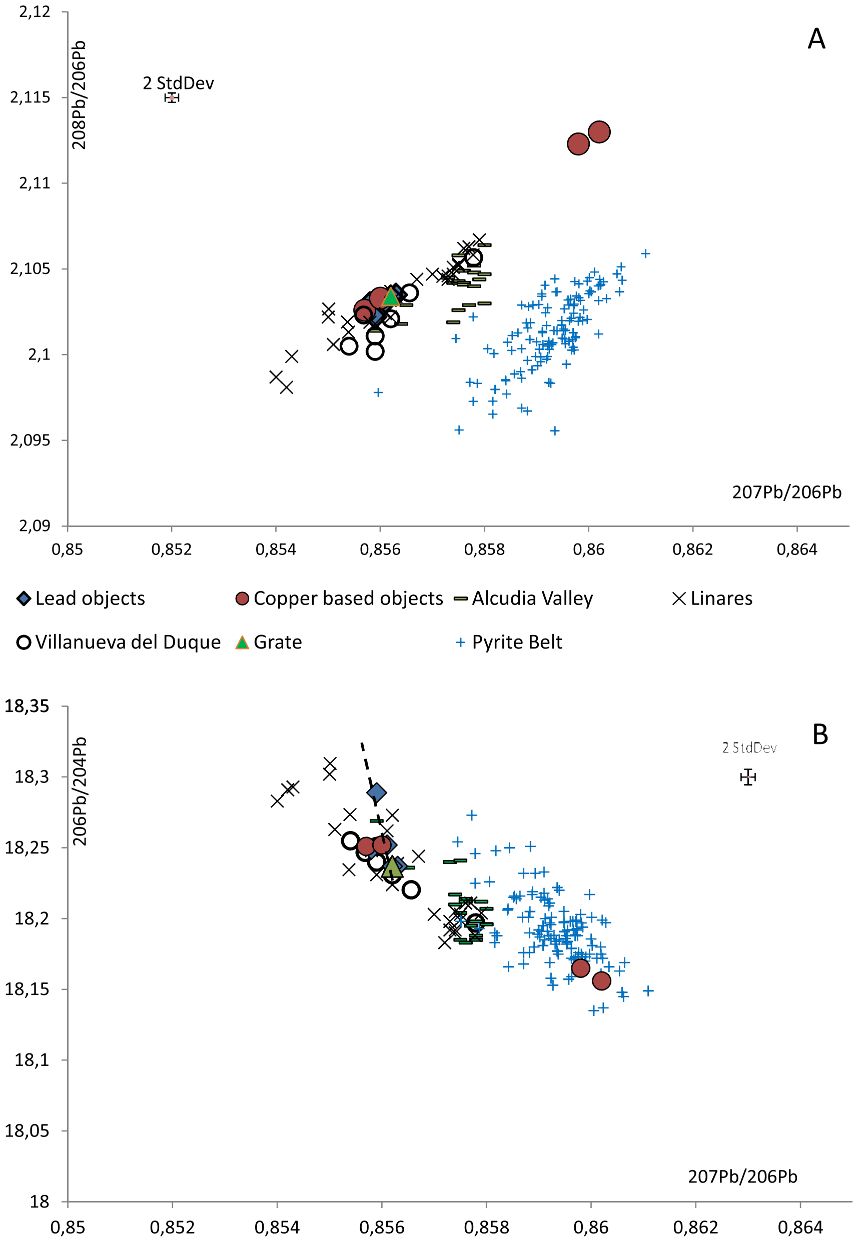

Fig. 6. Mirror scatterplots showing the LIA of the analysed objects of Madinat al-Zahra compared with relevant mineralisations of the south of the Iberian Peninsula. The dashed connects several samples that could be on the same mixing line, but see text for discussion.

(Jaén) and, on the other hand, those at Villanueva del Duque (Córdoba) in Los Pedroches area. LIA from the mines located in Villanueva del Duque are those identified as El Soldado, Morras de Cuzna and Guadalupe by Santos Zalduegui et al. (2004: Table 3) and Cuzna by Klein et al. (2009: Table I n° 45–47). Some of the mines at the Alcudia Valley (CIZ) are also isotopically close to them, but the results for our archaeological samples fall at the outskirts of their general isotopic field (Fig. 6): only three of 94 samples from the Alcudia Valley could be related to the archaeological results (single samples from Grupo el Guijo, Mina María Aurora and Lomo del Perro published by Santos Zalduegui et al., 2004), hence the options of Linares or Villanueva del Duque seem more consistent. Other single mines at Los Pedroches can be ruled out with certainty, as also can the mines of the Murcia and Almería provinces, as well as the various belts at Ossa Morena (mainly the Azuaga formation) (Fig. 7), and at the Huelva Pyrite Belt (Fig. 6).

Although we have no statistically reliable data to decide between Linares and Villanueva del Duque, the graphs (Figs. 6 and 8) show that all the lead and leaded brass samples appear always more centred in relation with the Linares isotopic field than in relation with the one for the mines at Villanueva del Duque.

Only the sample from the capital stone, with a higher value in the ^{206}Pb/^{204}Pb and ^{207}Pb/^{206}Pb ratios is displaced in the set (Figs. 6b and 8), clearly away from the mines at Villanueva del Duque, and in the boundary of the Linares isotopic field. It has already been noted that this sample, although known to be composed of recycled metal because of its high Sn content (4645 ppm), showed a slightly different impurity patterns from that of the other lead objects.

From the point of view of the analytical results there is no definite evidence in favour of, or against, either of the two most likely origins for the lead, but some further reasoning can be put forward:

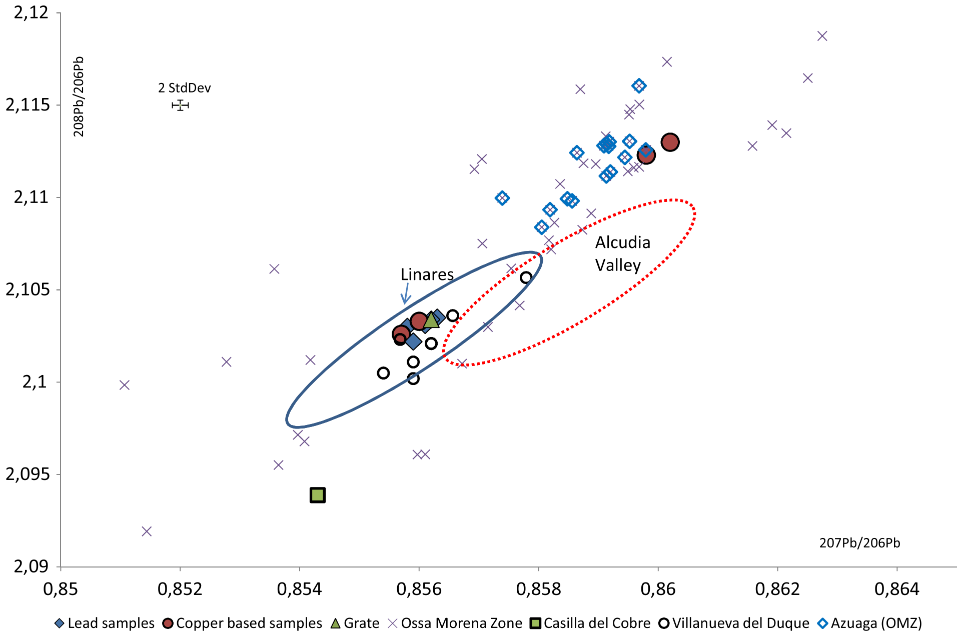

Fig. 7. LIA of the analysed objects of Madinat al-Zahra compared with ores from Ossa Morena Zone (OMZ). The distribution of ores from Linares (CIZ) and Alcudia (CIZ) are included as ellipses for clarity. Their detailed distribution can be observed in Fig. 6a.

- Most of the lead seems to have its origin in the Linares area.
- Being recycled lead, it is possible that both mining areas (Linares and Villanueva del Duque) might be in use, and that the apparent shift of the final isotopic value of the mix in favour of Linares in the majority of objects is simply due to the fact that this area features a wider isotopic field. In this sense, the sample from the grate, considered as primary lead, falls always inside the isotopic field of Villanueva del Duque. The rest of the recycled lead objects are slightly slanted towards Linares (Fig. 8).
- The lead from the capital stone suggests the possibility of a contribution from a third, unidentified, mining area. This contribution is minor but could affect the possible recycling of other lead objects, because there is an alignment in isotopic signatures (shown in Figs. 6b and 8 as a dashed line) between the primary lead of the grate and the position of the capital stone lead, with the large pipe in an intermediate position.
- This purported third lead source would have values higher than 15.66 (^{207}Pb/^{204}Pb) and 18.3 (^{206}Pb/^{204}Pb), and lower than 0.855 (^{207}Pb/^{206}Pb). However, there are no lead ores in the Iberian Peninsula with such a signature (Fig. 9, projection of the alignment shown as a dashed line). Therefore, this strongly indicates that, in fact, the origin for this recycled lead is the Linares area, and there is no such third provenance area.

Historical data should now be considered to weigh the possibilities that the lead isotope analyses establish. Both areas have a known record of lead mining in Roman times and there are also some references to Islamic works (Contreras and Dueñas, 2010;

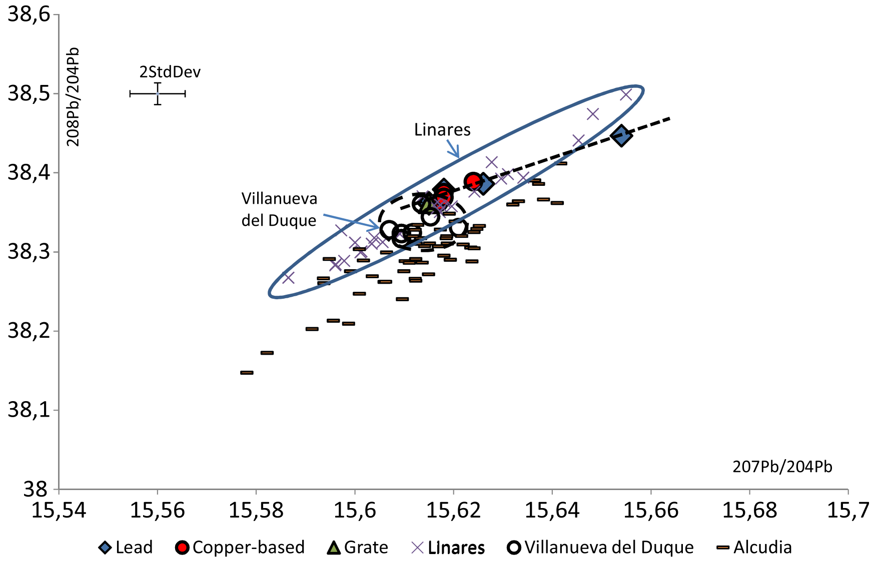

Fig. 8. LIA of the analysed objects of Madinat al-Zahra compared with ores from Linares, Villanueva del Duque and Alcudia (CIZ) in different ratios from those shown in Fig. 6. The dashed connects several samples that could be on the same mixing line, but see text for discussion. The sample outside the Linares ellipse is the capital stone.

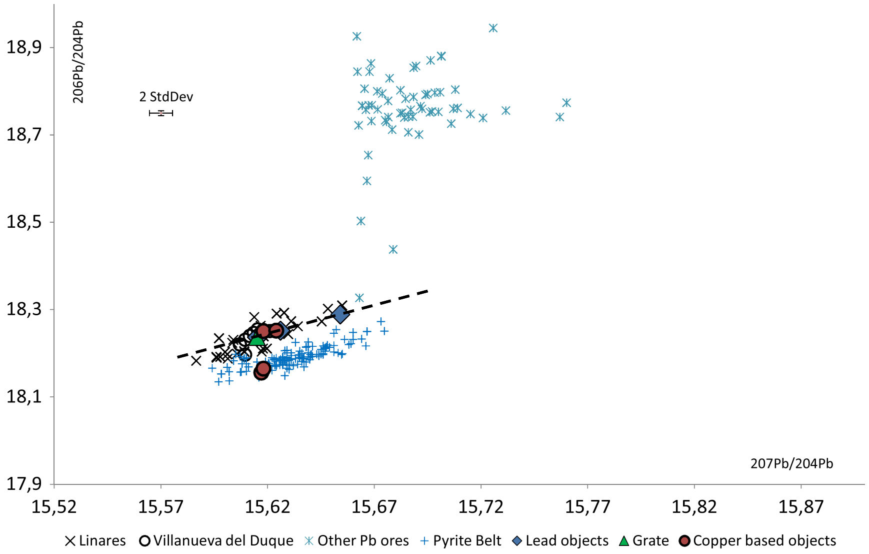

Fig. 9. Lead isotope ratios of the analysed objects of Madinat al-Zahra, relevant mineralisations of the south of the Iberian Peninsula and other Pb mineralisations from the rest of the Iberian Peninsula. The dashed connects several samples that could be on the same mixing line, but see text for discussion. No other lead ores from the rest of Iberian Peninsula seem consistent as source for recycled metal.

Domergue, 1987; Graneda, 2008), especially in Villanueva del Duque, where Caliphal remains were recovered in El Soldado group of mines. The main difference is that the Villanueva mines are argentiferous, silver content in galena reaches up to 9 kg/Tm (cf. Graneda, 2008: 26), whilst the ones at Linares have a low silver content and their production was lead. In this context, an isotopic study of silver coins minted at Madinat al-Zahra could give new arguments to support or discard a lead provenance from Villanueva.

As for the origin of the two unleaded copper alloy objects, their position in the graph is very distant from those of the lead or leaded objects, with higher values in the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (Fig. 6). They do not match the isotopic signatures for the mines at Linares, Villanueva del Duque and the Alcudia Valley, where copper minerals occur. The Iberian Pyrite Belt is also excluded due to lower values than 2.105 in $^{208}\text{Pb}/^{206}\text{Pb}$ ratio.

The presence of a high amount of tin in the brass, and the ternary alloy with tin and zinc could be the results of recycling, at least in part, of tin bronzes for the production of brass. It is assumed that the amount of lead added by tin to bronze alloys is too little to distort the isotopic signature of the copper: lead levels in tin minerals are generally under 100 ppm Pb (Pernicka, 1995; Stos-Gale, 1989) and, for example, in the majority of the tin ingots from the Uluburun shipwreck, lead is below the ICP detection limit of 100 ppm (Hauptmann et al., 2002) – which means that less than 10 ppm Pb would be added by tin to a 10% tin–bronze alloy. In the case of zinc, although zinc sulphide (sphalerite) occurs together in paragenesis with galena, the cementation process to produce brass implies the evaporation of zinc and therefore it brings relatively little of the lead that may be associated to the zinc. Following Allan (1979: 43), a maximum of 0.2% Pb is quantified in zinc oxide bars obtained by smelting zinc and lead minerals, and subsequently used for brassmaking. Afterwards, zinc would have to evaporate once again to be alloyed to copper by cementation and consequently, lead levels in the final brass alloy are minimal. If brass was produced from zinc oxides or carbonates, as seems to be usual in Western Europe (Craddock et al., 1990: 78), those minerals are usually nearly free of lead, as was stated for the Riopar Mines in Albacete province (Larruga, 1792) and thus the amount of lead carried by the zinc ores would not be high enough to modify the isotopic signature of copper. Consequently, lead isotope analyses of these objects are related to the provenance of copper.

In this case, the lead isotope analyses only allow us to propose the belts of Ossa Morena in Iberia, with the Azuaga belt in particular as a possible source for the metal (Fig. 7), but it should be noted that copper ores are not the main resource in this formation (Tornos et al., 2004). There is a lack of comparative data to offer a more specific hypothesis of origin. However, what is beyond doubt is that copper mines of Cerro Muriano and Casilla del Cobre in OMZ (Klein et al., 2009), the closest to Madinat al-Zahra, have clearly different isotopic ratios (lower than 2.1 in $^{208}\text{Pb}/^{206}\text{Pb}$ ratio) than those of the objects studied here and cannot be a primary origin of the recycled metal. In any event, still considering the possibility of imported objects, copper has a different provenance than the one proposed for lead.

5. Conclusions

Islamic mining and metallurgy in the Iberian Peninsula are still poorly known, although the main features about copper alloys were described years ago by Craddock (1979). This study reveals some new data, helpful to understand not only the technology but also the provenance of the metal in a key site such Madinat al-Zahra, where official Caliphal workshops supplied the city. The origin of brass gilding is not clear, but must be related to the general use of brass in Islamic metallurgy. The fire gilding technique was successful in this type of copper alloy, and was in use after the 10th century. However, we have no knowledge of earlier gilt brasses, except for a brass belt terminal found in Brno (Czech Republic), which dates back to the 8th century, but whose gilding technique is not clearly described (Hložek et al., 2012).

Recycling was a normal practice in Islamic metallurgy, not only in copper alloys, but also in metallic lead. In spite of this, we have provided strong evidence that lead supply came mainly from a single source, as was the case for some other materials employed in the building of the city. The most probable origin is the Linares mining district, 100 km to the east following the Guadalquivir River, although another option is the Villanueva del Duque silver–lead mines, located 75 km north of the city. There are other lead mines in close locations at Sierra Morena, mainly in Posadas or Villaviciosa (belonging to OMZ) but, following Graneda's (2008) chronology, they began to be exploited later, in the first part of the 12th century. LIA suggests that they did not supply lead in Caliphal time.

The provenance of copper could not be determined due to the likely use of recycled metal. At the copper mines of Cerro Muriano and Casilla del Cobre, close to Madinat al-Zahra, intensive Roman works are well documented (Domergue, 1987), as well as somewhat doubtful evidence of works from the Caliphal period, but the results of the lead isotope analyses of the copper-based objects are clearly not related to them.

The role of Iberian non-ferrous ore resources during Islamic times needs further research. The splendour of the activity in Roman times has eclipsed the number of studies on later periods. This work constitutes a first approach to confirm the use of some of these resources, such as Linares or Villanueva del Duque mining districts, for lead supply. Furthermore, it confirms that mineral exploitation decreased at other locations such as Cerro Muriano or Rio Tinto, where there are no clear archaeological or documental references related to this early Islamic period – with the only exception of the Almohade period in the case of Rio Tinto (Pérez Macias and Delgado Domínguez, 2011: 14).

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