

STUDY OF ISOTOPIC LEAD IN ONE INGOT DEPOSITED IN THE
MINING MUSEUM OF RIOTINTO FOUND IN PLANES LODE
(RIOTINTO MINES, HUELVA – SPAIN)
Estudio de plomo isotópico del lingote depositado en el
Museo Minero de Riotinto hallado en Masa Planes
(Minas de Riotinto, Huelva – España)

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RESUMEN

El plomo fue un elemento necesario para los trabajos metalúrgicos romanos, por lo que poder determinar su origen es muy importante para conocer los circuitos comerciales de las materias primas en el mundo romano. El 27 de febrero de 2015 se encontró un lingote romano de plomo en Masa Planes (Minas de Riotinto, Huelva-España), dentro del área del Proyecto Riotinto liderado por Atalaya Mining, aprovechamos para agradecer a esta compañía el apoyo para este proyecto. Siendo el primer lingote de plomo hallado en Riotinto con una ubicación conocida.

PALABRAS CLAVE

Plomo; Lingote; Romano; Isótopos; Riotinto.

ABSTRACT

Lead was a necessary element for Roman metallurgical work, so being able to determine its origin is very important to know the commercial circuits of commodities in the Roman world. On February 27th, 2015, a Roman lead ingot was found in Planes Lode (Riotinto Mines, Huelva, Spain), within the area of the Riotinto Project led by Atalaya Mining, we take the opportunity to thank this Company for supporting this Project. It's the first lead ingot found in Riotinto with a known location.

KEY WORDS

Lead; Ingot; Roman; Isotopes; Riotinto.



Figure 1. Location of the finding of the lead ingot in Planes Lode, Minas de Riotinto (Huelva, Spain).



Figure 2. Photo from the north of the place where the ingot was found in Planes Lode, Minas de Riotinto (Huelva, Spain), Photo ADD.



Figure 3. Photo of the ingot found in Planes Lode, Minas de Riotinto (Huelva, Spain), Photo ADD.

INTRODUCTION

On February 27th, 2015, a Roman lead ingot was found in a secondary position. Specifically, the discovery occurred in the area known as Planes Lode (coordinates X: 7146876 Y: 4155889, Minas de Riotinto, Huelva). This discovery is inserted within the Riotinto Project (See fig. 1, 2 and 3), led by Atalaya Mining¹.

The ingot under study was recovered in good conditions of preservation and practically intact. Morphologically it is rectangular, with a semicircular section and a flat back. It has the following dimensions: 50 cm long; 8.4 cm high and 7 cm width. Its total weight is 26.3 kg (ca. 90 Roman pounds) (See fig. 4 and 5). On the two shorter sides it presents a “*sigillum*” in a rectangular gusset with rounded ends of 3 cm. long by 1.2 cm. wide that, unfortunately, none of it is legible (See fig. 6).



Figure 4. Photo of the Roman lead ingot found in Planes Lode, Minas de Riotinto, (Huelva, Spain), Photo ADD and MBA.



Figure 5. Drawing of the Roman lead ingot found in Planes Lode, Minas de Riotinto (Huelva, Spain).

¹ We take this opportunity to thank the Atalaya Mining company for the facilities offered to carry out this Study Project.



Figure 6. View of the illegible seal with the lead ingot on the short side. Photo ADD.

The good state of conservation, as well as the interest of this find has led us to propose the work presented in this paper ². The purpose of this study is to assess, starting from the results of isotopic lead, the provenance of this metal used in Roman times as “metallic” to obtain silver by cupellation. This is the first time that an ingot found in Rio Tinto with a known location has been analysed.

This paper presents additional data on silver production at Rio Tinto, Spain. The lead ingot was analysed for isotopic data at ALS Scandinavia. The material was studied in collaboration with the students of the archaeometallurgy module of the MSC in cultural heritage offered by the University of Sassari in the academic year 2017-2018, to increase the understanding of the metallurgical activities carried out at Rio Tinto, in particular concerning the provenance of lead metal used in Rio Tinto (Wood and Montero, 2019, 272 -285; Wood *et al.*, 2019, 1-31)

This work will give an introduction of silver production in Roman time, the importance of lead isotope analyses and the relevant analytical techniques and then it presents the data on the ingot, and how they fit within the regional isotopic fingerprint.

² On October 6th, 2017, a Project for the Study of Isotopic Lead of the ingot was presented at the Territorial Delegation of Culture of Huelva, which was approved by resolution dated 10/31/2017

1.1 Roman silver production in Rio Tinto

Anguilano suggests that the lead at Rio Tinto was imported from Cartagena because the Jarosite veins were often too impoverished in lead to effectively work as silver collector, and then recycled in the system, showing an isotopic mixing line (Anguilano *et al.*, 2010, 275). This was also confirmed by instructions *Carthago Nova* recorded in some of the ingots (Charlesworth, 1970, 161-164). Work carried out by (Murillo-Barroso *et al.*, 2019, 23) further reinforces and summarises the use of all the sources of the Iberian Pyrite Belt and rich sources of Cartagena available further South.

The analysis of this newly recovered ingot will add on the dataset of information related to the link between Rio Tinto and the lead produced in other areas.

1.2 Roman Silver Metallurgy and its need for Lead

Silver metallurgy is documented for the first time in the Riotinto Mining Area. Specifically, we refer to the findings that occurred in the "Parrita" Necropolis (Nerva, Huelva) in the middle of the second millennium (Pérez and Frías, 1990, 11-22). Silver production will reach its peak in Roman times, following the wake of Punic metallurgy.

The Iberian Peninsula became an important ore source both for silver and copper linked with the rich geological deposit of the Iberian pyrite belt (Barriga, 1990, 369-379). The minerals exploited for the extraction of silver in ancient times were jarositic types (jarosite, plumbojarosite and argentojarosite) as it was at the time documented by Williams (Williams 1934, 630 - 635 and William, 1950, 7-10). In the specific case of the Riotinto area, another mineral variant was also exploited, the jarositic gossan and complex minerals with silver sulfosalts (tetrahedrite), located in the secondary enrichment zone (Pérez and Delgado, 2007b, 293-294). The process of these minerals was possible thanks to the tillage developed in Roman times, this was based on the chamber, shaft and gallery system, which allowed reaching greater depths than in past times (Willies, 1997, 8-11; Pérez and Delgado, 2011, 8-9). This also forced the use of drainage systems (Luzón, 1968, 101-120; Delgado and Regalado, 2010, 659-676; Delgado *et al.*, 2013, 275-294).

In Rio Tinto there are mineral species that contain lead, such as cerussite (lead carbonate) or gale-

na (lead sulphide), but this was not enough to sustain silver production. Thus, from the 4th and 3rd centuries BC, a greater quantity of lead was needed for the cupellation operations, which had to be imported from other locations (Craddock *et al.*, 1985; 209; Tylecote, 1987; 302-310; Domergue, 1990, 51; Hunt, 2003, 35; Pérez and Delgado, 2007b, 293-295; Anguilano *et al.*, 2010, 274-275; Anguilano, 2012, 296).

The need for lead was due to a significant increase in metallurgical operations in the Republican era, characterised by the presence of a type of fayalite type of fayalite -rich slags in the form of plates between 30 and 35 cm and with a thickness of about 6 cm. From the Augustan period (Delgado *et al.*, 2017, 895-924), in addition to the beginning of the exploitation of copper minerals (Blanco and Rothenberg, 1981, 111), there will be a change in the metallurgical techniques that resulted in a change in the type of furnaces, which had larger dimensions and capable of withstanding higher temperatures, therefore, it was able to process another kind of minerals such as arsenides (Pérez and Delgado, 2007b, 293). This is seen in the appearance of a new type of slag -large conical "lupias"- that usually exceed a meter in diameter and where the superposition different levels generated by continuous tapping (Rothenberg *et al.*, 1990, 57-71; Pérez and Delgado, 2007b, 292-296). At this time, a new metallurgical by-product began to appear, the white metal or speiss, which is the result of the processing of silver sulfosalts (Pérez and Delgado, 2007b, 292-294). Finally, cupellation techniques that had been improved since the Republican era continued to develop with the addition of significant amounts of lead that allowed large amounts of silver to be recovered. Given this, Craddock's words would be justified: "Rio Tinto was one of the greatest sources of silver in the ancient world, especially in the late Republican and early Imperial period" (Craddock *et al.*, 1985, 209). This productive reality would not have been possible without the contribution of lead from other mines where this metal was extracted.

The importance of Riotinto as a mine in Roman times is confirmed both by more than 20 million tons of slag, studied by Salkield (1970, 85-90), and by the isotopes found in the fossil ice in Greenland which indicated that between the 150 BC and 50 A.D. 70% of the metallurgically operated metals

came from the Riotinto Mining Area (Rosman *et al.*, 1997, 3413-3416), making Riotinto the largest metal producing centre in the ancient world.

Silver production continued until the crisis of the early third century AD. The recovery will not occur until the end of that same century or the beginning of the fourth century when the mining operations focused on the copper lodes. Thus the exploitation of Planes lode was promoted, the works in North Lode and South Lode were abandoned and the population was concentrated in the Marismilla settlement where the archaeological items documents an occupation in centuries IV - V d. C., as demonstrated by the presence of Terra sigillata African Red Slip Ware -ARSW- (Pérez, Delgado and Regalado, 2012, 45-83).

Riotinto went from being a silver mine in republican times, to a silver and copper mine in imperial times, and a copper exploitation during the Late Roman Empire (Pérez and Delgado, 2007b, 296)

1.3 Silver content in lead ingots

The silver content can be used to indicate if the lead is obtained by desilvered litharge (by-product of the cupellation process) or by smelting (reduction) of galena depleted in Ag.

Records from the late 19th and early 20th century indicate silver concentrations of around 0.2% in the ore (Pérez and Delgado, 2007a, 49-51). But, since there is an absence of reliable documentary sources and intact Roman mine workings, the lead ingots commonly known as "lead pigs" constitute the primary evidence for the understanding of the lead industry in Roman times: by examination of the inscriptions, weights, compositions and find-spots of all the known Romano-British lead pigs, it has been possible to answer a number of important questions concerning the lead industry during the Roman period (Gardiner, 2001, 11-13).

1.3.1 Use of lead isotopes in archaeometallurgy (in particular for lead/silver production)

Lead has 38 isotopes, with an atomic mass between 178 and 215. Only four of these isotopes are stable and only Pb-204 is natural. This isotope formed at the formation of planet Earth hence it is called "primary lead" and its concentration is stable. The other three stable lead isotopes are: Pb-206; Pb-207 and Pb-208. These form from radiogenic decadence of Uranium 238, Uranium 235 and

Thorium 232. Lead that is found on Earth is called "common lead" and is made of the 4 isotopes just described (Pb-204; Pb-206; Pb-207 and Pb-208) and it does not contain any significant proportion of Uranium or Thorium hence its composition does not vary. The origin of the different lead isotopes is the reason why the ratio between them can be linked with specific geological origins hence indicate the provenance of minerals and consequently of the metal produced by them.

An important goal for archaeo-metallurgists is to establish the geological provenance of the metal used to manufacture a particular artefact in order to understand trade relationships and movement of raw materials and objects. The original approach was to make use of chemical analysis, beginning in 1934 (Noddack and Noddack, 1934, 637 - 641) and leading on to the large-scale chemical analytical programmes of Otto and Witter (Otto and Witter, 1952, 250 -264) and the Stuttgart group (Junghans *et al.*, 1960, 1968 and 1974), later reviewed by Härke (Harke, 1978, 268-276). But chemical analysis by themselves were not the optimal methodology to respond to this scientific question because of the variation of chemical composition in ore deposits, as well as the chemical changes between ore, slag and metal due to the production processes. To answer the quest of identifying the ore deposits, a comparative approach was needed, in terms of lead isotope analysis, between artefacts and metal ores (Brill and Wampler 1965, 63-77; Grögler *et al.*, 1966, 1167 - 1172). Systematic studies and applications of lead isotope provenance began in the 1970s when a group at the Max-Planck-Institut für Kernphysik in Heidelberg, comprising W. Gentner, G. A. Wagner and O. Müller, invited N.H. Gale at the University of Oxford.

They focused on studies of the provenance of ancient Greek silver coins using both trace element and lead isotope analysis with particular attention on lead-silver deposits in and around the Aegean. So it became possible, for the first time, to relate with high probability metal artefacts to specific ore deposits. Since the mid-1970s, all of the projects on lead isotope provenance studies at Oxford and Heidelberg have been based on parallel geological and archaeo-metallurgical collection of samples for analysis and mapping the ore deposits, ancient mines and slag heaps significant to Bronze Age archaeology.

The classic method for the measurement of lead isotope ratios, developed largely for isotope geochemistry (Faure, 1986, 237-239), is thermal ionisation mass spectrometry with a magnetic sector mass spectrometer (TIMS). It was usual before, around 1970s, to mount the sample as lead sulphide on a Rhenium strip filament, which, on heating, emitted ions into the mass spectrometer. But this was a method which required micrograms amounts of sample and achieved only about $\pm 1\%$ accuracy. So Cameron and Barnes and their teams devised a thermal ionisation method based on the use of a silica gel/ phosphoric acid emitter on a Rhenium filament which allowed the sample size to be reduced by an order of magnitude and the accuracy of lead isotope ratio measurement to be greater than $\pm 0.1\%$ (Cameron *et al.*, 1969, 525-526; Barnes *et al.*, 1973, 1881-1884; Arden and Gale 1974, 687-697). A further step in sample throughput and accuracy was accomplished with the introduction of magnetic sector mass spectrometer using multi collectors. In this way, the absolute 2σ errors were reduced to $\pm 0.002\%$. In more recent times the introduction of an inductively coupled plasma source fitted to a magnetic sector multi-collector mass spectrometer (MC-ICPMS) allowed to reduce the sample size, using nano-grams samples of lead (Hirata, 1996, 1956-1411; Rehkämper and Halliday, 1998, 123-133; Belshaw *et al.*, 1998, 51-58). The routine use of small samples necessitated also the development of low blank chemical separation methods carried out in special laboratories over-pressured by highly filtered air to reduce contamination to very low levels. But lack of chemical separation can expose one to problems arising from the fact that large amounts of matrix included with the sample may cause differential mass bias behaviour between samples and standards, as well as the possibility of introducing isobaric interferences. Matrix effects were limited by Baker *et al.* (Baker *et al.*, 2006, 45-56), who included an external standard glass (NIST 610) for normalisation of the laser ablation isotopic analyses. But the laser ablation method (using NIST 610 glass as an external standard to monitor instrumental mass bias), though is suitable for metals containing high concentrations of lead, must be used with care for lower-lead metals, as it is demonstrated in the contrasting accuracy between the high-lead silver and copper samples and the relatively low-lead Uluburun copper ingot sample (Baker *et al.*, 2006, 45-56).

Comparison between analysis from different laboratories became possible thanks to the introduction, by the US National Bureau of Standards, of three isotope standards for lead. One of these is the SRM 981, which has been used in the present paper.

1.3.2 Possible fractionation of lead isotopes during ancient metallurgical processes.

Another point of discussion amongst archaeo-metallurgists is if the lead isotope ratios in the metal extracted from a metal ore is the same of the metal ore or different because of the possible fractionation occurred in one or more of the steps of smelting, refining, working, casting, cupellation or corrosion processes. This was remarked by Budd *et al.* (1995, 143-150) and Pollard and Heron (2008, 144-152), who hypothesised that changes in lead isotope composition due to non-equilibrium evaporation during smelting, for example, could produce changes in lead isotope composition sufficient to move the isotopic composition in the smelted metal quite outside the field of isotopic composition of the ores being smelted. Experiments by Barnes *et al.* (1978, 273-277) gave empirical proof that anthropogenic processes produced no measurable change in lead isotope composition ($\pm 0.05\%$). But the accuracy of the lead isotope analyses of the results of these experimental procedures depends on the analytical methods known at that time, which were not as accurate as modern analyses. In fact, Pollard and Heron, 2008, 302-382 were correct to observe that the overall loss of lead in the experiments of Barnes *et al.* (1978, 273-277), did not exceed circa 5%, so that it had not been established that isotopic fractionation of lead might not occur in procedures where the loss of lead was larger.

Since we have no exact knowledge of metallurgical processes practiced in ancient times and modern simulations are thus uncertain, it seems obvious that the most rigorous tests of possible lead isotope fractionation should involve the actual remains of ancient metallurgical processes. To this end, isotopic analyses were made in the Oxford Isotrace Laboratory of the traces of lead (from 0.5% to a maximum of 3% Pb) in a series of Archaic and Classical Athenian silver tetradrachms together with argentiferous galena ores from the Lavrion mines (Marinos and Petrascheck, 1956, 245-247) in Attica. In fact, thanks to ancient authors, we certainly know

these coins were made (between 525 and 450 B.C.) from silver that had been obtained from Lavrion argentiferous lead ores, first by smelting to produce argentiferous lead and then by cupelling this silver-rich lead to produce the silver. The conclusions were that the lead isotope analyses for the tetradrachms all fall within the data for the Lavrion ores; there certainly are no large-scale fractionations of the isotope ratios away from those characteristic of the argentiferous lead ores from which the ancient authors show that they were made. Consequently, these data support the hypothesis that there is no measurable fractionation of lead isotopes when the ores are subjected to smelting, two separate cupellations, and one silver refining step. So, it can be concluded that anthropogenic processes do not affect the lead isotopic composition of the original ore but we must bear in mind that possible dishomogeneities could be due to corrosion (Gale and Stos-Gale, 2000, 503-584).

1.3.3 The interpretation of lead isotope analyses for provenance studies.

It is the precise coincidence of lead isotope compositions of particular artefacts with particular ore deposits that is required before it can be concluded that the metal of the artefacts most probably came from the named ore deposits. It can happen that differences between deposits are so small that we need very accurate analytical methods to make certain comparisons. If, instead, some ore deposits have overlapping lead isotope compositions, then the conclusions for artefacts plotting in such regions must necessarily be better defined. Moreover, it can be possible that the isotopic lead composition in an ore deposit is not uniform. So it is necessary to use methods suitable not only to define the range of lead isotope composition that identifies a particular ore deposit (ideally it requires the analysis of about 30 to 50 of different ore samples), but also to choose the possible ore deposits from which the artefact come from.

To make assertions in terms of provenance, two possible approaches can be followed: the graphical method and the statistic one. From the beginning, the interpretation of the data was based on comparison of the three lead isotope ratios in two-dimensional plots where the horizontal axis was always $^{207}\text{Pb}/^{206}\text{Pb}$ and the two vertical ones $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. The choice of these particular three independent ratios was partly due

to the method of representation of lead isotope measurements in isotope geology (Gulson, 1986, 1167-1172), partly for convenience, because these three ratios always differ by one order of magnitude (e.g. 0.8..., 2.07..., 18.8...) and, therefore, are easy to distinguish. Pollard first introduced multivariate statistical interpretation into lead isotope provenance work but, initially, a main problem encountered with this approach was the rather small number of data points available for most of the ore deposits. Later this limit was overcome with the introduction of multi-collector mass spectrometer. But Stos-Gale *et al.* (1997, 237-246), explained in 1997 and later papers (Gale *et al.*, 1999, 1-19) that they no longer used multivariate statistics and had reverted to the simple two bivariate plots and point-by-point comparisons of lead isotopic analysis for artefacts and ores because multivariate statistics was based on the normal distribution of the data while lead isotope data are not normally distributed. However, today very large datasets of isotopic data are available for comparison between artefacts and ores / slags sample, so it could be very time-consuming and potentially inaccurate to make use only of the traditional graphical method. To avoid such a difficult task it would be useful to make an initial statistical screening between the artefact and the ore to identify the possible ore deposits and then to submit to graphical analysis only such cases that appear uncertain, using point-by-point comparisons between isotopic data for ores and artefacts. Finally, the geochemistry and history of exploitation of the ore deposits identified as possible sources has to be evaluated. The method suggested by Gale and Stos-Gale follows this logic. (Stos-Gale and Gale, 2009, 503-584).

Researchers can find the lead isotopic composition of different objects in the database OXALID (oxalid.arch.ox.ac.uk), which contains many data for ancient metals, glass, paint and pigments. Another important database is PARADOX, created in 1988, with data obtained in the Isotracer Laboratory. To the development of these databases contributed Professor Colin Renfrew that suggested to Noel Gale that it would be interesting to apply lead isotope studies to the earliest Aegean metallurgy to test the old theories of the 'diffusion' of metallurgy from the Near and Middle East to Europe and to identify the sources of the earliest metals and the Bronze Age metal trade routes. The scientific

plan for this project included a survey of lead–silver mines and sampling of lead and silver artefacts from Bronze Age sites excavated in Greece using multi-collector TIMS analysers capable of producing data for 10–12 samples a day.

2. METHODOLOGY

The samples obtained by the lead ingot subject of this study were measured for trace analyses, in particular to evaluate the concentration of silver in the lead ingot, using a Quadrupole ICP-MS NexION 300X at the CESAR laboratory at Sassari University.

The samples were measured for isotopic composition using the ALS Scandinavia AB facilities, in particular their MC-ICP-MS (Neptune Plus).

The samples for both ICP-MS analyses were prepared through digestion using nitric acid and their preparation will not be further described. Three samples were analysed for elemental compositions and two for isotopic analysis to ascertain repeatability and accuracy of the data.

2.1. Description of the statistical methods used to investigate the precision of the results and to take into account the errors due to preparation and instrument

In analytical chemistry we are usually interested in the precision of a series of data obtained in the same way, i.e. the reproducibility of measures. In other words, we want to understand how the measures are distributed around the average value. To answer this question, statistics give us four parameters: the standard deviation, the variance, the coefficient of variance and the range.

In order to identify the right way to calculate standard deviation and the other parameters relate to it, first of all we must distinguish if we have a population of data or a smaller number of measure that approximate it, i.e. a sample. A population is not usually easy to define and in the majority of cases it remains a conceptual quantity, so we often deal with a sample that is representative of the population of interest.

The *standard deviation of the population* (σ) is defined by:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \mu)^2}{N}}$$

where :

x_i : i-measure;

μ : average value of the population;

N: number of measures.

If it cannot be measured, the estimate of the standard deviation of the population, i.e. *the standard deviation of the sample* (s), is given by :

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

where:

$\bar{x}$: average value of the sample;

n-1: number of degree of freedom.

Another quantity is the *variance*, that is defined as the square of the standard deviation; for the population, the variance σ^2 is:

$$\sigma_x^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{N}$$

For the sample, instead, the variance (s^2) is :

$$S^2 = \frac{1}{n - 1} \sum_{i=1}^n (x_i - \bar{x})^2$$

The standard deviation has the same units of measure of the data, so scientists prefer it to variance but sometimes the latter is better than the first because in many cases this is additive while standard deviation is not.

Another parameter useful to describe the precision of a set of measures is the *coefficient of variation* (CV), that is the relative standard deviation (SRD), i.e. the standard deviation of the sample divided for the average value, multiplied for 100:

$$CV = \text{SRD} \cdot 100 = 100$$

Finally, the *range* (w) is easily the difference between the bigger value and the smallest one of the set of the data:

$$w = x_{\max} - x_{\min}$$

Standard deviation allow us to take into account the uncertainty of the results due both to casual errors than systematic errors due to the dilution of the samples throughout the *interval of confidence (IC)*, that is to say the range of values in which we expect to find the true value μ with a certain level of probability.

If we have a small set of data, like in this case, we must know a parameter, the “Student’s t”, that allow us to calculate the interval of confidence. The “Student’s t” describes the distribution of the error when we have a small number of measure, instead of the normal or Gaussian distribution that deals with a big number of repeats, usually for $N > 30$. This parameter is printout in manuals of statistics and depends on the degrees of freedom and on the level of confidence chosen. The interval of confidence is described as following:

$$\mu = \bar{x} \pm (t s) / \sqrt{N}$$

2.2 Inter-laboratory data comparability

If we want to investigate, for example, if two different analytical methods have the same precision or one of these is more precise than the other or if two average values calculated with the same method by different analysts are statistically different, we have to execute a “*test of significance*”, as it was defined by Ronald Fisher in 1925 (Fisher, 1925, 79). A test of significance is based on the formulation of two hypothesis: the *null hypothesis*, that postulates that two or more quantities examined are tantamount and the *alternative hypothesis*, that has two possible ways to be expressed: the first one assumes that the two quantities are different (the so called *two-tailed test*) and the second one tries to understand if one quantity is greater or lower than the other one (the so called *one-tailed test*). Before data analysis, we must choose the *level of significance* α as it was called by Neyman and Pearson (Neyman and Pearson, 1933, 492 – 510) α is the probability of mistakenly rejecting the null hypothesis when it is true. Sometimes researchers talk about the *confidence level* $\gamma = (1 - \alpha)$ instead. This is the probability of not making errors accepting the null hypothesis. Confidence levels and confidence intervals were introduced by Neyman (Neyman 1937, 333–380). This manner of investigation implies the possibility of making two kind of errors: the *type I error*, that happens when

the null hypothesis is refused though it is true, and the *type II error* that happens when the null hypothesis is accepted though it is wrong. Because of this two types of errors are inversely bonded with each other, trying to minimize a one type error means to maximize the other, so we must find a right compromise, that is usually achieved setting $\alpha = 5\%$. This decision is made in order to minimize the type II error because it is considered more serious than a type I one.

3 RESULTS

3.1 Isotopic results

Standard data:

The quality of the MC-ICP-MS data is controlled by the correction for isotopic mass fractionation monitored by repeated measurement of the standard SRM981, which in the Isotrace Laboratory over several years consistently reproduces to within $\pm 0.1\%$ for each lead isotope ratio (Stos-Gale et al. 1995, 407–412). The data presented below (table 2) were produced at the ALS Scandinavia AB facilities and the standard deviation, calculated from 2 consecutive measurements is also presented.

3.2 Quantitative results

Quantitative results were obtained from Quadrapole. Using the results as not calibrated and only as a measure to evaluate the required procedure for the isotopic ratio calculation; they can be used to estimate the ratio between silver and lead in the ingot. The results (table 1) show the concentration in ppb as estimated by the instrument, without dilution correction and a consequent preliminary percentage of silver content in the lead ingot can be estimated at $0.6\% \pm 0.2$.

	Ag (ppb)	Pb (ppb)	ratio	%
Sample 1	0.514	114.264	0.004498	0.4
Sample 2	0.682	109.139	0.006248	0.6
Sample 3	0.603	96.160	0.006271	0.6

Table 1. Concentrations measured in the ingot for the elemental composition (prior corrections) and consequent ratio and silver concentration estimated for the ingot.

Sample ID	206/207	2SD	207/206	2SD	206/204	2SD	208/204	2SD	207/204	2SD
Lead ingot	2.4832	0.0006	0.84010	0.00012	18.663	0.004	38.934	0.011	15.679	0.006
Lead ingot r2	2.4838	0.0007	0.83980	0.00008	18.666	0.006	38.935	0.015	15.675	0.007

Table 2. Isotopic data.

If the TotalQuant data are used applying the dilution factor of 1:4.000.000 used for the sample preparation, then the concentration of silver in the samples can be calculated as follows: 2056 ppm for Sample 1, 2728 ppm for Sample 2 and 2412 ppm for sample 3.

4. DISCUSSION

4.1 Concentration of silver in lead ingots

The quantitative data obtained during this study (presented in section 3.2) conform to the previously mentioned records, which estimated the silver concentration in the ore to be around 0.2% (Pérez y Delgado, 2007a, 49-51). This would be an indication that this ingot is a direct result of smelting and not a silver-free ingot imported solely for cupellation purposes.

Due to the absence of reliable documentary sources and intact Roman mine workings, we shall obtain information through specific lead artefacts obtained from different locations, which may give us important indications on the mining exploitation, metal use and trade routes: lead pigs from Britannia and lead pipes from *Conimbriga* (Portugal).

Regarding the Romano-British context, lead pigs that bear the EX ARG inscription have been studied and analyzed (Gardiner, 2001, 11.13) to see if there was a standard policy for the desilverisation of argentiferous lead. Of the 32 lead pigs analyzed (both with and without EX ARG inscription), 75% contained between nil and 0.012% (120 ppm) silver. No appreciable variations were detected between those with the EX ARG markings and those without, suggesting that EX ARG is not indicative of desilverisation and that there is no clear pattern concerning this activity.

In the case of Portugal, forty four lead pipes (*fistulae plumbeae aquariae*) from the hydraulic systems installed at *Conimbriga*, a large Roman town in Central Portugal, were analyzed using a quadrupole based ICP-MS (Gomes *et al.*, 2016,

184-193). Ag content was quantified in all samples reaching a maximum value of 346 ppm, 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 [5,6]. According to some authors [3,5], during Roman period, litharge or galena ores with a Ag content of 400 ppm or higher would have been used to extract silver.

However, the low Ag content (63-98 ppm) of some of the samples also suggests that the lead of some of the pipes was obtained by reduction of litharge.

The results obtained in this study indicate a concentration of silver an order of magnitude higher, potentially pointing towards a source of silver and not a desilvered ingot.

4.2 Isotopic fingerprint

Initial evaluation was conducted to ascertain the comparability of the new ingot presented in this study with the ingots and slags characterised by Anguilano (Anguilano *et al.*, 2010, 269 - 276) and the overall composition of the Spanish ores as published in the OXALID database.

At first evaluation the data obtained from the ingot (highlighted by the red arrow) are positioned in the mixing line defined between the Cartagena ores and the Rio Tinto mines ores, closer towards the Cartagena data (Fig. 7 and Fig. 8), but not overlapping with the ingot identified as from Cartagena by Anguilano (Anguilano *et al.*, 2010, 275) (highlighted by the blue arrow in the same figures).

A further evaluation considering sources from outside Spain shows that the data deriving from this ingot are in fact at the edge of the Spanish field, closer to the data deriving from the Mazarron mine, but could also show a signature from Greece (Euboea or Lesbos) and Italy (Tuscany). Indicating a potential origin from outside Spain

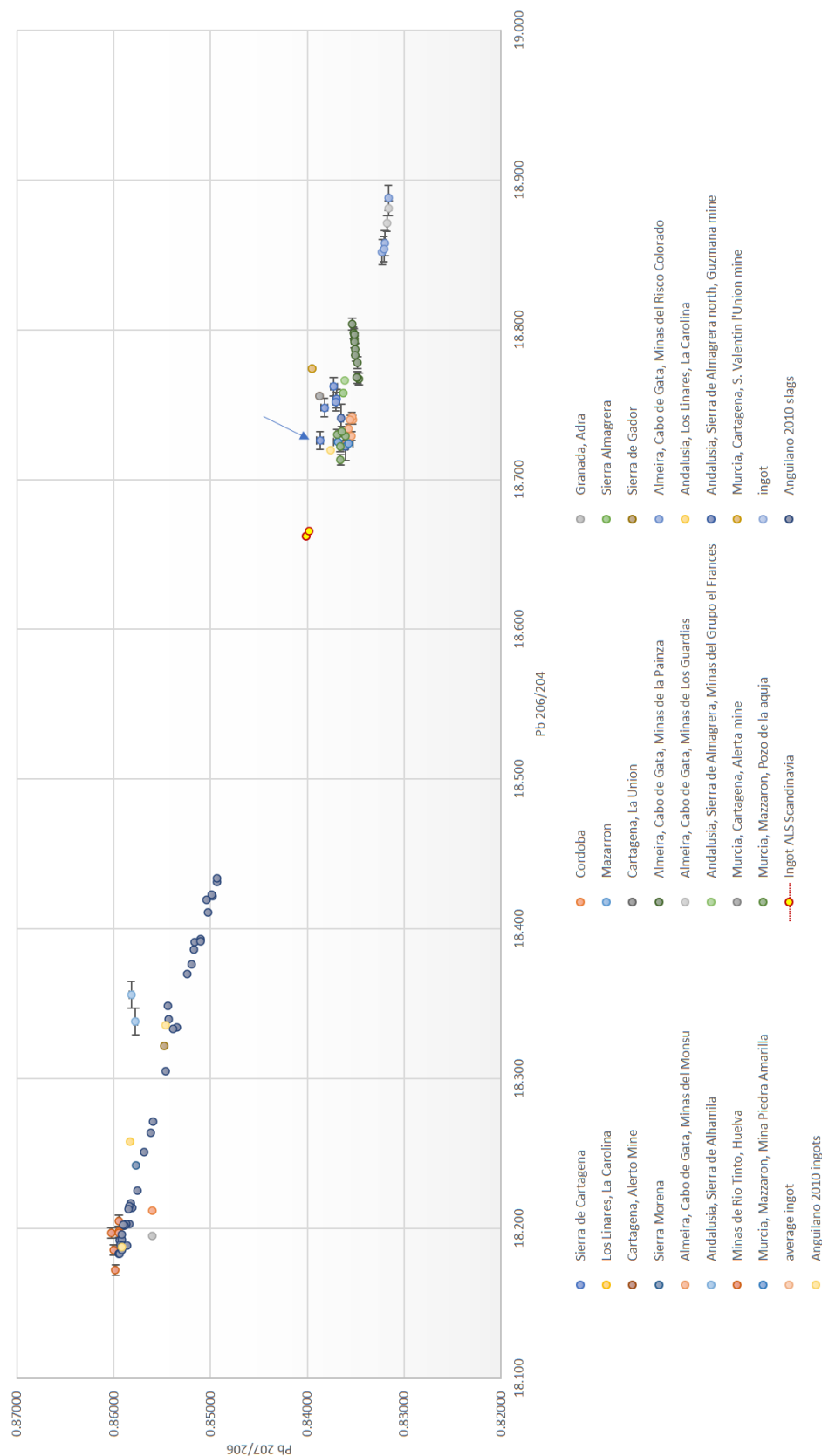


Figure 7. Graphical Spanish mines isotopic fingerprints and data obtained by Anguilano 2010 compared with the new ingot data (point in yellow with dark red contour).



Figure 8. Graphic 1b Spanish mines isotopic fingerprints and data obtained by Anguilano 2010 compared with the new ingot data (point in yellow with dark red contour).

5 CONCLUSIONS

The lead samples from the Riotinto ingot were analysed by ICP-Q-MS to trace their isotopic signature and to determine its origin. The data were compared with the tabulated data from the Oxford database (Oxford Archaeological Lead Isotope Database, (1997), Isotracer Laboratory), along with previously analysed samples (Anguilano *et al.*, 2010, 269–276). It was taken into account that the data referred to are on galena minerals, since this is the most important mineral species for the production of metallic lead (Boulakia, 1972, 139–144). Two comparisons were made, one with samples from mines from the Iberian Peninsula (See fig. 7 and 8) and the other with known data from mining deposits in countries of the Mediterranean Basin (See fig. 9 and 10). All of the above seem to indicate that the lead isotopes obtained in this investigation can be within the peninsular ratio, and within this they can potentially indicate the result of smelting of minerals plus a mixed lead metal source (RioTinto/Cartagena) further strengthening the hypothesis of the use of metal from the mines of Cartagena and the re-use of litharge after cupellation. This will indicate a continuous mix of the lead sources at the Rio Tinto site to allow for the high volume of silver smelting and cupellation processes (Anguilano *et al.*, 2010, 275; Pérez and Delgado 2014, 249) since the end of the republic and the beginning of the principality of Augustus (Rothenhoefer *et al.*, 2016, 127 – 133).

Morphologically, this ingot would be included within the type I, defined by Domergue (1994, 62–63) which is identified by Anguilano *et al.* (2010) as a period of technological change and increase in the volume of production. The dimensions are framed in the normal ones of this type of pieces as it was already approached by Domergue. This piece was developed in a very rough ceramic mould as it can be seen from the surface that has been printed on the piece.

Furthermore, as we have already indicated, it presents a cold *sigillum* on one of the edges, something that is far from the usual practice of presenting several seals on one of the spines in this type of piece (Díaz Ariño, 2006, 291–292). The weak impression on the piece means that we cannot provide more information on whether this stamp was printed directly from the mould or if, on the contrary, it was cold printed afterwards. Unfortunately,

the present *sigillum* can not be read. In relation to the significance of this type of impressions it is difficult to determine. Despite this, Domergue (1994, 73–82) indicated that these stamps on the side could indicate data about the intermediary in charge of marketing.

Overall this ingot seems to show a different picture compared to the ones previously recovered at Rio Tinto: (1) the ingot seems to contain a higher silver concentration similar to the one reported in the ores of Rio Tinto, hence indicating that it could be an ingot deriving directly from smelting; (2) the ingot seems to present a different isotopic signature from the RioTinto ores and corresponds to the mixing line as presented by Anguilano (2010), closer to the Cartagena end member, seeming to indicate that lead from Cartagena was already added at the smelting step.

However, as hypothesised by Angelini (Angelini *et al.*, 2019, 4959–4970) for the Marengo silver objects, the mixing line Cartagena/Rio Tinto could mimic the French ores of the Massif Central. In this case, also, the potential overlapping with Greek ores from Lesbos and Euboea can be seen in the graphs presented, it is possible that Spanish material was mixed at different mines to enrich the silver concentration and reuse the lead available in the region for the industrial recovery and cupellation needs. However, it is also possible that a wider movement of ingots was happening within the Roman empire to ensure the stock of raw material in the larger manufacturing areas. This would open an interesting perspective on the level of material sourcing and transport logistics within the Empire.

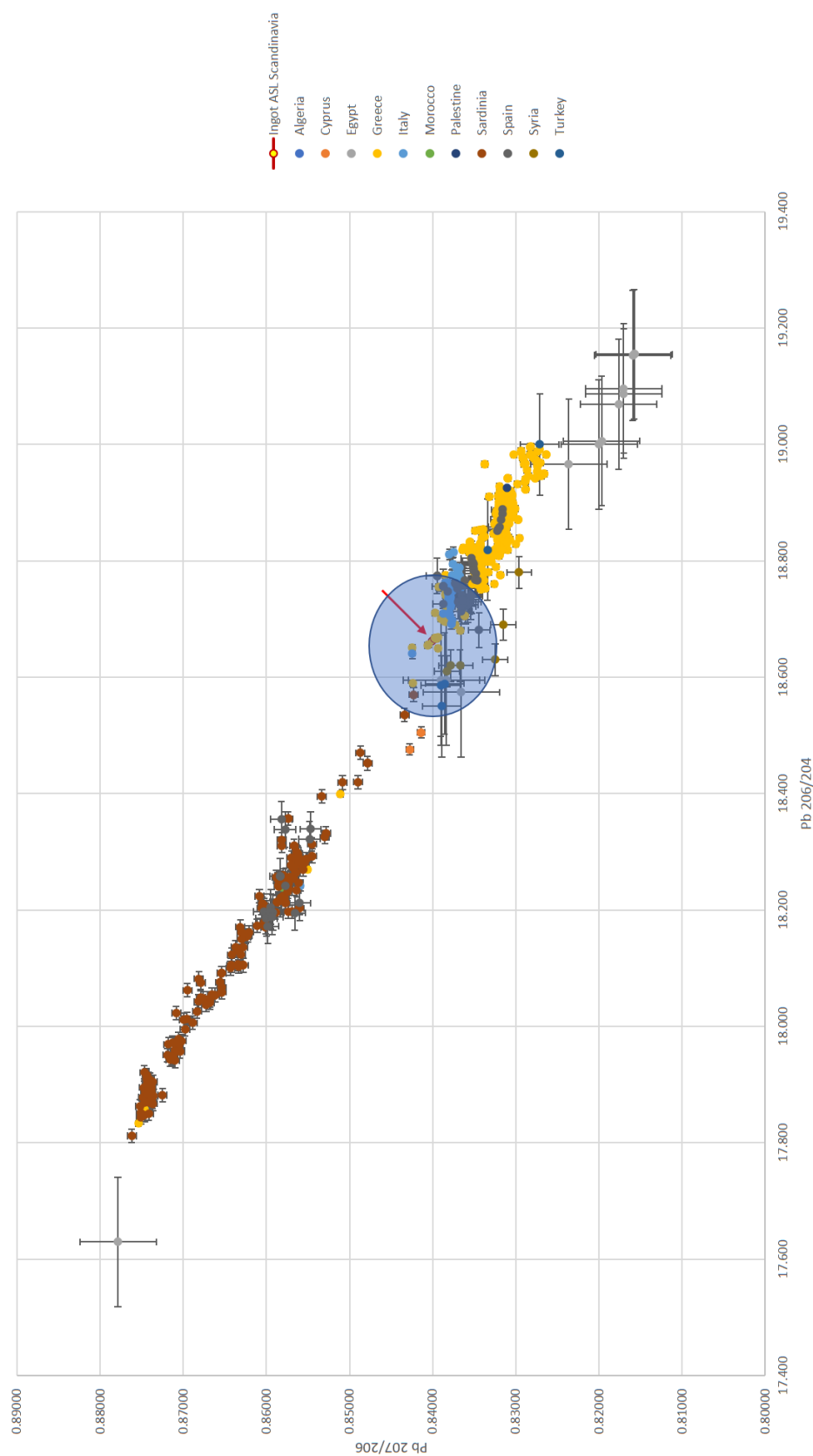


Figure 9. Graphic 2a Isotopic fingerprints and data from the OXALID database compared with the new ingot data (red arrow).

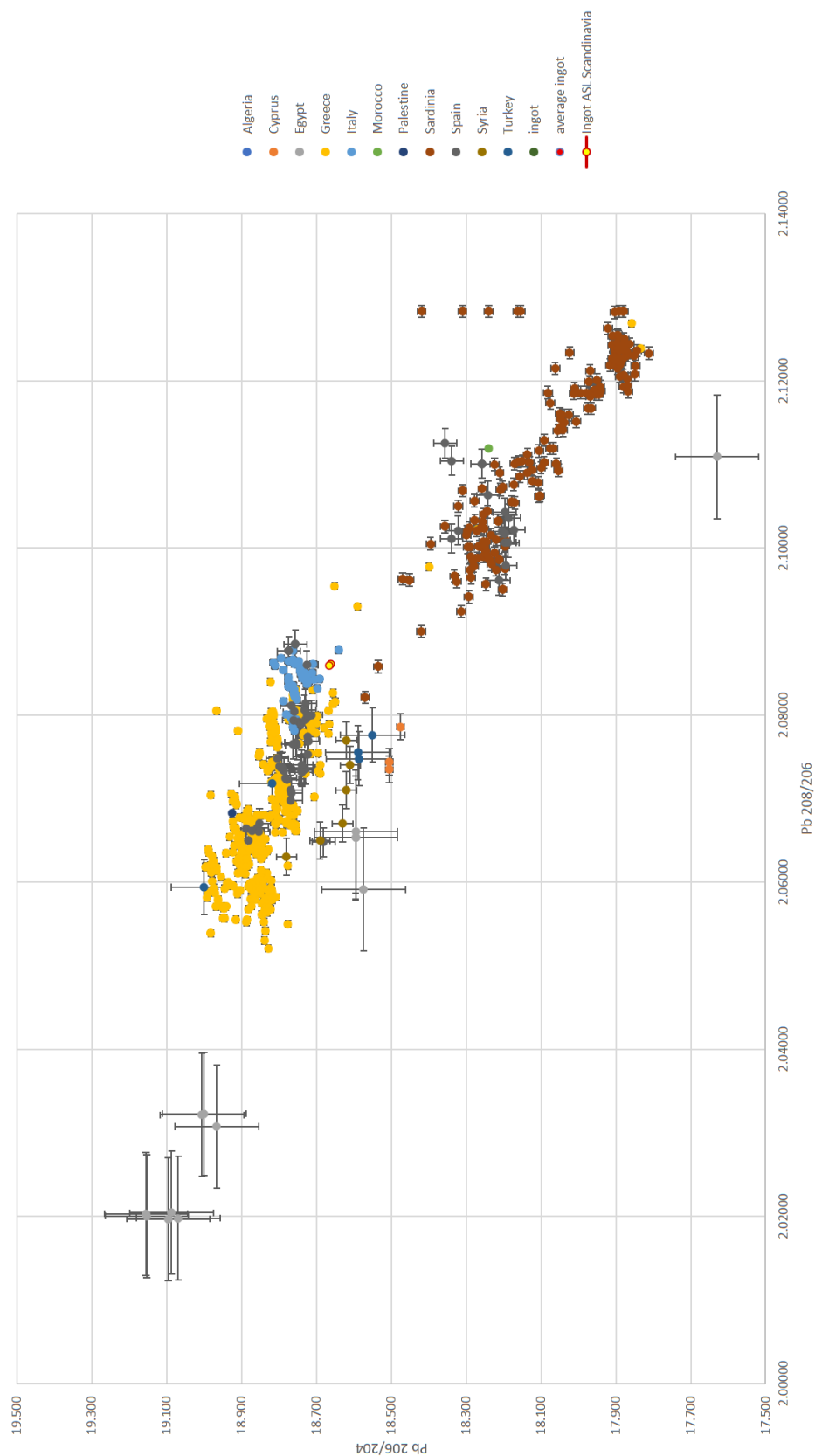


Figure 10. Graphic 2b Isotopic fingerprints and data from the OXALID database compared with the new ingot data (red arrow).

BIBLIOGRAPHY

- Arden, J.W. and Gale, N.H. (1974), "Separation of Trace Amount of Uranium and Thorium and Their Determination by Mass Spectrometric Isotope Dilution", *Analytical Chemistry* 40, 687–691.
- Angelini, I., Canovaro, C., Venturino, M.; Artioli, G. (2019), The silver treasure of Marengo: silver provenancing and insights into late antiquity Roman and Gallo-Roman hoards. *Archaeological and Anthropological Science* 11, 4959–4970.
- Anguilano, L., Rehren, T., Müller, W. and Rothenberg, B. (2010), "The importance of lead in the silver production at Riotinto (Spain)", *ArcheoSciences, revue d'archéométrie* 34, 269–276.
- Anguilano, L. (2012), *Roman lead silver smelting at Riotinto, the case study of Corta Lago*, London, (inédita).
- Baker, J., Stos, S. y Waight, T. (2006), "Lead isotope analysis of archeological metals by Multiple-Collector Inductively Coupled Plasma Mass Spectroscopy", *Archeometry* 48, 45–56.
- Barnes, I. L., Murphy, T.J., Gramlich, J.W. and Shields, W.R. (1973), "Lead separation by anodic deposition and isotope ratio mass spectrometry of microgram and smaller samples", *Analytical Chemistry* 54, 1881–1884.
- Barnes, I. L., Gramlich, J.W., Diaz, M.G. and Brill, R.H. (1978), "The possible change of lead isotope ratios in the manufacture of pigments: a fractionation experiment". Carter, G.F. (ed.) *Archaeological chemistry II, Advances in chemistry series 171*: American Chemical Society, Washington, 273–277.
- Barriga, F. J. A. S., (1990), "Metallogenesis in the Iberian Pyrite Belt". Dallmeyer R. D. and Martinez Garcia E. (eds.), *Pre-Mesozoic Geology of Iberia*, Springer-Verlag, 369–379.
- Belshaw N.S, Freedman PA, O'Nions R.K, Frank M, and Guo, Y (1998), "A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes", *International Journal of Mass Spectrometry*, 18, 51–58.
- Brill, R. H., Wampler, J. M. (1967), "Isotope studies of ancient lead", *American Journal of Archaeology* 71. 63–77
- Blanco, A. y Rothenberg, B. (1981), *Exploración Arqueometalúrgica de Huelva*, Barcelona.
- Boulakia, J.D.C., (1972), "Lead in the Roman world", *American Journal of Archaeology*, 76(2), 139–144.
- Budd P, Pollard AM, Scaife B, Thomas RG (1995), "The possible fractionation of lead isotopes in ancient metallurgical processes", *Archaeometry* 37:143–150
- Cameron, A. E., Smith, D. H. and Walker, R. L. (1969), "Mass spectrometry of nanogram-size samples of lead", *Analytical Chemistry* 41, 525–526.
- Charlesworth, M.P. (1970), *Trade-Routes and Commerce of the Roman Empire*, Cambridge University Press.
- Craddock, P.T., Freestone, I.C., Gale, N.H., Meeks, N.D., Rothenberg, B. and Tite, M.S. (1985), "The investigation of a small heap of silver smelting debris from Rio Tinto, Huelva, Spain". *Furnaces and Smelting Technology in Antiquity*, Craddock P.T. y Hughes, M.J. (Eds.), British Museum Occasional Papers 48, London, 199–217.
- Delgado, A. and Regalado, M.C. (2010), *Rotae urionensis*. Las norias romanas de Riotinto (Huelva, España). *Patrimonio Geológico y Minero. Una apuesta por el desarrollo local sostenible*, Romero Macías, E. M. (Eds.), Huelva, 659–676.
- Delgado, A., Monge, A. and Queiroz, P.F. (2013), "La datación por radiocarbono de los elementos de las norias romanas de madera de Filón Sur (Minas de Riotinto, Huelva)", *Onoba*, 1, 275–284.
- Delgado, A.; Bustamante, M. and Martins, A. (2017), "La Faja Pirtica Ibérica en época de Augusto", *La Hispania de Augusto*, Mangas, J. y Mayorgas, A. (Eds.), Gerión 35, 895–924.
- Díaz Ariño, B. (2006): "Sello sobre lingote de plomo inédito conservado en el Museo Nacional de Arqueología Marítimo de Cartagena", *Salduie* 6, 291–295.
- Domergue, C. (1990), *Les mines de la Peninsule Ibérique dans l'antiquité romaine*, Collection de l'École Française de Roma, 127, Roma.
- Domergue, C. (1994), "Production et commerce des métaux dans le monde romain. L'exemple des métaux hispaniques d'après l'épigraphie des

- lingots”, *Epigrafia della produzione e della distribuzione*. Actes de la VIIe rencontre franco-italienne sur l'épigraphie du monde romain, 61-91.
- Faure, G. (1986), *Principles of isotope geology*, John Wiley & sons., New York.
- Fisher, R. (1925), *Statistical Methods for Research Workers*, Edinburgh.
- Gale, N. H., Stos-Gale, Z., Houghton, J. and Speakman, R. (1997), “Lead isotope data from the Isotrace Laboratory, Oxford, Archaeometry data base 4, ores from Cyprus”, *Archaeometry* 39, 237-246.
- Gale, N.H., Woodhead, A.P., Stos-Gale, Z.A., Walden, A. and Bowen, I. (1999), “Natural variations detected in the isotopic composition of copper: possible applications to archaeology and geochemistry”, *International Journal of Mass Spectrometry and Ion Processes*, 184, 1-9.
- Gale, N.H.; Stos-Gale Z.A. (2000), “Lead isotope analyses applied to provenance studies”. Ciliberto, E.; Spoto, G. (Eds.), *Modern analytical methods in art and Archaeology*, Wiley, New York, 503-584.
- Gardiner, V. (2001), “Romano-British Lead Pigs”, *IAMS*, 21, 11-13
- Grögler, N., Geiss, J., Grünenfelder, M. and Houtermans, F. G. (1966), “Isotopenuntersuchungen zur Bestimmung der Herkunft römischer Bleirohre und Bleibarren”, *Zeitschrift für Naturforschung*, 21a, 1167-1172
- Gomes, S.S., Monge Soares, A., Araújo, M.F. and Correia, V.H. (2016), “Lead isotopes and elemental composition of Roman *fistulae plumbeae aquariae* from Conimbriga (Portugal) using Quadrupole ICP-MS”, *Microchemical Journal*, 129, 184-193.
- Gulson, B.L. (1986), *Lead isotopes in mineral exploration*, Elsevier, Oxford.
- Härke, H. (1978), “Probleme der optischen Emissionsspektralanalyse in der Urgeschichtsforschung”, *Prähistorische Zeitschrift*, 53, 165-276
- Hirata, T. (1996), “Lead isotopic analyses of NIST standard reference materials using multiple collector inductively coupled plasma mass spectrometry coupled with a modified external correction method for mass discrimination effect”, *The Analyst*. 121, 1407-1411.
- Hunt Ortiz, M.A (2003), *Prehistoric Mining and Metallurgy in South West Iberian Peninsula*, B.A.R. International Series, 1118, Oxford.
- Junghans, S., Sangmeister, E. and Schröder, M. (1960), *Metallanalysen kupferzeitlicher und frühbronzezeitlicher Bodenfunde aus Europa*, Gebr, Mann
- Junghans S, Sangmeister E. and Schröder, M (1968), *Kupfer und Bronze in der frühen Metallzeit Europas 1-3*, Gebr, Mann.
- Junghans S, Sangmeister E. and Schröder, M (1974), *Kupfer und Bronze in der frühen Metallzeit Europas 4*, Gebr, Mann.
- Luzón Nogué, J. M^a (1968), “Sistemas de desagüe en las minas romanas del suroeste peninsular”, *Archivo Español de Arqueología*, 41, 101-120.
- Marinos, G. and Petrascheck, W.E. (1956), “Laurium. Institute of geology and underground researches in Greece”, *Greece. Geological and Geophysical Research* 4(1), 1-247.
- Murillo-Barroso, M., Montero-Ruiz, I., Nieto, J.M., Camalich Massieu, M.D. and Martín Socas, D. (2019), “Trace elements and lead isotopic composition of copper deposits from the eastern part of the Internal Zone of the Betic Cordillera (SE Iberia): application to provenance of archaeological materials”, *Journal of Iberian Geology*, 45/4, 585-608.
- Neyman, J. and Pearson, E.S. (1933), “The testing of statistical hypotheses in relation to probabilities a priori”, *Mathematical Proceedings of the Cambridge Philosophical Society*, 29, 492-510.
- Neyman, J. (1937), “Outline of a Theory of Statistical Estimation Based on the Classical Theory of Probability”, *Philosophical Transactions of the Royal Society*, 236, 333-380.
- Noddack, I. and Noddack, W. (1934), “Herkunftsuntersuchungen”. *Angewandte Chemie* 74, 637-41.
- Otto H, and Witter W (1952), *Handbuch der ältesten vorgeschichtlichen Metallurgie in Mitteleuropa*, Barth Verlag, Leipzig.
- Pollard, A.M. and Heron, C. (2008), *Archaeological chemistry*, RSC, London
- Pérez Macías, J.A. and Delgado Domínguez, A. (Eds.) (2007a), *Las minas de Riotinto en época Julio-Claudia*, Universidad de Huelva.

- Pérez, J. A. and Delgado, A. (2007b), "Tecnología metalúrgica en Riotinto y el SO Ibérico desde la Edad del Bronce a la Edad media", *Coloquio Annaberg*, 281 - 308.
- Pérez, J. A. and Delgado, A. (2011), "Ingeniería minera antigua y medieval en el suroeste ibérico", *Boletín Geológico y Minero* 122/1, 3-16.
- Pérez, J. A. and Delgado, A. (2014), "La Minería Romana en el SO Ibérico", *Cuadernos de Prehistoria y Arqueología de la Universidad de Granada* 24, 239-275.
- Pérez, J. A., Delgado, A. and Regalado, M.^a C. (2012): "El asentamiento romano en el paraje de Marismilla (Riotinto-Nerva, Huelva)", *Paisajes, Tiempos y Memoria*, Pérez, J. A., Carriazo J.L. y Ceballos, B., (Eds.), Universidad de Huelva, Huelva, 45-83.
- Pérez, J.A. and Frías, C. (1990), "La necrópolis de La Parrita (Nerva, Huelva) y los inicios de la metalurgia de la plata en Minas de Riotinto", *Cuadernos del Suroeste*, 1, 11-22.
- Rehkämper M, and Halliday, AN (1998), "Accuracy and long-term reproducibility of lead isotopic measurements by multiple-collector inductively coupled plasma mass spectrometry using an external method for correction of mass discrimination", *International Journal of Mass Spectrometry*, 181, 123-33.
- Rosman, K. J. R., Chisholm, W., Hong, S., Candelone, J.P. and C. F. Burton (1997), "Lead from Carthaginian and Roman Spanish Mines Isotopically Identified in Greenland Ice Dated from 600 B.C. to 300 A.D.", *Environmental Science and Technology*, 31, 3413 - 3416
- Rothenberg, R., García, F., Bachmann, H.G. and Goethe, J. (1990), "The Río Tinto enigma", *Minería y Metalurgia en las antiguas civilizaciones mediterráneas y europeas, I*, Madrid, 57-71.
- Rothenhoefer, P., Bode, M. and Hanel, N. (2016), "Old Finds – new insight: remarks on two romana lead ingots from Minas de Riotinto (Huelva, Spain)", *Onoba*, 4, 127 – 133.
- Salkield, L.V. (1970), "Ancient slag in the south west of the Iberian península", *La minería Hispana e Iberoamericana. Contribución a su estudio*, León, 85-99.
- Stos-Gale, Z.A., Gale, N.H., Houghton, J. and Speakman, R. (1995), "Lead isotope analyses of ores from the Western Mediterranean", *Archaeometry*, 37(2), 407-415
- Stos-Gale, Z.A. and Gale, N.H. (2009), "Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID)", *Archaeol Anthropol Science* 1, 195-213.
- Tylecote, R. F. (1987), *The early history of metallurgy in Europe*. Longman, London.
- Williams, D. (1934), "The geology of the Río Tinto Mines, Spain", *Bulletin of the Institution of Mining and Metallurgy*, 355, 593-678.
- Williams, D. (1950), "Gossanized Breccia-ores, Jarosites, and Jaspers at Riotinto (Spain)", *Transaction of Institution of Mining and Metallurgy*, 71, 1-12
- Willies, L. (1997), "Roman mining at Río Tinto", *Bulletin of the Peak District Mines Historical Society* 13:3, 1-30.
- Wood, J.R. and Montero Ruíz, I. (2019), "Semi-refined silver for the silversmiths of the Iron Age Mediterranean: A mechanism for the elusiveness of Iberian silver", *Trabajos de Prehistoria*, 76/2, 272-285,
- Wood, J. R., Montero-Ruiz, I. and Martínón-Torres, M. (2019), "From Iberia to the southern Levant: the movement of silver across the Mediterranean in the Early Iron Age". *Journal of World Prehistory*, 32 (1), 1-31.