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ENHANCING UNDERSTANDING OF THE EMERGENCE OF GLOBAL TRADE: ANALYSIS OF 17TH- TO 19TH-CENTURY SPANISH COINS RECOVERED FROM WESTERN AUSTRALIAN SHIPWRECKS USING LASER ABLATION – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (LA–ICP–MS)*

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This research uses legacy data from shipwrecks to further our understanding of global silver movement in the 17th to 19th centuries by analysing a collection of silver coins held by the Western Australian Museum. Three hundred and eighty-nine silver coins were analysed for their trace element fingerprint in order to identify provenance. The coins are a selection from the ships Batavia, Vergulde Draeck, Zuytdorp, Rapid and Correio da Azia, all wrecked off the coast of Western Australia between 1629 and 1816. Analysis was undertaken using laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS), a relatively non-destructive technique with a sensitivity of parts per million to parts per billion. Data were interpreted using linear discriminant analysis (LDA), which allowed the coins of known provenance to be sorted into identifiable subgroups on the basis of their trace and minor elemental fingerprints, while 27 unidentified coins were compared with this database and their mint of origin predicted. These results have implications for the provenance determination of archaeological artefacts of many materials.

KEYWORDS: LA–ICP–MS, SILVER COINS, TRACE ELEMENT FINGERPRINT, PROVENANCE, SHIPWRECKS

INTRODUCTION

This paper details the use of laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) for determining the elemental distribution of 17 analytes from a selected series of 389 silver coins from five ships wrecked off the Western Australian coast between 1629 and 1816. The coins are in the collection of the West Australian Museum.

By demonstrating the application of trace elemental analysis on the provenance identification of the coins used in this study, our understanding of global silver movement during the 17th to 19th centuries is enhanced. Further, this technique is applicable to artefacts of any material, and as demonstrated, has the capability of characterizing and revealing much more about an object than may be known otherwise.

Most of the coins analysed had already been successfully identified by their mint markings by a numismatist. The database created from LA–ICP–MS analyses was used to characterize the

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trace elemental fingerprints of different mints. Coins that could not been visually identified could be compared to the database and their mint of origin identified on the basis of their trace elemental fingerprint.

Linear discriminant analysis (LDA), an interpretational statistical technique, was used to identify the place of minting of coins that had previously not been identified, based on a statistical comparison against a database of compositional analysis of silver coins of known provenance.

The wrecks

The coins for this study were recovered from the wrecks of the *Batavia*, *Vergulde Draeck, Zuytdorp*, *Rapid* and *Correio da Azia*. All five of these ships were wrecked off the coast of Western Australia. A summary of each ship's voyage is detailed in Table 1.

Trace elements and provenance determination

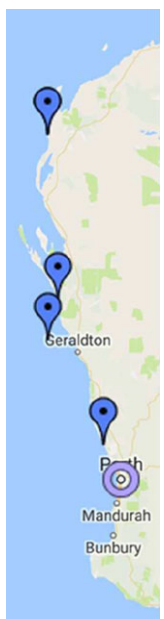
The inter-elemental ratios between trace elements (or trace elemental 'fingerprint') of any geological material is indicative of its provenance, due to the unique mineralizing event that created the material. The same necessarily holds true for silver ore, and indeed, it has been demonstrated that silver ores and refined silver can be traced back to a mine of origin on the basis of the trace elemental fingerprint, as discussed below. Analysis has shown that there is an identifiable trace elemental composition between slag, bullion and silver coins originating from the same ore (Schneider 1994; Rehren *et al*. 1999). In many cases, coinage metals are recycled and recoined: in the present case, American coinage was often recoined in Spain. The recycling of coinage metals has been identified as presenting unclear and indistinct trace elemental fingerprints, in some cases to such a degree that assemblages of recycled coins become homogenous in their composition, and the origin of the coin metal is not readily identifiable via trace elemental analysis (Butcher and Ponting 1998). It follows that unidentified coins can be traced to their mint of origin, where an assemblage of recycled coins of known mint display a homogenous trace elemental composition.

Trace elemental analysis and provenance determination of archaeological silver is an established method that has been used in a number of different studies, on silver from varied spatial and temporal contexts. Provenance determination of silver using trace elements was first attempted in the 1970s and 1980s after an extensive field survey and laboratory analysis of Aegean lead and silver using both trace elemental and lead isotope analysis (Gale *et al*. 1980). Guerr*a et al*. (1999) used ICP–MS to provenance precious metal ores in an attempt to explore the possibilities of using ICP–MS in this field of study. The circulation of gold and silver in 17th-century Brazil has been investigated using a combination of LA–ICP–MS, neutron activation analysis (NAA) and proton activation analysis (PAA) (Guerra 2004). LA–ICP–MS analysis was used in a study of ancient silver coins in order to overcome problems arising from their inhomogeneous nature (Sarah *et al*. 2007). Analysis of Athenian style tetradrachms discovered in Israel using ICP – atomic emission spectrometry (AES) and ICP–MS was conducted by Ponting *et al*. (2011; see also Gitler *et al*. 2009).

Problems identified with provenance determination of archaeological metals using trace elemental analysis have been identified by Pernicka (2014). First, ores are inhomogeneous, and so it can be problematic to attempt to match a metal to its provenance ore on the basis

Table 1 *The ships represented in this study*

Ship	*Country of origin*	*Port of departure*	*Departure date*	*Destination*	*Date of wrecking*	*Rediscovery*	*Wreck locations*
Batavia	The Netherlands	Texel	27 October 1628	Batavia (Jakarta)	4 June 1629	1963	
Vergulde Draeck	The Netherlands	Texel	4 October 1655	Batavia (Jakarta)	7 May 1656	1963	
Zuytdorp	The Netherlands	Vlissingen	1 August 1711	Batavia (Jakarta)	1712	1927	*Rapid* and *Correio da Azia*
Rapid	USA	Boston	28 September 1810	Canton (Guangzhou)	7 January 1811	1978	
Correio da Azia	Portugal	Lisbon	1816	Macau	26 November 1816	2004	
							Zuytdorp Batavia Vergulde Draeck (Perth)



of their trace elemental fingerprints. Also relevant to the provenance ore of a metal, one must understand how the trace and minor elements present in the ore will behave during the refining and smelting process, as they will not all be retained in the finished product at the same rate (Pernicka 2014). A problem with the refining of silver in terms of trace elemental composition is that silver is refined either using lead, following the cupellation technique, or later using mercury, following the Patio process. Further, the silver in question is alloyed with copper. It is difficult to determine if trace elements have been introduced by the lead, mercury or copper rather than the silver, and if they have, what affect this will have on the total trace elemental composition, and hence the ability to determine the provenance of the silver in question. Further, the addition of copper and lead or mercury can distort the trace elemental composition of the silver, especially if additions are made in different locations (Desaulty *et al*. 2011), which would have been the case through trade when silver coins were exported and reminted or resmelted.

The reliability of surface analyses to be representative of the bulk of silver coins and artefacts has been investigated (Beck *et al*. 2004; Beck *et al*. 2008; MacLeod and Schindelholtz 2004; Wanhill 2012; Ager *et al*. 2013; Borges *et al*. 2017). Similarly, analysis has been undertaken to confirm the reliability of surface LA–ICP–MS analysis on the coins in the present study (Gentelli 2017). Electron probe microanalysis (EPMA) and scanning electron microscopy – energy-dispersive spectroscopy (SEM–EDS) quantitative elemental mapping were used to investigate the cross-section of a number of silver coins. The results indicated that while the coins displayed clear surface layers of corrosion, the elemental make-up of this layer could be considered representative of the bulk of the coin.

Changes in an inhomogeneous sample matrix, analyte composition and laser power result in unpredictable variations in the amount of material sampled (Scadding *et al*. 2015). As such, LA–ICP–MS has been defined as a semi-quantitative technique, which produces a compositional 'fingerprint' of a sample (Guerra and Calligaro 2003, 2004; Vlachou-Mogire *et al*. 2007; Giussani *et al*. 2009). Quantification of counts per second LA–ICP–MS data is possible and ideally requires calibration of the instrument using a matrix-matched standard (Giussani *et al*. 2009): a non-matrix-matched standard can also be used for successful quantification, most commonly a NIST 610–617 glass standard, combined with an internal standard. This method has been applied in an archaeological context, to a number of different materials (e.g., Cucina *et al*. 2007; Duwe and Neff 2007; Peacock *et al*. 2007; Resano *et al*. 2007; Shortland *et al*. 2007; Hoffmann *et al*. 2008; Whitaker *et al*. 2008: Resano *et al*. 2010).

Despite the above-mentioned limitations, semi-quantitative data have many applications in archaeometric research. For example, a number of studies on various materials conducted by Watling *et al*. have demonstrated the use of inter-elemental ratios in the form of elemental 'fingerprints' for provenance determination. Watling *et al*. have successfully determined the provenance of gold, paint and pigment (Watling *et al*. 1994; Smith *et al*. 2005; Green and Watling 2007; Scadding *et al*. 2015) on the basis of semi-quantitative trace elemental data gained through LA–ICP–MS analysis. Similarly, the provenance of silver artefacts has been determined using inter-elemental ratios based on semi-quantitative trace elemental data gained using LA–ICP–MS (Gentelli 2016). In these cases, as in the present study, these results were achieved by measuring and correcting for instrumental drift, by normalizing counts per second data based on repeat analyses of NIST 610 and/or 612 glass standard reference materials. This normalization of data leads to a reproducible and reliable trace elemental fingerprint, characteristic of a sample, which can be used in a database of trace elemental fingerprints from other samples. As noted by Resano *et al*. (2010), semi-

quantitative, normalized LA–ICP–MS counts per second data are suitable to build databases for statistical comparison of unknowns, as conclusions are being drawn on the basis of the ratios of signal intensities. While no quantitative data are obtained, data interpretation is based on the variations and similarities in the relative abundances of analytes (Scadding *et al.* 2015).

In the case of the silver coins used in this study, the majority of the silver has been mixed from silvers from a number of different mines, and so the trace elemental composition will be altered from those of the original silver ores. The possible exception to this is silver known to have originated from the Americas, where there is a higher likelihood that it represents refined silver sourced from a single mine. Further, silver that is known to have been minted in Spain will almost certainly be a combination of silver from the Americas, while silver minted outside Spain has less certain origins. It has been demonstrated, however, that silver from a mint that is not associated with a specific silver mine, and which is suspected to have multiple sources of silver, will still demonstrate an identifiable trace elemental signature, unique to the mint (Guerra *et al.* 1999). It is proposed that this is due to the combination of trace elements present in silver from different sources and, in this case, trace elements associated with the copper added to the alloy, combining to create a new combination of trace elements unique to the mint in question at the time (Gentelli 2012).

The coins analysed in this study have been cleaned and identified by the Western Australian Maritime Museum, as well as being used in studies to find the optimal method of removing concretion and corrosion from silver (MacLeod and North 1979).

Corrosion mechanisms of silver in marine environments

The coins and silver artefacts used in this study have all been affected by corrosion to varying degrees. All of the coins and silver artefacts in this study have been submerged in seawater for between 169 years (for coins aboard the *Rapid*) and 336 years (for coins aboard the *Batavia*). In order to determine how representative surface analyses are of the bulk of a corroded coin, it is necessary to understand the corrosion processes and products of silver in a marine environment.

The marine environment of the shallow reefs of Western Australia is generally aerobic, with oxygen concentrations above 75% saturation. The shipwreck sites mentioned in this study are all in similar marine environments of shallow reefs in tropical to subtropical waters, with a mean temperature of approximately 24°C. The sites of the wrecks vary somewhat in the turbulence to which they are subjected (MacLeod 1991).

This type of environment will typically produce chlorargyrite (AgCl) as well as some bromian chlorargyrite or embolite (Ag (Cl,Br)) as a corrosion product on submerged silver. If the silver has been buried in sand or covered by an iron concretion, sulphate-reducing bacteria will produce sulphide ions, which in turn create silver sulphide corrosion products (Craig *et al.* 2002). Under the same conditions, when copper has been used as an alloying metal with silver, copper(I) chloride ions are more stable and thus more soluble than silver. In this case, the copper in the alloy will either be lost to the environment as $CuCl_2^-$ complexes, or precipitate on the surface of the metal as cuprite (Cu_2O) or as a copper (II) chloride (MacLeod 1991).

As the coins were generally transported in chests, the degree of corrosion evident on an individual coin will depend on its location within the chest. The coins closest to the outside of the

chest will be more heavily corroded than those in the centre. The extent of corrosion on silver coins recovered from shipwrecks at the Western Australian Museum range from corrosion that has progressed to completion, leaving no solid metal core at all, to a crystalline metallic silver forming in the corrosion layer of a coin and by and large protecting the coin from further corrosion. Typically, corroded silver coins from ships wrecked in Western Australian waters will consist of a core of uncorroded metal surrounded by a corrosion layer of silver compounds, which is covered in a concretion layer of shell, sand and copper compounds (MacLeod and North 1979).

The corrosion layer on the coins used in the present study was consolidated using the sodium dithionite method (MacLeod and North 1979).

MATERIALS AND METHODS

Instrumentation and operating conditions

LA–ICP–MS was undertaken using a New Wave Research Co. Ltd (Cambridgeshire, UK) UPI 213 nm Nd:YAG laser system coupled with an Agilent Technologies (Tokyo, Japan) 7500cs inductively coupled plasma mass spectrometer. A spot size of 50 µm diameter (and approximately 75 µm deep) was ablated for 30 s, with a pulse rate of 6 Hz and a laser power of 60%. Seventeen analytes were detected: Fe, Ni, Zn, Cu, As, Se, Pd, Cd, In, Sn, Sb, Te, Pt, Au, Hg, Pb and Bi. These analytes were chosen as they are known to be found in archaeological silver coins, and have been demonstrated to be able to be used to distinguish different groups of coins (Sarah *et al*. 2007). In sum, analytes that are associated with silver-bearing minerals, refining and the manufacture of silver coins were included, while those that may be associated with corrosion (e.g., Cl, S, O and Br) (MacLeod and Schindelholtz 2004) or the conservation of the coins (e.g., Na and S) (MacLeod and North 1979) were excluded.

The ICP–MS was tuned for optimal system sensitivity and to eliminate mass bias effects prior to the commencement of each day's analysis using a National Institute of Standards and Technology (NIST) 612 glass standard. After every 10 samples, a NIST 610 glass standard was analysed to facilitate retrospective normalization of the data for instrumental drift. Approximately 10 s of instrumental gas blank was collected prior to each analytical run, to allow for background correction.

While a comparable certified reference material in a similar matrix to the samples would have been ideal, no such silver standard was available. An attempt to dose silver with a selection of other relevant trace metals to use as a standard was attempted, albeit unsuccessfully.

All samples were analysed in triplicate in order to allow for the possibility of analysing a non-silver inclusion, which would provide non-representative results for the sample. In addition, sites selected for ablation were visually appraised prior to analysis for inclusions, via the instrumentation's camera and display.

Samples

Three hundred and eighty-nine coins were selected for this study from the Western Australian Museum's collection of almost 68,000 coins. The study coins included 71 coins from the *Batavia*, 142 coins from the *Vergulde Draeck*, 70 from the *Zuytdorp*, 79 from the *Rapid* and 51 from the *Correio da Azia*. The sample coins were minted between 1568 and 1816. All coins selected

for analysis are of 'Good' or 'Poor' grade according to the Museum's classification system and, as such, are unsuitable for display purposes. The Museum had not performed any compositional analysis on any of the coins in their collection prior to this study.

Sample preparation All coins were spot cleaned in order to remove surface contaminants before being analysed. Previous cleaning by the Western Australian Maritime Museum had consisted of using 10% v/v nitric acid solution to separate the coins from each other and to remove concretion. The coins were then subjected to the alkaline–dithionite method to remove concretion and to consolidate the corrosion layer (MacLeod and North 1979). After a visual appraisal of each coin, a specific area for ablation was selected based on its being relatively clean and flat, and the selected area was then cleaned using a suspension of ultra-fine-grained alumina powder in water. The chosen area was rubbed with a cotton bud dipped in the suspension with excess solution being wiped away using a tissue dampened with acetone.

Spot cleaning of the coins for sample preparation removes the patina and results in some visible damage to the coin of approximately 5 mm diameter. LA–ICP–MS analysis removes material from the sample coins, which means that some damage to the coins is inevitable. However, the damage is almost invisible to the naked eye and consists only of the laser crater itself. The crater is approximately 50 μm in diameter and 75 μm deep.

Data interrogation

The laser ablation ICP–MS results are presented in the form of counts per second. Through the use of matrix-matched, certified reference materials, it is possible to quantify LA–ICP–MS results; however, this was not possible for the present study, as discussed above. The following data interrogation methods rely upon the inter-elemental ratios present in the data (the trace elemental 'fingerprint'), and their relationship to the provenance of a coin, rather than the absolute trace elemental composition of the coins. For the purposes of this study, quantitative data is not necessary; however, here it should be noted that since the data presented are non-quantitative, there are invariably some limitations present in terms of possible further interpretations of the data.

Representative counts per second data produced by LA–ICP–MS analysis were selected using a commercially available computer program called Glitter™. The median for each analyte was determined and used as the total concentration, representative of the sample.

Linear discriminant analysis (LDA) requires the user to assign the data to separate groups, in this case the mint of origin, prior to analysis. Assuming that the groups have a normal multivariate distribution and the same covariance matrix, LDA is used as the simplest approach to discriminant analysis (Baxter 1994). LDA generates functions that maximize between-population to within-population differences using factor analysis. Factor analysis was used in preference to principal component analysis in order to identify those factors—in this case, combinations of analytes—which are most representative of a latent factor (Baxter 1994), in this case the mint of origin. LDA analysis was undertaken using the commercially available computer program XLSTAT.

It is then possible to project samples of known population into the two-dimensional LDA plot on the basis of their elemental fingerprint. Samples are plotted on the x- and y-axes by being 'pulled' in the direction of the vectors that represent the different analytes of which each sample is composed. In order to identify the probability that the assigned groups of data are correct on the basis of similarities in their elemental fingerprints, a number of validation samples per

analysis are taken from the square root of the total number of samples in the analysis. These samples are withheld from LDA and are plotted in the final stage of analysis as if they were of unknown origin. The accuracy with which the validation samples have been assigned to subpopulations helps to assess the appropriateness of the linear classifiers in separating assigned populations and predicting the correct population for any given sample.

Further, samples of unknown population can also be projected into the LDA plot and potentially identified as belonging to a particular population on the basis of their elemental fingerprint, with a percentage confidence assigned to their belonging to any particular population.

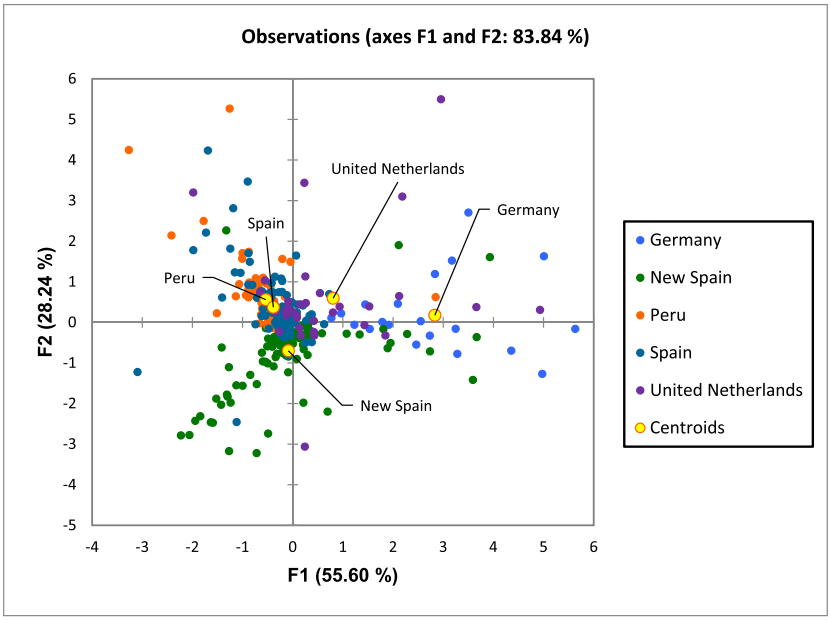
RESULTS

A note on the interpretation of LDA plots follows: Linear discriminant analysis allows samples with more than two variables to be plotted in two dimensions. The algorithm first determines those variables that are most indicative of separation between pre-identified populations using factor analysis. Factor analysis plots are included in the following results, so that the elements that are indicative of each population's separation from other populations can be identified. The variables are arranged in vectors on two axes, with individual samples able to be plotted in terms of all variables, by being 'pulled' in the direction of their composite variables. The level to which each axis, as a combination of variables, distinguishes between populations is given above the plot. In this study, the variables are the elements of which the coins are made up. Pre-identified populations of coins, in terms of country or mint of origin, are plotted in such a way as to maximize the separation between populations on the basis of their elemental fingerprints. It is worth noting that the vector on which a coin has plotted, in relation to the centre of the plot, is what is particularly indicative of the population to which it belongs, rather than its x,y coordinates. Coins of unidentified origin can then be included in the algorithm, and are plotted according to their trace elemental fingerprint. The algorithm will generate a prediction as to which of the assigned populations that sample best fits into, with an associated level of confidence. The confidence level is based on random known samples being taken out of the algorithm and treated as unknowns. The accuracy with which these known samples are then plotted is used to determine the accuracy with which unknown samples will be predicted.

Identification of country of origin

The results from all 389 samples were subjected to LDA analysis, detailed in Figure 1. In Figure 1 it can be seen that 83.84% of the variation between samples is described by the two components (F1 and F2); these components are made up of a combination of all 17 analytes. In order to be able to plot each sample in two dimensions, on the basis of their trace elemental fingerprint, each of the two components is represented on an axis in the plot, further detailed in the lower right section of Figure 1. The samples are plotted with centroids representing the locations of the means of the relevant subpopulations.

It can be seen that coins of Spanish and Peruvian origin have a distinct overlap due to their similar elemental fingerprints. Samples from the United Netherlands and Germany can also be seen to have some similarities in their trace elemental fingerprints in the main scatter plot. These samples are less uniform in composition than Spanish and Spanish American coins, reflected in how widely dispersed coins from the United Netherlands and Germany are from their relevant centroid.



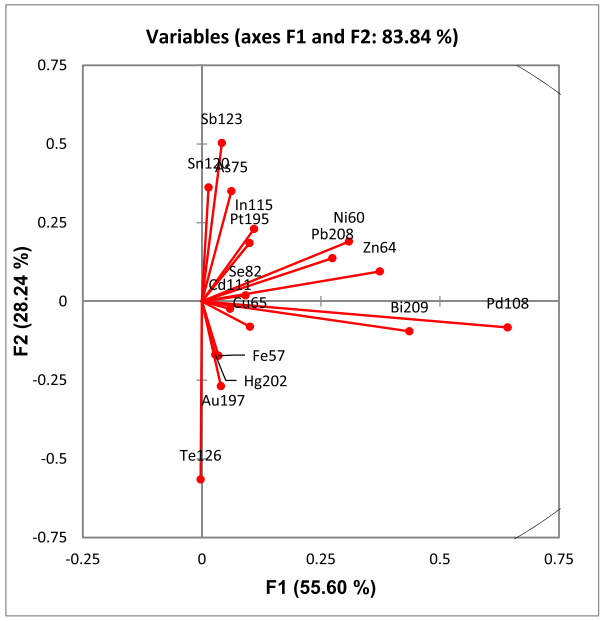


Figure 1 *(a) The LDA plot showing populations of coins on the basis of their country of origin: observations (axes F1 and F2, 83.84%). (b) Factor analysis: variables (axes F1 and F2, 83.84%). [Colour figure can be viewed at wileyonlinelibrary.com]*

German coins would appear to be relatively high in zinc, palladium and bismuth. Coins from New Spain are separated on the basis of their relatively high tellurium content, while Peruvian and Spanish coins are characterized by their antimony and tin contents.

When German and Dutch coins are removed from the LDA, clearer separation between Spanish populations can be established, which indicates that it is possible to distinguish between countries of origin of a coin on the basis of its trace elemental fingerprint. Coins minted in New Spain are characteristically higher in tellurium, palladium and bismuth than those minted in Spain or Peru. Spanish coins are relatively high in platinum, while Peruvian coins are relatively high in antimony and indium. According to factor analysis, gold is indicative of separation between populations, and it would appear to be a significant component in both New Spanish and Spanish minted coins.

Twenty-seven samples of unknown country of origin were also run through the algorithm, to be placed in the population representing the country with the most similar trace elemental fingerprint. In order to identify the mint of origin of these 27 unknown coins, they were placed into a database with coins from their predicted country of origin in order to further predict their mint of origin the results of which are detailed in below.

Identification of the mint of origin

United Netherlands Figure 2 shows the separation of the 33 samples known to have originated from mints in the provinces of Gelderland, Holland, Utrecht, West Friesland or Zeeland, all in the United Netherlands. Two coins identified as being from the United Netherlands, but with an unknown mint of origin, have been predicted as having been manufactured at the Holland and West Friesland mints.

Coins minted in Holland can be seen to be relatively high in mercury, while coins from West Friesland are characterized by their cadmium and mercury contents. Coins minted in Gelderland, Utrecht and Zeeland/Middleburg can be seen to have significant compositional overlap. When discriminant analysis is performed on only those three populations it can be seen that Zeeland/Middleburg is relatively high in nickel, while Gelderland is higher in mercury and platinum. In this case, Utrecht is characterized by being lower in characteristic analytes than coins of the other populations.

New Spain The Viceroyalty of New Spain consisted of all Spanish American territories north of Panama as well as the West Indies, Venezuela and the Philippines. Two New Spanish mints are represented in this study, Mexico and Guatemala. As only two populations were available to be plotted in LDA the plot is one-dimensional, resulting in samples being plotted only along factor 1 (the *x*-axis).

Guatemalan silver is separated from Mexican silver on the basis of its higher tellurium content, while Mexican coins display higher bismuth and palladium contents. All 19 unidentified samples were predicted to be Mexican in origin.

Peru The Viceroyalty of Peru consisted of all Spanish American territories south of Panama except for Venezuela. The Peruvian mints represented in this study are Lima, Potosí and Santa Fe. Seventy-two coins in this study are of known Peruvian provenance, while one coin of unknown mint, identified as being Peruvian using LDA in terms of country of origin rather than mint (Fig. 1), has been included in the following LDA (Fig. 3) in order to predict its mint of origin.

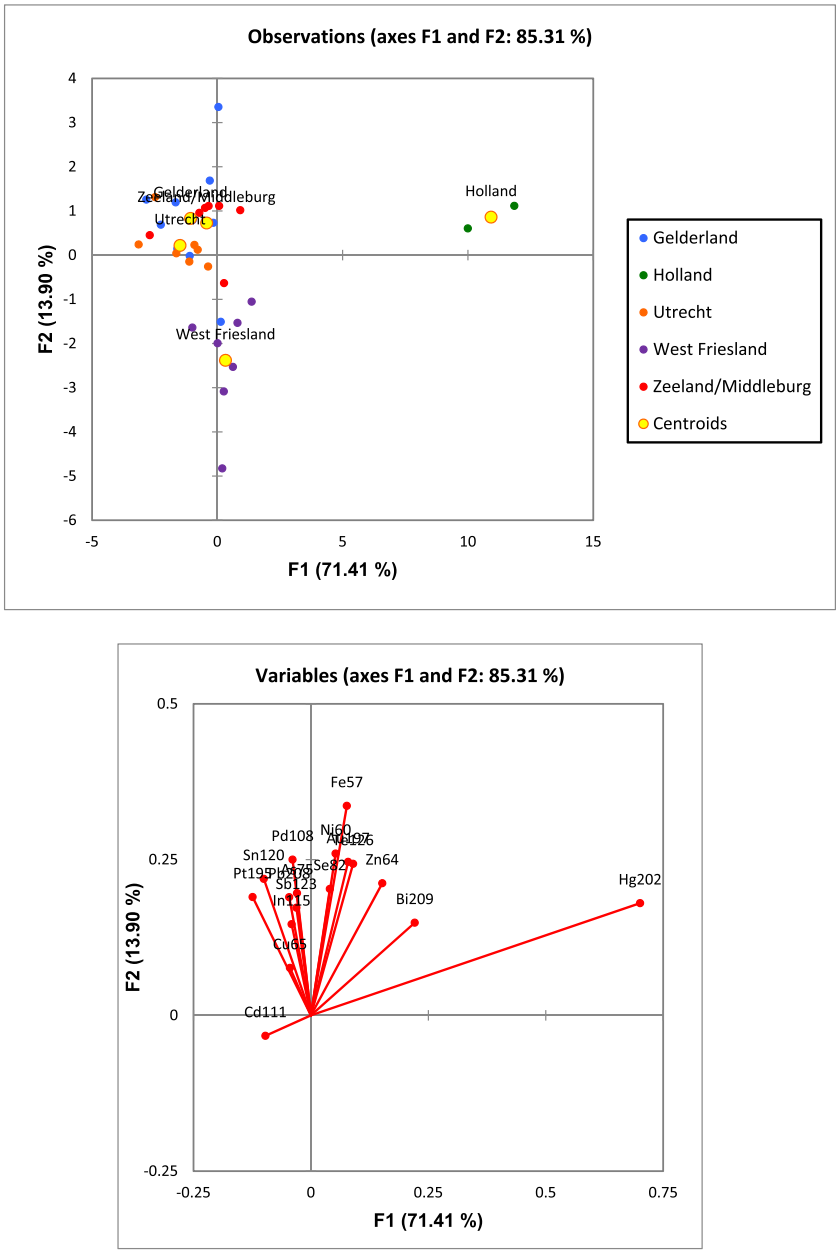
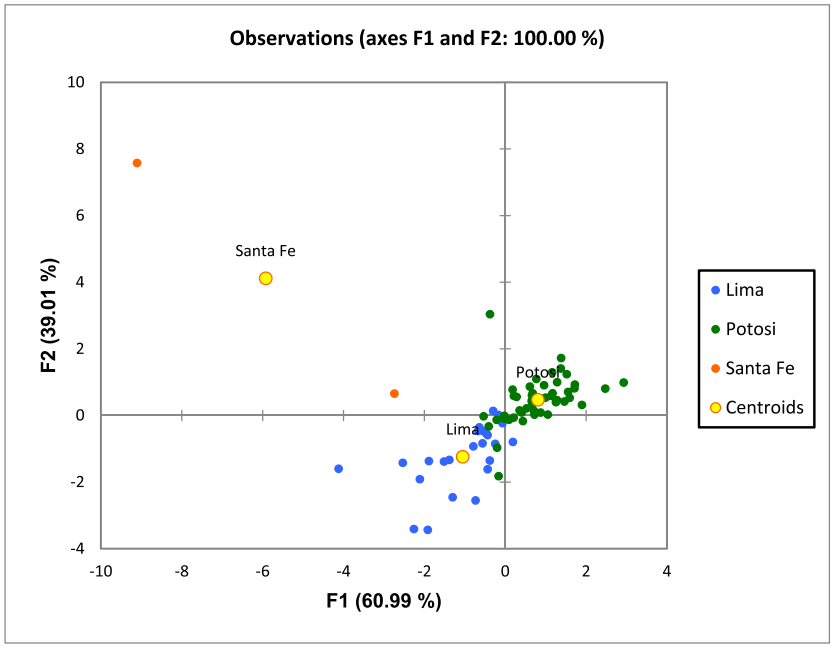


Figure 2 *(a) The LDA plot showing populations of coins on the basis of their mint of origin in the United Netherlands: observations (axes F1 and F2, 85.31%). (b) Factor analysis: variables (axes F1 and F2, 85.31%). [Colour figure can be viewed at wileyonlinelibrary.com]*

Coins minted in Lima are separated on the basis of their relatively high mercury content, and coins minted at Potosí are relatively high in zinc, tin and indium, while coins minted in Santa Fe are distinguished by their relatively high gold, iron, and tellurium contents. The single unidentified coin, S086, has been identified as originating at the Santa Fe mint.



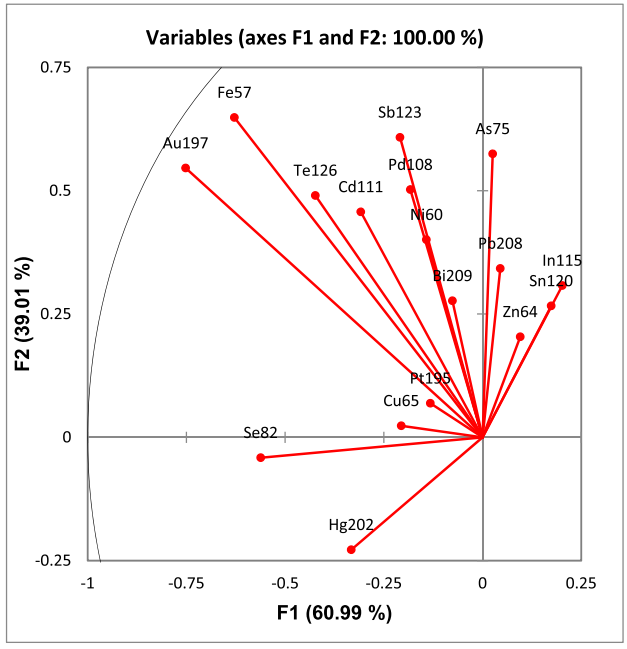


Figure 3 *(a) The LDA plot showing populations of coins on the basis of their mint of origin in Peru: observations (axes F1 and F2, 100%). (b) Factor analysis: variables (axes F1 and F2, 100%). [Colour figure can be viewed at wileyonlinelibrary.com]*

Spain A large group of coins were identified as having been minted in Spain at Cadiz, Madrid, Segovia or Seville. Linear discriminant analysis of these 105 coins is detailed in Figure 4.

Coins minted in Cadiz appear to be relatively high in platinum, palladium, bismuth and gold compared with coins minted elsewhere in Spain. Coins minted in Segovia are high in tin and indium. Coins minted in Seville are differentiated on the basis of their mercury content, while coins minted in Madrid are higher in copper and nickel.

Two unidentified Spanish coins were predicted to have originated in Seville and Segovia.

Germany Twenty coins from three German mints were analysed, from Lubeck, Nuremberg or Sachsen. The results of LDA are detailed in Figure 5. Two previously unidentified coins were predicted to have been minted in Lubeck, and one in Sachsen.

Distinct separation can be seen between the three German mints. Coins from Lubeck would appear to be relatively high in lead, selenium, indium and platinum when compared to coins from the other two German mints. Sachsen coins are relatively high in bismuth and nickel, while coins minted at Nuremberg are separated on the basis of their relatively high combined concentration of zinc and palladium.

DISCUSSION

Country of origin

This research shows that the vast majority of the silver minted in Spain came from the mines of Spanish America in the 16th to 19th centuries.

The significant overlap of the elemental fingerprint of silver coins minted in Spain and Peru is to be expected, as at the time the Spanish were reminting all coins minted in Peru. However, it is of interest to note that the elemental fingerprint of coins from New Spain does not overlap more with the Spanish population in the LDA plot. By order of the Council of the Treasury in 1620, all Spanish American treasure imported to Spain, whether owned privately or by the Crown, passed through the House of Trade in Seville upon its arrival in Spain (Hamilton 1965). A certificate from one of the Castilian mints to prove that the bullion had been coined was to be presented to the House of Trade (Hamilton 1965). Spanish mints, therefore, minted almost exclusively silver that had been mined and refined in the Americas. Coins and cobs struck in the Americas would occasionally go directly into circulation in Spain or more often were used to pay off Crown debts if they were pressing, or when the Crown believed that the price offered for bullion by its creditors was more than its minted value (Hamilton 1965).

The significant similarities in trace elemental fingerprint between Spanish and Peruvian coinage can be explained by an illegal debasement of Peruvian coinage in the 1640s and 1650s, requiring Peruvian coinage in Spain to be reminted. Of the 72 Peruvian coins in this study, 48 were recovered from the 1656 wreck of the *Vergulde Draeck*, and were minted between 1650 and 1653. In Castile in 1650, it was discovered that Peruvian silver coins minted in a few preceding years had been illegally debased, with a silver content as low as half the required content (Hamilton 1965). To remedy the situation, all Peruvian coins were recalled by the Spanish government and required to be refined and recoined, while simultaneously, a new coinage design was ordered for coins minted in Peru (Pradeau 1939; Burzio 1958). Despite immediate action being taken to remedy the debasement in Peru, the communication did not reach the Americas for two more years, during which time defective coins continued to be imported into Spain. Philip

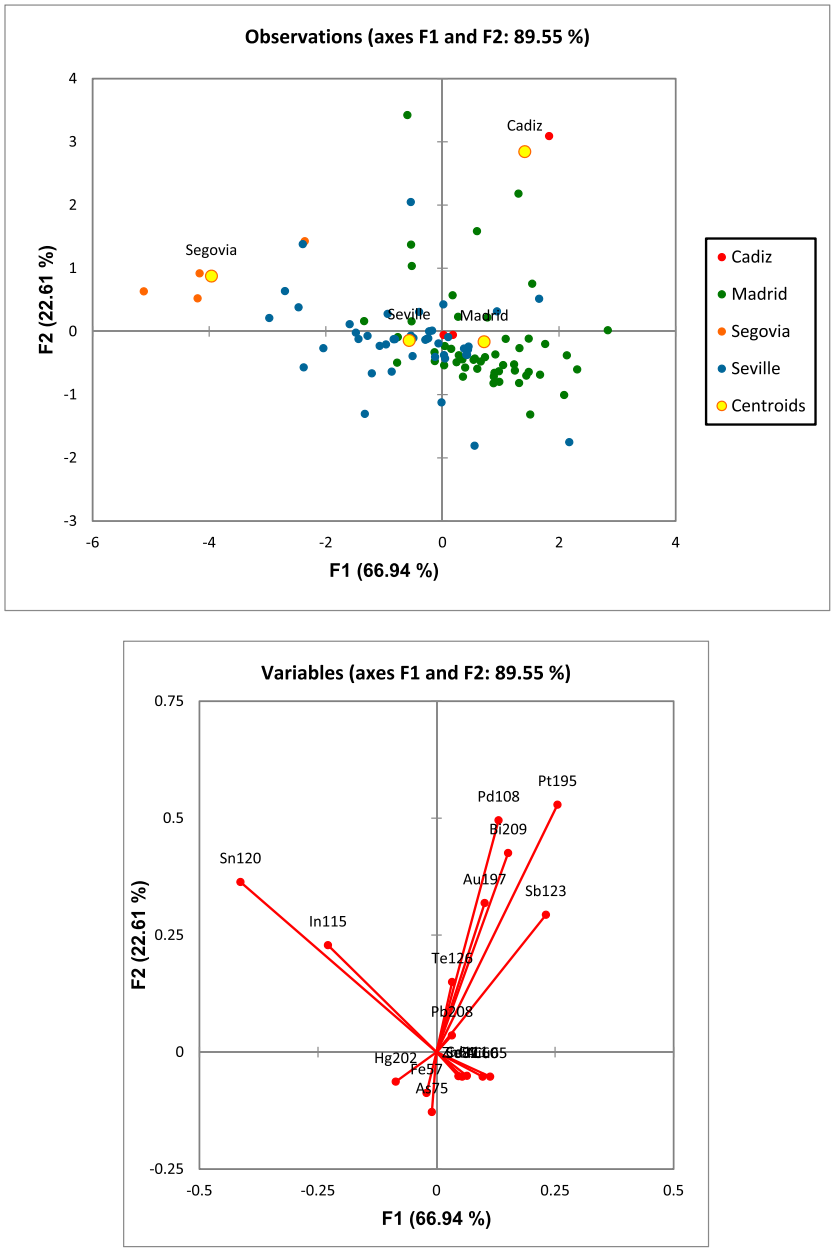
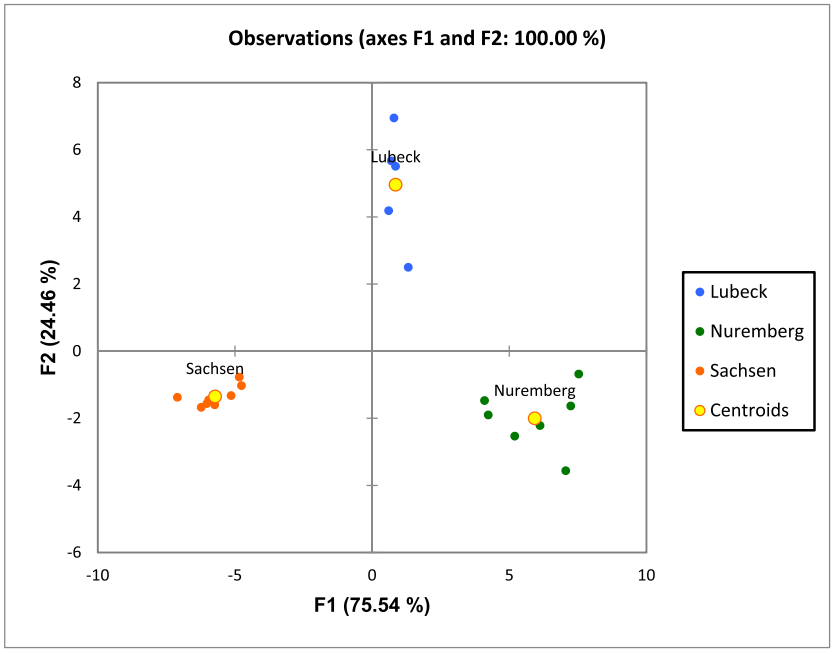


Figure 4 *(a) The LDA plot showing populations of coins on the basis of their mint of origin in Spain: observations (axes F1 and F2, 89.55%). (b) Factor analysis: variables (axes F1 and F2, 89.55%). [Colour figure can be viewed at wileyonlinelibrary.com]*

IV ordered that all coins arriving from Peru be refined and recoined before being delivered to their owners (Pradeau 1939; Burzio 1958). By 1653 the problem had been resolved and Philip IV issued a royal order stating that all Peruvian marked coinage was guaranteed to be of equal fineness to that minted in Castile (Hamilton 1965). It would appear that the close compositional



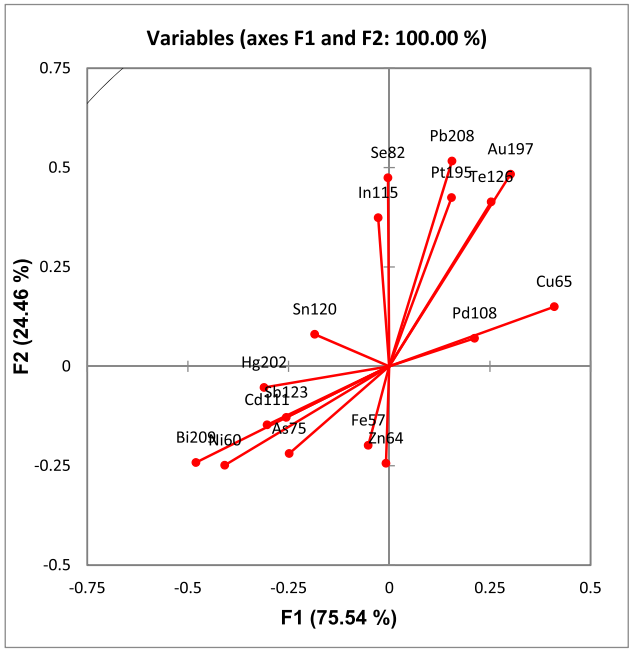


Figure 5 *(a) The LDA plot showing populations of coins on the basis of their mint of origin in Germany: observations (axes F1 and F2, 100%). (b) Factor analysis: variables (axes F1 and F2, 100%). [Colour figure can be viewed at wileyonlinelibrary.com]*

overlap between Peruvian and Spanish coins, a far greater overlap than that between Spanish and New Spanish coins, would be the result of the reminting between 1650 and 1653 of Peruvian coinage in Spain into Spanish metropolitan currency.

It is interesting to note that there are some similarities in the trace elemental fingerprints of Dutch- and German-minted coins, when the vast majority of silver in circulation at the time would have originated in the Americas. This would indicate that a significant amount of Dutch silver originated in Germany, despite the influx of American silver into Europe. Prior to and during the Spanish utilization of American silver mines, Germany also mined and produced silver, but on a significantly smaller scale. With trade embargoes in place between Spain, the main supplier of precious metals in Europe, and the United Netherlands, it might be expected that silver and gold circulating in the United Netherlands would have decreased, and that the silver in circulation at the time may have originated predominantly in Germany. However, it is also widely demonstrated that despite the Spanish Crown's best efforts to retain their precious metals, silver and gold drained out of Spain to the rest of Europe at a very rapid rate (Hamilton 1965). Despite trade embargoes, the Dutch still had relatively easy access to Spanish precious metals via other European trading partners, and some private Spanish merchants.

Predictions of the provenance country of unidentified coins have yielded promising results. As explained above, there is significant compositional overlap between coins minted in Spain and Peru, meaning that it has been somewhat difficult to provenance at least one coin; sample 148 from the wreck of the *Correio da Azia*. The results for sample 148 were inconclusive between Spain, New Spain and Peru. However, the other samples of unknown country have been predicted to belong to a particular country of origin using LDA and so this information has been used in further provenance studies, by inserting these coins into populations corresponding to their predicted country of origin when investigating the mint of origin of unknown coins.

Mint of origin

A successful identification of the provenance mint of 27 coins was made, on the basis of trace elemental fingerprints and validation of known samples included in the algorithm as unknowns. This research has demonstrated that coins that are too heavily damaged for visual identification can still be identified on the basis of their trace elemental fingerprint, and can further contribute to the understanding of the larger assemblage and context in question.

The analytes found to be most indicative of separation between populations of coins using factor analysis, would appear to have little correlation with the analytes expected to separate coins on the basis of the mineralogy of the relevant silver-producing regions. It should be remembered that silver-bearing ores, while identifiably different in different geographical locations based on the minerals of which they are composed, are still very similar to each other. It follows that non-silver elements associated with silver-bearing minerals and/or ores may not be the most indicative of where silver is from.

CONCLUSION

This research addresses a previously unstudied aspect of the silver coin collection of the Western Australian Museum. For the first time a selection of coins from the collection were subjected to chemical analysis, yielding results with implications that go beyond the scope of the study. As a preliminary investigation, the work has not only created many new areas of research interest but has also been successful in achieving the initial aims.

Three hundred and eighty-nine coins were subjected to trace elemental analysis using LA–ICP–MS. The trace elemental fingerprints of 27 coins of unidentified origin were statistically compared to the remaining 362 identified coins using linear discriminant analysis, and their mint of origin predicted. These results have added to our understanding of silver movement during the great maritime empires of the 16th to 19th centuries.

This research has demonstrated the use of trace elemental fingerprinting for provenance determination of archaeological artefacts. Further, the techniques involved are applicable to many different items of cultural heritage significance.

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