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Lead isotopes and elemental composition of Roman *fistulae plumbeae aquariae* from *Conimbriga* (Portugal) using Quadrupole ICP-MS

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ABSTRACT

Lead metal and lead artefacts were widespread over the Roman world, as consequence of its large use in public buildings, namely as plumbing on hydraulic systems of Roman cities and *villae*. The determination of Pb isotope ratios combined with minor and trace element contents of such lead artefacts may constitute a powerful tool for provenance studies as well as in the assessment of trade routes during the Roman period. In the present work forty four *fistulae plumbeae* from the hydraulic systems installed at *Conimbriga* were analysed using a quadrupole based ICP-MS. The overall results demonstrate the suitableness of this well-established and economic analytical technique involving simple sample preparation and high throughput. Pb isotopic patterns present high scattered distributions which suggest different provenances of the raw material. Ag, As, Bi, Cu, Ni, Sb, and Sn contents were determined in an attempt to identify the type of raw materials and the metallurgical process used to obtain the lead metal. Sn content points to the frequent use of recycled lead. The Pb isotope ratios of samples of lead pipes made with metal probably not recycled indicate the use of raw materials (galena ores) from Sierra Morena mines or desilvered litharge resulting from silver cupellation probably using argentiferous jarosite ores from the Iberian Pyrite Belt (Rio Tinto mines).

1. Introduction

The spread of Romanization increased the demand of metals due to economic and military reasons and, at the same time, new areas of ore supply came within the sphere of exploitation of the Roman Empire. The Iberian Peninsula became an important ore source, being even referred by some authors as the Hispanic mining district. One of the largest mining activities was located in Huelva district (Southern Spain), notably at Rio Tinto, where jarosite-type minerals became a main silver source. But, as it is known, on the silver metallurgy the smelting of these ores usually requires the addition of a large amount of lead in order to collect the silver, which is later separated from the lead by cupellation. Pliny, the Elder, in the 1st century AD, wrote on his book *Naturalis Historia* [1] about the need of this metal for the silver extraction.

Therefore, lead became of great economic importance, not only due to the large scale of silver production, but also due to its frequent use in hydraulic and architectural structures. On the other hand, it seems that there was a lead scarcity for the silver cupellation process in the Iberian Pyrite Belt, as suggested by findings of imported lead ingots from Cartagena-Mazarrón region (Eastern Iberian Peninsula) at Rio Tinto mines [2–4]. Thus, research on provenance of lead metal or lead artefacts, which were fairly widespread at this time, may give important indications on the mining exploitation, metal use and trade routes.

The relevance of Pb isotope characterization is widely recognized as a powerful tool for provenance research. Since Pb isotope ratios do not change during metallurgical processes remaining identical on the produced artefacts to those on the ores, the Pb isotopic signature may associate artefacts to a particular/distinct mineral deposit [5–9]. However, some difficulties may arise in the interpretation of isotopic data. For instance, Craddock [2] mentions that Pb isotope analyses on Roman metallurgical remains of silver production at Rio Tinto mines indicate that the lead found in slag resulting from the smelting of argentiferous jarosites has its origin at different mining regions (being difficult the attribution to a particular provenance) although the imported lead ingots found at the mines were from the mining region of Cartagena-Mazarrón.

Nevertheless, Pb isotope characterization of artefacts and metallurgical remains can be complemented with the determination of the concentrations of minor (content between 1000 mg kg^{-1} and 10,000 mg kg^{-1}) and trace (content $<$1000 mg kg^{-1}) elements to achieve a better discrimination of lead ore sources. Contrary of Pb

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isotope distribution, which remains constant during metallurgical processes, the elemental composition is often changed in the process, but it can provide some indication on the source and type of raw materials used. Accordingly to Gale and Stos-Gale [5], the resulting lead from litharge (a by-product from the cupellation process) could contain As, Cu, Sb and Sn, among other impurities, because jarosites and argentiferous lead ores are enriched with a diversity of elements which are reduced and/or oxidized with lead during the smelting and the cupellation processes. However, Au and most of Bi remain with the silver [2]. Consequently, the concentrations of those elements in lead artefacts can be a good indicator to the type of lead ores used as the metal source. Also the Ag content in the lead metal is a good fingerprint concerning the origin of lead: litharge reduction or smelting of a galena ore. Moreover, the Sn content can be an important indicator for the existence of recycling of lead metal [10,11]. Chemical analysis of lead ingots has shown, in general, a very low Sn content, in the order of few mg kg^{-1} [12,13].

The analytical technique frequently used for determination of Pb isotope ratios, and also of minor and trace elements composition, is the inductively coupled plasma mass spectrometry (ICP-MS). In the last decade, this technique has been increasingly used in Archaeometry for elemental analysis [14,15] and for provenance studies of metal artefacts [16–22]. An ICP-MS instrument is composed by a plasma ion source which operates with a high efficiency, allowing the analysis of very small samples. The sample introduction system consists in a continuous nebulisation of a solution with a higher throughput for fast and routine analysis [17]. Sometimes an ICP-MS can be associated with laser ablation (LA-ICP-MS) for the almost non-destructive analysis of valuable objects or artefacts, easing the sample preparation and allowing a better spatial resolution [23,24].

The present work is focused on the determination of Pb isotope ratios and minor and trace elements composition on lead artefacts by a quadrupole based ICP-MS. Results were obtained on the analysis of the Roman lead pipes (*fistulae plumbeae aquariae*) from the hydraulic systems used at *Conimbriga*, a large Roman town in Central Portugal. These results were essential on the attribution of the type and origin of the raw materials.

2. Experimental

2.1. Studied material and archaeological context

The set of 44 lead water pipes (*fistulae plumbeae aquariae*) selected for this study belong to the collection of the Museu Monográfico e Ruínas de Conimbriga (Condeixa, Portugal), one of the richest sites in archaeological collections and excavated buildings (residential, public baths and aqueduct) belonging to the Roman world. *Conimbriga* was an important urban centre located in ancient *Lusitania,* which apogee occurred between I and IV centuries AD, with architectural structures built up along several periods. In particular, important hydraulic engineering changes began since the Augustan period with the building of the first public bath and aqueduct, *c.* 10 BCE. Afterwards, it was implemented the generalization of water distribution, *c.* 40–50 CE, and a creation of garden architecture with an outstanding complex water system, known by “house of water jets”, *c.* 117–138 CE. The analysis of such structures can provide information about the materials sources and the metallurgical techniques used on the manufactured of lead plumbing pipes. For the present work, small samples were collected from distinct parts of the pipes of the *Conimbriga* hydraulic systems, namely: seven from pipes of Aqueduct (41–54 CE) [25]; one from the Southern Baths (69–117 CE) [25]; one from the House of Cantaber (69–96 CE) [26]; 32 samples from the House of water jets (117–138 CE) [26,27]; two from Northern *Insulae* (41–68 CE) [25]; and one from an unknown (not recorded) archaeological context (Table 1).

2.2. Analytical method

All procedure of sample preparation and analysis by quadrupole ICP-MS were performed in a clean room, Class 5, with a laminar flow hood. Only polypropylene (PP), low polyethylene density (LPDE), polytetrafluoroethylene (PTFE or TEFLON) or perfluoralcoxy (PFA) materials were used in the sample preparation.

Pb isotopic ratios determinations and elemental measurements were carried out with a quadrupole ICP-MS, ELAN DRC-e (Axial Field Technology) from Perkin Elmer Sciex. This equipment is composed by a peristaltic pump, a concentric nebulizer, a cyclonic spray chamber with a Peltier cooled PC3, sampler and skimmer Ni cones, a quadrupole filter as mass analyser, and a discrete dynode electron multiplier with a simultaneous pulse and analogue detector. The operating conditions and the acquisition parameters of the instrument are presented in Table 2.

In each session operating conditions were optimized to reach the performance criteria recommended by the manufacturer: low levels of oxides CeO^+/Ce^+ and double charged ions Ba^{2+}/Ba^+ ($\leq 0.03\%$); sensitivity for Mg ≥ 50,000 count s^{-1}; U ≥ 200,000 count s^{-1} and In ≥250,000 count s^{-1}.

2.2.1. Reagents and standard

Samples and the reference materials were dissolved with 20% HNO_3 solution from HNO_3 65% (MERCK) purified by sub-boiling distillation (bi-distilled) and diluted with water ultra-pure (18.2 MΩ cm) obtained with a MilliQ water purification system (Millipore).

NIST 981 (Common Lead Isotopic Standard) from National Institute of Standards and Technology was used as a mass bias correction solution for isotope ratio analysis. To correct the mass bias discrimination, the software package ELAN version 3.4 calculates a ratio correction factor (RCF) [28,29], based on the following equations:

$$RCF = {}^{Sknown}\Big/_{Smeasured} \tag{1}$$

Sknown is the certified isotope ratio of the NIST 981 and *Smeasured* is the measured, blank-corrected isotope ratio of the standard. Once determined the RCF, the correction factor is applied to the results to get the real isotope ratio:

$$Xtrue = {}^{Xmeasured}\Big/_{RCF} \tag{2}$$

Xmeasured is the isotope ratio measured by the instrument and RCF is the correction factor previously calculated. The certified Pb isotope ratios of standard NIST 981 are: $^{206}Pb/^{204}Pb = 16.973$; $^{207}Pb/^{206}Pb = 0.9146$; $^{208}Pb/^{206}Pb = 2.1681$. A stock solution was prepared with 80 μg L^{-1} concentration. The accuracy of the analytical determinations was ≤0.2%.

A calibration method was used for elemental composition determination with external standardization. Two Multi-element Calibration Standard 3 and Standard 4 solutions (Perkin Elmer) were used for the calibration. BCR 288 (Lead Containing Added Impurities) standard from Community Bureau of Reference was used as a reference material (Table 3). A stock solution 20 g L^{-1} was prepared from 1 g of the BCR 288 standard. In order to minimize drift effects, instrument instability and matrix effects an internal standard of 10 μg L^{-1} Re was added to each sample and standard solutions.

SmartTune Solution-Std Elan & DRC-e and ELAN 6100 Set up/Stab/MassCal standards solutions by Perkin Elmer Pure Atomic Spectroscopy Standard were used for daily and monthly optimization and tuning. Measurement sequences begin with blank and standard solutions (NIST 981 for Pb isotope measurements and the multi element calibration standards and BCR 288 for elemental determinations). A blank and a standard solution for quality control were analysed between each set of six samples.

Table 1
Samples of the Roman lead water pipes from *Conimbriga* and their archaeological contexts following Alarcão and Etienne [25], Correia [26], and Pilar and Correia [27].

Laboratory sample reference	MMC inventory number	Archaeological context	Chronology
MMC1		House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC2		Northern *Insulae*(*NI*)	Claudius-Nero (41–68 CE)
MMC4	260	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC5	270	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC6	272	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC7	275	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC8		House of Cantaber(*HC*)	Flavian dynasty (69–96 CE)
MMC9		Aqueduct(*A*)	Claudius (41–54 CE)
MMC10		House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC12		Southern Baths (*SB*)	Flavian dynasty or Trajan (69–117 CE)
MMC13		Aqueduct(*A*)	Claudius (41–54 CE)
MMC14		Aqueduct(*A*)	Claudius (41–54 CE)
MMC15		Aqueduct(*A*)	Claudius (41–54 CE)
MMC16		Aqueduct(*A*)	Claudius (41–54 CE)
MMC17		Aqueduct(*A*)	Claudius (41–54 CE)
MMC18		Aqueduct(*A*)	Claudius (41–54 CE)
MMC19	238	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC20	239	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC21	240	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC22	241	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC23	242	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC24	243	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC 25	244	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC26	245	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC27	246	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC28	247	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC29	248	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC30	249	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC31	250	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC32	251	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC33	252	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC34	253	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC35	254	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC37	255	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC38		Northern *Insulae*(*NI*)	Claudius-Nero (41–68 CE)
MMC39	258	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC40	259	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC42	261	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC44	263	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC46	271	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC47	273	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC49	276	House of water jets(*HWJ*)	Hadrian (117–138 CE)
MMC52	269 (A55)	House of water jets (*HWJ*)	Hadrian (117–138 CE)
MMC53		Unknown. Not recorded	

Table 2
Operating conditions for Quadrupole ICP-MS ELAN DRC-e (Number of readings: 1; number of replicates: 5).

Plasma gas	Argon
RF Power	1100 W
Plasma gas flow	15 L min^{-1}
Auxiliar gas flow	1.20 L min^{-1}
Nebulizer gas flow	0.80 L min^{-1}
Sample uptake rate	1 mL min^{-1}
Acquisition parameters	
Pb isotope measurements	
Dwell time	^{204}Pb 50 ms ^{206}Pb and ^{207}Pb 20 ms ^{208}Pb 10 ms
Sweeps	400 ms
Scan mode	Peak hopping
Detector mode	Dual stage discrete dynode electron multiplier
Ag, As, Au, Bi, Cd, Cu, Ni, Sb, Sn measurements	
Dwell time	Variable
Sweeps	30
Detector mode	Dual stage discrete dynode electron multiplier

2.2.2. Sample preparation

The corroded superficial layer was removed (to avoid exogenous materials contamination) in an area of *ca.* 1 cm^2 prior to sample collection for elemental and isotopic analysis. Afterwards, a small amount (~50 mg) was taken with a drill (HSS DIN 338 bits) with 1 or 1.5 mm in diameter on the cleaned area (Fig. 1).

Due to the archaeological and museological relevance of the studied samples and in order to preserve the characteristics of artefacts the amount of collected sample allowed the preparation of a single sample dissolution for analysis.

Each sample was transferred to a polypropylene tube, where it was dissolved with 25 mL of the 20% HNO_3 solution and heated for 90 min at 35 °C in an ultrasonic bath. The certified reference materials, NIST 981 and BCR 288, were prepared following the same procedure. An aliquot of each sample solution was diluted to 100 μg L^{-1} in 1% HNO_3 for Pb isotope ratio determinations.

Due to the wide variation range on the minor and trace elements contents, analytical measurements implied variable calibration ranges and dilutions. An aliquot of each sample solution was diluted 1:20 for the determination of the elements present in trace amounts (Ag, As, Au, Bi, Cd, Cu, Ni, Sb and Sn). For the elements present as minor contents, usually Sb and Sn, the sample solution was diluted 1:100. Detection limits (DL) were determined following the Validation of Analytical Procedure Methodology Guidelines reported by the

Table 3
Results obtained for Certified Reference Material BCR 288 (Mean and standard deviation for 4 determinations).

BCR 288	Certified values (mg kg^{-1})	Experimental values (mg kg^{-1})	Accuracy (%)
Ag	30.5	28 ± 0.54	9
As	55.7	48 ± 0.26	14
Bi	215.8	173 ± 2.61	20
Cu	19.3	14 ± 0.29	25
Sn	30.6	27 ± 1.18	7
Sb	32.5	35 ± 5.8	11

International Conference on Harmonisation (ICH) Expert Working Group [30]. Calculations were based on the low range concentrations of the standards used for each calibration curve and obtained results correspond to the following values for the analysed samples: Ag 0.52 mg kg^{-1}; As 1.43 mg kg^{-1}; Au 12.29 mg kg^{-1}; Bi 0.94 mg kg^{-1}; Cd 0.95 mg kg^{-1}; Cu 0.81 mg kg^{-1}; Ni 0.87 mg kg^{-1}; Sb 1.32 mg kg^{-1}; Sn 0.81 mg kg^{-1}.

3. Results and discussion

3.1. Elemental analysis

Elemental compositions of the 44 analysed lead Roman pipes of *Conimbriga* are presented in Table 4.

The results show a high variability on the elemental concentrations. Cu is present as minor or trace element, ranging concentrations from 0.02 to 0.19%. Sn and Sb are higher being present as minor elements in most of the lead pipes (28 and 37 samples, respectively). Sb concentrations vary from 0.03 up to 0.36%, while Sn concentrations present a quite distinct behaviour. For a significant number of samples (10) Sn concentrations are very low (≤5 mg kg^{-1}) while for a larger group of pipes (28) Sn concentrations are above 0.1%, and for the majority of them (24) higher than 0.3%, reaching values of about 0.9%. A probable explanation to this enriched Sn values is the common use of tin solders by Romans in the manufacture of such lead water pipes [12,31]. The used solders would be an alloy composed by two parts of Pb and one part of Sn (called *tertiarium* by Pliny on *Naturalis Historia* [32]), but a solder richer in Sn (two parts of Sn and one part of Pb) was found in two *fistulae* seals from *Conimbriga* [33]. In general, the Sn amount in galena ores is different at each mining area, but usually is <100 mg kg^{-1}, although in a restricted region in the Northeastern Iberian Peninsula some galena ores have a mean Sn content value of 800 mg kg^{-1} [10, 11]. Therefore, the presence of Sn with concentrations around or above 1000 mg kg^{-1} (0.1%) in the lead metal might indicate the existence of recycling operations [11]. Thus, lead water pipes with very low Sn content would have most likely been made with not recycled lead. Ag, As, Bi and Ni are systematically present as trace elements. Ag content is quantified in all samples reaching a maximum value of 346 mg kg^{-1}, which means, in a first approach, that the lead was obtained from reduction of desilvered litharge or from the smelting of silver-poor galena ores [10]. According to some authors [2,10], during Roman period, litharge or galena ores with a Ag content of 400 mg kg^{-1} or higher would have been used to extract silver. Arsenic (As) is not detected in two samples, being 379 and 903 mg kg^{-1} the higher measured concentrations. Bi and Ni contents are below the quantification limits (3.15 mg kg^{-1} and 2.9 mg kg^{-1}, respectively) in two and three samples, and average values are 54 mg kg^{-1} and 30 mg kg^{-1}, respectively. Au and Cd were also analysed, but not measurable (below to detection limits).

The elemental distribution determined in the analysed *fistulae plumbeae* from *Conimbriga* (Table 4) is presented in the following diagrams: Cu—Sn and Cu—Ni (Fig. 2a, b), Ag—Cu, Ag—Sn and Ag—Bi (Fig. 3a–c), and Sb—Ag and Sb—As (Fig. 4a, b). As it is known, metal recycling usually leads to a substantial change in concentrations of the various chemical elements (and isotopic compositions as well) making it impossible to determine with accuracy the sources of raw materials. As a consequence of the recycling process identified in our set of samples, the following discussions and inferences will discriminate samples with low tin contents, namely those from Aqueduct, Southern Baths, Unknown and MMC20, MMC24, MMC30, MMC39, MMC49, MMC52 from the House of water jets.

In the analysed lead pipes from *Conimbriga* the higher Cu contents (>0.1%) mostly occur in those having low Sn concentrations (<0.1%). It is evidenced that the seven samples from Aqueduct, the sample from the Southern Baths and two samples from the House of water jets (MMC49 and MMC52) have significantly higher Cu content (0.11–0.19%) although rather low Sn concentration values (mostly below or close to the quantification limit, Table 4). Besides, the same group of samples also present significantly higher Ni contents, which is not usual in lead ores. Ni may occurs associated with Cu [16] and the existence of enriched values in both elements in the lead metal is probably provided by the smelting of a complex polymetallic ore containing Cu

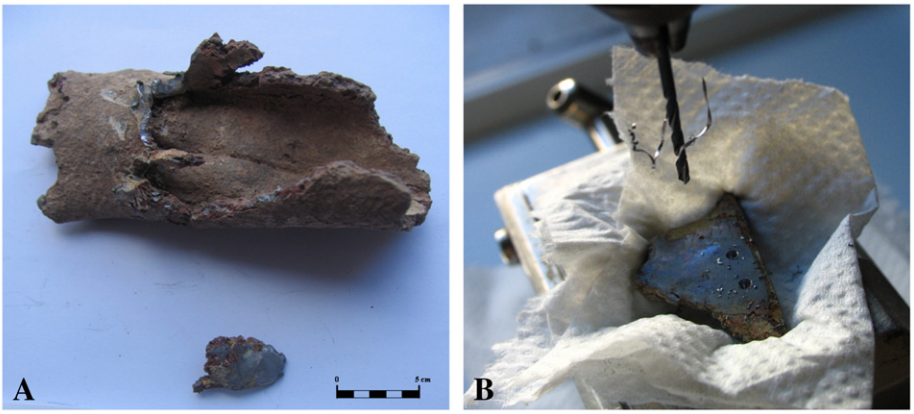

Fig. 1. A – Fragment of a *fistula plumbeae* deposited in Museu Monográfico e Ruínas de Conimbriga; B – Drilling of a sample with the corroded superficial layer removed.

Table 4
Minor and trace elements content of *fistulae plumbeae* from *Conimbriga* performed by a Quadrupole ICP-MS (Single determination of Cu, Sb, Sn in %, unless otherwise stated, and Ag, As, Bi, Ni in mg kg^{-1}, n.d. – not detected; (a) – not recorded).

Laboratory sample reference	Archaeological context	Cu	Ag	As	Bi	Ni	Sb	Sn
MMC1	*HWJ*	0.04	170	323	65	<2.92	0.14	0.34
MMC2	*NI*	0.05	160	39	50	9.6	0.09	0.57
MMC4	*HWJ*	0.07	210	122	90	16	0.13	0.34
MMC5	*HWJ*	0.10	200	134	94	3.0	0.17	0.89
MMC6	*HWJ*	0.07	200	132	108	8.9	0.17	0.45
MMC7	*HWJ*	0.04	225	379	75	<2.92	0.27	0.22
MMC8	*HC*	0.05	170	49	82	7.1	0.07	0.48
MMC9	*A*	0.12	95	40	4.0	36	0.16	3.1 mg kg^{-1}
MMC10	*HWJ*	0.11	190	18	68	17	0.04	0.11
MMC12	*SB*	0.17	350	903	4.2	200	0.36	2.7 mg kg^{-1}
MMC13	*A*	0.17	100	133	45	43	0.16	<2.69 mg kg^{-1}
MMC14	*A*	0.19	90	92	30	97	0.12	<2.69 mg kg^{-1}
MMC15	*A*	0.18	80	46	15	187	0.11	0.03
MMC16	*A*	0.17	85	33	15	105	0.10	0.01
MMC17	*A*	0.13	60	35	6.6	35	0.14	<2.69 mg kg^{-1}
MMC18	*A*	0.18	80	46	15	185	0.11	0.05
MMC19	*HWJ*	0.03	130	34	18	12	0.16	0.09
MMC20	*HWJ*	0.02	140	nd	4.6	7.7	0.05	2.8 mg kg^{-1}
MMC21	*HWJ*	0.03	140	38	18	14	0.17	0.10
MMC22	*HWJ*	0.05	150	187	52	4.7	0.14	0.32
MMC23	*HWJ*	0.07	180	139	60	6.8	0.17	0.43
MMC24	*HWJ*	0.03	150	14	<3.15	7.8	0.23	2.8 mg kg^{-1}
MMC25	*HWJ*	0.06	170	129	77	4.8	0.19	0.38
MMC26	*HWJ*	0.06	150	29	53	5.6	0.03	0.72
MMC27	*HWJ*	0.02	150	204	27	43	0.23	0.39
MMC28	*HWJ*	0.08	150	91	80	8.8	0.13	0.40
MMC29	*HWJ*	0.02	160	189	28	18	0.24	0.37
MMC30	*HWJ*	0.03	170	13	<3.15	7.6	0.23	3.3 mg kg^{-1}
MMC31	*HWJ*	0.07	180	150	65	6.2	0.22	0.34
MMC32	*HWJ*	0.06	170	207	59	6.9	0.16	0.33
MMC33	*HWJ*	0.06	180	130	73	5.9	0.19	0.38
MMC34	*HWJ*	0.06	170	123	75	5.3	0.17	0.38
MMC35	*HWJ*	0.06	160	125	80	5.9	0.19	0.32
MMC37	*HWJ*	0.06	170	127	68	5.1	0.19	0.35
MMC38	*NI*	0.04	160	39	45	<2.92	0.06	0.44
MMC39	*HWJ*	0.02	125	nd	4.9	8.6	0.05	5.0 mg kg^{-1}
MMC40	*HWJ*	0.03	150	38	18	10	0.17	0.10
MMC42	*HWJ*	0.08	180	144	75	7.7	0.22	0.42
MMC44	*HWJ*	0.02	160	190	28	16	0.24	0.39
MMC46	*HWJ*	0.07	180	122	86	4.2	0.16	0.45
MMC47	*HWJ*	0.16	150	71	89	7.9	0.10	0.74
MMC49	*HWJ*	0.11	320	278	131	16	0.35	0.02
MMC52	*HWJ*	0.15	110	37	167	19	0.21	0.05
MMC53	(*a*)	0.03	60	18	3.7	10	0.24	3.7 mg kg^{-1}

and Ni. This might have happened if the lead was obtained from litharge resulting from a metallurgical process that had as primary ore an argentiferous jarosite with crusts of malachite, like those found in the gossan zone of the mines of the Iberian Pyrite Belt [3]. It must be noted that three samples of the House of water jets (MMC5, MMC10 and MMC47) also present high Cu contents (0.10–0.16%) but high Sn and low Ni concentrations. Two of them present the highest values of Sn (0.74–0.89%), pointing to the use of recycled material but also suggesting a different origin for primary lead used in these *fistulae*.

Besides those samples with high Cu and Ni and very low Sn contents, another group of samples with very low Sn content but also with low Cu and Ni contents can be identified (Fig. 2). It consists of samples MMC20, MMC24, MMC30 and MMC39 from the House of water jets and sample MMC53 from unknown provenance. In a first approach, the source of this type of lead metal would be galena ores due to the low content of Ni as mentioned above.

Consequently, the differences between Cu and Ni contents of the two groups can be probably attributed to different primary ores used in the production of the lead metal.

Fig. 3a, b and c display the distribution of Ag *versus* Cu, Sn and Bi, respectively. Obtained results showed that the highest Ag content determined in the analysed set is 346 mg kg^{-1} for MMC12 (Table 4). Therefore, one can assume that the lead metal used in the lead pipes at *Conimbriga* was obtained from reduction of desilvered litharge or from the smelting of silver-poor galena ores [2,10].

The dataset composed by samples from Aqueduct (MMC9, MMC13–MMC18), Southern Baths (MMC12) and House of water jets (MMC49 and MMC52) can be differentiated in two groups according to the Ag content related to the used raw materials. The Ag content has been used to indicate if the lead is obtained by desilvered litharge (cupellation process) or by smelting (reduction) of galena depleted in Ag [10,34]. The low Ag content (63–98 mg kg^{-1}) of the Aqueduct samples to which we can add the sample from a not recorded context (MMC53) suggests that the lead of the pipes was obtained by reduction of litharge. Healy [35] refers that Romans were able to desilver lead successfully to Ag content of 20–100 mg kg^{-1}. Examples are the roman lead ingots found with the inscription EX ARG or EX ARGENT [35] or those, with one exception, found in Great Britain and Switzerland analysed by Wyttenbach and Schubiger [12] or even those with the inscription L. *Carulius Hispallus* with probable origin in Spain [13]. The high Cu content of the Aqueduct samples suggests distinct ores from that one of MMC53, probably argentiferous copper ores or argentiferous jarosites contaminated with malachite or with other copper ore. These would have been used to extract Ag by the cupellation process “followed” by

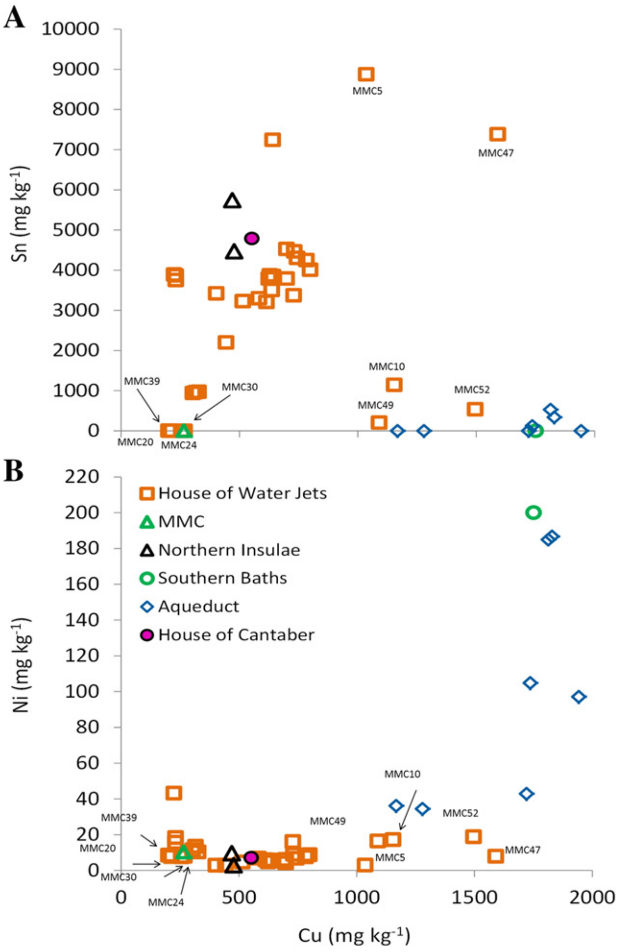

Fig. 2. a) Cu *versus* Sn and b) Cu *versus* Ni for *fistulae plumbeae* from *Conimbriga*.

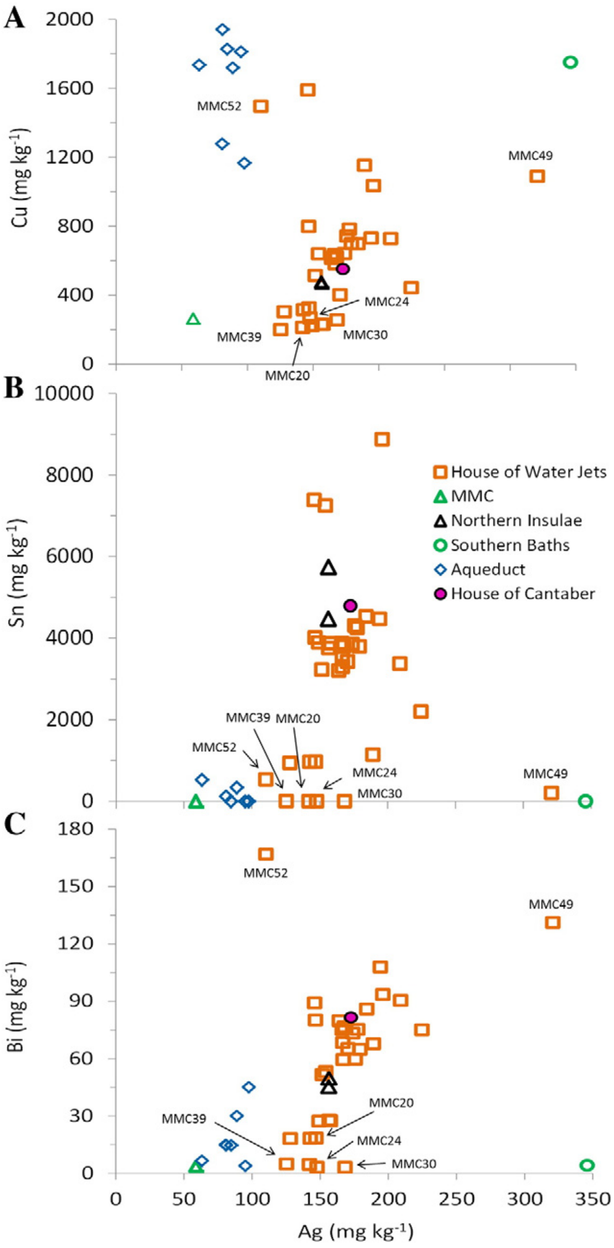

Fig. 3. a) Ag *versus* Cu, b) Ag *versus* Sn and c) Ag *versus* Bi for *fistulae plumbeae* from *Conimbriga*.

a litharge reduction to obtain the "pure" lead [10]. Concerning Bi, as it remains preferentially in molten lead with the silver during the cupellation process [2], the lower concentrations of Ag and Bi and the direct "correlation" between them (Fig. 3c) is an indication of the lead produced from desilvered litharge.

On the contrary, the Southern Baths sample presents the highest Ag content of the analysed samples but a lower Bi content (346 mg kg^{-1} and 4 mg kg^{-1}, respectively) indicating that in this case the lead is obtained by smelting galena depleted in Ag (<400 mg kg^{-1}) [10]. It must be also noted that the higher Cu content of this sample suggests a copper ore contamination during the smelting process. The other two samples (MMC49 and MMC52) of the House of water jets present the highest values of Bi and high values of Cu, but different content of Ag becoming difficult to identify a specific metallurgical process.

Samples MMC20, MMC24, MMC30, and MMC39, all from the House of water jets, have very low content values of Bi, low contents of Cu and Ag concentrations between 125 and 168 mg kg^{-1}, suggesting that the lead could have been also produced from galena ore depleted in Ag.

Fig. 4a and b present the Sb content *versus* Ag and As contents, respectively. A positive correlation between Sb and Ag is often found in lead ores, while a correlation between the volatile elements As and Sb can be found in desilvered lead metal [16]. These correlations must be obliterated in the samples of recycled lead and therefore, as done previously, in the following discussion we only will consider the samples with very low Sn content, *i.e.* samples from lead probably not recycled. Fig. 4a.I displays a positive correlation ($R^2 = 0.200$) between Ag and Sb for the set of lead samples compose by the House water jets (MMC20, MMC24, MMC30, MMC39, MMC49, MMC52), Aqueduct (7 samples), Southern Baths and the unknown sample. Otherwise, if we exclude the lead samples probably produced by lead obtained from litharge, where we include all samples from Aqueduct, MMC52 (House of water jets) and MMC (the unknown sample) the correlation ($R^2 = 0.631$) between these elements is improved (Fig. 4a.II). Therefore, such lead samples would have been produced from a galena ore source depleted in silver.

In what regards the pair Sb—As (Fig. 4b) a general tendency of a positive correlation ($R^2 = 0.428$) is observed, in particular for samples from Aqueduct pointing out to their common origin (litharge) and manufacturing processes.

3.2. Pb isotope analysis

Pb isotope ratios of *fistulae aquariae* (44 artefacts) are presented on Table 5 and Fig. 5.

Results (^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb) are presented as usual in two "mirror" plots [36] in Fig. 5 with two vertical axes ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb, and a horizontal one ^{207}Pb/^{206}Pb. Values

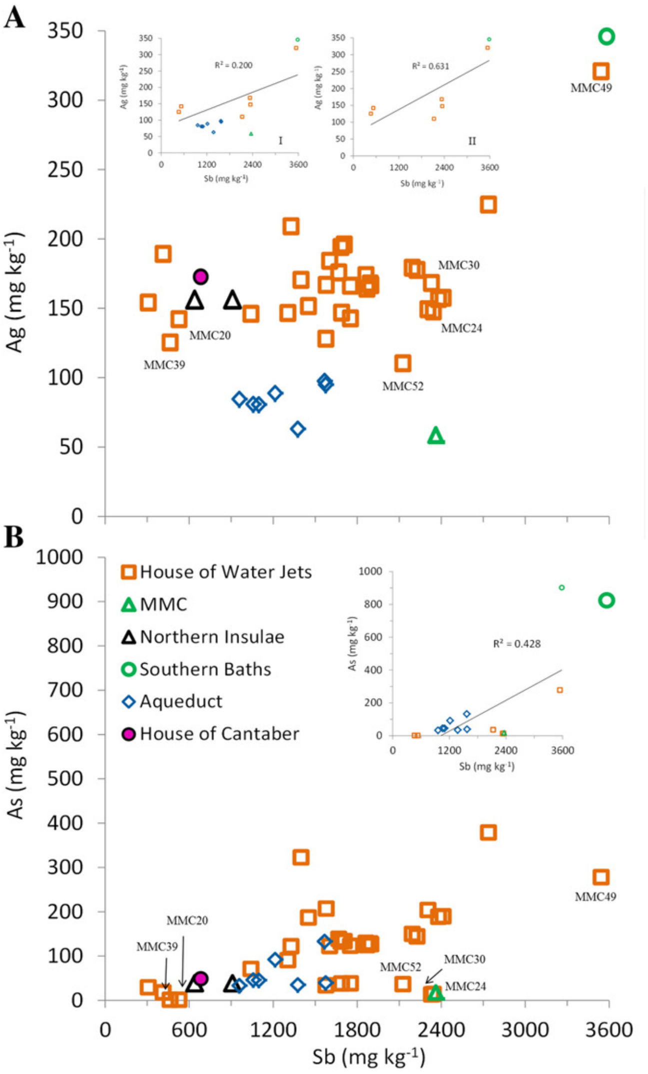

Fig. 4. a) Sb *versus* As and b) Sb *versus* Ag of *fistulae plumbeae* from *Conimbriga*.

Table 5
Pb isotope ratios of *fistulae plumbeae* from *Conimbriga* performed by Quadrupole ICP-MS (±SD).

Laboratory sample number	Archaeological context	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
MMC1	*HWJ*	18.264 ± 0.12	0.856 ± 0.002	2.119 ± 0.004
MMC2	*NI*	18.332 ± 0.04	0.855 ± 0.003	2.122 ± 0.005
MMC4	*HWJ*	18.308 ± 0.06	0.855 ± 0.001	2.120 ± 0.009
MMC5	*HWJ*	18.154 ± 0.06	0.856 ± 0.002	2.121 ± 0.007
MMC6	*HWJ*	18.153 ± 0.06	0.855 ± 0.003	2.127 ± 0.011
MMC7	*HWJ*	18.276 ± 0.04	0.856 ± 0.002	2.113 ± 0.008
MMC8	*HC*	18.332 ± 0.05	0.857 ± 0.002	2.124 ± 0.005
MMC9	*A*	18.292 ± 0.03	0.855 ± 0.002	2.108 ± 0.006
MMC10	*HWJ*	18.295 ± 0.08	0.856 ± 0.002	2.118 ± 0.008
MMC12	*SB*	18.368 ± 0.05	0.856 ± 0.003	2.119 ± 0.004
MMC13	*A*	18.176 ± 0.09	0.857 ± 0.002	2.103 ± 0.007
MMC14	*A*	18.189 ± 0.07	0.858 ± 0.004	2.105 ± 0.003
MMC15	*A*	18.159 ± 0.07	0.857 ± 0.002	2.099 ± 0.006
MMC16	*A*	18.172 ± 0.06	0.857 ± 0.002	2.101 ± 0.006
MMC17	*A*	18.235 ± 0.03	0.860 ± 0.002	2.109 ± 0.008
MMC18	*A*	18.166 ± 0.08	0.859 ± 0.003	2.110 ± 0.007
MMC19	*HWJ*	18.214 ± 0.05	0.855 ± 0.003	2.103 ± 0.011
MMC20	*HWJ*	18.256 ± 0.04	0.858 ± 0.002	2.106 ± 0.004
MMC21	*HWJ*	18.151 ± 0.05	0.858 ± 0.003	2.107 ± 0.007
MMC22	*HWJ*	18.158 ± 0.05	0.858 ± 0.003	2.104 ± 0.009
MMC23	*HWJ*	18.184 ± 0.04	0.859 ± 0.003	2.104 ± 0.008
MMC24	*HWJ*	18.123 ± 0.04	0.859 ± 0.001	2.106 ± 0.005
MMC25	*HWJ*	18.162 ± 0.11	0.859 ± 0.003	2.102 ± 0.010
MMC26	*HWJ*	18.185 ± 0.06	0.860 ± 0.002	2.101 ± 0.003
MMC27	*HWJ*	18.275 ± 0.05	0.857 ± 0.004	2.094 ± 0.004
MMC28	*HWJ*	18.153 ± 0.05	0.858 ± 0.001	2.105 ± 0.002
MMC29	*HWJ*	18.292 ± 0.03	0.853 ± 0.001	2.093 ± 0.008
MMC30	*HWJ*	18.104 ± 0.07	0.858 ± 0.003	2.110 ± 0.004
MMC31	*HWJ*	18.146 ± 0.10	0.860 ± 0.003	2.109 ± 0.004
MMC32	*HWJ*	18.156 ± 0.05	0.859 ± 0.002	2.107 ± 0.005
MMC33	*HWJ*	18.201 ± 0.04	0.857 ± 0.002	2.102 ± 0.007
MMC34	*HWJ*	18.144 ± 0.07	0.859 ± 0.002	2.109 ± 0.009
MMC35	*HWJ*	18.234 ± 0.07	0.859 ± 0.002	2.117 ± 0.005
MMC37	*HWJ*	18.170 ± 0.06	0.861 ± 0.002	2.111 ± 0.008
MMC38	*NI*	18.170 ± 0.07	0.859 ± 0.002	2.107 ± 0.006
MMC39	*HWJ*	18.075 ± 0.11	0.859 ± 0.002	2.112 ± 0.007
MMC40	*HWJ*	18.125 ± 0.07	0.862 ± 0.001	2.118 ± 0.002
MMC42	*HWJ*	18.210 ± 0.09	0.859 ± 0.003	2.109 ± 0.007
MMC44	*HWJ*	18.251 ± 0.05	0.857 ± 0.001	2.103 ± 0.009
MMC46	*HWJ*	18.180 ± 0.06	0.860 ± 0.002	2.112 ± 0.005
MMC47	*HWJ*	18.164 ± 0.05	0.861 ± 0.001	2.112 ± 0.005
MMC49	*HWJ*	18.186 ± 0.04	0.860 ± 0.003	2.111 ± 0.010
MMC52	*HWJ*	18.152 ± 0.09	0.860 ± 0.003	2.115 ± 0.007
MMC53	(*a*)	18.141 ± 0.07	0.861 ± 0.004	2.114 ± 0.015

are plotted using different symbols according to the archaeological context of the lead pipes. The high scattered lead isotope ratio distribution can be a consequence of the use of recycled lead (at least 28 samples in 44 samples) and probable different origins of the raw materials. Aqueduct samples seem to exhibit a more homogeneous distribution: $^{206}Pb/^{204}Pb$ 18.159–18.235, $^{207}Pb/^{206}Pb$ 0.857–0.860 and $^{208}Pb/^{206}Pb$ 2.099–2.110, except for one of the samples (MMC9) that presents somehow different values: 18.292, 0.855 and 2.108, respectively. Concerning the isotopic distribution defined for the samples of lead with very low Sn content, where are included the House of water jets, MMC20, MMC24, MMC30, MMC39, MMC49, MMC52, Aqueduct, Southern Baths and the unknown sample (MMC) these also display a more or less homogeneous isotopic distribution: $^{206}Pb/^{204}Pb$ 18.075–18.368, $^{207}Pb/^{206}Pb$ 0.855–0.861 and $^{208}Pb/^{206}Pb$ 2.099–2.119 (Fig. 5).

In order to infer about provenances, all lead isotope distribution were plotted together with available published data of raw materials from several mining areas of the Iberian Peninsula which have been mined during the Roman Empire (Fig. 6). Several mining districts were considered, namely: the mining districts of Cartagena-Mazarrón, the main source of Roman lead during Republican times; the Sierra Morena mines (Los Pedroches, Alcudia Valley, Linares-La Carolina, and Azuaga–Fuente Obejuna in the Ossa Morena Zone), the main source of lead during the first two centuries of the Empire; the Iberian Pyrite Belt, a major metallogenic province in Europe, composed by a large massive sulphide body, where below the gossan zone argentiferous jarosites were mined by the Romans as a silver ore; and, the Almeria zone, where some small galena mines were also worked during the Roman Empire [19,37–44].

Fig. 6 displays the Pb isotope distributions showing that the analysed samples are clearly distinct from those of galena mining districts of Cartagena-Mazarrón and Almeria. Although due to the high proportion of recycled lead found in our analysed samples raw materials would come from distinct areas. A similar situation was found with the isotopic analysis of the lead used in the Roman water pipes of Pompeii which showed a mixed provenance involving "recyclings of a rather heterogeneous lead supply" [45].

If we exclude all the samples with high Sn content (recycled lead) and consider the five remaining mining districts mentioned above, we obtained the following diagrams (Fig. 7).

On the overall, Pb isotope compositions of lead pipes from *Conimbriga* with low Sn content are similar to data published for galena ores of the Sierra Morena mines, namely those of Alcudia Valey, Linares - La Carolina, and Ossa Morena. A mixture of lead from the Iberian Pyrite Belt with lead from Linares - La Carolina or from the Alcudia Valey is suggested by the isotopic compositions of some samples, namely MMC13, MMC14, MMC15, and MMC16 from Aqueduct. It must be taken into account that although the Pb isotopic field of Sierra Morena mining districts is partially overlapped by the Sardinian Pb isotopic

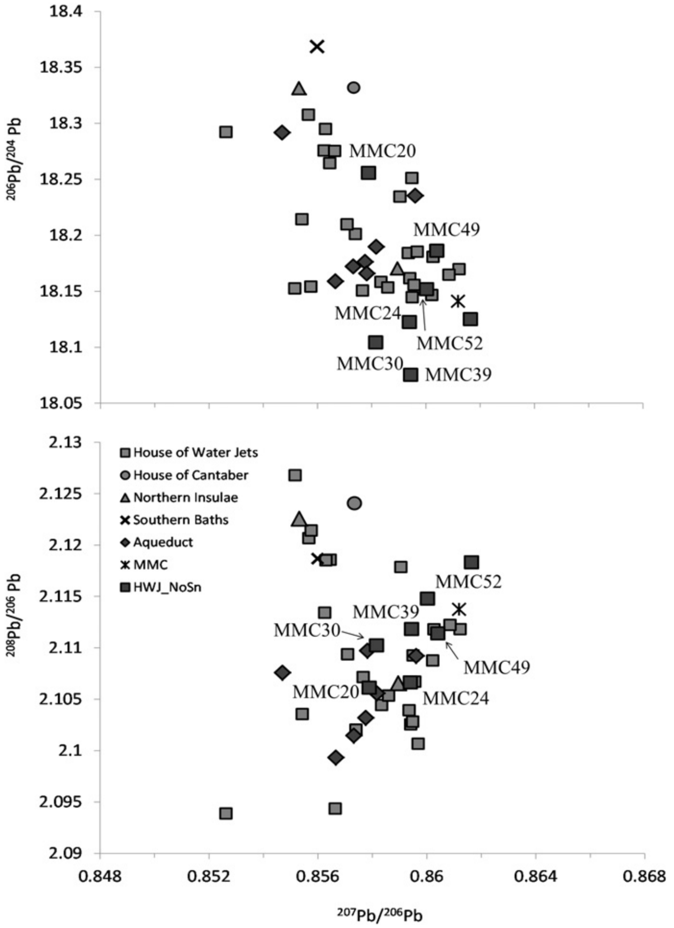

Fig. 5. ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb plots for *fistulae plumbeae* from *Conimbriga*.

field [20], samples with higher ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb and lower ^{206}Pb/^{204}Pb ratios would have their provenance in Iberian Peninsula, since the lead metal produced in *Hispania* was exported and there was no need for the importation of this metal from abroad.

4. Conclusion

The present study has clearly shown the usefulness of a Quadrupole ICP-MS to determine elemental contents and Pb isotopic composition of lead metal in order to ascertain about the provenance of the raw material used in the manufacture of the Roman lead pipes of Conimbriga. Minor and trace elements provided some insights in our study concerning the metallurgical techniques used on the manufacture of the Roman lead pipes in *Conimbriga*. At the same time they allowed to determine what kind of raw material was used for the production of the lead metal, a galena ore or litharge, a by-product of silver cupellation. Such results combined with data of the Pb isotopic analyses have allowed to obtain relevant hints on the provenance of the studied materials. In this regard, the lead metal used for the manufacture of the most of *fistulae aquariae* from *Conimbriga* was recycled as the Sn content clearly indicates. A similar situation was also found with the water lead pipes from the Roman town of Pompeii. Nevertheless, it must be noted that the use of not recycled lead in Aqueduct may be due to be fact of being the oldest and a public hydraulic work at *Conimbriga*. The frequent use of recycled lead in later hydraulic systems may be due to their private nature or also due to the simple result of increasing local availability and reuse of lead metal over time.

At *Conimbriga*, all the lead used in the water pipes was very probably produced by the smelting of galena ores depleted in silver, or by reduction of desilvered litharge, taking into account the low Ag content of the samples. Also Ag contents lower than 100 mg kg^{-1} together with high concentrations of Cu and Ni are indicative of lead produced as a by-product of the cupellation of silver. This is the case of the lead used in the large water pipes of Aqueduct. However, water pipes of the House of the water jets (made of lead probably not recycled) would be obtained from galena ores depleted in silver.

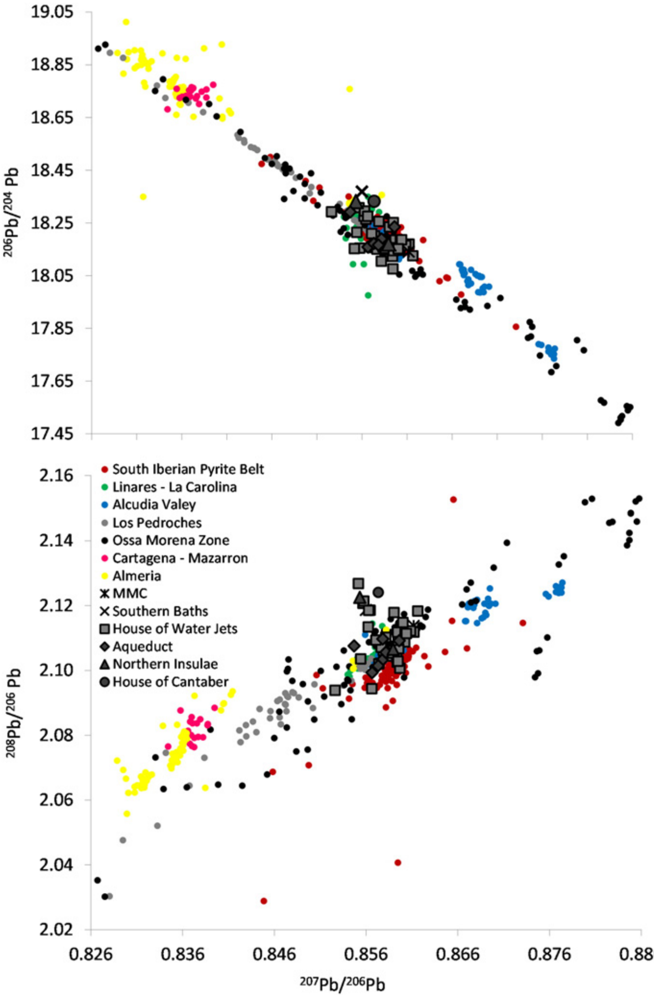

Fig. 6. ^{206}Pb/^{204}Pb and ^{208}Pb/^{206}Pb *versus* ^{207}Pb/^{206}Pb plots for the *fistulae plumbeae* from *Conimbriga* compared with mineralizations from *Hispania*.

The isotopic composition of lead used on *fistulae aquariae* from *Conimbriga* show that most of the lead would have its origin in the mines of Sierra Morena, probably mixed, in some cases, with lead from the Iberian Pyrite Belt. Some samples from Aqueduct, perhaps the oldest of the analysed samples, fit within this group. Yet the Pb isotopic compositions of other samples, including some of the House of water jets (more recent than those from Aqueduct) suggest a provenance from the galena ores of Sierra Morena mines, which were exported for all the Empire during the first centuries of our era.

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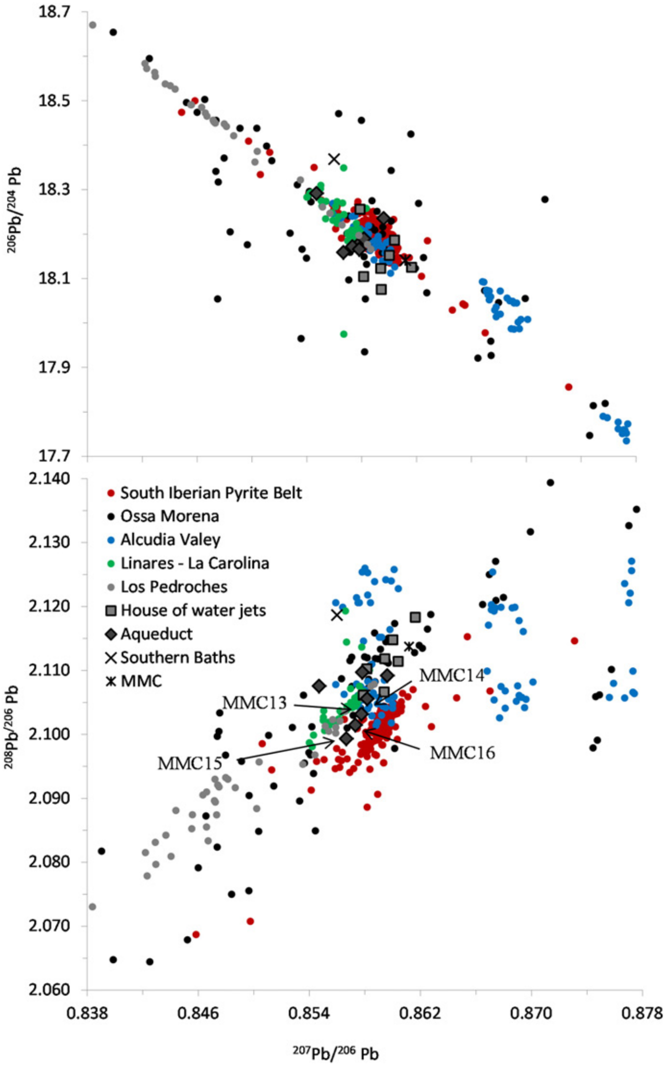

Fig. 7. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ *versus* $^{207}Pb/^{206}Pb$ plots for *fistulae plumbeae* ($Sn < 600$ mg kg^{-1}) from Conimbriga compared with mineralizations from Sierra Morena and the South Iberian Pyrite Belt.

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