

## FINGERPRINTING OF ROMAN MINTS USING LASER-ABLATION MC–ICP–MS LEAD ISOTOPE ANALYSIS\*

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*In this paper we present data to demonstrate the applicability of laser-ablation MC–ICP–MS isotope analysis to archaeological artefacts, in this case Roman silver coins. The technique requires no chemical preparation, does minimal damage to the sample and yields external reproducibility that is better than conventional TIMS analysis;  $^{207}\text{Pb}/^{206}\text{Pb} = \pm 0.015\%$   $2\sigma$  in comparison with  $^{207}\text{Pb}/^{206}\text{Pb} = \pm 0.04\%$   $2\sigma$ , respectively. We show that Pb isotope compositions give isotope fingerprints to mints despite the likely reworking of the metal during coin production.*

**KEYWORDS:** THIRD CENTURY, PB ISOTOPES, ROMAN, SILVER, COINS, LASER ABLATION, MINTS

### INTRODUCTION

In this study we set out to demonstrate the application of laser-ablation multi-collector inductively coupled plasma mass spectrometry (LA–MC–ICP–MS) lead analysis to archaeological problems and its enhanced precision over conventional thermal ionization analysis. We use lead isotopes to fingerprint the products of two Roman mints during the late second century AD, and show that mints have their own isotope signature that fingerprints their ore sources and production processes.

The production of currency is of fundamental importance to a state, and so an understanding of the origins of the metals—particularly the precious metals—that are used in the production of metal coinage improves our understanding of technology, trade routes, foreign policy and communication.

Geochemical fingerprinting of coins has been used to investigate many such aspects for several years. This approach looks at the distributions of geochemically linked elements to identify trends that can be diagnostic of different production centres (mints or workshops). These elements can be linked to the source of the ores from which the metal was smelted, such as gold and bismuth in silver or nickel, arsenic and cobalt in copper, or relate to the smelting and recycling technology, such as lead in silver or tin in copper. The former relates to the ore used and the production process, and the latter to the use of bronze rather than copper in the alloying process. The application of this approach has generated knowledge not revealed by traditional archaeological and numismatic approaches; for example, the discovery that the mint of Rome struck coins for circulation in various parts of the empire at different times (Carradice

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and Cowell 1987; Butcher and Ponting 1994), and that the influx of captured bullion during Trajan's Dacian wars can be identified by shifts in the elemental profile of coins produced from this metal (Butcher and Ponting 1998, 313). Trace element 'fingerprints', however, can lack resolution, making chemical distinction between possible groups unclear and indistinct. This is particularly a problem with later (post-first-century) coins, where there must have been such a degree of recycling that any trace element patterning has been homogenized to such a degree that little or no patterning is discernable (Butcher and Ponting 1998, 314). The issue of whether Roman silver was recycled and re-refined through the addition of lead (liquation) also needs to be addressed. The Roman coinage underwent numerous re-coinages, involving the calling-in of old coins and the subsequent issue of new coins (Burnett 1987, 89). Often, the new coins were issued on a lower standard of fineness, and occasionally on a higher one (e.g., Domitian's reform in AD 83). In either case, it would have been necessary to re-refine the silver from the old coins and then re-alloy it in order to achieve the high standards of alloy control that the Roman law demanded (Burnett 1987, 20–8).

Because they can distinguish between different sources of a given element, isotopes provide a more powerful complimentary tool to geochemical fingerprinting (Stos-Gale and Stos-Gale 1989; Stos-Gale 1998; Gale and Stos-Gale 2000). Extensive studies have been made of the Pb isotope composition of European ore fields, with the aim of providing provenance fields for sourcing artefacts. In some cases, lead–silver ores have unique compositions, such as those at Lavrion and from Siphnos, but many show overlapping fields. Stos-Gale (1998) concludes that it is only possible to trace metals back to their ore-field origins if the artefacts were made from material originating from a single source.

Identifying geological source regions for lead in human artefacts is difficult and is hampered by three main problems:

- (1) Imprecision in conventional thermal ionization Pb analyses arising from uncertainties in mass fractionation corrections when double or triple spiking techniques are not employed (Thirlwall 2002).
- (2) The very variable composition of natural sources and the problems of ensuring that defining fields are drawn through the analysis of very well provenanced material.
- (3) The re-working, re-refining and re-melting of metals that blur the primary geological signature.

This last point is seen as being particularly the case with later Roman silver coinage, where the silver would have been re-refined from coinage alloys (by liquation) by the addition of lead (Craddock 1995, 232) and then re-alloyed with copper (or copper alloy) with its own lead component.

To address these problems, we present the first Pb isotope analysis of Roman coins undertaken using MC–ICP–MS analysis on carefully selected coins of well-known origin (as defined by both stylistic and chemical analyses). Our approach is to define the Pb isotope signature of a mint or workshop (which includes the effects of all of its procedures of metal processing and recycling) and to test the hypotheses that with higher-precision analysis and well-provenanced material it is possible to define the Pb isotope range of specific mints. If this is possible, then it provides a valuable tool for sourcing less well-constrained samples, once the main discrimination fields are established.

#### SAMPLE DETAILS

The chemical analysis of silver coins of the Roman Emperor Septimius Severus (AD 193–211) had been conducted several years ago on drilled samples taken from British Museum coins,

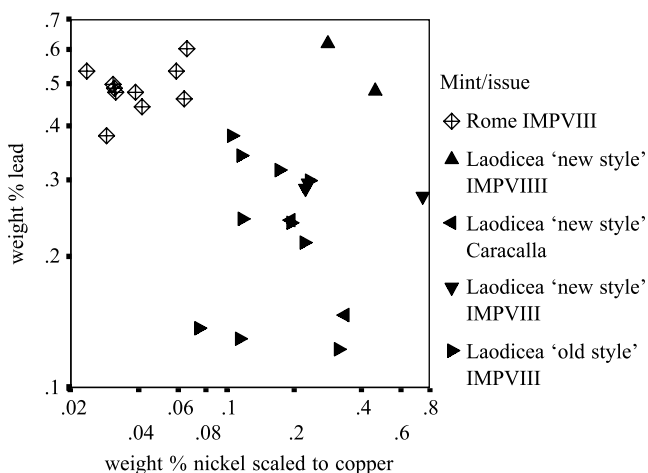


Figure 1 A geochemical discrimination diagram of denarii from the mints at Rome and Laodicea, based on the nickel and zinc contents of the copper component in the coins.

and the results were subsequently published (Butcher and Ponting 1997). Enough sample remained from some of the coins for MC-ICP-MS to be conducted and the results compared with the chemical analysis. The denarii of Severus have a silver content of *c.* 45% (Butcher and Ponting 1997; Gitler and Ponting forthcoming) and were produced at a number of different mints; Rome and some eastern mints, including Alexandria in Egypt, Laodicea ad Mare and Emesa (both in Syria).

This study focuses on the Rome and Laodicea mints. Over 50 silver denarii have now been analysed from these two mints (Gitler and Ponting forthcoming). The gold and bismuth contents of the silver portion of the alloy are often a good method of discriminating between alloys (Craddock 1995); however, no distinction could be made between the two mints on this basis. Trace elements associated with the copper proved more useful. The lead and nickel contents (the latter associated with the copper) provide grounds for discrimination (Fig. 1), with the samples falling into two distinct fields. Furthermore, the lead content is generally higher in the coins that are known to have been struck in Rome (a mean of 0.5% for Rome compared with a mean of 0.2% for Laodicea). This latter difference may reflect differences in the refining procedure, which resulted in more lead being left in the silver, or the possibility that the copper alloyed with the silver contained more lead. The characterization of the samples by conventional numismatic techniques, supported by geochemical discrimination, gave a good basis for testing the discriminatory power of Pb isotopes to fingerprint the mints.

#### LEAD ISOTOPE ANALYSIS TECHNIQUES

Drillings from the denarii were mounted in resin using standard procedures and analysed using a New Wave Research 266 nm Nd:YAG laser-ablation system attached to a VG P54 Elemental MC-ICP-MS (a multi-collector inductively coupled plasma mass spectrometer). The surface of the mount was ablated away until surplus resin was removed and the metal was exposed to the laser. The shavings were then ablated using a rastered sampling approach with the following conditions: raster spacing 100  $\mu\text{m}$ , scan speed 100  $\mu\text{m s}^{-1}$ , change of Z per pass

5  $\mu\text{m}$ , power 35%, frequencies 10 Hz, spot size 400  $\mu\text{m}$ . This resulted in *c.* 8 V total emission from the majority of the material, and the power was adjusted between 32% and 35% to maintain such a beam intensity. The results are based on 100 scans with a target internal precision of  $\pm 0.1\%$  1 SE, which the majority achieved. The data are presented in Table 1. A blank was

Table 1 *Laser-ablation Pb isotope ratios and reproducibility statistics for Roman coins*

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
<i>Roman coins</i>					
BMC 167a	18.3791	15.6241	38.4350	0.84993	2.09104
BMC 167b	18.3946	15.6374	38.4709	0.85010	2.09178
BMC 167c	18.3937	15.6338	38.4639	0.84999	2.09147
BMC 167d	18.4006	15.6402	38.4815	0.85008	2.09166
Average	18.3920	15.6339	38.4628	0.8500	2.0915
1 SD	0.0091	0.0070	0.0199	0.0001	0.0003
% 2 SD	0.10	0.09	0.10	0.02	0.03
BMC 152a	18.4978	15.6472	38.6066	0.84586	2.08723
BMC 152b	18.4880	15.6338	38.5759	0.84575	2.08670
Average	18.4929	15.6405	38.5912	0.8458	2.0870
1 SD	0.0069	0.0094	0.0218	0.0001	0.0004
% 2 SD	0.07	0.12	0.11	0.02	0.04
BMC 151a	18.4003	15.6317	38.4630	0.84970	2.09045
BMC 151b	18.3900	15.6276	38.4498	0.84983	2.09087
Average	18.3951	15.6296	38.4564	0.8498	2.0907
1 SD	0.0072	0.0029	0.0094	0.0001	0.0003
% 2 SD	0.08	0.04	0.05	0.02	0.03
BMC 180a	18.4463	15.6384	38.5270	0.84768	2.08829
BMC 180b	18.4416	15.6328	38.5094	0.84766	2.08810
Average	18.4440	15.6356	38.5182	0.8477	2.0882
1 SD	0.0033	0.0040	0.0124	0.0000	0.0001
% 2 SD	0.04	0.05	0.06	0.00	0.01
BMC 169a	18.3748	15.6327	38.4396	0.85078	2.09200
BMC 156a	18.3703	15.6307	38.4254	0.85089	2.09180
BMC 161	18.3532	15.6259	38.3920	0.85134	2.09170
<i>Laodicea—old-style coins</i>					
BMC 445ai	18.5813	15.6465	38.6642	0.84202	2.08095
BMC 445aai	18.5754	15.6414	38.6473	0.842088	2.080817
BMC 445b	18.570691	15.64137	38.65115	0.842264	2.081405
Average	18.5783	15.6439	38.6558	0.8421	2.0809
1 SD	0.004	0.004	0.012	0.000	0.000
% 2 SD	0.04	0.05	0.06	0.01	0.01
1946 10-4-?	18.5679	15.64732	38.64393	0.842659	2.081277
BMC 466a	18.5416	15.6442	38.6241	0.843808	2.083034
1947 10-1-10a	18.543934	15.63681	38.60844	0.843189	20.81975
BMC 449a	18.637457	15.65106	38.71221	0.839849	2.077319
<i>Laodicea—new-style coins</i>					
BMC 451a	18.499241	15.64052	38.5732	0.845849	2.08603
BMC 463	18.548362	15.64503	38.63032	0.843493	2.082854

determined on the resin that, under the ablation conditions above, gave an insignificant beam intensity of  $1.8\text{E-}3$  V. The NBS 981 solution standard gave the following values and reproducibility for a 100 ppb Pb solution, doped with 10 ppb of Tl and run throughout the day:  $^{206}\text{Pb}/^{204}\text{Pb} = 16.933 \pm 0.007\% \ 2\sigma$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.485 \pm 0.01\% \ 2\sigma$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 36.688 \pm 0.019\% \ 2\sigma$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.91458 \pm 0.007\% \ 2\sigma$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1667 \pm 0.018\% \ 2\sigma$  ( $n = 11$ ). The data agree well with recently documented values from plasma analysis given in Thirlwall (2002) and so no normalization of the sample data set was required. Simultaneous aspiration of the thallium solution provides constant monitoring and correction for mass bias variations caused by sample matrices, when compared with the solution standard. Additional inaccuracies could result from interferences of individual lead isotope peaks as a result of the formation of polyatomic ions from the sample matrix. However, the high lead content (0.2–0.5 wt%) and the inorganic nature of the matrix would almost certainly render such interferences very small or negligible.

## RESULTS AND DISCUSSION

The reproducibility of the NBS 981 solution provides the evidence for the stability and the accuracy of the mass spectrometer. However, as the material was introduced by laser ablation, unpurified by chemical procedures, an estimate had to be made for the reproducibility of the data using this method of sample introduction. The external reproducibility (i.e., the heterogeneity of the coins) was tested by carrying out multiple or duplicate analyses on several of the coin shavings. Four determinations of different shavings were made for coin BMC 167; three determinations were made on BMC 445 and duplicate analyses were performed on three other coins (see Table 1). These data provide the current best estimate for external reproducibility, which is given as the average reproducibility of these multiple analyses,  $^{207}\text{Pb}/^{206}\text{Pb} = \pm 0.015\% \ 2\sigma$  and  $^{208}\text{Pb}/^{206}\text{Pb} = \pm 0.023\% \ 2\sigma$ , respectively. This demonstrates that the method is at least twice as precise as conventional thermal ionization analysis, which typically yields reproducibilities of the above ratios of  $\pm 0.04\% \ 2\sigma$  and  $\pm 0.07\% \ 2\sigma$ ,  $n = 5$ , respectively (NIGL unpublished data).

Fourteen coin samples were selected for analysis, seven from the mint at Rome and seven from the mint at Laodicea. All of the samples from Rome coins were struck during Severus' eighth imperatorship (IMP VIII, AD 196). Five of the Laodicean samples were 'old-style' coins from the same period. Two of the coins were of a different style, referred to as 'new-style'; one is from the same period as the coins above, while the other is younger and is from the later ninth imperatorship (IMP VIII, AD 197). The imperatorship was an official honour or acclamation bestowed upon the emperor in recognition of a military victory. When such acclamations are frequent, as in the case of Severus, they can be used to help date coinages where the imperatorships are enumerated. The data from the coins minted in Rome and Laodicea plot in two separate fields (Fig. 2). The coins from Rome lie at the more radiogenic (younger) composition end and those from Laodicea at the less radiogenic (older component) end.

The Pb isotope data from the mint at Rome and from the old-style coins from Laodicea show a similar pattern. The majority of the data cluster to form what might be viewed as the 'main field' for each mint. Two coins from the mint at Rome extend the field down to lower values and one coin from Laodicea is a low-values outlier. There is a compositional gap between the coins from the mint at Rome and the 'old-style' coins from Laodicea. The 'new-style' coins straddle this gap. BMC 451 IMPVIII plots within the error of coin BMC 152 from the mint at Rome, whereas the later 'new-style' coin BMC 463 plots within the Laodicea field of 'old-style' coins. The coins attributed to the Laodicea mint are of two types. BMC451 was

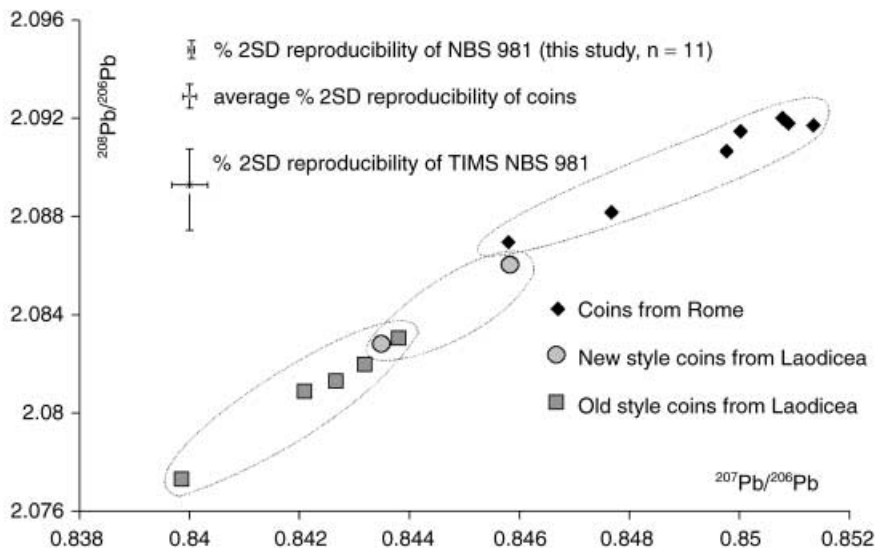


Figure 2 A  $^{207}\text{Pb}/^{206}\text{Pb}$  versus  $^{208}\text{Pb}/^{206}\text{Pb}$  discrimination diagram of data from the mints at Rome and Laodicea.

issued contemporaneously with the 'old-style' coins, marking Severus' eighth imperatorial acclamation (AD 196), while BMC463 was struck a year later, in AD 197, to mark Severus' ninth imperatorial acclamation. The interpretation of this may mean that the first production of the 'new-style' coins were struck in Rome and shipped out to Syria, and that production of that design was started in Syria in the following year when the 'old style' was ended.

#### CONCLUSIONS

The reproducibility of the coin analysis using laser-ablation MC-ICP-MS analysis ( $^{207}\text{Pb}/^{206}\text{Pb} = \pm 0.015\%$   $2\sigma$ ) was better than that of thermal ionization analysis (typically  $\pm 0.04\%$   $2\sigma$ ), demonstrating a higher-resolution method of analysis that is rapid and does not require prior chemical separation for Pb. Such an approach could be used on small samples where damage to the sample had to be kept to the minimum, or where it was not possible to remove a sub-sample for dissolution.

Pb isotope analysis has clearly distinguished between Roman denarii from the mint at Rome and 'old-style' coins from the mint at Laodicea. Twelve of the samples produced two well-defined fields within isotope space that are analytically separable. The two 'new-style' coins from Laodicea are chemically different from both of these groups and may form a third field in isotope space.

The study has demonstrated that isotope analysis provides a signature for a specific workshop or mint, and therefore has considerable potential as a technique for the study of ancient coinage and any other class of archaeological non-ferrous metalwork.

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