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Provenance evidence for Roman lead artefacts of distinct chronology from Portuguese archaeological sites

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ABSTRACT

In the present study, a set of 24 *glandes plumbeae* found at Alto dos Cacos, a Roman Republican military camp located in the Tagus valley, Portugal, was analysed by a quadrupole based ICP-MS to determine the tin (Sn) content and lead (Pb) isotope ratios. Results were compared with similar data previously obtained for *fistulae plumbeae aquariae* from *Conimbriga*, an important Lusitanian Roman centre during the Empire. Low Sn contents (≤ 0.01 wt%) were observed in 25% of *glandes plumbeae* indicating that were probably made with non-recycled lead. A similar situation was perceived for the set of *fistulae aquariae*, although most of the remaining *fistulae* present systematically higher Sn concentrations than those of *glandes* suggesting that lead recycling increased during the Empire. Pb isotope ratios distribution differentiated the analysed samples into two distinct groups: one composed by most of *glandes plumbeae* (15) and the other by the remaining *glandes plumbeae* (9) and all *fistulae aquariae*. The comparison with Pb isotope ratios of the published data for several lead ore deposits, exploited by the Roman in Iberian Peninsula, suggests that lead used in the manufacture of most of the *glandes plumbeae* would come from Linares-La Carolina, Alcudia Valley and Ossa Morena Zone. Also, some *glandes* could have been made using these ores, probably mixed with lead ores from *Gallia Narbonensis* (Southern France) or from Sardinia in the Mediterranean region. On the other hand, lead used in most *fistulae aquariae* came from Iberian mines, namely from Sierra Morena (Alcudia Valley and Linares-La Carolina mines) and Ossa Morena mining district, although in some cases, probably mixed with lead from the Iberian Pyrite Belt.

1. Introduction

Lead (Pb), an unaesthetic metal, became of great economic importance during Roman times due to its large scale use in silver production (cupellation process). Besides, it was widely used in architectural and hydraulic structures, and also in containers, sarcophagi and military weapons, as sling bullets used by Roman legions.

The Romanization of Iberia started during the 2nd century BCE becoming *Hispania* an important source of silver and lead, but also of copper, tin and gold (Edmondson, 1989; Rodà de Llanza, 2009). During the Republic, the mining district of Cartagena (*Carthago Noua*)/Mazarrón turned out to be the most important source of silver and lead in the Iberian Peninsula, exporting to other Roman regions as testified by lead ingots found in several shipwrecks ascribed to this period (Domergue et al., 1974, 2012; Trincherini et al., 2001, 2009). With the end of the Republic, the mines of Linares-La Carolina, Alcudia Valley, Fuente Obejuna and Los Pedroches, located in Sierra Morena region, replace Cartagena/Mazarrón as the most important source of lead and silver, supplying high amounts of these metals to the Roman Empire. Later on, during and after the Flavian period, Riotinto mining region, in the Iberian Pyrite Belt, became the region with the most productive silver mines in Iberia. However, it was necessary to import lead from other regions, since in Riotinto there was not enough lead to proceed with the silver cupellation process (Edmondson, 1989). It must be noted that other lead mines beyond those either during the Republic or during the Empire were exploited although on a smaller scale than those referred to above.

The abundance of lead made possible a diversity of applications including the manufacture of military weapons as sling bullets (*glandes plumbeae*) used by slingers of the Roman legions. *Glandes plumbeae* were long-distance light weapons widely used by legionaries mainly during the Republic and also during the Augustan-Tiberian period. These weapons, having diverse sizes, shapes, and weights, were usually made by casting lead in moulds (Dohrenwend, 2002; Rihll, 2009; Laharnar,

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Fig. 1. Geographical location of the Roman Republican military camp of Alto dos Cacos (Almeirim) and of the town of *Conimbriga*.

2011). On the other hand, high amounts of this metal were used to the manufacture of plumbing hydraulic systems (*fistulae plumbeae aquariae*) at public buildings and private houses, as occurred in *Conimbriga* or *Pompeii*, for instance. These two kinds of artefacts, *glandes* and *fistulae*, which have distinct chronology, but both found in the Portuguese territory, were subjected to analysis for this study.

Chemical analysis of lead artefacts, namely Pb isotopic ratios and elemental content determinations, may provide significant information on sources and trade routes of lead. In the particular case of the tin (Sn), a higher content may indicate the recycling of lead materials, since tin solders were largely used for joining components of lead artefacts or to seal the joints of lead pipes, (*e.g.* Gomes et al., 2016). Usually, lead obtained from galena ores and consequently lead from ingots has a Sn content $<$ 0.01 wt% (Wyttenbach and Schubiger, 1973; Asderaki and Rehren, 2006). However, galena ores from the Iberian Northeast (Molar-Bellmunt-Falset mining district, Catalonian region) can present much higher Sn contents, which may reach *c.* 0.4 wt% with an average of 0.08 wt%, following analyses of 46 samples (Montero-Ruiz et al., 2008, 2009, 2009). Therefore, when using Pb isotope ratios to assess an Iberian provenance of leaden raw materials, the first step is to see if a Catalonian source can be ascribed to the raw material. If not, only those artefacts with a Sn content $\leq$ 0.01 wt% (lead probably not recycled) can give the most reliable information. Nevertheless, it must be taken into account that, in some cases, a mixture of primary leaden raw materials or the recycled lead may also give some indication about the origins of the raw materials used in the manufacture of the artefact, if Pb isotope ratios of the respective ore sources are known (Durali-Müeller et al., 2007).

The present work is focused on variations of the Sn content and Pb isotope ratios distributions of *glandes plumbeae* found at Alto dos Cacos, ascribed to the Roman Republican period with a chronology of *c.* 60 BCE. Results were compared with those from a previous study of *fistulae plumbeae* from *Conimbriga* ascribed to the Empire (Gomes et al., 2016), intending to investigate whether the source of leaden raw materials changed over the time and, if so, trying to identify those different sources.

2. Archaeological collections

The first collection is composed by 24 *glandes plumbeae* of different typologies (biconical, truncated biconical, oblong or with an olive shape) and manufacturing processes (most of them cast in moulds but some seem to have been hammered into the desired shape), found at Alto dos Cacos (AC). This archaeological site (Fig. 1) is a Roman

Table 1
Sn content of *glandes plumbeae* from Alto dos Cacos (AC) and *fistulae plumbeae aquariae* from *Conimbriga* (MMC) performed by the Quadrupole ICP-MS (Gomes et al., 2016) (Results in wt %; n.d. – not detected; low Sn samples in mg kg^{-1} and italic; HWJ – House of Water Jets; A – Aqueduct; NI – Northern Insulae; Southern Baths – SB; HC – House of Cantaber; (a) – unknown).

Sample reference	Sn	Sample reference	Sn	Sample reference	Sn
AC316	*3.5 mg kg^{-1}*	MMC1 (HWJ)	0.34	MMC27 (HWJ)	0.39
AC317	*0.06*	MMC2 (NI)	0.57	MMC28 (HWJ)	0.40
AC318	0.13	MMC4 (HWJ)	0.34	MMC29 (HWJ)	0.37
AC319	*0.05*	MMC5 (HWJ)	0.89	*MMC30 (HWJ)*	*3 mg kg^{-1}*
AC320	*8 mg kg^{-1}*	MMC6 (HWJ)	0.45	MMC31 (HWJ)	0.34
AC321	*0.06*	MMC7 (HWJ)	0.22	MMC32 (HWJ)	0.33
AC322	*< 2.69 mg kg^{-1}*	MMC8 (HC)	0.48	MMC33 (HWJ)	0.38
AC323	*0.05*	*MMC9 (A)*	*3 mg kg^{-1}*	MMC34 (HWJ)	0.38
AC324	*0.07*	MMC10 (HWJ)	0.11	MMC35 (HWJ)	0.32
AC325	0.16	*MMC12 (SB)*	*3 mg kg^{-1}*	MMC37 (HWJ)	0.35
AC326	0.16	*MMC13 (A)*	*< 2.69 mg kg^{-1}*	MMC38 (NI)	0.44
AC327	0.39	*MMC14 (A)*	*< 2.69 mg kg^{-1}*	*MMC39 (HWJ)*	*5 mg kg^{-1}*
AC328	*86 mg kg^{-1}*	MMC15 (A)	0.03	MMC40 (HWJ)	0.10
AC329	0.04	MMC16 (A)	0.01	MMC42 (HWJ)	0.42
AC330	0.05	*MMC17 (A)*	*< 2.69 mg kg^{-1}*	MMC44 (HWJ)	0.39
AC331	*8 mg kg^{-1}*	MMC18 (A)	0.05	MMC46 (HWJ)	0.45
AC332	n.d.	MMC19 (HWJ)	0.09	MMC47 (HWJ)	0.74
AC333	0.44	*MMC20 (HWJ)*	*< 2.69 mg kg^{-1}*	MMC49 (HWJ)	*0.02*
AC334	0.30	MMC21 (HWJ)	0.10	MMC52 (HWJ)	*0.05*
AC335	0.07	MMC22 (HWJ)	0.32	*MMC53 (a)*	*4 mg kg^{-1}*
AC336	0.07	MMC23 (HWJ)	0.43		
AC337	0.05	*MMC24 (HWJ)*	*3 mg kg^{-1}*		
AC338	0.08	MMC25 (HWJ)	0.38		
AC339	0.06	MMC26 (HWJ)	0.72		

Table 2
Pb isotope ratios of *glandes plumbeae* from Alto dos Cacos performed by a Quadrupole ICP-MS (low Sn samples in italic).

Sample reference	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
AC316	*18.125 ± 0.06*	*15.527 ± 0.07*	*38.016 ± 0.19*	*0.857 ± 0.003*	*2.097 ± 0.010*
AC317	18.417 ± 0.03	15.629 ± 0.04	38.729 ± 0.11	0.849 ± 0.002	2.103 ± 0.002
AC318	18.365 ± 0.04	15.593 ± 0.03	38.378 ± 0.15	0.849 ± 0.003	2.090 ± 0.009
AC319	18.416 ± 0.05	15.586 ± 0.07	38.328 ± 0.14	0.846 ± 0.003	2.081 ± 0.004
AC320	*18.220 ± 0.06*	*15.622 ± 0.05*	*38.328 ± 0.10*	*0.857 ± 0.002*	*2.104 ± 0.005*
AC321	18.481 ± 0.07	15.662 ± 0.06	38.592 ± 0.16	0.847 ± 0.002	2.088 ± 0.006
AC322	*18.102 ± 0.04*	*15.581 ± 0.05*	*38.159 ± 0.09*	*0.858 ± 0.002*	*2.102 ± 0.003*
AC323	18.407 ± 0.04	15.652 ± 0.05	38.705 ± 0.11	0.848 ± 0.002	2.096 ± 0.009
AC324	18.351 ± 0.02	15.570 ± 0.03	38.268 ± 0.10	0.846 ± 0.002	2.079 ± 0.006
AC325	18.548 ± 0.05	15.683 ± 0.05	38.755 ± 0.19	0.845 ± 0.002	2.089 ± 0.012
AC326	18.436 ± 0.04	15.654 ± 0.06	38.549 ± 0.23	0.849 ± 0.002	2.091 ± 0.008
AC327	18.319 ± 0.04	15.634 ± 0.05	38.264 ± 0.19	0.853 ± 0.003	2.089 ± 0.010
AC328	*18.200 ± 0.08*	*15.582 ± 0.07*	*38.164 ± 0.15*	*0.856 ± 0.001*	*2.097 ± 0.010*
AC329	18.446 ± 0.10	15.633 ± 0.06	38.708 ± 0.25	0.847 ± 0.003	2.098 ± 0.007
AC330	18.282 ± 0.04	15.575 ± 0.03	38.330 ± 0.19	0.852 ± 0.003	2.096 ± 0.014
AC331	*18.207 ± 0.10*	*15.583 ± 0.07*	*38.213 ± 0.15*	*0.856 ± 0.001*	*2.099 ± 0.005*
AC332	*18.185 ± 0.13*	*15.600 ± 0.11*	*38.060 ± 0.32*	*0.858 ± 0.002*	*2.093 ± 0.007*
AC333	18.350 ± 0.11	15.606 ± 0.11	38.459 ± 0.23	0.850 ± 0.003	2.096 ± 0.010
AC334	18.178 ± 0.06	15.650 ± 0.08	38.495 ± 0.25	0.854 ± 0.004	2.101 ± 0.012
AC335	18.352 ± 0.12	15.698 ± 0.12	38.983 ± 0.26	0.849 ± 0.001	2.107 ± 0.014
AC336	18.342 ± 0.09	15.666 ± 0.09	38.695 ± 0.14	0.847 ± 0.001	2.093 ± 0.008
AC337	18.483 ± 0.06	15.621 ± 0.09	38.634 ± 0.21	0.845 ± 0.002	2.090 ± 0.008
AC338	18.436 ± 0.04	15.596 ± 0.06	38.568 ± 0.13	0.846 ± 0.003	2.092 ± 0.006
AC339	18.496 ± 0.02	15.660 ± 0.04	38.562 ± 0.15	0.847 ± 0.003	2.085 ± 0.009

Republican military camp probably associated to the *Caesar* military campaigns against Pompey in Hispania Ulterior (*c.* 60 BCE) (Guerra et al., 2014; Pimenta et al., 2014). It occupies a relevant strategic position, near the Roman town of *Scallabis*, which nearby region had been converted into a place for stationary troops since *Decimus Iunius Brutus* (138 BCE). The second collection consists of a set of 44 *fistulae plumbeae aquariae* recovered from public and domestic structures at *Conimbriga* (Fig. 1), an important urban centre in the *Lusitania* province during the Empire. Archaeological contexts and chronology of these *fistulae* are described in Gomes et al. (2016, Table 1).

3. Analytical methods

A small amount of sample (50 mg) was taken with 1 or 1.5 mm diameter drill bit on a cleaned area (without corrosion layers) of the artefact. Each sample was dissolved in 20% HNO_3 solution in an ultrasonic bath. Certified reference materials, NIST 981 (Common Lead Isotopic Standard) and BCR 288 (Lead Containing Added Impurities), were used to quality control of the measurements and they were prepared following the analytical procedure used for the samples (Gomes et al., 2016). The accuracy of the Pb isotope ratios determination using the NIST 981 is $\leq 0.2\%$. For the Sn determination a Multi-element Calibration Standard 4 solution (PerkinElmer) was used to external calibration. The accuracy of Sn quantification was determined based on

Table 3
Pb isotope ratios of *fistulae plumbeae* from *Conimbriga* performed by Quadrupole ICP-MS (HWJ – House of Water Jets; A – Aqueduct; NI – Northern Insulae; Southern Baths – SB; HC – House of Cantaber; (a) – unknown; low Sn samples in italic).

Sample reference	^{206}Pb/^{204}Pb	^{206}Pb/^{204}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{206}Pb
MMC1 (HWJ)	18.264 ± 0.12	15.643 ± 0.08	38.337 ± 0.18	0.856 ± 0.003	2.119 ± 0.004
MMC2 (NI)	18.332 ± 0.08	15.679 ± 0.04	38.910 ± 0.11	0.855 ± 0.003	2.122 ± 0.005
MMC4 (HWJ)	18.308 ± 0.06	15.665 ± 0.05	38.825 ± 0.11	0.855 ± 0.001	2.120 ± 0.009
MMC5 (HWJ)	18.154 ± 0.06	15.573 ± 0.05	38.242 ± 0.16	0.856 ± 0.002	2.121 ± 0.007
MMC6 (HWJ)	18.153 ± 0.06	15.593 ± 0.07	38.327 ± 0.20	0.855 ± 0.003	2.127 ± 0.011
MMC7 (HWJ)	18.276 ± 0.04	15.650 ± 0.05	38.625 ± 0.11	0.856 ± 0.002	2.113 ± 0.008
MMC8 (HC)	18.332 ± 0.05	15.720 ± 0.07	38.940 ± 0.12	0.857 ± 0.002	2.124 ± 0.005
MMC9 (A)	*18.292 ± 0.03*	*15.634 ± 0.06*	*38.552 ± 0.15*	*0.855 ± 0.002*	*2.108 ± 0.006*
MMC10 (HWJ)	18.295 ± 0.08	15.666 ± 0.08	38.758 ± 0.16	0.856 ± 0.002	2.118 ± 0.008
MMC12 (SB)	*18.368 ± 0.05*	*15.723 ± 0.05*	*38.917 ± 0.08*	*0.856 ± 0.003*	*2.119 ± 0.004*
MMC13 (A)	*18.176 ± 0.09*	*15.591 ± 0.06*	*38.228 ± 0.15*	*0.857 ± 0.002*	*2.103 ± 0.007*
MMC14 (A)	*18.189 ± 0.07*	*15.610 ± 0.12*	*38.300 ± 0.15*	*0.858 ± 0.004*	*2.105 ± 0.003*
MMC15 (A)	18.159 ± 0.07	15.556 ± 0.04	38.123 ± 0.11	0.857 ± 0.002	2.099 ± 0.006
MMC16 (A)	*18.172 ± 0.06*	*15.579 ± 0.08*	*38.189 ± 0.23*	*0.857 ± 0.002*	*2.101 ± 0.006*
MMC17 (A)	*18.235 ± 0.03*	*15.675 ± 0.02*	*38.463 ± 0.15*	*0.860 ± 0.002*	*2.109 ± 0.008*
MMC18 (A)	18.166 ± 0.08	15.583 ± 0.05	38.325 ± 0.16	0.859 ± 0.003	2.110 ± 0.007
MMC19 (HWJ)	18.214 ± 0.05	15.581 ± 0.07	38.315 ± 0.21	0.855 ± 0.003	2.103 ± 0.011
MMC20 (HWJ)	*18.256 ± 0.04*	*15.661 ± 0.06*	*38.450 ± 0.12*	*0.858 ± 0.002*	*2.106 ± 0.004*
MMC21 (HWJ)	18.151 ± 0.05	15.567 ± 0.09	38.250 ± 0.23	0.858 ± 0.003	2.107 ± 0.007
MMC22 (HWJ)	18.158 ± 0.05	15.586 ± 0.08	38.214 ± 0.20	0.858 ± 0.003	2.104 ± 0.009
MMC23 (HWJ)	18.184 ± 0.04	15.630 ± 0.06	38.260 ± 0.16	0.859 ± 0.003	2.104 ± 0.008
MMC24 (HWJ)	*18.123 ± 0.04*	*15.575 ± 0.04*	*38.178 ± 0.12*	*0.859 ± 0.001*	*2.106 ± 0.005*
MMC25 (HWJ)	18.162 ± 0.11	15.608 ± 0.09	38.186 ± 0.24	0.859 ± 0.003	2.102 ± 0.010
MMC26 (HWJ)	18.185 ± 0.06	15.634 ± 0.05	38.202 ± 0.09	0.860 ± 0.002	2.101 ± 0.003
MMC27 (HWJ)	18.275 ± 0.05	15.656 ± 0.06	38.276 ± 0.12	0.857 ± 0.004	2.094 ± 0.004
MMC28 (HWJ)	18.153 ± 0.05	15.586 ± 0.05	38.220 ± 0.13	0.858 ± 0.001	2.105 ± 0.002
MMC29 (HWJ)	18.292 ± 0.03	15.596 ± 0.03	38.302 ± 0.19	0.853 ± 0.001	2.093 ± 0.008
MMC30 (HWJ)	*18.104 ± 0.07*	*15.536 ± 0.02*	*38.205 ± 0.15*	*0.858 ± 0.003*	*2.110 ± 0.004*
MMC31 (HWJ)	18.146 ± 0.10	15.610 ± 0.10	38.267 ± 0.20	0.860 ± 0.003	2.109 ± 0.004
MMC32 (HWJ)	18.156 ± 0.05	15.606 ± 0.06	38.250 ± 0.14	0.859 ± 0.002	2.107 ± 0.005
MMC33 (HWJ)	18.201 ± 0.04	15.605 ± 0.03	38.259 ± 0.06	0.857 ± 0.002	2.102 ± 0.007
MMC34 (HWJ)	18.144 ± 0.07	15.595 ± 0.06	38.272 ± 0.11	0.859 ± 0.002	2.109 ± 0.009
MMC35 (HWJ)	18.234 ± 0.07	15.664 ± 0.09	38.620 ± 0.20	0.859 ± 0.002	2.117 ± 0.005
MMC37 (HWJ)	18.170 ± 0.06	15.648 ± 0.07	38.372 ± 0.19	0.861 ± 0.002	2.111 ± 0.008
MMC38 (HWJ)	18.170 ± 0.07	15.607 ± 0.04	38.277 ± 0.16	0.859 ± 0.002	2.107 ± 0.006
MMC39 (HWJ)	*18.075 ± 0.11*	*15.535 ± 0.07*	*38.172 ± 0.20*	*0.859 ± 0.002*	*2.112 ± 0.007*
MMC40 (HWJ)	18.125 ± 0.07	15.617 ± 0.08	38.395 ± 0.12	0.862 ± 0.001	2.118 ± 0.002
MMC42 (HWJ)	18.210 ± 0.09	15.651 ± 0.08	38.411 ± 0.14	0.859 ± 0.003	2.109 ± 0.007
MMC44 (HWJ)	18.251 ± 0.05	15.643 ± 0.05	38.379 ± 0.19	0.857 ± 0.001	2.103 ± 0.009
MMC46 (HWJ)	18.180 ± 0.06	15.640 ± 0.03	38.394 ± 0.14	0.860 ± 0.002	2.112 ± 0.005
MMC47 (HWJ)	18.164 ± 0.05	15.637 ± 0.06	38.368 ± 0.15	0.861 ± 0.001	2.112 ± 0.005
MMC49 (HWJ)	18.186 ± 0.04	15.647 ± 0.05	38.398 ± 0.16	0.860 ± 0.003	2.111 ± 0.010
MMC52 (HWJ)	18.152 ± 0.09	15.611 ± 0.10	38.387 ± 0.22	0.860 ± 0.003	2.115 ± 0.007
MMC53 (a)	*18.141 ± 0.07*	*15.623 ± 0.03*	*38.345 ± 0.15*	*0.861 ± 0.004*	*2.114 ± 0.015*

the analysis of BCR 288, being about 7%. Quantification limit (QL) was determined following the Validation of Analytical Procedure Methodology Guidelines reported by the International Conference on Harmonisation Expert Working Group (International Conference on Harmonisation (ICH) of Technical Requirements for the Registration of Pharmaceuticals for Human Use, 1996). The value obtained was based on the low range concentrations of the standards used to establish the calibration curve, being 2.69 mg kg^{-1}.

Measurements were carried out with an ICP with a Quadrupole mass spectrometer, ELAN DRC-e (*Axial Field Technology*) from Perkin Elmer *Sciex* installed at CTN, IST, Lisbon University. Further details of this analytical method and operating conditions have been described elsewhere (Gomes et al., 2016).

4. Results and discussion

Pb isotope ratios and Sn contents

Sn content values of lead artefacts from both sets (*glandes* and *fistulae*) are presented in Table 1.

Results point to variable Sn content, ranging from values below the detection limit (0.81 mg kg^{-1}) up to 0.44 wt% for *glandes plumbeae*, while for *fistulae aquariae* the Sn content varies between *c.* 2.69 mg kg^{-1} (the quantification limit) and 0.89 wt%.

Lead isotopes have different origins: ^{206}Pb, ^{207}Pb and ^{208}Pb are radiogenic nuclides produced by radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively, while ^{204}Pb is not a product of radioactive decay and its concentration remains constant along the time. Therefore, terrestrial rocks have Pb isotope ratios (^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb) that continuously increase and their values depend on the age of geological deposits. Pb isotope ratios of *glandes plumbeae* and *fistulae aquariae* are presented in Tables 2 and 3, respectively.

In Fig. 2 are displayed the binary diagrams of ^{206}Pb/^{204}Pb *versus* ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb (Stos-Gale and Gale, 2009) for all the analysed samples.

Results make possible to distinguish two groups: one made up of 15 out of 24 *glandes plumbeae* and the other by all *fistulae aquariae* and the remaining (nine) *glandes plumbeae*. The first group of artefacts suggests the use of raw materials with a distinct origin from those used on *fistulae aquariae*. Lead samples of *fistulae aquariae* from *Conimbriga* define the following isotopic distribution: ^{206}Pb/^{204}Pb 18.075–18.368, ^{207}Pb/^{206}Pb 0.853–0.862, and ^{208}Pb/^{206}Pb 2.093–2.127, while the isotopic signature of those 15 *glandes plumbeae* from Alto dos Cacos presents a different distribution: ^{206}Pb/^{204}Pb 18.342–18.548, ^{207}Pb/^{206}Pb 0.845–0.850, and ^{208}Pb/^{206}Pb 2.079–2.107. These results point to distinct raw materials from different mineral deposits used in the manufacture of the two sets of artefacts, which are of different

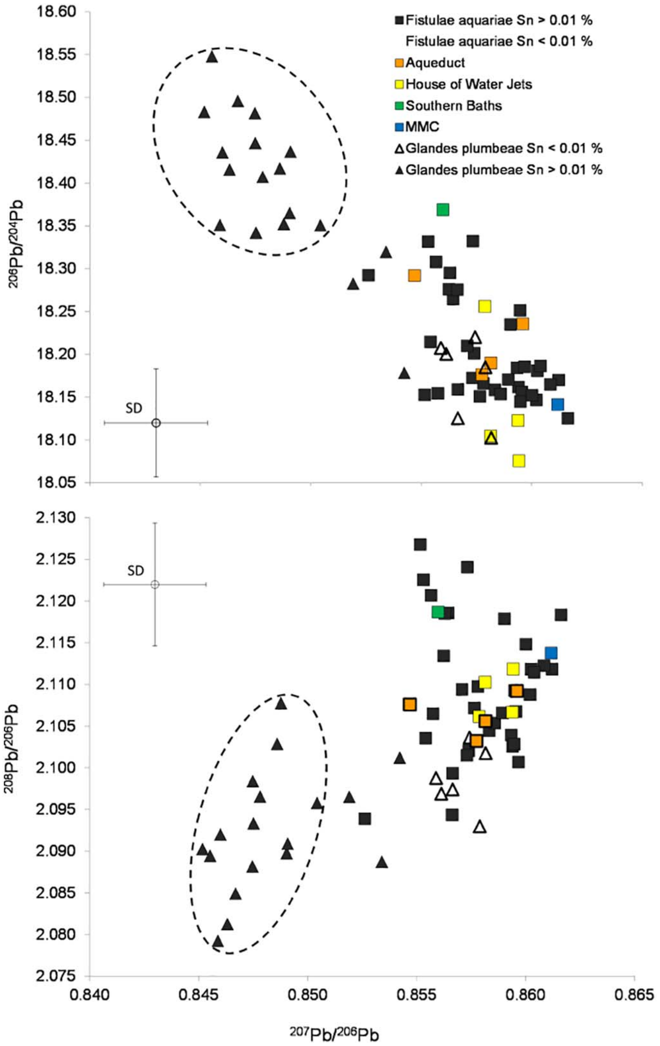

Fig. 2. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ *versus* $^{207}Pb/^{206}Pb$ plots for *glandes plumbeae* from Alto dos Cacos and *fistulae aquariae* from *Conimbriga*.

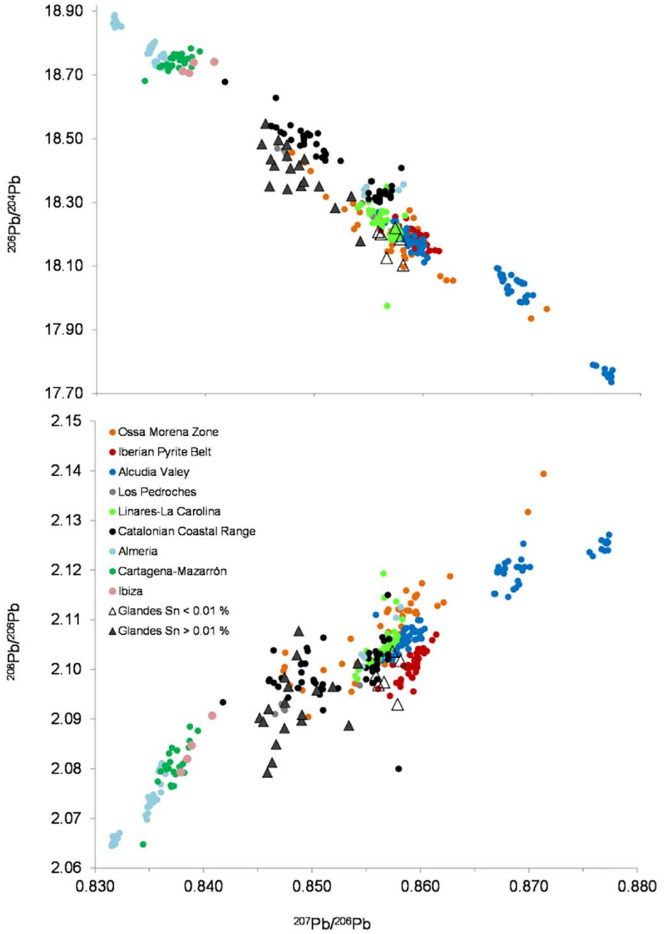

Fig. 3. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ *versus* $^{207}Pb/^{206}Pb$ plots for *glandes plumbeae* compared with Pb isotope ratios of lead ore sources from the Iberian Peninsula.

chronology and recovered at two sites of the Portuguese territory. Accordingly, 15 *glandes plumbeae* seem to be produced with raw materials from ores mined in geological deposits older than those used in the manufacture of *fistulae aquariae* from *Conimbriga*. On the other hand, it can be seen that the distribution of Pb isotope ratios of *glandes plumbeae* is approximately rectilinear in the plot $^{206}Pb/^{204}Pb$ *vs* $^{207}Pb/^{206}Pb$ occupying the samples of lower Sn content one of the extremes, which also correspond to the lower values of $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$.

Since the mines of the Catalonian region were in operation during the Republic and the Empire, a provenance of lead raw materials from the Catalonian region is possible. Then it should be investigated if the data obtained with our samples is coincident with the isotopic field from that region. Pb isotope ratios of the *glandes plumbeae* are plotted in Fig. 3 together with published Pb isotopic data of lead ores sources collected from several Iberian mining areas, including the Catalonian Coastal Ranges (see Gomes et al., 2016 and Canals and Cardellach, 1997 for references concerning the database used). Besides, the Pb isotope ratios of the published data by other authors of Cartagena mining district and also of Ibiza mines (early exploited by Phoenicians) were also added (Ramon et al., 2011). Results show that Pb isotopic ratios are clearly distinct from Cartagena-Mazarrón, Almeria and Ibiza, and somehow inconclusive concerning Catalonian Coastal Range, since they do not entirely match the Catalonian isotopic field.

Pb isotope ratios of the *fistulae plumbeae* are plotted in Fig. 4 together, as in Fig. 3, with the same isotopic field of lead ores. This set of artefacts clearly indicates that a Catalonian source for the raw materials must be discarded.

In order to be able to ascertain about artefacts provenance, discussion will be focused on those presenting evidence of being manufactured with not recycled materials (Sn $<$ 0.01%). Then 25% of *fistulae aquariae* (11 out of 44) are possibly made of non-recycled metal and the same occurred for *glandes plumbeae* (6 out of 24). Nevertheless, it must be noted that only 25% of the sling bullets have a Sn content between 0.1 and 0.4 wt%, while 64% of the lead pipes have a Sn content between 0.1 and 0.9 wt%. Since the Sn content do not introduce any improvements in the properties of the lead metal (Wyttenbach and Schubiger, 1973), then Sn concentrations certainly result from the use of tin solders in lead artefacts that were later recycled. However, the higher Sn content of most lead pipes compared with that of *glandes* may be related with the necessity to use tin solders in large amounts to join the various sections of the pipes and also in repairs. On the other hand, the Sn solder was more available in lead scrap at the producing pipes workshops. Besides, a large-scale lead production began with the Republic and continued throughout the Empire. Therefore the availability of scrap metal has been increasing over time and the same will have occurred with the recycling operations. It must be noted that five out of seven samples of the Aqueduct from *Conimbriga*, the oldest sampled plumbing system of this Roman city, built during the reign of Claudius (41–54 CE) (Correia, 2013), belong to the group of 11 lead pipes with a Sn content $\leq$ 0.01 wt% (Table 1). Also four samples from the House of Water Jets (HWJ), which was built during the 1st century and had a large refurbishment during the reign of Hadrian (117–138 CE), have a

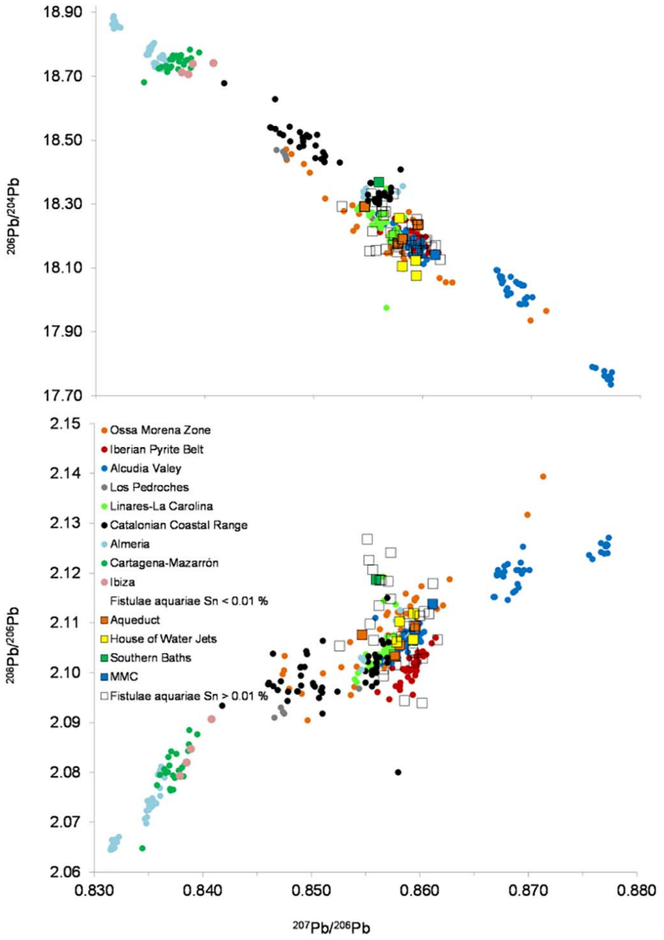

Fig. 4. ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb plots for *fistulae plumbeae aquariae* compared with Pb isotope ratios of lead ore sources from the Iberian Peninsula.

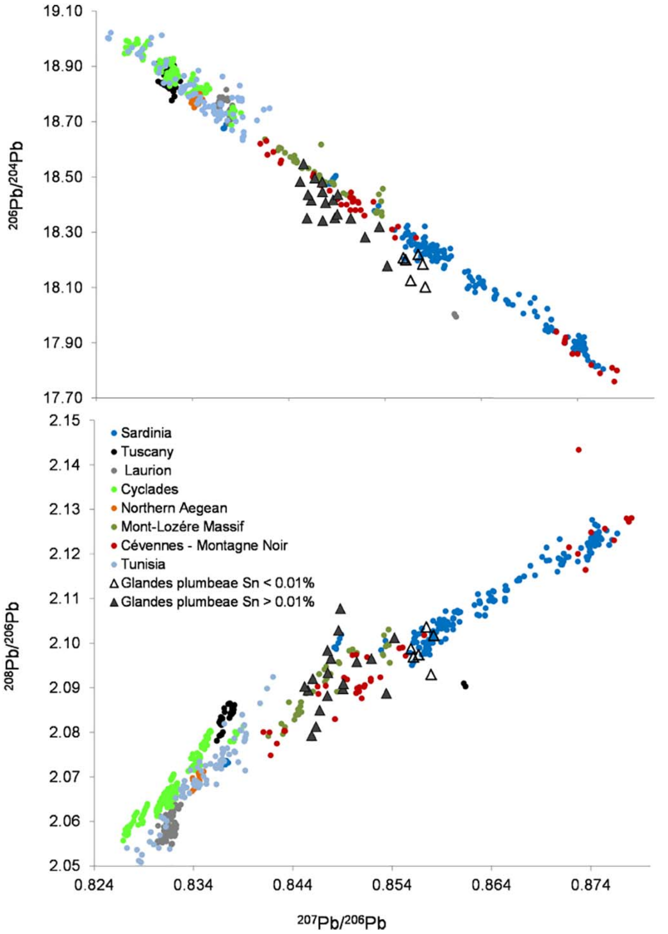

Fig. 5. ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb plots for *glandes plumbeae* compared with Pb isotope ratios from lead ore sources in the Mediterranean regions.

low Sn content, perhaps pointing out that these four lead pipes belong to the first building. The remaining two samples, one corresponds to a lead pipe which archaeological context is unknown, while the other is from *fistulae aquariae* recovered from the Southern Baths, a public building also built during the 1st century CE.

Since we are assuming a Sn content of 0.01 wt% as the boundary between lead raw material probably not recycled and recycled, then the Pb isotope ratios of four of those six *glandes* manufactured with no-recycled materials, point to the use of ores from Linares-La Carolina, Alcudia Valley and Ossa Morena Zone (Fig. 3). Nevertheless, the Pb isotope ratios of some Mediterranean ore fields overlap partially with those corresponding to Sierra Morena and Ossa Morena Zone mining districts. On the other hand, it must be taken into account that these leaden sling bullets are small artefacts easily transported from one place to another by Roman legionaries, and a comparison with data from the main ore bodies of the Mediterranean regions exploited during Roman times must be also performed. Therefore, Pb isotope ratios of galena and other lead ore sources from different Mediterranean regions, namely Greece, Sardinia, Tuscany (Boni and Koeppel, 1985; Stos-Gale et al., 1995, 1996), Mont-Lozére Massif and Cévennes-Montagne Noir, in *Gallia Narbonensis* (Trincherini et al., 2001; Baron et al., 2006) and Tunisia (Skaggs et al., 2012) were plotted in Fig. 5 together with those of *glandes plumbeae*.

It can be seen that four samples with Sn ≤ 0.01 wt% can also be ascribed to Sardinian ores, while some of those made with recycled lead may have been made with lead with this origin (or with the Iberian origins referred to above) mixed with a leaden raw material which source can be ascribed to the *Gallia Narbonensis* (regions of Cévenne-Montagne Noir and Mont-Lozére Massif). Nevertheless, there are several lead samples which source or sources remain unknown. However, one may consider that leaden sling bullets could be of local production and the slingers themselves indigenous from Iberia. These were famous in Antiquity, namely the slingers from the Balearic Islands, first mentioned fighting for Carthaginians in Sicily at the battle of *Ecnomo* (310 BCE; *Diodorus Siculus Bib*. *Hist*. V.17.1) (Walton, 1963) and later mentioned by *Strabo* (*Geog*. III.5.2), *Livius* (A.U.C. 18.5-7) and *Vegetius* (*De Re Militari*, I) (Jones, 1923). A recent research concerning lead sling bullets from different Spanish sites, with similar dating and contexts, was carried out also using Pb isotope ratios (Müller et al., 2015). Sling bullets from Sanisera (Baleares), Monzon (Northern Spain) and Cerro de Balas (Southern Spain) seem to be manufactured with lead imported from Sierra Morena (Monzon and Cerro de Balas) and Cartagena (Sanisera) regions. Besides, it cannot be discarded that Iberian lead ore sources not explored by the Romans may have been previously exploited in small scale by indigenous communities and also that values for Pb isotope ratios of many ore deposits are still quite limited. Moreover, the main supply of legions from Italy along the *Via Domitia* could explain the use of ores from *Gallia Narbonensis*. However, as mentioned above, other *glandes* have isotope ratios that cannot be assigned with certainty to any known Mediterranean source. This fact probably is due to the Roman legions movements during the conquests of the western territories in 1st century BC. Our current knowledge of the conformation of legionary forces stations in West and their *auxilia* is insufficient for a further discussion on this topic.

Concerning Pb isotope ratios of lead pipes with low Sn content, those ratios point to ore sources located at the Sierra Morena, namely Alcudia Valley and Linares-La Carolina, and also the Ossa Morena

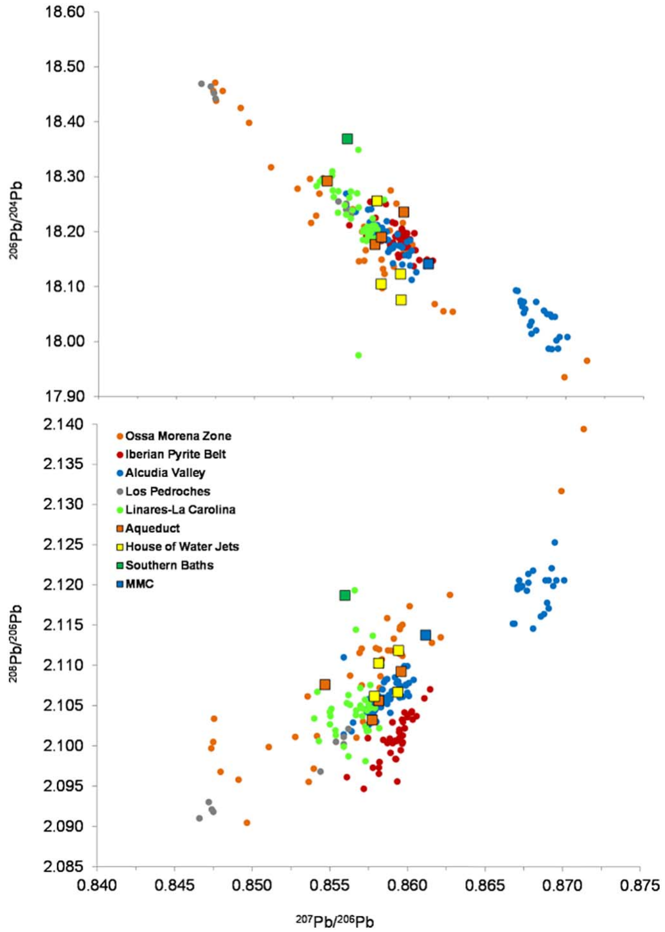

Fig. 6. ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb plots for *fistulae aquariae* with Sn ≤ 0.01% compared with Pb isotope ratios from lead ore sources in the Iberian Pyrite Belt, Ossa Morena Zone, Alcudia Valley, Linares-La Carolina and Los Pedroches.

mining district (Figs. 4 and 6). In addition, it is possible that some artefacts have been made with lead mixed from the Iberian Pyrite Belt ore sources. This raw material mixture could be explained by the lead obtained of litharge reduction, a by-product resulting of cupellation process, where it is added lead in order to facilitate the recovery of the silver directly from plumbojarosite or argentiferous jarosite ores (Anguilano et al., 2010).

A similar situation occurs with the roman lead pipes from *Pompeii* which evidence a mixed provenance due to a local recycling of older pipes and lead objects (Boni et al., 2000). The wide heterogeneity of the Pb isotopic ratios in *Pompeii* and *Conimbriga*, together with a high Sn content, suggests the recycling of lead in which tin solder had been used. The recycling of lead becomes a common practice probably also due to economic constraints. Pernicka (2014) refers, as a good example, the lead pipes of the late Roman Empire, as well as the analysis of a Byzantine shipwreck discovered on the Mediterranean coast (Kahanov et al., 2015). As already mentioned, an ore source identification becomes problematic due to the use of this practice.

5. Conclusion

The research based on the Sn content and Pb isotope ratios distribution of *glandes plumbeae*, ascribed to the Roman Republic, and *fistulae aquariae* (Roman Empire), recovered in Portuguese territory, allows to differentiate several ore sources with chronological meaning for the raw materials used in their manufacture.

A lower Sn content (≤ 0.01 wt%) indicates that artefacts were made probably with pure lead, while higher Sn contents point to the recycling of lead in which tin solder had been used. About 25% of the sling bullets have a Sn content between 0.1 and 0.4 wt%, while 64% of the chronologically later lead pipes have a Sn content between 0.1 and 0.9 wt%, indicating that recycled lead became more frequent as time passed.

Pb isotope ratios allow to distribute the studied artefacts into two groups: one composed of all *fistulae aquariae* and some *glandes plumbeae* (44 and nine, respectively), and the other with the remaining *glandes* (15). Although some *glandes plumbeae* have a comparable isotopic signature with that one of *fistulae*, a reliable provenance cannot be assigned to the same ore sources.

The isotope signature of *fistulae* suggests the mines from Alcudia Valley, Linares-La Carolina and Ossa Morena, or a mixture of these with lead ores from the Iberian Pyrite Belt as the most probable provenance for the (non-recycled) lead samples. Some samples with high Sn content (probably recycled) may be a result of mixtures of the above mentioned raw materials or, according to our present knowledge, even with others from diverse sources which isotopic signatures have not been published.

On the other hand, the provenance of lead of the most of *glandes plumbeae* should be sought in the Mediterranean region. The Pb isotope compositions of samples with a Sn content ≤ 0.01 wt% match the Pb isotope signature of ores from Linares-La Carolina, Alcudia Valley, and Ossa Morena Zone, which overlap with that one of Sardinian ores. However, *glandes* with high Sn content seem to have been made with raw materials resulting from a mixture of Mediterranean or Iberian lead with a provenance mentioned above with lead from *Gallia Narbonensis* (regions of Cévenne-Montagne Noir or Mont-Lozére Massif). Also in this case of sling bullets, there are several samples of lead whose provenance is not possible to determine.

This research also shows the importance of the evaluation of the Sn content on lead samples for a reliable interpretation of the Pb isotopic compositions, since recycling operations were very common all over the Roman Empire and during the Republic. A spreading out of the Pb isotope ratios database from Iberian lead ores is also necessary since the results obtained in this work indicate that there will certainly be many lead mines which ores are not yet analysed for Pb isotope signatures.

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