



Simultaneous lead isotope ratio and gold-lead-bismuth concentration analysis of silver by laser ablation MC-ICP-MS

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ABSTRACT

A new approach is presented for the simultaneous analysis of lead isotope ratios and gold, lead, and bismuth concentrations in metallic silver using nanosecond laser ablation multi-collector inductively-coupled plasma mass spectrometry (LA-MC-ICP-MS). Corrections for both isotope and concentration analyses are performed using an in-house matrix matched silver reference material RM3834. Accuracy and external reproducibility are demonstrated by repeat analyses of a further seven silver reference materials all characterised by solution (MC)-ICP-MS approaches. Typical internal precisions, expressed as two relative standard errors (S.E.) of the mean of the cycles comprising one analysis, are <0.5% for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and <0.03% for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. External reproducibilities, based on repeat analyses over a 10 month period and expressed as two relative standard deviations (S.D.) of the mean, are <0.4% for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ and <0.2% for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. Internal precisions and external reproducibilities of gold, lead and bismuth concentration analyses are typically <25%. Data are consistent with solution-based approaches. Methods are further demonstrated through analyses of a set of Islamic silver dirhams from the mint of al-Muhammadiyah, highlighting their applicability to geochemical studies of archaeological artefacts.

1. Introduction

The isotopic and elemental signature of archaeological objects are important archives of information regarding the societies who created and used them, shedding light on aspects including: location of raw material source, technological processing, circulation of metal pools, and patterns of trade and exchange (e.g. Bevins et al., 2012; Bray and Pollard 2012; Standish et al., 2015; Merkel 2016). A key analytical method employed in studies that investigate metallic objects is Pb isotope ratio analysis, the signature of which may vary between objects depending on the source(s) of the Pb incorporated either as a trace or major element (Albarède et al., 2012; Baron et al., 2014). Whilst traditionally such analyses have been performed using either Thermal Ionisation Mass Spectrometry (TIMS) or solution Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), such approaches require destructive sampling of the object, and, for the most

accurate and precise results, time-consuming chemical preparation of the samples prior to analysis (Northover et al., 2001; Stos-Gale and Gale 2009; Desauty et al., 2011). In contrast, laser ablation (LA)-MC-ICP-MS can allow minimally destructive analysis of objects, with the added benefit of faster sample through-put due to the absence of time-consuming sample digestion and purification procedures (Standish et al., 2013). With artefact conservation being a key consideration for curators of culturally important artefacts worldwide, this technique is increasingly becoming a key method in the field of archaeological science despite typically lower precisions (Dussubieux et al., 2016).

Considerations of artefact conservation are especially pertinent when studies focus on objects made from precious metals, and indeed a number of studies have begun to investigate the suitability of LA-MC-ICP-MS techniques with regards to Pb isotope analysis of silver artefacts (Ponting et al., 2003; Baker et al., 2006; García de Madinabeitia et al., 2017). However, accuracy was investigated only by Baker et al.

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Table 1

Details of reference materials used in this study for laser ablation MC-ICP-MS. Uncertainties are ± 2 S.E. in the last decimal place for all Pb isotope data except for NIST SRM610 which, along with concentration data, are ± 2 S.D. in the last decimal place. Cert. refers to certified reference values. Asterisks indicate solution MC-ICP-MS measurements where ion-exchange chromatography was not performed prior to analysis.

ID.	Description	Method	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Au (wt. %)	Bi (wt. %)	Pb (wt. %)	Ref.
NIST SRM610	Glass (NIST)	Solution MC-ICP-MS	17.052 ± 2	15.515 ± 2	36.991 ± 5	0.90986 ± 1	2.1694 ± 1	–	–	–	Baker et al. (2004)
133X AGA1	Silver Reference Material (MBH Analytical Ltd.)	ICP-AES	–	–	–	–	–	1.48 ± 6	0.194 ± 12	0.207 ± 14	Cert.
133X AGA3	Silver Reference Material (MBH Analytical Ltd.)	Solution MC-ICP-MS*	17.409 ± 1	15.545 ± 1	37.280 ± 5	0.89304 ± 5	2.1413 ± 1	–	–	–	This study
RM12467	Silver Reference Material	ICP-AES	–	–	–	–	–	0.258 ± 4	0.048 ± 2	1.89 ± 10	Cert.
		Solution MC-ICP-MS*	18.533 ± 6	15.660 ± 6	38.650 ± 10	0.84490 ± 10	2.0854 ± 3	–	–	–	Merkel (2016, 2019)
		Solution MC-ICP-MS	18.532 ± 1	15.657 ± 1	38.644 ± 2	0.84490 ± 2	2.0852 ± 1	–	–	–	This study
		Solution ICP-MS	–	–	–	–	–	0.20 ± 1	0.066 ± 3	1.18 ± 6	Merkel (2016, 2019)
		fsLA MC-ICP-MS	18.535 ± 4	15.662 ± 4	38.660 ± 10	0.84490 ± 10	2.0856 ± 3	–	–	–	Merkel (2016, 2019)
		nsLA ICP-QMS	–	–	–	–	–	0.17 ± 1	0.063 ± 3	0.94 ± 4	Merkel (2016, 2019)
		nsLA ICP-QMS	–	–	–	–	–	0.21 ± 2	0.066 ± 6	1.08 ± 11	Merkel (2016, 2019)
RM3834	Silver Reference Material	Solution MC-ICP-MS	18.452 ± 4	15.639 ± 4	38.480 ± 20	0.84750 ± 10	2.0855 ± 4	–	–	–	Merkel (2016, 2019)
		Solution MC-ICP-MS	18.447 ± 2	15.634 ± 2	38.466 ± 5	0.84749 ± 1	2.0851 ± 1	–	–	–	This study
		Solution ICP-MS	–	–	–	–	–	0.35 ± 2	0.014 ± 1	0.52 ± 3	Merkel (2016, 2019)
		fsLA MC-ICP-MS	18.457 ± 17	15.643 ± 16	38.490 ± 40	0.84750 ± 40	2.0855 ± 11	–	–	–	Merkel (2016, 2019)
		nsLA ICP-QMS	–	–	–	–	–	0.42 ± 4	0.016 ± 1	0.49 ± 2	Merkel (2016, 2019)
		nsLA ICP-QMS	–	–	–	–	–	0.39 ± 4	0.013 ± 1	0.46 ± 5	Merkel (2016, 2019)
Ag-4817-14	Silver Reference Material	Solution MC-ICP-MS	20.059 ± 5	15.799 ± 3	40.900 ± 5	0.78762 ± 1	2.0390 ± 2	–	–	–	This study
RMAg981	Silver Reference Material	Solution MC-ICP-MS	16.938 ± 2	15.490 ± 1	36.706 ± 4	0.91452 ± 2	2.1670 ± 1	–	–	–	This study
Ag-Du	Galena	Solution MC-ICP-MS*	18.690 ± 3	15.653 ± 1	38.780 ± 4	0.83753 ± 10	2.0749 ± 3	–	–	–	This study
Ag-Sl	Silver Reference Material	Solution MC-ICP-MS	18.686 ± 1	15.651 ± 2	38.774 ± 5	0.83758 ± 3	2.0750 ± 2	–	–	–	This study
	Silver Reference Material	Solution MC-ICP-MS*	18.051 ± 1	15.582 ± 1	38.104 ± 2	0.8634 ± 1	2.1110 ± 3	–	–	–	This study
		Solution MC-ICP-MS	18.048 ± 4	15.579 ± 3	38.096 ± 8	0.86321 ± 2	2.1108 ± 7	–	–	–	This study

(2006) who, in a study of 6 hack-silver objects, showed consistency between the results of LA-MC-ICP-MS, bulk MC-ICP-MS analyses, and analyses by Thermal Ionisation Mass Spectrometry (TIMS) performed after sample purification. Demonstrations of reproducibility have been limited to repeat analyses (between two and ten) of selected artefacts. None of these studies state whether analyses were performed over multiple analytical sessions and due to the small number of objects analysed it is presumed that the stated reproducibilities are not long-term assessments of the approach (e.g. over months). The true capabilities and limitations of the technique are therefore yet to be fully recognised.

Here we present methods for LA-MC-ICP-MS Pb isotope analysis of metallic silver, demonstrating accuracy and external reproducibility through repeat analyses of a series of metallic silver reference materials over a 10 month period. A key factor holding back the development of this technique is the absence of well characterised matrix-matched standards relevant to this type of analysis. We therefore demonstrate our approach on a suite of seven reference materials, including some that are available on the open-market and could be adopted as an inter-laboratory reference material by the wider scientific community. In addition, we incorporate Au, Pb and Bi concentration analysis into the

analytical set-up. These elements have been demonstrated to be of use in geochemical studies of archaeological silver because they can directly reflect the compositions of the ore exploited (McKerrell and Stevenson 1972; Pernicka and Bachmann 1983; L'Héritier et al., 2015); they therefore add an extra level of possible discrimination between objects. These data are collected simultaneously with the Pb isotope ratios, and thus come at no extra analytical cost and do not require a secondary analytical approach. Finally, the methods are further demonstrated through the analyses of a set of early Abbasid Islamic silver coins, *dirhams*, from the mint of al-Muhammadiyah, Iran, held by the Fitzwilliam Museum, Cambridge.

2. Materials and methods

2.1. Reference materials

All reference materials analysed as part of this study are detailed in Table 1. NIST SRM610 was trialled as a Pb isotope standard for mass bias corrections (Baker et al., 2004), whilst silver reference materials 133X AGA1 and 133X AGA3 were used for both Pb isotope and concentration analyses (MBH Analytical Ltd., Barnet, UK). These are currently

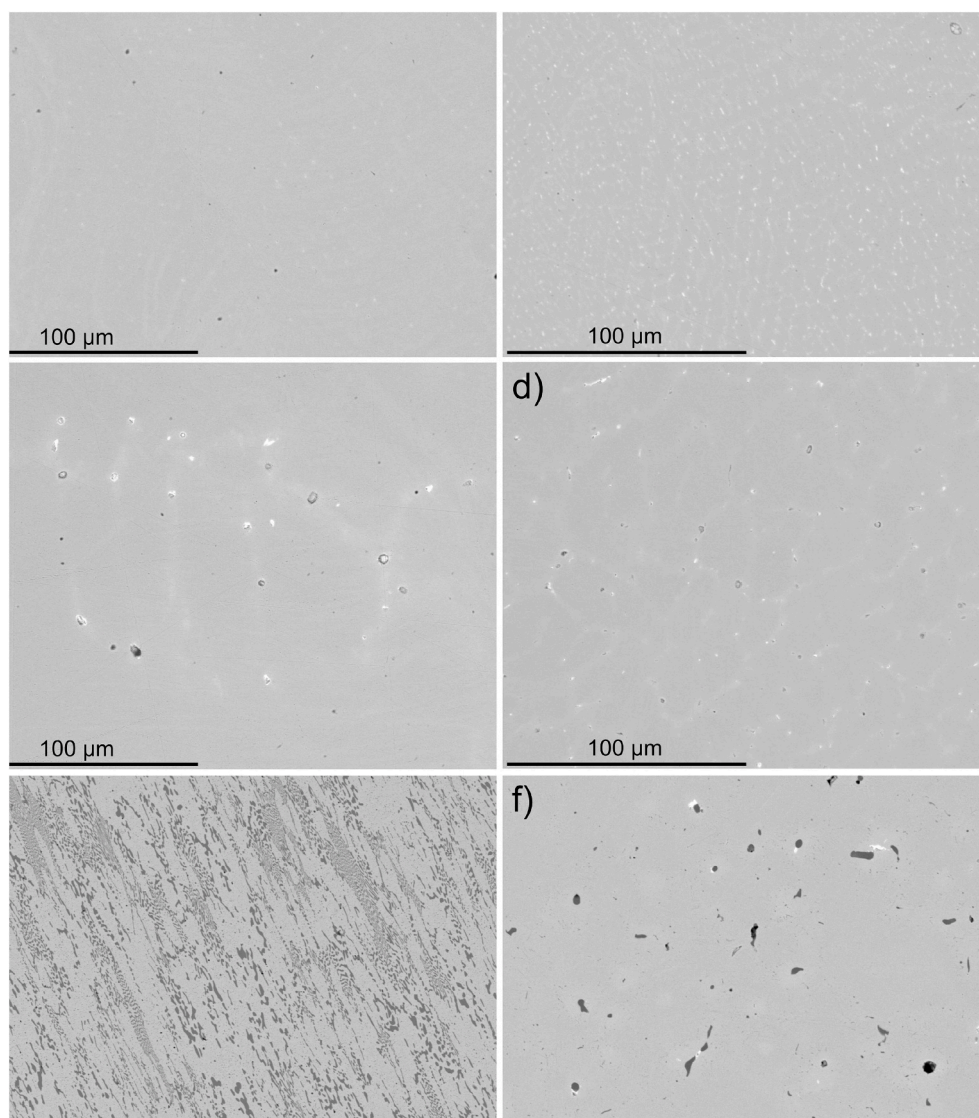


Fig. 1. Backscattered electron SEM images detailing the microstructure of silver reference materials: a) Ag-Du, b) Ag-SI, c) Ag-4817-14, d) RMAg981, e) 133X AGA1, f) 133X AGA3. Reference materials were polished prior to imaging. Metallic Pb inclusions are white and in c) and d) Pb is enriched in the silver between the grains (light grey).

available on the open market. A series of further in-house silver reference materials were also employed. RM3834 and RM12467 are samples of Viking period (c. 750–1050 CE) hack-silver from Hedeby, Germany, previously analysed by a range of instrumentation for both Pb isotopes and elemental concentrations (Merkel 2016, 2019). A further reference material was created by melting nearly pure metallic silver (MBH 131X AGP4) with universal Pb isotope ratio standard NIST SRM981 (procured as a solid) together in a clean lidded graphite crucible at 1060 °C and cast into hot water; the resulting silver contains c. 1.5% Pb and is named RMAg981. Ag-4817-14 was created by melting metallic silver with radiogenic lead using the above methods. Ag-Du and Ag-SI were both created from ore: Ag-SI was produced from argentiferous galena, and Ag-Du was made from silver ore and galena. For these two reference materials, the galena was first roasted and then smelted in graphite crucibles at 1100°C. Ag-SI was created by cupelling the resulting argentiferous lead, remelting in a graphite crucible and casting into hot water. Ag-Du was made by cupelling the smelted lead together with rich silver ore consisting of argentiferous tetrahedrite and silver sulphide. The resulting metallic silver was then remelted in a graphite crucible and cast into hot water. The silver produced from ore is low in impurities, consisting of Cu (<0.5%) and Pb.

The microstructure of both the created and commercial silver reference materials was investigated by scanning electron microscopy in polished section (Fig. 1). The two reference materials that underwent a cupellation step were highly homogenous: Ag-Du and Ag-SI have sub-micron Pb phases distributed evenly throughout the metal (Fig. 1a and b). However, the two materials created by melting together metallic Pb and Ag (Ag-4817-14 and RMAg981) have discrete globules of Pb up to several microns in size that are not equally distributed throughout the metal (Fig. 1c and d): this metal is more heterogeneous than the Ag that underwent cupellation and could have a different ablation behaviour. Regarding the commercial reference materials, 133X AGA1 has no separate Pb phase that is visible (Figs. 1e) and 133X AGA3 has micron-size Pb inclusions that are evenly distributed (Fig. 1f). Both these reference materials are homogenous in the volumes ablated in this study.

2.2. Solution MC-ICP-MS

Solution MC-ICP-MS analyses of RM3834 and RM12467 are previously published (Merkel 2016, 2019). Solution MC-ICP-MS analyses of RM3834, RM12467, Ag-4817-14, 133X AGA3, RMAg981, Ag-Du, and Ag-SI were performed on a Nu Plasma high resolution (HR) MC-ICP mass spectrometer (Nu Instruments Ltd., Wrexham, UK) in the Department of Earth Sciences at the University of Oxford using a well-established Tl-doping technique for mass-bias correction (Belshaw et al., 1998). Silver reference materials were digested in dilute HNO₃ and were purified using anion-exchange resin (Bio-Rad AG1-X8) with dilute HBr and HCl. Silver with greater than 1 wt % Pb were additionally analysed without purification. In brief, reference materials and samples were prepared in 2% HNO₃ acid to give ~40 ppb Pb solutions, and a High-Purity Tl standard (Lot# 0927427) was added to achieve Tl/Pb = ~0.2 for internal mass-bias correction. The measured ratios of ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb, and ²⁰⁶Pb/²⁰⁴Pb in NIST SRM981 are 2.1662 ± 3, 0.91449 ± 10, and 16.933 ± 2 (2 S.D., n = 62) using the exponential fractionation law with ²⁰⁵Tl/²⁰³Tl = 2.3875. The data are in good agreement with previous studies using solution MC-ICP-MS (Hirata 1996; Belshaw et al., 1998; Rehkämper and Halliday, 1998).

To correct for instrumental drift, and for comparisons with

previously published data using different techniques, all Pb isotopic data presented in this study have been normalised to NIST SRM981 through sample-standard bracketing using the following values: ²⁰⁸Pb/²⁰⁶Pb = 2.16701, ²⁰⁷Pb/²⁰⁶Pb = 0.91459, and ²⁰⁶Pb/²⁰⁴Pb = 16.9356 for (Todd et al., 1996). The normalised ratios of ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb, and ²⁰⁶Pb/²⁰⁴Pb in NIST SRM982 are 1.0003 ± 1, 0.46701 ± 2, and 36.730 ± 3 (2 S.D., n = 3), which are consistent with previous studies (Hirata 1996; Todd et al., 1996; Rehkämper and Mezger, 2000). The results of silver reference materials are reported in Table 1.

2.3. LA-MC-ICP-MS

Nanosecond (ns) LA-MC-ICP-MS analyses were performed at the University of Southampton using a Neptune Plus MC-ICP mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), equipped with 9 Faraday cup detectors and a central ion counter, coupled to an Elemental Scientific Lasers (Bozeman, MT, USA) NWR193 excimer laser ablation system with a TwoVol2 ablation chamber (sample cell dimensions of 100 × 100 × 25 mm). Reference materials were either mounted in epoxy resin and polished or secured in adhesive putty. The coins were mounted whole in sheets of polyethylene foam customised to their individual shapes. Lead isotope ratio and Au, Pb and Bi data were collected simultaneously using the Faraday cup array detailed in Table 2.

Operating conditions and tune parameters, detailed in Table 3, were optimised for stability, sensitivity, and low oxide production (²⁵⁴UO⁺/²³⁸U⁺ <1%) whilst ablating glass reference material NIST SRM610. A minimally invasive approach was also a key consideration considering the high cultural value of early medieval silver dirhams from museum collections. The laser was therefore operated in spot

Table 3
Typical operating conditions for laser ablation MC-ICP-MS analysis.

Instrumentation	
Mass Spectrometer	Thermo Scientific Neptune Plus MC-ICP mass spectrometer
Laser Ablation System	Elemental Scientific Lasers NWR193 excimer laser with TwoVol2 ablation cell
RF Power	1200 W
Cones	Nickel skimmer (X) and jet sample
Gas Flows	
Cool Gas	16 l min ⁻¹
Auxiliary Gas	0.7 l min ⁻¹
Helium ablation cell carrier gas	0.8–1.0 l min ⁻¹
Additional nitrogen	0.001–0.003 l min ⁻¹
Argon make-up gas	1.0 l min ⁻¹
Ablation Conditions	
Laser power density	~6 J cm ⁻²
Laser repetition rate	5 Hz
Laser spot size	60 µm
Ablation mode	spot
Dwell Time	210 s
Data Collection	
Integration time	4.194 s
n cycles of preceeding gas blank	15
n cycles of ablation	50
n cycles of succeeding gas blank	15

Table 2
Faraday cup configuration for laser ablation MC-ICP-MS analysis.

	L4	L3	L2	L1	C	H1	H2	H3	H4
Mass	¹⁹⁷ Au	–	²⁰² Hg	²⁰⁴ Pb	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb	²⁰⁹ Bi	–
Resistor	10 ¹¹ Ω	10 ¹² Ω	10 ¹² Ω	10 ¹² Ω	10 ¹¹ Ω	10 ¹¹ Ω	10 ¹¹ Ω	10 ¹² Ω	–

mode, with a beam diameter of 60 μm , repetition rate of 5 Hz, power density of $\sim 6 \text{ J cm}^{-2}$, and dwell time of 210 s. The preferred operating conditions are similar to those used in related studies, e.g. Ponting et al. (2003) and Baker et al. (2006). Typical sensitivities for RM3834, with a composition of $\sim 0.4 \text{ wt } \% \text{ Au}$, $\sim 0.5 \text{ wt } \% \text{ Pb}$, $\sim 0.015 \text{ wt } \% \text{ Bi}$ (Merkel 2016, 2019), were $\sim 1 \text{ V}$ for ^{197}Au , $\sim 6 \text{ V}$ for ^{208}Pb , and $\sim 0.2 \text{ V}$ for ^{209}Bi .

Data were collected over 50 integration cycles of 4.194 s. An on-peak gas blank was analysed immediately before and after ablation, both over 15 cycles of 4.194 s. All corrections were applied offline. Dynamic blank corrections were applied on all masses cycle by cycle assuming a linear relationship between the preceding and succeeding blank measurements. Each sample was ablated once, and samples were analysed in groups of three bracketed by analyses of reference materials with known isotopic and elemental compositions: glass reference material NIST SRM610 and/or the silver reference material RM3834. For Pb isotope analysis, a mercury correction was performed cycle by cycle on ^{204}Pb following the method outlined in Standish et al. (2013), instrumental mass bias was corrected by sample-standard bracketing, and cycles falling outside of 2 SD of the mean were omitted. Both mercury and mass bias corrections employed either RM3834 or NIST SRM610 and used the isotopic compositions published in Table 1.

Gold, lead and bismuth concentrations were calculated by normalising the mean signal intensity (^{197}Au , ^{206}Pb and ^{209}Bi) of the samples to those of the bracketing RM3834 analyses and the elemental compositions published in Table 1. The first 24 cycles were omitted from this calculation to allow stabilisation of the signal, which can be highly variable at the beginning of an analysis, e.g. due to perturbation or contamination of the unpolished surface, or loss of optimal focus. Limits of detection (l.o.d.), defined as 10x the blank intensities of each mass, equate to concentrations of 24 ppm Au, 45 ppm Pb, and 5 ppm Bi. Au/Pb and Bi/Pb ratios were first calculated for all integration cycles from the blank-corrected intensity data after abundance-correcting the ^{206}Pb signal, then resulting mean ratios were also normalised to the bracketing RM3834 analyses.

The role of matrix matched standards in laser ablation MC-ICP-MS has been discussed in numerous studies. Whilst some have argued that they are not always critical (Kimura et al., 2013; Standish et al., 2013) others have shown that in some cases they are absolutely necessary if data of the highest accuracy and reproducibility is to be achieved (Zhang et al., 2016; Standish et al., 2019). Here the roll of matrix-matched standards to Pb isotope analysis of metallic silver has been investigated. Twelve analyses of silver reference material RM12467 were bracketed by both the unmatched, but well characterised, global reference material NIST SRM610 (silicate-rich glass) and the well-matched silver reference material RM3834. Both accuracy and reproducibility of RM12467 are superior when employing the matrix matched reference material RM3834 for both mercury and mass bias corrections (Fig. 2). Offsets to the solution values presented in Table 1 are as great as -1.91% for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, and $+0.70\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ when bracketing with NIST SRM610, compared to $+0.53\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, and $+0.20\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ when bracketing with silver reference material RM3834 (Table S1). External reproducibilities, expressed in % as 2 S.D. of the mean of the repeat analyses, are $\leq 1.92\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, and $\leq 0.28\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ when bracketing with NIST SRM610, compared to $\leq 1.21\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, and $\leq 0.16\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ when bracketing with silver reference material RM3834 (Table S1). Silver reference material RM3834 was therefore adopted as the primary standard for subsequent analyses. This has the added benefit that it can also be used to normalise Au, Pb, and Bi concentration data, which would not be possible with NIST SRM610 due to the considerable compositional differences with archaeological silver.

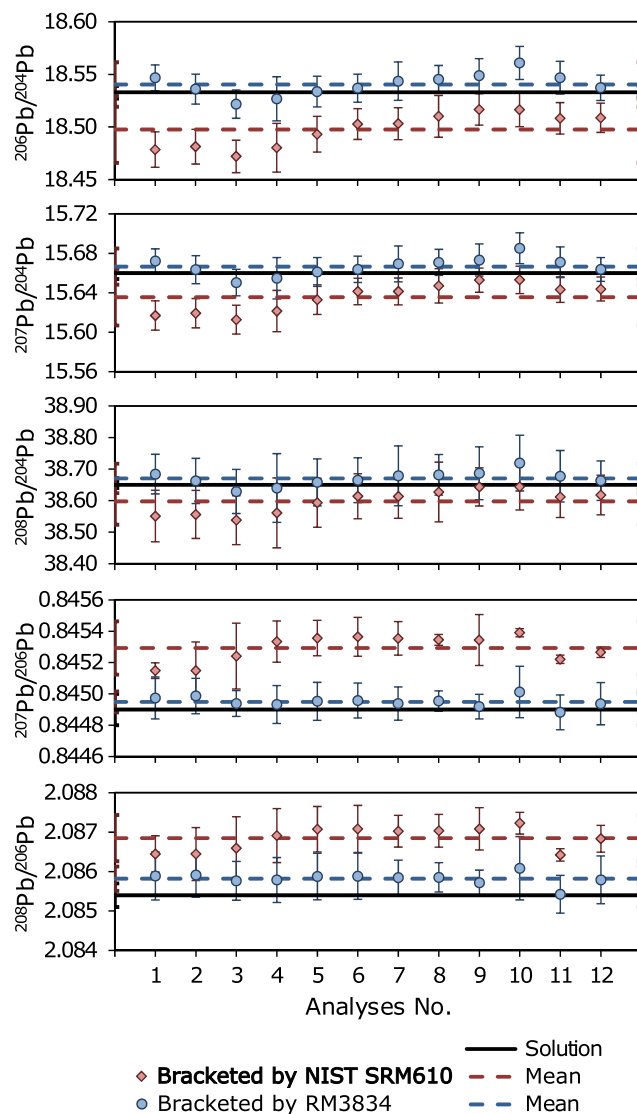


Fig. 2. Lead isotope ratio analysis of silver reference material RM12467 by laser ablation MC-ICP-MS analysis. Mass bias corrections are applied using both the non-matrix matched NIST SRM610 (red diamonds) and matrix matched silver reference material RM3834 (blue circles). Error bars on each data point are ± 2 S.E. of the mean of the 50 integration cycles of a single analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

3.1. Pb isotope analysis

Accuracy, internal precision and external reproducibility of Pb isotope analysis by LA-MC-ICP-MS is demonstrated through repeat analysis of silver reference materials RM12467 ($n = 30$) and RMAg981 ($n = 17$) over multiple analytical sessions (6 and 5 respectively) across a 10 month period, eight repeat analyses of the 133X AGA1 and 133X AGA3 silver reference materials, and three repeat analyses on each of the Ag-4817-14, Ag-SI, and Ag-Du silver reference materials (Fig. 3 and Table 4).

Typical internal precisions on all silver reference materials, expressed as two relative S.E. of the mean of the cycles comprising one analysis, are $< 0.5\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and $< 0.03\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. These vary between reference materials, most likely as a response to both differences in Pb content and

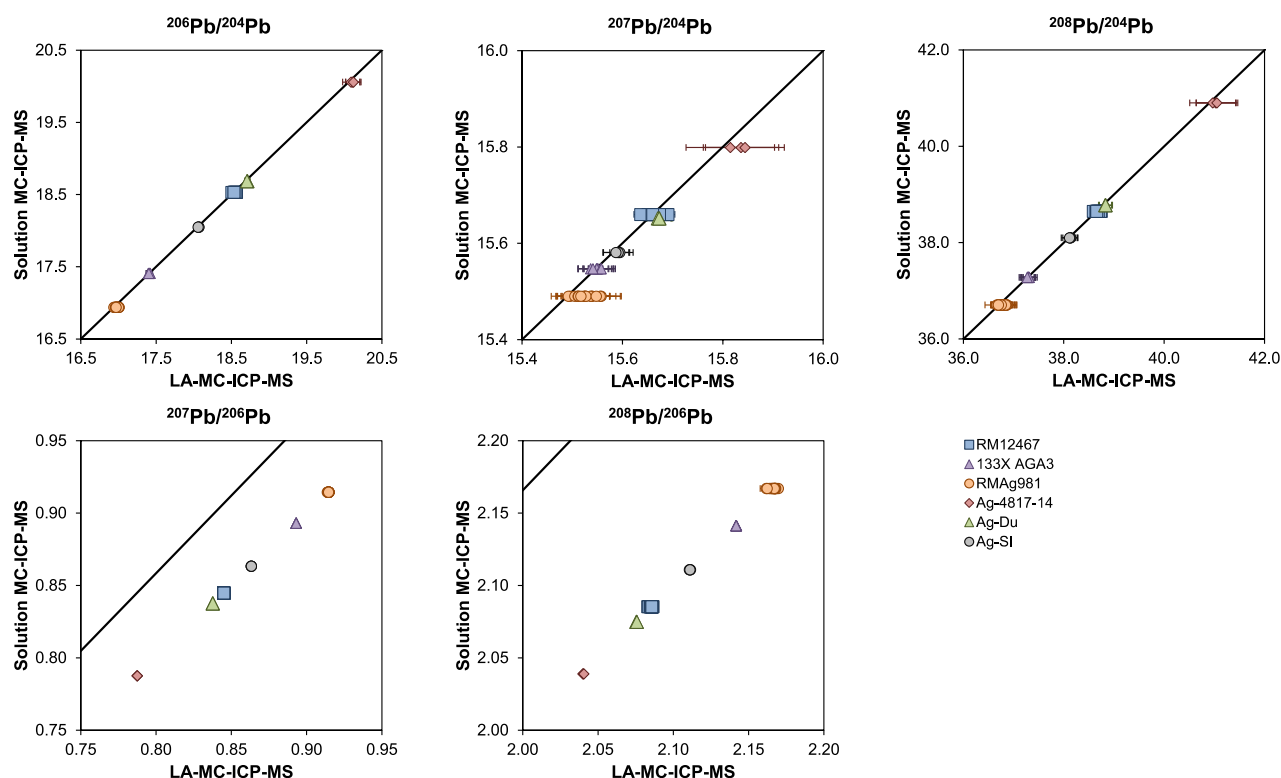


Fig. 3. Comparison of lead isotope ratio analysis of silver reference materials by laser ablation and solution MC-ICP-MS. Error bars on each data point for LA-MC-ICP-MS are ± 2 S.E. of the mean of the 50 integration cycles of a single analysis.

alloy homogeneity; the highest internal precision achieved was for 133X AGA1, highlighting this reference material in particular as a promising reference material for Pb isotope analysis of silver: $<0.2\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and $<0.01\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$. These precisions are comparable to that achieved by Baker et al. (2006) for analyses of metallic silver.

External reproducibilities, expressed as two relative S.D. of the mean of the repeat analyses, are $<0.4\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ and $<0.2\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for all reference materials, and as low as $\leq 0.1\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ and $<0.02\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for 133X AGA1 and 133X AGA3. This is comparable to the reproducibilities published by Baker et al. (2006) for analyses of metallic silver. Within-session external reproducibilities were similar to those of longer-term data compilations. With no clear relationship to Pb concentration, internal homogeneity and melting behaviour are likely to be the key causes of the differences in reproducibility recorded between the reference materials. Indeed this likely explains the superior reproducibility for analyses of silver reference materials 133X AGA1 and 133X AGA3 — the modern, commercially available, reference materials — again highlighting that they are most suited as primary standards in future Pb isotope studies. However, by using hack-silver reference material RM3834 as the bracketing standard in our analytical set-up, and fully propagating both internal precision (2 S.E.) of individual analyses and external reproducibility (2 S.D.) of suitable reference materials, calculated uncertainties will reflect typical geochemical variation seen in archaeological metals on a larger (cm) scale. Furthermore, external reproducibility of hack-silver reference material RM12467 ($\leq 0.18\%$ for ratios normalised to ^{204}Pb and $\leq 0.08\%$ for ratios normalised to ^{206}Pb), is only slightly larger than that of 133X AGA1 and 133X AGA3, suggesting differences between ablating modern and archaeological silver are minimal. LA analyses are consistent with solution MC-ICP-MS values within their estimated uncertainties (i.e. the external reproducibility) in almost all cases.

3.2. Au-Pb-Bi concentration analysis

Accuracy, internal precision and external reproducibility of elemental analysis is demonstrated through analyses of silver reference materials RM12467, RMAg981, 133X AGA1, and 133X AGA3 (Fig. 4 and Table 4). Internal precision of Au, Pb and Bi analyses are typically $<20\%$. This is typically $\leq 10\%$ for 133X AGA1 and $\leq 15\%$ for 133X AGA3, highlighting that these reference materials are also well suited to studies concerned with elemental analysis. External reproducibilities are $\leq 25\%$, except for the analyses of Pb in RMAg981 which was $\sim 40\%$. This likely relates to the heterogeneity of the metal which is apparent in the SEM image (Fig. 1d); discrete globules of Pb up to several microns in size, unequally distributed throughout the metal, are visible. As with the Pb isotope analysis, one way in which external reproducibility could be improved in the future is through selection of a more suitable, homogenous, bracketing reference material than that used in this study, e.g. 133X AGA1 instead of RM3834. LA-MC-ICP-MS analyses are consistent with LA and solution ICP-MS values within their estimated uncertainties in almost all cases, although Pb concentrations are typically lower than the certified value for 133X AGA3.

Internal precision of Au/Pb and Bi/Pb are typically $\leq 10\%$ and $\leq 5\%$, respectively, whilst external reproducibilities are $\leq 10\%$ for both. By expressing the elemental data in ratio form, it is therefore possible to achieve smaller uncertainties than if intensities were first used to calculate elemental concentrations. This is likely because in ratioing the intensities of pairs of elements cycle by cycle, much of the signal noise seen throughout an ablation that impacts on the calculation of elemental concentrations is effectively eliminated through internal normalisation. LA-MC-ICP-MS analyses are consistent with LA and solution ICP-MS values within their estimated uncertainties in most cases, although Bi/Pb are typically elevated above the certified ratio for 133X AGA3.

It is accepted that more resolved Au, Pb and Bi data would be achievable using other analytical techniques, e.g. those tailored specifically to elemental concentration analyses such as single collector ICP-

Table 4

LA-MC-ICP-MS analyses of silver reference materials. Uncertainties are either 2 S.D. or 2 S.E. as specified, and are displayed in the last decimal place. Individual LA-MC-ICP-MS analyses are presented in Table S2.

Reference Material	Method	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Au (wt. %)	Bi (wt. %)	Pb (wt. %)	Au/Pb	Bi/Pb
RM12467	Reference Value (mean \pm 2 SD)	18.533 ± 6	15.660 ± 6	38.650 ± 10	0.8449 ± 1	2.0854 ± 3	0.19 ± 4	0.065 ± 3	1.07 ± 24	0.181 ± 57	0.061 ± 14
	LA-MC-ICP-MS (mean \pm 2 SD)	18.544 ± 29	15.668 ± 25	38.672 ± 68	0.8449 ± 2	2.0854 ± 16	0.18 ± 4	0.062 ± 16	0.96 ± 25	0.179 ± 20	0.062 ± 4
RMAG981	Reference Value (mean \pm 2 SE)	16.938 ± 2	15.490 ± 1	36.706 ± 4	0.91452 ± 2	2.1670 ± 1	–	–	–	–	–
	LA-MC-ICP-MS (mean \pm 2 SD)	16.976 ± 41	15.525 ± 39	36.779 ± 120	0.9145 ± 6	2.1663 ± 43	–	–	1.52 ± 61	–	–
Ag-4817-14	Reference Value (mean \pm 2 SE)	20.059 ± 5	15.799 ± 3	40.900 ± 5	0.78762 ± 1	2.0390 ± 2	–	–	–	–	–
	LA-MC-ICP-MS (mean \pm 2 SD)	20.108 ± 31	15.832 ± 30	41.017 ± 84	0.7874 ± 1	2.0403 ± 6	–	–	0.44 ± 6	–	–
Ag-Du	Reference Value (mean \pm 2 SE)	18.688 ± 3	15.652 ± 1	38.777 ± 4	0.8376 ± 1	2.0749 ± 3	–	–	–	–	–
	LA-MC-ICP-MS (mean \pm 2 SD)	18.711 ± 8	15.672 ± 4	38.831 ± 10	0.83762 ± 6	2.0756 ± 3	–	–	0.44 ± 7	–	–
Ag-SI	Reference Value (mean \pm 2 SE)	18.050 ± 4	15.581 ± 4	38.100 ± 11	0.8633 ± 3	2.1109 ± 3	–	–	–	–	–
	LA-MC-ICP-MS (mean \pm 2 SD)	18.065 ± 12	15.591 ± 8	38.126 ± 23	0.8632 ± 2	2.1110 ± 7	–	–	3.07 ± 32	–	–
133X AGA1	Reference Value (mean \pm 2 SE)	–	–	–	–	–	1.48 ± 6	0.194 ± 12	0.207 ± 14	7.150 ± 564	0.937 ± 86
	LA-MC-ICP-MS (mean \pm 2 SD)	17.424 ± 14	15.558 ± 15	37.311 ± 39	0.8929 ± 1	2.1415 ± 4	1.47 ± 27	0.191 ± 46	0.178 ± 38	7.997 ± 573	1.042 ± 82
133X AGA3	Reference Value (mean \pm 2 SE)	17.409 ± 1	15.547 ± 1	37.278 ± 5	0.89304 ± 5	2.1413 ± 11	0.258 ± 4	0.048 ± 2	1.89 ± 10	0.137 ± 8	0.025 ± 2
	LA-MC-ICP-MS (mean \pm 2 SD)	17.411 ± 16	15.549 ± 14	37.292 ± 26	0.8930 ± 1	2.1418 ± 2	0.211 ± 41	0.049 ± 13	1.57 ± 34	0.137 ± 10	0.031 ± 2

MS. However, the approach outlined here allows collection of Au, Pb and Bi compositional data simultaneously with the Pb isotope ratio analysis and therefore comes at no extra analytical cost, e.g. in terms of artefact conservation, time, or finances. Furthermore, it means that isotopic and elemental data correspond to the same sample location, and are directly comparable. Au, Pb, and Bi concentration analyses are therefore routinely incorporated into our analytical set-up for Pb isotope ratio analysis as it allows discrimination, to some degree, of archaeological silver based on further geochemical variables.

4. Case study: silver dirhams from the mint of Al-Muhammadiyah

4.1. Abbasid dirhams and the mint of al-Muhammadiyah

During the early Abbasid period (132–205 AH or 750–820 CE), dirham production expanded greatly and the large scale production of highly pure, unalloyed, silver coins made them into a desirable commodity that was exported throughout much of the known world. Minting was concentrated in four major regions: Iraq, Iran, North Africa and Central Asia. While the caliphal capital at Madinat al-Salam (Baghdad) dominated in terms of total dirham production, al-Muhammadiyah (Tehran) was often second in productivity (Noonan 1986). Al-Muhammadiyah, which was known as al-Rayy before 148 AH/765 CE, was located in the region of Jibal and was the primary mint in Iran. Unlike Iraq, which is poor in metallic resources, Iran is rich in ore deposits (Momenzadeh 2004). Silver deposits in Jibal and the neighbouring Alborz Mountains are known to have been worked during the early Islamic period on the basis of archaeological evidence (Hallier 1972, 306; Stöllner 2004; Stöllner and Weisgerber 2004). Up until now, only two dirhams from al-Muhammadiyah have been analysed to characterise their Pb isotope ratios and elemental composition using mass spectrometry techniques, for example laser ablation inductively-coupled plasma quadrupole mass spectrometry (LA-ICP-QMS), femtosecond (fs) LA-MC-ICP-MS, and TIMS (Merkel 2016; Sarah 2008). These previous analyses are augmented with new analyses of eight coins from the collection of the Fitzwilliam Museum, Cambridge (Fig. 5; Table 5). The aim of this study was to characterise the dirhams isotopically and elementally and to draw conclusions concerning the potential source or sources of the metal used in their manufacture.

4.2. Theory behind provenance analysis of silver

Before discussing the dirham analyses, it is first necessary to explain the interpretive approach and the underlying theoretical basis of silver provenance studies (for a fuller discussion, see Merkel 2019; Sarah 2019). A combination of elemental and Pb isotope ratio characterisation is key for interpreting silver sources, and for identifying cupellation, recycling and/or the mixing of silver stocks.

Lead isotope analysis provides information about the Pb in the silver being studied. This Pb may stem from a number of different sources. Almost without exception, medieval silver was cupelled to refine it from impurities; cupellation by definition is the high temperature process of refining precious metals through the oxidation of Pb, leaving metals like silver in a metallic state. Cupellation could have been carried out at the end of primary silver production using lead produced from associated ore, or it could have been a secondary process undertaken anywhere, using exogenous lead from any available source: in the case of the former the Pb isotope ratio signature relates to the original ore, but in the latter, the added lead confers a new Pb isotope ratio signature which no longer corresponds to the original silver. In addition, it is possible that the Pb isotope signature results from recycling through the melting-down of multiple objects, which may or may not have been secondarily cupelled. This form of recycling homogenises the silver isotopically and hence reflects a mix of Pb isotope ratios controlled by the ratio values of

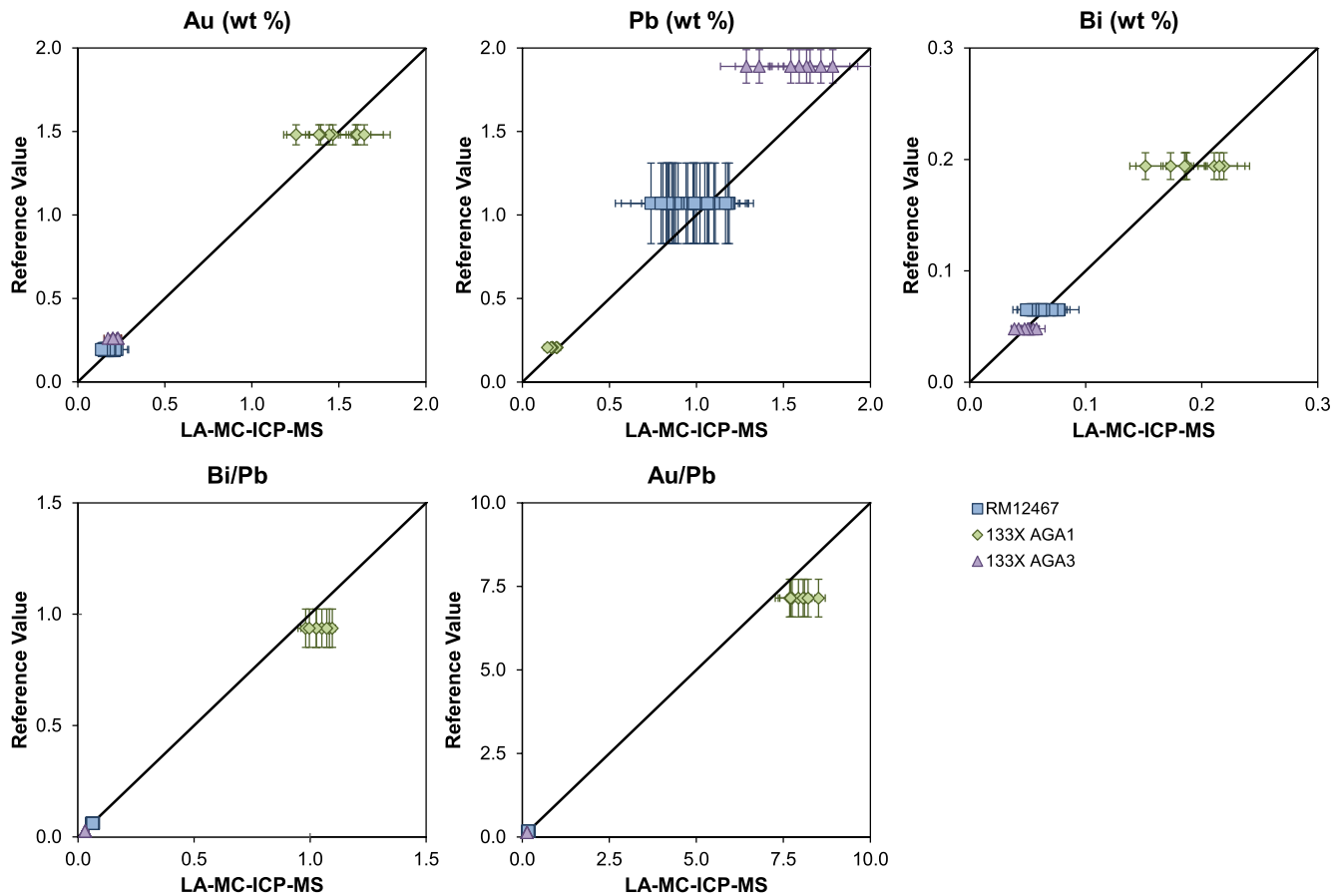


Fig. 4. Gold, lead and bismuth concentration analysis, and Au/Pb and Bi/Pb analysis, of silver reference materials analysed by laser ablation MC-ICP-MS compared to reference values (see Table 4). Error bars for LA-MC-ICP-MS are ± 2 S.E. of the mean of the cycles comprising one analysis. Error bars for reference values follow those in Table 4. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the constituents in relation to their proportion and Pb content. It has the potential to create a new Pb isotope ratio signature that may correspond with another group of silver, providing a false link. A key issue with Pb isotope analyses in the context of archaeological provenance studies is

that signatures may not be unique, i.e. shared between multiple potential sources, or could reflect mixing or sources that have never been characterised.

Whilst the full elemental profile of silver is advantageous for finding clues regarding alloying, refining and recycling, Au and Bi stand out as being additional, well-tested, indicators of source; these elements can stem from the original ore, preserved through the refining process, with Au surviving completely and Bi resisting oxidation until the very end of processing, partially surviving (Merkel 2016; 2019; Sarah 2019; L'Héritier et al., 2015). Gold is frequently associated with silver ore in small amounts. In archaeological silver it can usually be found in quantities of less than 1 wt % (Gordus 1972; Mc Kerrell and Stevenson



Fig. 5. Set of silver dirhams mounted for LA-MC-ICP-MS, with standards mounted in adhesive putty. Two examples from the mint of al-Muhammadiyah are visible in the top row.

Table 5

Details of the analysed silver dirhams from the mint of al-Muhammadiyah.

No.	Ruler	Year	Description
Fitz1	al-Mansur	AH 148	Dirham, 2.93g. CM.IS.0146-R (Novak 469)
Fitz2	al-Mansur	AH 150	Dirham, 2.86g. CM.279-1939 (Novak 470)
Fitz3	al-Mansur	AH 154	Dirham, 2.49g (pierced in two places). CM.IS.0147-R (Novak 471)
Fitz9	al-Rashid	AH 180	Dirham, 2.73g (pierced). CM.IS.0175-R (Novak 519)
Fitz10	al-Rashid	AH 184	Dirham, 2.80g. CM.IS.0176-R (Novak 523)
Fitz24	al-Ma'mun	AH 200	Dirham fragment, found Torksey (Blackburn, 2011, no. 73), 0.78g. CM.150-2011
Fitz22	al-Rashid	c. AH 186	Dirham fragment, found Torksey (Blackburn, 2011, no. 62), 0.39g. CM.79-2011
Fitz11	al-Rashid	AH 188/9	Dirham fragment, found Caldecote, Norfolk, 0.56g. CM.384-1991 (Novak 525)

1972; Pernicka and Bachmann 1983; Meyers 2003). While it is unlikely that Au was deliberately added to silver, it may occasionally have an exogenous origin, entering silver through contamination with Au or gilding during recycling. The survival of Bi during the cupellation of silver is connected to the Pb content, so the ratio of these elements appears to stay constant regardless of factors controlling the degree of refining, i.e. temperature, duration, etc. When reliable Bi and Pb contents are available, their ratio is a useful way to compare silver without the influence of variation in the cupellation procedure.

When combined with Pb isotope data, Au and Bi contents and Bi/Pb ratios provide additional variables which can help to characterise silver stocks. It must be stressed that while this archaeometric information is to some degree independent from the historical and archaeological record, their full potential is reached only when the data are placed within the historical, archaeological and geochemical context. The stronger the foundation is, and the more known variables there are, the more valuable isotope and elemental data can be in answering archaeological/historical questions.

4.3. Al-Muhammadiyah dirhams results and discussion

The geochemical composition of the eight dirhams analysed for this study are detailed in Table 6. Uncertainties are expressed at 2σ and combine both the internal precision of a specific analysis and the external reproducibility of the methodology based on analyses of 133X AGA1 and 133X AGA3. These measurements augment two analyses that were performed using different techniques that specialise on elemental and isotopic analysis. While standard deviations (2SD) of 10% are often obtainable by LA-ICP-QMS for elements like Au, Bi and Pb (Sarah 2008), we demonstrate here that it is still possible to distinguish compositional groups using nsLA-MC-ICP-MS despite the typically larger uncertainties of 20–25% (2SD), whilst elemental ratios have uncertainties of ~10% (2SD). Also, despite the higher uncertainties associated with Pb isotope analysis compared to solution based techniques (<0.4% for ^{204}Pb normalised ratios, and <0.2% for ^{206}Pb normalised ratios), nsLA-MC-ICP-MS still allows isotopic variation to be identified and is of a high enough resolution to be useful for many archaeological applications. It therefore constitutes a powerful geochemical tool for studies where use of a minimally invasive technique is paramount.

The Au, Bi and Pb contents of the dirhams shows that there is a difference between the early coins minted under al-Mansur and the later coins of Harun al-Rashid and al-Ma'mun. The earlier coins have higher Au (0.13–0.20%) and the later have much less (<0.05%). The two al-Muhammadiyah dirhams analysed in independent studies (Sarah 2008; Merkel 2016) have directly comparable lead isotope ratios and Au, Bi, and Pb contents to those of this study (Figs. 6 and 7). Both are

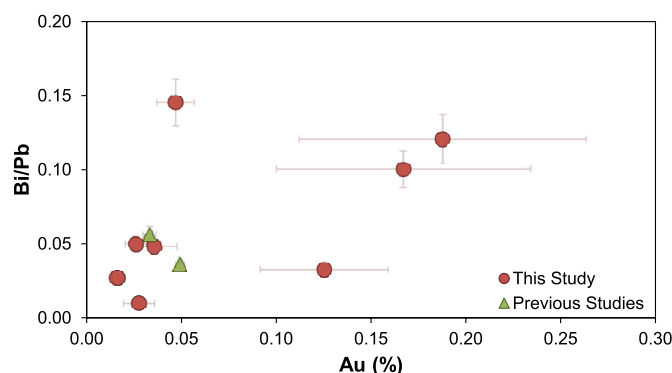


Fig. 6. Au (wt. %) and Bi/Pb of al-Muhammadiyah dirhams from this and previous studies (Sarah 2008; Merkel 2016). The three dirhams with the highest Au contents are the earliest. There is a cluster of six coins with relatively homogeneous Au and Bi/Pb ratios probably reflecting silver from a single source. Error bars from this study reflect the fully propagated uncertainties at 2σ (see text for details). For the previous dirham analyses, given errors are smaller than the symbol: 10% for Sarah (2008) and 95% confidence interval for Merkel (2016).

extremely pure, with 0.1 and 1.0% Cu, minted in 194 AH and 178–187 AH respectively, and thus fit with what is known about the typical purity of early Abbasid dirhams from this mint (cf. Ilisch et al., 2003). Both of these two previously analysed coins and a group of four coins from this study have a relatively homogenous Au contents and Bi/Pb ratios that likely indicate a single silver source (Fig. 6).

The Pb isotope ratios of the al-Muhammadiyah dirhams have a relatively narrow range. Based on Stacey and Kramers (1975) two-stage model using the method of Albarède et al. (2012), calculated Pb model ages are between ca. 292 and 147 Ma (Permian to Jurassic). The geology of Iran is divided into geological units with complex origins and it is clear that they are not isotopically distinct nor homogenous, but some trends can be determined. Based on published analyses of ore it can be said that the al-Muhammadiyah dirhams have Pb isotope ratios consistent with ore from the Central Iranian, Sanandaj–Sirjan and the Alborz zones, which occupy much of Central and North Central Iran (Bazargani-Guilani et al., 2011; Mirnejad et al. 2011, 2015; Pernicka et al., 2011; Stos-Gale 2004). The Urumieh–Dokhtar zone, with large Pb deposits that concentrate in NW Iran, has Pb isotope ratios that are generally younger (Cenozoic), and in the Zagros Fold Belt, in the south, there is only one major Pb deposit, which is significantly older geologically (Fazli et al., 2019; Mirnejad et al., 2011; Stos-Gale 2004). There are other geologic units, particularly in the east of Iran, which are poorly

Table 6

LA-MC-ICP-MS analyses of silver dirhams from the mint of al-Muhammadiyah. Uncertainties are expressed at 2σ in the last decimal place (see section 4.3 for further details).

Sample ID	Details	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	Au (wt. %)	Bi (wt. %)	Pb (wt. %)	Au/Pb	Bi/Pb
Fitz1	al-Mansur AH 148	18.451 ± 33	15.639 ± 29	38.665 ± 125	0.8476 ± 1	2.0957 ± 4	0.125 ± 33	0.054 ± 19	1.339 ± 429	0.075 ± 13	0.033 ± 4
Fitz2	al-Mansur AH 150	18.534 ± 45	15.679 ± 39	38.720 ± 189	0.8459 ± 2	2.0892 ± 10	0.187 ± 75	0.087 ± 29	0.838 ± 313	0.347 ± 90	0.121 ± 16
Fitz3	al-Mansur AH 154	18.658 ± 38	15.669 ± 33	38.876 ± 159	0.8397 ± 2	2.0837 ± 10	0.167 ± 67	0.019 ± 6	0.195 ± 72	0.872 ± 119	0.101 ± 12
Fitz9	al-Rashid AH 180	18.317 ± 51	15.605 ± 44	38.383 ± 205	0.8519 ± 1	2.0956 ± 5	0.047 ± 10	0.076 ± 20	0.519 ± 118	0.162 ± 38	0.146 ± 16
Fitz10	al-Rashid AH 184	18.510 ± 33	15.672 ± 31	38.707 ± 183	0.8466 ± 2	2.0913 ± 17	0.036 ± 12	0.054 ± 19	1.128 ± 383	0.032 ± 3	0.048 ± 5
Fitz24	al-Ma'mun AH 200	18.588 ± 31	15.696 ± 27	38.835 ± 114	0.8443 ± 1	2.0886 ± 8	0.028 ± 8	0.023 ± 8	2.325 ± 596	0.012 ± 1	0.010 ± 1
Fitz22	al-Rashid c. AH 186	18.502 ± 31	15.685 ± 27	38.676 ± 114	0.8477 ± 1	2.0902 ± 5	0.026 ± 6	0.068 ± 18	1.246 ± 342	0.018 ± 2	0.050 ± 5
Fitz11	al-Rashid AH 188/9	18.517 ± 38	15.631 ± 32	38.557 ± 147	0.8441 ± 1	2.0821 ± 5	0.016 ± 3	0.0017 ± 5	0.055 ± 16	0.223 ± 27	0.027 ± 3

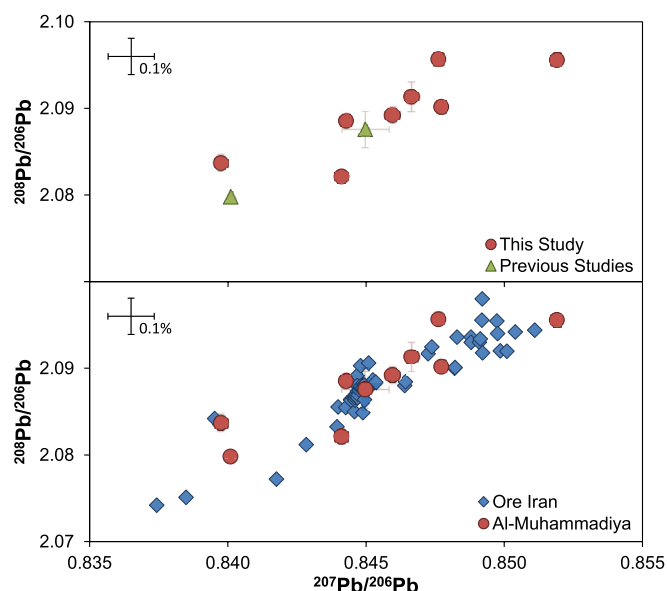


Fig. 7. Upper: Lead isotope ratios of al-Muhammadiyya dirhams from this study and from two previous studies (Sarah 2008; Merkel 2016). Lower: Lead isotope ratios of al-Muhammadiyya and a selection of comparable Iranian lead ore and related materials mostly from the Sanandaj–Sirjan zone, Central Iranian Zone and the Alborz Range (Stos-Gale 2004; Bazargani-Guilani et al., 2011; Mirnejad et al. 2011, 2015; Pernicka et al., 2011). The selection reflects a segment of the Iranian ore data between $^{207}\text{Pb}/^{206}\text{Pb}$ ratios 0.8375 and 0.8511. Error bars from this study reflect the fully propagated uncertainties at 2σ (see text for details), and, for the previous dirham analyses, the determined error is smaller than the symbol. For the ore analyses, errors (2SD) are expected to be below 0.1% for TIMS and MC-ICP-MS.

characterised and thus cannot be considered in this study.

As many of the Iranian ore deposits are only represented by a single analysis, it is difficult to say anything concrete about the origin of the metal. The best characterised deposit in the dataset is the Pb–Zn–Ag deposit of Nakhlak, which is very homogenous and plots in the centre of the al-Muhammadiyya dirham cluster. Considering uncertainties, it could be consistent with three dirhams. Nakhlak alone, however, cannot explain the range of Pb isotope ratios found in the coins and Pb from other deposits must have contributed to the stock. The Pb–Ag deposit of Duna in the Alborz, north of Tehran, frames the range on the geologically young side and several Pb–Ag deposits in the Arak–Kashan area (between Isfahan, Hamedan and Qom) are close isotopically to the geologically oldest al-Muhammadiyya dirhams. Each of these deposits/regions are proposed to be Pb–Ag sources during the early Islamic period based on archaeological and archaeometallurgical evidence (Allan 1979, 15; Gordus 1972, 138–140; Stöllner 2004; Stöllner and Weisgerber 2004). Geochemically, it is possible that the Pb-ratios of the al-Muhammadiyya dirhams could represent Pb or a mixture of Pb originating from these areas.

By combining the Pb isotope and Au, Bi and Pb datasets, some significant deductions can be made:

1. The dataset, though small, indicates that there are at least two sources, or, at least, a change occurred at al-Muhammadiyya during the early Abbasid period. Though there is a shift in Au contents between the early and late dirhams, the Pb isotope ratios appear to be independent of this change. The clearest indications of a distinct silver source are the clustering of six dirhams with exceptionally low Au and homogenous Bi/Pb ratios. This group is both too extreme in composition and too homogeneous to be a mixture and thus probably reflects freshly mined silver.

2. The relatively wide disparity in Pb contents (0.06–2.33%) suggests that this silver was struck into coins immediately following cupellation, the Pb contents reflecting varying cupellation parameters, i.e. duration

and temperature (see L'Héritier et al., 2015). Recycling via remelting has a homogenising effect, lessening the extremes and usually results in Pb contents around 0.5–1.0%. This can be demonstrated by the SD of the whole dataset: the dirhams have almost double the SD for Pb (0.68, $n = 10$) compared to previously analysed Viking-period jewellery and ingots from Scandinavia known to have been made of recycled silver (0.36, $n = 18$) (Merkel 2019).

If differences in silver source indicators (Au % and Bi/Pb ratios) are independent of Pb isotope ratios, it is likely that the latter reflect the Pb used in the last cupellation rather than the silver source. This appears to be the case for the al-Muhammadiyya dirhams. Cupellation may have been done at the mint with Pb sourced locally from the Jibal region and possibly the Alborz Mountains.

4. An alternative possibility is that the decrease in gold contents seen in the al-Muhammadiyya dirhams between al-Mansur and Harun al-Rashid reflects a change in ore type, but not source, as mining technology adapted to deeper mining (see Meyers 2003). Meyers suggests that such a shift in ore type visibly occurred at the transition of the Umayyad to the Abbasid dynasties (ca. 132 AH or 750 CE), and the change seen in the al-Muhammadiyya may be connected to this development.

Nonetheless, the geochemical characterisation of the al-Muhammadiyya dirhams presented here provides a key dataset for future studies concerned with tracing the flow of metal in the Islamic and wider early medieval world.

5. Conclusions

This study presents an approach to simultaneously determine Pb isotope ratios and Au and Bi concentrations of metallic silver by nano-second laser ablation MC-ICP-MS. It is demonstrated by repeat analyses on seven silver reference materials. Typical internal precisions, are $<0.5\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, and $<0.03\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ (2 S.E.). External reproducibilities, based on analyses over a 10 month period, are $<0.4\%$ for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ and $<0.2\%$ for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ (2 S.D.). Internal precisions and external reproducibilities are typically $<25\%$ for gold, lead, and bismuth concentration analyses, and $\leq 10\%$ for Au/Pb and Bi/Pb analyses. Data are consistent with reference values within the presented uncertainties in most cases.

The approach employs a laser with a 60 μm beam diameter, and therefore provides a minimally invasive method of characterising the geochemical signature, including the geologically informative lead isotope ratios, of silver objects. Furthermore, characterisation of a set of silver reference materials provides well characterised, matrix-matched, reference materials for use in future studies employing such techniques. In particular, 133X AGA1 and 133X AGA3 from MBH Analytical Ltd. are recommended as suitable, and easily available, reference materials for such analyses, and adoption of one of these into the analytical approach as the bracketing standard, e.g. for mass bias corrections, is likely to give improved internal precisions and external reproducibilities to those reported here.

Methods were further demonstrated through analysis of early Abbasid dirhams minted at al-Muhammadiyya, Iran. The internal precision and reproducibility, while not equal to solution based MC-ICP-MS and other specialised techniques, are sufficient to explore archaeological questions. The analyses from this study could be compared with previously analysed coins and potential Iranian silver and lead sources. Results indicate the use of at least two silver stocks with a change occurring between the reigns of al-Mansur and Harun al-Rashid. Although Pb isotope analysis is limited by the low numbers of Iranian ore analyses, it is clear that the origin of the Pb in the silver could originate from deposits in Jibal, possibly in addition to deposits in the nearby Alborz Mountains. It can be seen that the silver is freshly cupelled and likely reflects new metal production.

Declaration of competing interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jas.2020.105299>.

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