Analysis of 16th to 19th Century Silver Coins

LIESEL GENTELLI

Bachelor of Archaeology (Honours) La Trobe University

Bachelor of Arts (Philosophy) Murdoch University

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Technical assistance was kindly provided by Zakaria Quadir for electron backscatter diffraction analysis, Malcolm Roberts for electron probe microanalysis, and Alexandra Suvorova for focussed ion beam and transmission electron microscopy that is described in Chapter 6.

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Abstract

This thesis demonstrates the application of a number of analytical techniques on a selection of silver coins from the Western Australian Museum. Results of analysis are used to appraise the applicability of surface analytical techniques on samples that have corroded. Analysis has also been used to determine when, where and how coins too heavily corroded to visually identify were minted. Further, the importance of maintaining large collections and assemblages of objects in museum collections is demonstrated, and further applications of the techniques used are discussed.

Four hundred silver coins and a selection of silver artefacts were provided for analysis from the collection of the Western Australian Museum. The coins and artefacts were recovered from the following shipwrecks; the *Batavia* wrecked 1629; the *Vergulde Draeck*, wrecked 1656; the *Zuytdorp,* wrecked 1712; the *Rapid*, wrecked 1811; and the *Correio da Azia,* wrecked 1816. All of the ships were wrecked off the coast of Western Australia. The coins represent 22 mints in Spain, Spanish America, the United Netherlands, Germany, and the Spanish Netherlands, and 19 European sovereign issuers from Spain, Saxony, the Holy Roman Empire, Denmark and Norway, the United Netherlands, Holstein Gottorp, and Saxe-Coburg Saxe-Eisenach. The coins were minted between 1560 and 1816.

Samples were analysed using non-destructive analytical techniques: inductively coupled plasma mass spectrometry (ICP-MS) and scanning electron microscopy (SEM). These semi-destructive techniques were chosen in order to demonstrate their effectiveness in gleaning further information from items of cultural heritage significance, than is possible through a visual analysis alone. Silver coins and artefacts were chosen for analysis due to the large assemblage of silver coins held by the Western Australian Museum, making it possible to create a database of analytical results from coins of both known and unknown mint of origin and year of minting for the sake of effective comparison.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), a technique which facilitates multi-element analysis without causing significant damage to the coins themselves. Thirty-eight elements were determined in triplicate for each coin thereby providing individual elemental “fingerprints”. Data were interpreted using linear discriminant analysis (LDA) which allows the coins to be grouped into easily identifiable sub-groups. Using LA-ICP-MS plus LDA it was possible to use the trace and minor element composition of the coins to identify chemical signatures which are specific to the mints of origin. This information was then cross-referenced against the trace and minor elemental composition of damaged and unidentifiable coins to determine their mint of origin and year or decade of minting.

A selection of samples was also analysed using scanning electron microscopy (SEM), a technique which facilitates further understanding of the manufacturing history of the samples based on backscattered electron (BSE) images and electron backscatter diffraction (EBSD) structural maps. Diffracted backscattered electron images can be used to assess the crystallographic structure of the sample and to assess areas of possible inhomogeneity, both of which are indicative of techniques used to manufacture objects of silver and silver alloys. This analysis complements LA-ICP-MS analysis by providing the manufacturing history of the samples, on top of the identification of their provenance and year of manufacture.

This research gives new information about economic networks, including trade between the Americas, Europe and the Far East during the 16th, 17th and 18th centuries, the height of the great maritime empires, and more specifically, the procurement, manufacture and trade of silver as a global commodity at this time. Further, the techniques used in this study are applicable to many other items of cultural heritage significance for future analysis.

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List of Abbreviations

BSE	Backscatter electron
EBSD	Electron backscatter diffraction
EDS	Energy dispersive spectroscopy
EPMA	Electron probe microanalysis
FIB-SEM	Focussed ion beam scanning electron microscopy
HAADF-STEM	High-angle annular dark-field scanning transmission electron microscopy
ICP-MS	Inductively coupled plasma mass spectrometry
LA-ICP-MS	Laser ablation inductively coupled plasma mass spectrometry
LDA	Linear discriminant analysis
New Spain	The Viceroyalty of New Spain – Spanish controlled land north of the Isthmus of Panama
Peru	The Viceroyalty of Peru – Spanish controlled South America except for the coast of Venezuela
SEM	Scanning electron microscopy
SEM-EDS	Scanning electron microscopy energy dispersive spectroscopy
TEM	Transmission electron microscopy
VOC	*Verenigde Oostindische Compagnie* (United Dutch East India Company)

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Chapters 4 and 5

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Chapter 1 – Introduction

Chapter introduction

This study applies different analytical techniques in a holistic approach to understanding the history and use of historical silver coins found in archaeological assemblages. The silver coins that form the basis of this study were minted during the 17th to 19th centuries, and originated both from the Americas and Europe. They were recovered from five shipwrecks off the coast of Western Australia. The 400 coins in this study have been subjected to a number of different analytical techniques in order to glean more information from them than a visual appraisal alone would give.

Historically, the years represented in this study are those of the Spanish conquest of the Americas beginning with Christopher Columbus in 1492, followed by the establishment of the great European maritime empires set up to establish trade routes with the Far East. The majority of the silver used in coins originated from mines in the American Spanish dominions. Movement of silver from the Americas to Spain through Europe and to the East was mostly well recorded and through legal, established channels. However, often silver was won through war, piracy and illegal trade, and restruck or counter stamped.

The influx of American silver into Spain proved to be both a blessing and a curse for the nation, with it quickly draining into other European nations through trade and warfare. From Europe, precious metals were an important trading commodity with the Far East for spices and other Asiatic goods; tea coffee, textiles, ceramics etc. Conversely, European states struggled to produce trading goods other than precious metals that were in demand internationally. The world's first true corporations were the maritime empires of the Portuguese, the Spanish, the Dutch and the British. These maritime empires were set up seeking to find safe and quick passage to the Far East, to then set up trading posts and make enormous profits on imported goods back in Europe. The trading post approach would later be replaced in many cases with settler colonialism.

There are many scientific methods which can be used to glean more information from a coin than a visual appraisal alone. Most commonly used are non-destructive compositional analyses such as x-ray fluorescence (XRF), in order to gain bulk compositional information, while maintaining the integrity of the coin as an item of cultural heritage significance. Somewhat more expensive and time consuming is LA-ICP-MS, which provides minor and trace elemental analysis, and is relatively non-destructive. Through chemical analyses of silver coins of known place and year of minting, this study shows that the trace elements in a coin can be indicative of its mint of origin and year of minting. Further, the microstructure of the silver is indicative of the method of manufacture, and the manufacturing history if the silver has been reworked. The analyses used, in terms of their application to archaeological science, have been critically compared using the results of this study.

1.1 Aims of this study

The purpose of the present study is to apply chemical analyses to silver in order to determine provenance, date, and method of manufacture. This thesis is a methodological study for the analysis of archaeological silver, with further aims to broaden the understanding of the silver items analysed. This study also provides a comparative assessment of different analytical techniques, and also their effectiveness in combination with one another. Further, the results of this study are used to demonstrate the importance of maintaining collections and assemblages of artefacts to provide future researchers with the opportunity to study collections as a whole. The specific aims of this thesis are:

1.1.1 To identify the mint of origin of a coin from chemical analysis

It has been found that the trace elemental composition of silver is indicative of the mint where it was manufactured (Gentelli, 2012). In order to use this information to identify the mint of manufacture of a coin the trace elemental composition can be determined and then compared to a database of the elemental composition of coins identified through other means, for example legible dates and mintmarks. In this way we can identify the mint of origin of previously unidentified silver coins from this collection, while the technique can be applied to any material, given a large enough database of samples of known origin.

1.1.2 To identify the year of minting of a coin from chemical analysis

It has been found that the trace elemental composition of silver can also be used to date the coin. In some cases, it may also be possible to identify the precise year of minting of a coin based on its trace elemental composition, given a large enough database of samples of known place and year of minting (Gentelli, 2012). We can also apply this technique to identify the year of minting of previously unidentified silver coins.

1.1.3 To determine the manufacturing history of individual coins

Backscatter electron (BSE) imaging detects phases of different elements in a sample, the layout of which can be indicative of the manufacturing technique of a metal. Electron backscatter diffraction (EBSD) can be used to detect the crystal structure of the cross-section of a sample, which can also be indicative of their method of manufacture. In general, the microstructure of a worked metal is known to be closely associated with the manufacturing history of the metal, with particular characteristics being indicative of different methods of working at different stages of heating, cooling or annealing.

1.2 The wrecks

Coins used in 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 1.1, and a map of the location of the wreck sites is detailed in Figure 1.1.

Table 1.1– Ships represented in this study

Ship	Departed	Departure Date	Destination	Date of Wrecking	Wreck Location	Rediscovery
Batavia	Texel, The Netherlands	October, 27th, 1628	Batavia (Jakarta)	June 4th, 1629	Houtman Abrohlos	1963
Vergulde Draeck	Texel, The Netherlands	October 4th, 1655	Batavia (Jakarta)	May 7th, 1656	Ledge Point	1963
Zuytdorp	Vlissingen, The Netherlands	August 1st, 1711	Batavia (Jakarta)	June, 1712	Zuytdorp Cliffs	1927
Rapid	Boston, USA	September 28th, 1810	Canton (Guangzhou)	January 7th, 1811	Ningaloo Reef	1978
Correio da Azia	Lisbon, Portugal	1816	Macau	November, 26th, 1816	Ningaloo Reef	2004

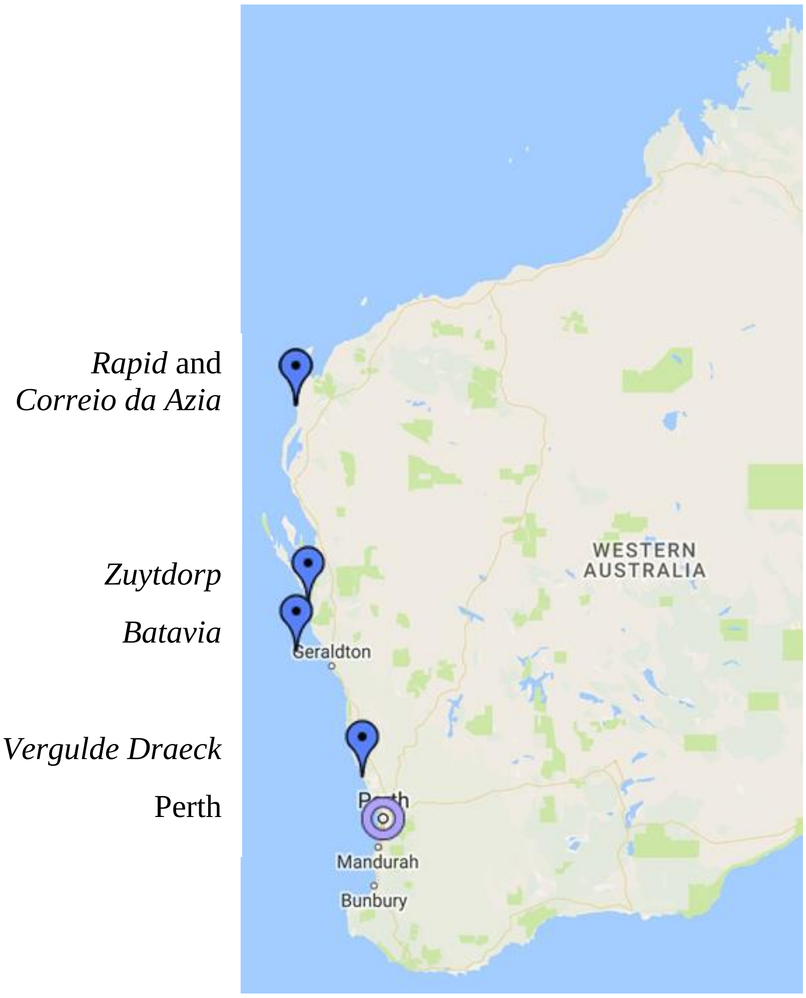


Figure 1.1 – The location of the five wrecks represented in this study. From top: the *Rapid* and *Correio da Azia* wrecked on Ningaloo Reef, the *Zuytdorp* wrecked on the Zuytdorp Cliffs, the *Batavia* wrecked off the Houtman Abrohlos, and the *Vergulde Draeck*, wrecked off Ledge Point.

1.3 Summary of analytical methods

1.3.1 ICP-MS analysis

1.3.1.1 LA-ICP-MS

Approximately four hundred samples from the Western Australian Museum were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This technique facilitates multi-elemental analysis without causing significant damage to the sample. The identification of trace elements in the samples enables the creation of an elemental "fingerprint" characterisation of each sample. Different samples of known provenance were compared using their fingerprints. Grouping those samples with similar fingerprints, groups of similar composition tended to correlate with having been produced in the same mint.

Sample data was investigated using linear discriminant analysis (LDA) to sort the samples into easily identifiable sub groups based on their principle components. Within these subgroups was a mix of previously identified coins and unidentified coins, from which it is possible to identify the mint of origin of the unidentified coins, based on the consistency in each subgroup of the identified coins.

It has also been found that combinations of trace elements in silver coins change over time, providing a platform for the identification of the year in which a coin was minted (Gentelli, 2012). Following on from this finding, the present study applied LDA to sort the samples, in terms of their trace elemental composition, into populations based on their year or decade of minting. Using the same protocol for identifying the provenance of previously unidentified coins in comparison to a database of coins of known provenance, coins of unidentified date were similarly identified.

1.3.1.2 Solution ICP-MS

Solution ICP-MS provides quantitative compositional information with a sensitivity of parts per billion. In this study, solution ICP-MS has been used on a selection of samples allowed for destructive analysis, in order to demonstrate that LA-ICP-MS compositional results from the surface of a coin are comparable to results from solution ICP-MS, which provides results for the whole digested area of a sample.

1.3.2 Electron microscopy analysis

1.3.2.1 SEM-EDS BSE imaging and TEM

Scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) analysis of samples focus primarily on determining the method used to manufacture coins, and secondly, to complement and further our understanding of the elemental composition of a coin by also determining its elemental distribution. This is achieved by investigating the microstructure of samples via EBSD and BSE imaging.

1.3.2.2 FIB-SEM

Using a focussed ion beam (FIB) to mill a section of a sample coin whilst simultaneously using backscattered electrons to image the milled surface facilitates the understanding of the three dimensional microstructure in a sample. Understanding the microstructure is important when interpreting the elemental composition of a sample, in terms of size, shape and distribution of the copper-rich phases within the silver matrix, as well further understanding the manufacture of the coin through imaging of indicators of porosity and stress at the surface of the coin.

1.3.2.3 EPMA

Electron probe microanalysis (EPMA) facilitates large area mapping of the polished cross-section of coins, in order to measure the corroded surface layer of coins, and to provide quantitative elemental distribution maps of the surface layer and the interior of the coin. This has enabled an appraisal on the suitability of surface analytical techniques, by determining how representative the surface composition of a coin is of the whole of the coin.

1.3.2.4 EBSD

Samples which have been allowed by the Western Australian Museum for destructive analysis were mounted in resin and polished to allow electron backscatter diffraction (EBSD) determination of the crystal structure of the samples. It is known that these crystalline structures can be indicative of the method of manufacture of the coin in terms of its thermo-mechanical history (Canovaro, 2013).

1.4 Overview of samples

Coins from shipwrecks are central to the analysis in this study because a shipwreck serves as a (maritime) hoard. An assemblage of coins on a shipwreck represents the trading interests of an identifiable nation or company at a given time. Historical records can give details of the origin and destination of the cargo.

Sample coins were chosen for analysis in consultation with Prof. Walter Bloom, the Honorary Numismatist at the Western Australian Museum. Criteria for the selection of coins to be chosen for analysis included compiling a range of identified and unidentified coins, coins which were below display grade quality, and an even spatial and temporal coverage of the mints, countries and centuries in question. The coins selected for analysis from the larger Museum collection are summarised in Table 1.2 and 1.3. Of the selected coins for analysis, the proportion of coins from the various countries of origin of the coins per ship wreck can be considered to be representative of the larger collection held by the Western Australian Museum.

Table 1.2 – Silver coins analysed in this study from the collection of the Western Australian Museum

Ship	Number of coins in the Museum's collection	Number used in this study
Batavia	7,730	71
Vergulde Draeck	8,404	142
Zuytdorp	20,281	70
Rapid	17,630	79
Correio da Azia	1,023	51

The locations of the mints in question are shown in Figure 1.2 and are further detailed in Table 1.3. A schematic overview of the movement of coins from their country of origin, per shipwreck, is detailed in Figure 7.1 in the Discussion chapter.

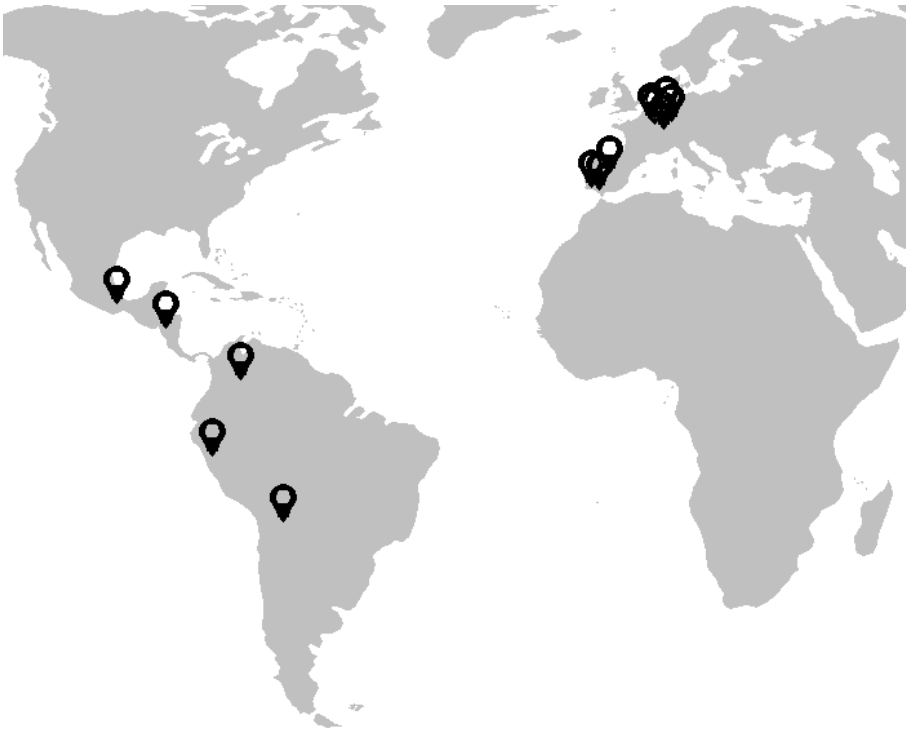


Figure 1.2 – Location of the mints represented in the sample

Table 1.3 – A schematic of all coins analysed for this study

			Sovereign Issuer																					
			Felipe II	Felipe III	Felipe IV	Carlos II	Felipe V	Carlos III	Carlos IV	Joseph Napoleon Bonaparte	Fernando VII	Unidentified	Augustus I	Christian I	Christian II	Johann Georg I	Johann Casimir & Johann Ernst	Rudolf II	Ferdinand II	Frederik III	Unidentified	Estates General	Unidentified	Unidentified
			Spain										Saxony					Holy Roman Empire				United Netherlands		Unidentified
Mint or Province	Cadiz	Spain									4													
	Madrid			1	4				26	6	14													
	Segovia			1	3																			
	Seville				20				20		3	2												
	Unidentified									1														
	Guatemala	New Spain[1]							8															
	Mexico								24															
	Lima	Peru[2]			55	3	29				3	27												
	Potosí				46																			
	Santa Fe				2																			
	Unidentified	Spanish America			1			2	6	1	2	5												
	Friesland	United Netherlands																1						
	Gelderland[3]		1																			3	6	
	Holland																						2	
	Overijsell																					1		
	Utrecht[3]		1																			6		
	West Friesland																					7		
	Zeeland																					7		

	Unidentified																						1	
	Holstein Gottorp	Germany																		1				
	Lubeck																	1	3		1			
	Nuremberg																		7					
	Saxony												2	2	1	2	1							
	Brabant	Spanish Netherlands	1		2	2						1												
	Unidentified	Unidentified							1		1													7
	[1]New Spain refers to Spanish American territories north of Panama as well as the West Indies, Venezuela and the Philippines [2]Peru refers to Spanish American territories south of Panama except Venezuela [3]Gelderland and Utrecht were administered by both the Spanish and United Netherlands at different times, ultimately coming under the control of the United Netherlands																							

1.5 Structure of thesis

Chapter 2 – The Background chapter details aspects of historical silver production, movement, archaeological excavation, conservation and storage. The purpose of this chapter is to provide the reader with sufficient understanding of the production, use, deposition and subsequent recovery of the coins in this study in order to fully engage with the research presented.

Chapter 3 – The Literature Review and Methodology chapter seeks to address the numerous analytical methods available for both destructive and non-destructive analysis of items of cultural heritage significance. This is followed by an explanation and a justification of the techniques chosen to be used in the present study.

Chapter 4 – The Methods chapter details the methods used for this study, in such a way as to ensure they are replicable and adaptable to other items of cultural heritage significance.

Chapter 5 – The Results of ICP-MS chapter details the results of investigations into the applicability of surface analysis on the coins used in this study, provenance determination of unidentified coins and artefacts, and absolute dating of coins based on their trace elemental composition.

Chapter 6 – The Results of Electron Microscopy chapter details the results of investigations into the measurement of corrosion and silver surface enrichment in terms of the applicability of surface analytical techniques on the coins used in this study, the structure and morphology of the coins, and a determination of the manufacturing methods used based on the structure of the coins.

Chapter 7 – The Discussion chapter seeks to synthesise the results detailed in chapters five and six together within the context of the history of the coins. When presented in context, the findings are explored in more depth and the significance of the results in terms of the sample coins is identified.

Chapter 8 – The Conclusion chapter aims to summarise the results of chapters five and six and the discussion in chapter seven, in terms of the significance of the findings in the broader terms of numismatics and archaeology. Further, the applications of the methods used in this study are indicated, with recommendations for future research.

Chapter conclusion

This thesis demonstrates, through the use of complementary analytical techniques, the information that can be gleaned from an archaeological artefact beyond visual identification. Further, the importance of keeping museum collections together for future research is demonstrated by the use of a collection of silver coins which have been in the collection of the Western Australian Museum for several decades. In terms of the coins themselves, results of analysis have been used to determine their method of manufacture, the year or decade they were minted, their mint of origin and to measure the differences between the surface and bulk of the coins due to corrosion.

Chapter 2 - Background

Chapter introduction

The following chapter aims to provide a detailed understanding of the coins used in this study, by providing a broad understanding of global silver movement and use during the 17th to 19th centuries. Further, aspects of the coins' manufacture, use, deposition and conservation will be discussed in terms of the effect on the composition and structure of the coins that has been observed through the present research study.

To this end, silver extraction and refining in the Americas is discussed, followed by a discussion on the movement of silver throughout the world in the 17th to 19th centuries. The mints which are represented in this study will be detailed, with a discussion on the development of minting technology at the time. The wrecks which are represented in this study are also discussed; from the wrecking event and salvage attempts, through to the rediscovery, excavation, and conservation of the wreck material. Finally, the conservation and identification of the coins in the Western Australian Museum's collection is discussed, followed by an overview of deaccessioning policies of museums around the world particularly in relation to coin collections.

2.1 Silver extraction and refining in the New World, 1450-1880

2.1.1 The application of developed technologies to new environments

Silver sourced from Spanish America as a trade commodity was the backbone of the European and global economies during the 16th to 19th centuries (Hamilton, 1965; Attman, 1986). As demand increased for silver for the Spanish war effort, paying off royal debt and trading within Europe and around the known world, innovations had to be made in order to increase the efficiency of silver refining with a long-term, centralised approach.

This section considers previously studied techniques for silver extraction and refining and argues that established industrial processes developed in Europe to refine silver had to change when applied to the different conditions in Spanish American colonies. The adaptation of established industries to a new and different colonial setting is well documented in industrial archaeology literature. For example, the development of iron smelting technologies from Britain to Australia (Jack, 1994), the use of pre-existing perceived tribal traits to increase productivity in South African gold mining (Guy and Thabane, 1988), the transition between British and American technologies for quartz roasting in Australia (Gojak and Allen, 2000), the application of British technology to irrigation in India (Gilmartin, 1994), the identification of a previously unknown type of furnace at the Howqua Hills goldfield (Hoey *et al.,* 2000) all demonstrate the adaptation of technologies to new environments.

The different silver refining techniques used in Europe and Spanish America respectively, had been adapted to the unique conditions existing in those places in terms of optimizing extraction efficiency cheaply and easily. However these silver refining techniques were all incompatible with the European exploitation of Spanish American silver deposits, and consequently new methods of production were necessarily established.

In Europe, the cupellation technique (Biringuccio, 1540) and the Saiger process of extracting silver from copper ores (L'Heritier and Tereygeol, 2010) were used in order to achieve high metal yields from European ore. In pre-Columbian Americas, the *huayrachina*,, a furnace used to refine silver from ore (Cohen *et al.*, 2009), was primarily used, achieving an incomplete metal yield from high quality, abundant ore, and at the same time using minimal fuel. None of these techniques were satisfactory for the long-term, intensive exploitation of silver mines by Europeans in the Americas.

2.1.1.1 Silver ores

Silver in Europe is generally found in galena (lead sulphide ore) and sphalerite (zinc sulphide ore) as well as trace minerals such as pyrite, arsenopyrite, tetrahedrite and freibergite. Spanish American silver is commonly found in relatively high concentrations in polymetallic ores, which are significantly different in their mineralogy from European ores where the silver is often found at relatively low concentration, associated with or included in base metallic ore minerals. For example, Potosí silver ore, when it was first mined by the Spanish, was found to contain as much as 30 to 40 per cent silver (Omiste, 1893), while the richest silver ores in Germany contain only 10 to 15 per cent silver (Bartels, 2009).

The mineralogy and compositional variability between different silver ores is discussed further in section 2.3.1.

2.1.1.2 Colonial forced labour

Mining for precious metals in Spanish colonies initially took the form of *encomienda*, a forced labour system relying on native labour. In Hispaniola, Spain's first Caribbean colony, gold mining heavily utilising native forced labour with a minimum input of Spanish financial investment and European technologies had been exhausted by the 1520s (Vilar, 1976; Stein and Stein 2000). Due to the relatively quick exhaustion of gold in Hispaniola the Spanish did not have the opportunity to recognise the long-term negative effects of the *encomienda* system on both mining and the native population, and so a similar system was ultimately unsuccessfully introduced for later silver mining in the Americas (Stein and Stein 2000).

Neither European nor Spanish American silver extraction and refining techniques were appropriate to fulfil the European demand for silver in the New World. The scale of operations required was something which had never been encountered in Europe or European colonies due to the abundance of ore in the Americas (Stein and Stein, 2000), and the cost of efficient extraction and refinement of large amounts of silver, using both European and Spanish American technologies, eventually made mining all but the richest ores almost prohibitively expensive. A new, centralised, efficient, large-scale silver extraction technique was therefore required, and delivered in the form of the Patio process (Probert, 1997).

2.1.2 European silver extraction and refining techniques

2.1.2.1 European silver sources before the Americas

Prior to European colonisation of the Americas, European silver originated from mines in Germany, from Saxon-Erzgebirge and the Kuttenberger mines in Bohemia (Soetbeer, 1879). Silver was also acquired through trade from the Arabian silver mine of Penjir in the mountain range of Hindu Kush in present day Afghanistan, and from Shash, a silver mine in present day Tashkent, Uzbekistan (Attman, 1981). France had very few profitable silver mines in Ariege, Bearne, and the Massif Central, which produced on a very small scale, and they did not produce enough silver for French currency (Vilar, 1969). Output from these mines was quickly dwarfed by the unprecedented output from American silver mines. To put this into perspective, in the six centuries between 250BCE and 350 CE, 40,000-50,000 tonnes of silver were produced in the Mediterranean world. The silver mines of the Americas produced the same amount of silver in only 200 years (Stein and

Stein 2000). Individual silver mines in Europe did not produce more than 2,300kg of silver per year before 1530. With advances in technology, particularly in Germany, some mines went on to produce as much as 11,500kg of silver per year (Vilar, 1969). However, the majority of German mines were shut down by 1600, and those that were still open were losing miners overseas, in particular to more lucrative colonial mines (Vilar, 1969).

In terms of trade, prior to the discovery of the trade route round Africa and direct trade between Europe and the Far East, a trade imbalance existed between Europe and the Baltic, and Europe and the Levant (Attman, 1986). Areas that are now Russia, Poland, and Lithuania provided goods to the European market in exchange for precious metals. The same is true of trade between the Levant and Europe. In section 2.2, the similar trade imbalance between Europe and the Far East is described, in which demand for European goods in exchange for goods from the Far East was far outstripped by demand for precious metals from Europe in exchange for goods.

2.1.2.2 Cupellation

Cupellation relies upon the principle that lead oxidises more easily than silver or gold when exposed to a blast of air at high temperatures. The lead metal oxidises to lead oxide (‘litharge’), which is either removed from the cupellation hearth through tapping or soaked up by the porous hearth material (Agricola, 1556). At the end of the process, a pure gold-silver regulus remains in the centre of the hearth on top of the litharge soaked up by the hearth material where it can be easily recovered (Rehren and Klappauf, 1995). This process can be represented by the following equation:

$$Ag + 2Pb + O_2 \rightarrow 2PbO + Ag$$

It is claimed that cupellation has been used as a technique for refining silver since the fourth and third millennia BCE in Anatolia,Mesopotamia and Iran (Hess *et al.,* 1998; Pernicka *et al.,* 1998, Pernicka *et al.,* 2011). For example, at the sites of Habuba Kabira in East Anatolia, Fatmali-Kalecik in Syria, and Arisman in Iran, artefacts of refined silver and lead have been found associated with pieces of lead oxide (litharge) and slag. Analysis of the slag indicates that silver was being extracted from lead ores using the cupellation technique (Karsten *et al.,* 1998; Pernicka *et al.,* 1998; Pernick *et al.,* 2011). Archaeological evidence in the form of litharge cakes indicates that large-scale cupellation continued to be employed as a refining technique through Roman and medieval periods (Bayley and Eckstein, 2006).

The method of cupellation remained essentially unchanged for centuries. A description of cupellation by Paul of Taranto in the 13th Century can be found essentially replicated in the writings of 16th Century metallurgists (Martinon-Torres and Rehren, 2005). The practice of cupellation varies only slightly depending on if it is used to separate precious metal from base metal, to purify precious metal that is being reused, or to assay precious metal (Bayley and Eckstein, 1997). In order to refine large quantities of silver, a cupelling hearth was incorporated as part of a furnace, with a cover of brick, iron, clay or wood (Biringuccio, 1540) (Figure 2.1). Archaeological evidence for the separation of silver from argentiferous lead ore by cupellation can be found in the form of litharge and cupellation hearth lining, which is identifiable as a porous material impregnated with lead oxide (Bayley *et al*., 2008). Litharge itself is a comparatively rarer archaeological find than hearth lining, as litharge was often re-smelted to extract the remaining lead (Bayley, 2008).

Figure 2.1 - A cupellation furnace with hearth in place. "A – Furnace. B – Sticks of wood. C – Litharge. D – Plate. (E – The foreman when hungry eats butter, that the poison which the crucible exhales may not harm him, for this is a special remedy against that poison.") (Agricola, 1950 [1556]:474)

2.1.2.3 The Saiger process

While much of the European silver was produced in association with lead refining, with lead being a bonus of silver refinement, copper-lead-zinc ores were also processed, as they were more abundant and contained high levels of silver. However, due to the difficulty of separating copper from silver (copper was present at a much higher level than silver in these ores, as is also the case in lead-rich silver ores), these ores were often not used as a source of silver and consequently a valuable source of this metal was being lost. In 1451, the Duke of Saxony introduced the Saiger process (*Saigerprozess*) to the silver mines of Germany to more easily separate silver from copper (Vilar, 1976; L'Heritier and Tereygeol, 2010). The Saiger process greatly increased production of silver from many European silver mines. For example, the Schneeberg mine (Germany) went from producing only a few hundred marks (a mark weight corresponds to an English pound) of silver per year to 4,400 marks per year, while the Schwaz mine (Austria) went from producing 2,800 to 9,000 marks of silver per year (Vilar, 1976:72). Indeed, silver production in Germany rose 500 per cent between 1450 and 1540 as a result of the use of the Saiger process (Suhling, 1994).

The Saiger process consists of melting together argentiferous copper (previously smelted in a normal furnace step) with lead metal, at a temperature where both metals are liquid (approximately 1,000°C). Charcoal furnaces at the time were capable of reaching up to 1,400°C. The resulting mixture was then cast into cakes and allowed to cool. When cooling, the silver migrated from the copper into the lead due to its strong affinity for the latter element. The cakes were then heated in a reducing atmosphere and the lead was separated from the copper at a temperature above the melting point of lead (327.5^{o}C) and below that of the copper (1085^{o}C), so that the silver-rich lead would flow out and be cooled, leaving the copper behind. The silver-rich lead was then cupelled and the silver removed.

2.1.3 Pre-Columbian silver refining in the Americas

Initially, American native silver would have been readily available from surface outcrop in silver-bearing veins. This silver would have simply required melting followed by casting (Barba, 1640). When these sources had been depleted, more complex silver ores, for example argentite (AgS) present as inclusions in lead sulphide (PbS – galena), a mineral which often would have been found in association with chalcopyrite ($CuFeS_2$) and sphalerite (ZnS), would have been available, requiring a different refining process.

These ores, unlike contemporary European ores, were silver-rich (often poor in lead minerals). European silver extraction relied on lead, either naturally occurring as a sulphide in the lead rich ore to be refined, or as an addition during the refining process based on the same principles as the Saiger process (Cohen *et al.,* 2010; Rehren, 2011). However, it would have been necessary for the lead sulphides to have been reduced to lead metal to facilitate the transfer of silver into the molten lead, requiring a large amount of charcoal to achieve a smelting.

2.1.3.1 Huayrachina and tocochimbo

Smelting of silver from lead rich ores in the pre-Columbian Americas, particularly the Andes, was undertaken in a furnace known as a *huayrachina* (Figure 2.2). These furnaces were cylindrical, about 80-100cm high, containing many small openings to allow oxygen flow. *Huayrachinas* operated in locations with consistent, strong winds in order to provide large amounts of air to assist in maintaining an adequate temperature for production (Van Buren and Mills, 2005). The process worked under the principle of inter-metallic eutectic formation. The silver and lead would combine, while the rest of the ore would separate in the form of slag. The *huayrachina* has an incomplete metal yield due to its low operating temperature, as evidenced by the discovery of slag with beads of silver still remaining (Cohen *et al.*, 2009; Cohen *et al.*, 2010). However, the silver-rich slag was sometimes further processed in small crucibles (Schultze *et al.*, 2009). One significant problem with all smelting furnaces and this particular method of silver removal was that a reducing environment had to be maintained inside the furnace to produce metallic lead from the lead sulphide. An accidental ingress of air into the furnaces could therefore change the internal furnace environment and reduce the extraction efficiency for the silver.

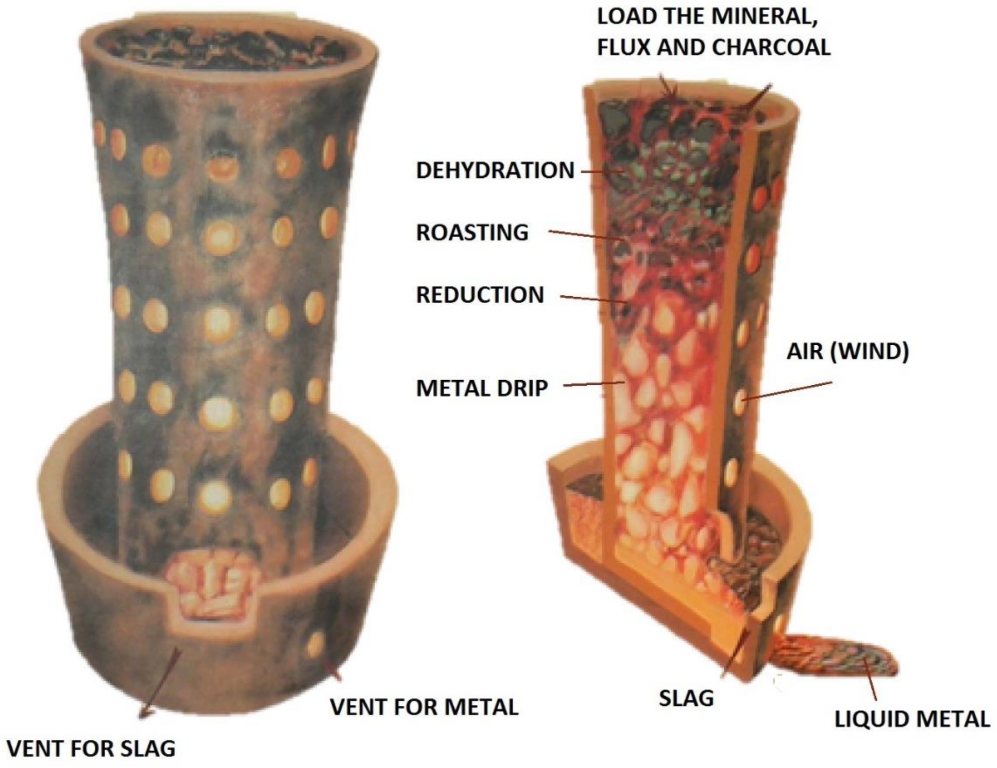


Figure 2.2 - Schematic of a *huayrachina* (Archive Sicán-Peru National Museum, 2013, used with permission)

The lead metal produced by the *huayrachina* was then processed by cupellation to extract the silver, probably in an installation called *tocochimbo*. The *tocochimbo* was a cupellation hearth described as a round muffle furnace with a diameter less than one meter. The dome shaped furnace had two doors on opposite sides, one for ventilation and one to insert both the muffle (a perforated piece of ceramic) and the lead metal. An opening in the *tocochimbo* allowed the introduction of charcoal (Figure 2.3) (Barba, 1640; Oehm, 1984). The *tocochimbo* was used mostly for silver refining, but could also be used for the smelting of small amounts of gold or silver (Barba, 1640). There is a distinct lack of contemporary descriptions of the *tocochimbo* in comparison particularly to the *huayrachina*, probably due to the fact that *tocochimbo*s were located inside domestic dwellings of local workers, rather than out in the open on hills (Van Buren and Mills, 2005).

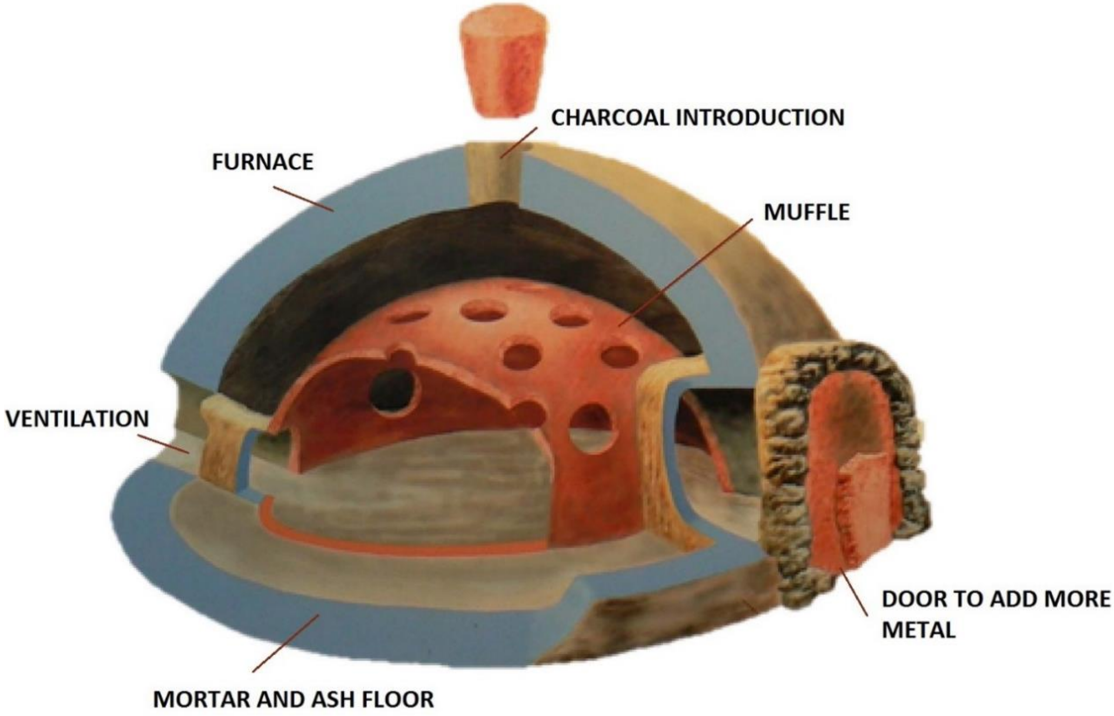


Figure 2.3 - Schematic of a *tocochimbo* (Archive Sicán-Peru National Museum, 2013, used with permission)

In contrast to European cupellation, traditional Spanish American cupels are made from plant ash, with animal dung used for fuel instead of charcoal (Cohen *et al.*, 2009). Analysis of the cupel material indicates that the lower temperature used for silver processing, like the *huayrachina*, also results in an incomplete silver yield, evidenced in higher amounts of silver being absorbed into Spanish American cupels than their European counterparts (Cohen *et al.*, 2010; Rehren, 2011).

2.1.4 Europeans in Spanish America

2.1.4.1 Dragon furnaces

Following European colonisation of the Americas, silver mining and refining was practiced on a much larger scale. However, small scale, decentralised, individual operations were in place near silver mines, in the interest of short-term profits for individuals rather than the creation of a long term, sustainable economy. The most common of these private silver refining processes involved the use of the dragon furnace (Figure 2.4), which functioned similarly to the *huayrachina*.

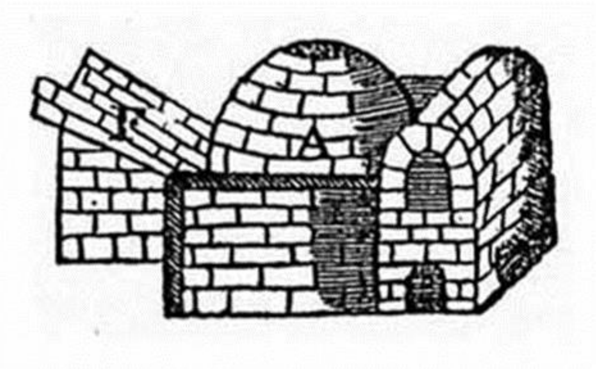


Figure 2.4 - A dragon furnace (Barba, 1640)

Dragon furnaces were hemispherical in construction, with long chimneys and adjacent fire boxes. Some of these furnaces have been discovered in southern Bolivia and analysis of the slag associated with them has indicated that they had much higher fuel consumption than the *huayrachina* leading to a greater silver yield (Cohen, 2008; Cohen *et al.*, 2009). This observation has also been used to support the argument above that the individuals running the dragon furnaces were more concerned with immediate profits than with a sustainable economy, and so continued using a method that would deplete fuel reserves at an increased rate (Cohen *et al.,* 2010; Rehren, 2011).

2.1.4.2 The turning point

It would appear that the European and Native American perspectives towards silver extraction differed enormously, with Europeans placing more importance on a high metal yield, whilst the Native Americans placed more importance on minimal fuel consumption (Cohen *et al.,* 2010; Rehren, 2011). Neither European nor Native American silver extraction techniques were adequate for the sudden increase in demand for Spanish American silver after European colonization due to a complex combination of socio-economic factors. This was evident by the mid-sixteenth century, when silver yields from Spanish America had begun to decline due to the depletion of high-grade ores and increased costs of production (Probert, 1997:102).

2.1.4.3 Mining effort and scale of production

The labour intensity of different methods of silver extraction and refinement greatly influence how widespread a technique is. While all methods of silver extraction and refining discussed above are relatively labour intensive, the success of a method will also depend on other factors.

By 1545, surface outcrops of silver-rich ore in Spanish America had been all but exhausted, necessitating deeper mining of lower quality ores which involved considerably more infrastructure and effort for the mining itself, ore processing, silver extraction and refinement (Vilar, 1976).

Silver production in Mexico and Peru employed roughly 15,000 mineworkers each year, producing 40,000 tons of silver in two centuries, an amount which took six centuries to produce in the Mediterranean world (250BCE-350CE) (Patterson, 1972). The volume of silver ore necessitated the construction of large amounts of mining infrastructure such as dams, waterwheels, adits and shafts. This was a scale of production not seen before in Europe or the Americas and required extensive investment of both capital and labour only possible with a centralised system rather than small private enterprise.

2.1.4.4 Cost of production

The cost of production of silver in Spanish America increased over time, due mainly to the depletion of high grade, easily accessible silver ores, and the increased cost of labour. Operational costs for mine owners included various royalties, fees and taxes to be paid to the Spanish Crown (Garner, 1988) in addition to those of infrastructure and labour. While output from Spanish American silver mines remained relatively high, particularly at Potosí, the costs to mine, extract and refine silver often meant that profits were not substantial.

Immediately after Columbus’ arrival in the Americas in 1492, Ferdinand and Isabella of Castile obtained a Papal grant to facilitate the enslavement of any non-Christians of the Americas in precisely the same wording as the Papal grant of 1454, which allowed the King of Portugal to enslave West Africans. A decade later, the formalised *encomienda* system was established to provide colonists with native labourers, but requiring the colonists to take responsibility for their labourers, and to teach them the Spanish language and the Catholic faith (Rodriguez, 2007).

Some Spanish colonists evidently did not agree with the enslavement of the natives, of note was Bartolomé de Las Casas, Bishop of Chiapas and Protector of the Indians. Las Casas strongly believed that the Native Americans were free men, deserving of the same treatment as all others (Crow, 1992). In 1515, Las Casas achieved an audience with King Ferdinand to argue for the end of the *encomienda* system. Initially unsuccessful, Las Casas’ argument gained popularity, and in 1530 Charles I of Spain (Charles V, Holy

Roman Emperor), decreed in the “New Laws of the Indies for the Good Treatment and Preservation of the Indians” that the enslavement of Native Americans was prohibited.

Despite the enacted laws, oppression of native labourers in silver mines continued. The work was harsh, with men spending eight hours inside the mine every working day. Owners and overseers routinely verbally and physically abused labourers, who were also vulnerable to pneumonia silicosis of the lung and generally dangerous working conditions. Finally, despite the requirement to pay forced labourers, the pay was low, and could fluctuate depending on whether an individual met specific targets (Vilar, 1976).

2.1.4.5 Fuel consumption and efficiency

As discussed above, the problem of fuel consumption was of less importance to European colonists than to Native Americans (Rehren, 2011), as European silver extraction and refining had been developed in an environment where smaller volumes of silver ore could be smelted without significantly depleting fuel sources. Private, enterprising European colonists who had set up extraction and refining enterprises near mines often relied on the dragon furnace, which gave a higher silver yield than the Native American *huayrachina* albeit with a much higher fuel consumption. Depleting fuel reserves in Spanish America led to increased cost of production, often making private extraction and refining enterprises prohibitively expensive.

Efficiency was a related factor in the issue of fuel consumption. An efficient extracting and refining technique was necessary to minimize consumption and maximize output. Both the *huayrachina* and Saiger process were relatively inefficient in terms of fuel consumption, with the dragon furnaces even less efficient.

2.1.4.6 Combination of factors

The labour intensity required to mine silver increased as rich surface veins were exhausted. Mining deeper underground required the construction of shafts, and methods to keep the shafts free from water, both expensive operations. Native labour became more expensive with the introduction of laws to protect the Native Americans, and the combination of taxes to be paid to the Spanish Crown for the privilege of mining, extracting and refining silver meant that profits were decreasing, despite an output of silver from Spanish America that still eclipsed anything seen in Europe.

As a result, silver production in Spanish America had declined. For many mine owners, the decreasing quality of ore and increasing cost and effort for production made silver mining prohibitively expensive. For production to continue and profits to be made, an efficient, large-scale, centralized method of silver extraction and refinement was necessary, to process large volumes of relatively low-grade silver ore, cheaply and simply. This was to be found in the mercury amalgamation, or Patio process.

2.1.5 The introduction of the Patio process

The Patio process was developed and used to refine both silver and gold in the 15th century, principally in the European silver mines that were producing silver for Venice (Vilar, 1976). The process was first described in 1540 by Biringuccio in *De La Pirotechnia* and is notably missing from Agricola's 1556 publication *De Re Metallica*. Biringuccio, however, seems to have described the mercury amalgamation as a small scale solution to recovering precious metals from slag and sweepings, rather than a primary method of silver extraction (Biringuccio, 1540).

The Patio process was introduced to Mexico in 1556 by the German Gaspar Lomann and was followed a year later by the Spaniard Bartolome de Medina who is most often credited with the introduction of the process to the New World (Vilar, 1976). Medina was instructed in the process in Spain by a German known as Lorenzo as follows;

Grind the ore fine. Steep it in strong brine. Add mercury and mix thoroughly. Repeat mixing daily for several weeks. Every day take a pinch of ore mud and examine the mercury. See? It is bright and glistening. As time passes, it should darken as silver minerals are decomposed by the salt and the silver forms an alloy with mercury. Amalgam is pasty. Wash out the spent ore in water. Retort residual amalgam; mercury is driven off and silver remains (Probert, 1997).

Medina then spent two years in Pachuca experimenting with the process with mixed success due to the different silver ore compositions from Europe to the Americas before successfully adapting the process to the local silver-rich, polymetallic ore (Zavala, 1962).

The process was then introduced at Potosí in 1570 by the Viceroy Francisco de Toledo, where silver production increased by 800 per cent in a decade as a result (Vilar, 1976) (Figure 2.5).

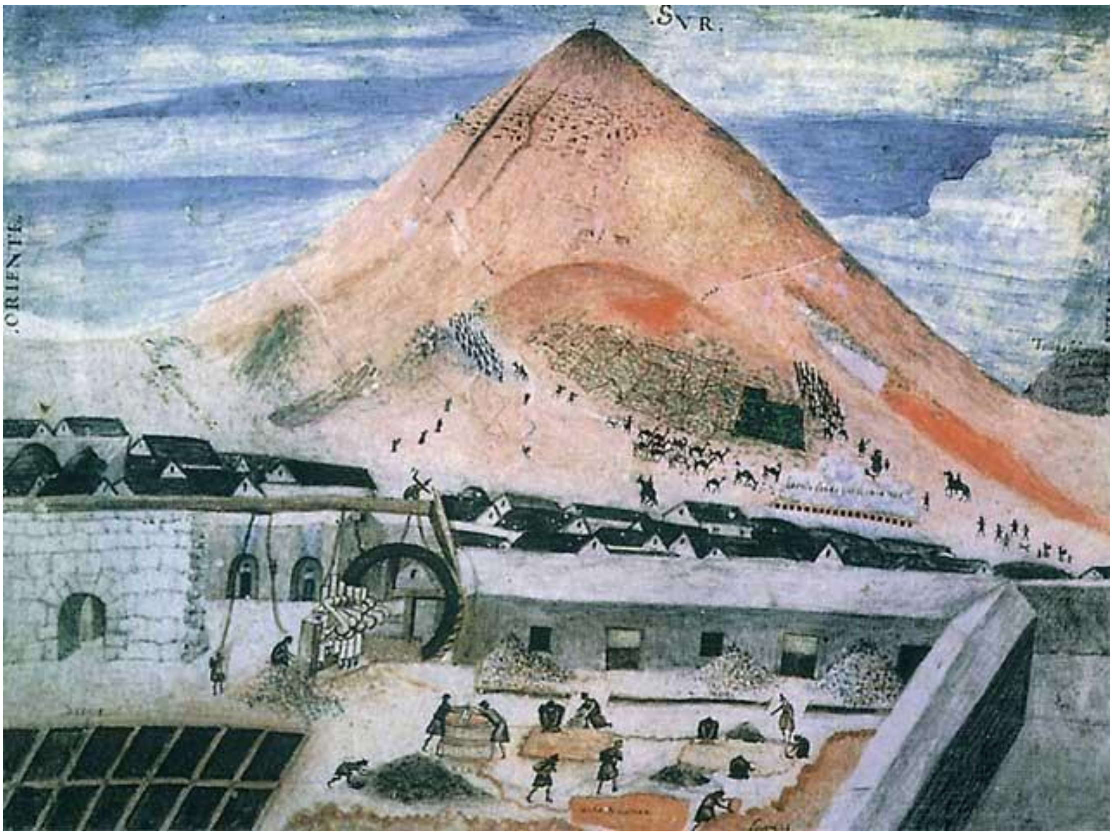


Figure 2.5 - Silver production at the Cerro Rico, Potosí, utilising the Patio process (unknown artist, 1584)

The rate at which the process was adopted in Spanish America was rapid, which can be gauged by the amount of mercury being imported from the Almaden mercury mine in Spain to be used in the process at the time. During the period 1550-1556, 40,370kg of mercury was imported, increasing to 136,080kg during 1561-1565 (Vilar, 1976). When the Huancavelica mercury mine in Peru began large-scale operations in 1563, the abundance of mercury available for silver extraction in Spanish America meant that minimal effort was put into recovering used mercury for further use. As a result, it is estimated that up to 200,000 tons of mercury evaporated into the atmosphere or washed down rivers in Spanish America during the use of the Patio process from 1556 to the 1880s, causing long term environmental impacts (Pirrone *et al.*, 1998).

The process, as briefly discussed by Lorenzo (Probert, 1997), consists of crushing the ore in brine (salt water) to make a fine paste, and mixing it with mercury. Copper sulphate is added as a later refinement to the process. The resulting paste was then spread out in a shaded area (generally on a patio) to about 30-60cm thick, and further mixed by mules, horses or occasionally people walking through it over a period of several weeks. At this point, the silver would have formed an amalgam with the mercury and could be recovered from the rest of the ore (Dennis, 1963). The silver was then extracted from the amalgam by heating and evaporating the mercury (Vilar, 1976). The amount of mercury lost during the whole process was between one and two times the mass of the silver recovered (Egleston, 1883).

The Patio process can be described using the following equations. Silver sulphides are first converted to silver chloride, before the mercury reduces the silver chlorides to elemental silver, which is then amalgamated by the excess mercury. The elemental sulphur produced will also combine with the mercury to create cinnabar (Hg_2S) (Johnson and Whittle, 1999).

$$Ag_2S(s) + 2Cu^{2+}(aq) + 8Cl^{-}(aq) \rightarrow 2AgCl(s) + 2[CuCl_3]^{2-}(aq) + S(s)$$

$$(n + 2)Hg(l) + 2AgCl(s) \rightarrow Ag_2Hg_n(l) + Hg_2Cl_2(s)$$

The process is now understood to be equivalent to hydrometallurgical chloride leaching, in which metal sulphide ores, which have been reacted with chloride ions in brine (NaCl), are oxidised by air in the presence of coppers salts acting as a catalyst. The oxidation process is continuously regenerated by the constant agitation of animals and humans walking through the mix and breaking it up to expose new surfaces to the air (Johnson and Whittle, 1999).

The Patio process was the principle method of silver extraction until the adoption in the 1880s and 1890s of the MacArthur-Forrest process for extracting gold and silver from ores using cyanide extraction (Scheidel, 1894).

2.1.6 Conclusion

In this section, it has been proposed that the Patio process for extracting silver from ores using mercury amalgamation was a necessary innovation when Old World demand for silver met abundant New World silver ore, and indeed was an essential requirement for the unprecedented large scale, centralised production.

Silver refining processes developed in Europe were satisfactory for European based production and supply of silver. The Saiger process, combined with cupellation, provided an adequate production of silver from the silver ore produced in Europe. However, this process required a significant use of timber for the production of charcoal, and while this was acceptable in wood-rich Europe, there were problems when applying this technology to wood-poor South American environment, especially after the high-grade ores were exhausted.

European exploitation of native labour for colonial mining in Africa and the Caribbean had been successful prior to the European discovery of the Americas, as an ore deposit as rich as those discovered there had never been encountered before and so the long-term effects of a forced labour system had not been discovered.

When Europeans arrived in Spanish America their demand for high metal yields from abundant ores over a relatively long period of time necessarily required a new silver extraction technique to be developed. Initially, high metal yields were achieved using privately run Dragon furnaces and high quality silver ore. However, this was not sustainable due to a number of factors, including the labour required to mine ever deeper, poorer quality ores, the increasing cost of production in terms of payment for labour, infrastructure and taxes, and fuel consumption and efficiency in terms of extracting and refining silver from ore. To enable the continued exploitation of silver mines in the long-term, an innovation in silver extraction and refining was necessary.

The Patio process was introduced in 1556 initially using mercury imported from Spain. Over time, and using mercury from the Peruvian mine of Huancavelica, it was possible to process much lower quality silver ores than previously, both efficiently and economically. The introduction of the Patio process was a necessary result of the unprecedented Old World desire for silver and the New World’s decline in profitable silver extraction and refining.

2.2 World silver movement from 1450

During the 16th century, precious metals in Europe were almost exclusively sourced from the Americas (Attman, 1986). The Spanish Crown held a monopoly on much of this American treasure which, upon arrival in Spanish ports, was quickly dispersed throughout Europe and beyond, through trade, warfare and the payment of royal debts (Hamilton, 1934).

Quantifiable estimates of silver produced in the Americas and imported to Spain have been made by a number of scholars, and are subject to variation based on the sources the figures are estimated from. Estimates are derived from figures from the Seville House of

Trade, the registration of mining royalties in the Americas, tax and mintage records, mercury consumption in the Americas (as mercury was used to refine silver), French consulate reports, and contemporary newspaper reports.

2.2.1 Spanish colonisation of the Americas

In competition with the Portuguese for control of international trade and trade routes, the Spanish Crown financed a large part of Christopher Columbus' expedition west, searching for a sea route to India. Columbus himself seems to have been motivated by a desire for gold, slaves and conversions to Christianity, mentioning these things repeatedly in his diary and letters (Vilar, 1969).

The Spanish Crown did not engage in any mining activities in the Americas, with the exception of mercury mining at Huancavelica in Peru. In this way the Spanish Crown gained a monopoly on mercury, which was necessary for silver extraction and refining (Hamilton, 1934). By royal decree (*Recopilacion,* 1681), mining of precious metals was run privately by individuals who had staked claims. Interestingly, the royal decrees dictated that natives had as much of a right to stake a claim as Spanish colonists, however in practice this was rare.

Native American labour was used in silver mines between 1545 and 1570. Labourers would be sold the silver ore they had extracted in a day's work by the mine owner. They would then be responsible for the refining of the metal, and would sell the metal back to the mine owner at a profit (Vilar, 1969). After 1570, a forced Native American labour system was introduced. Administrators would allocate a certain number of natives to a mine, who would mine all the ore they could in a day, and be allowed to keep whatever they could carry. They were no longer responsible for refining the ore. Further labourers were hired at a rate of four *reales* per day. Those who were required for forced labour were soon ruined financially, having uprooted their families from their community and abandoned their land.

Prospectors in Spanish America were bound by oath to present their bullion for assay at a royal assay office (*Recopilacion*, 1681), where it was assayed, cast, marked and subjected to the royal quint, a Crown tax of 20% of all precious metals mined in Spanish America.

Assaying involved checking the bullion for fineness, and for fraudulent mixing of base metals with precious metals. The punishment from 1535 for mixing base metals with gold was death, and this legislation was extended in 1646 to include mixing base metals with silver (*Recopilacion*, 1681). Precious metals were then cast into bars which had to be a manageable and easily quantifiable size and shape. From 1635, legislation dictated that the maximum size allowed for a bar of silver was 120 marks (approximately 28kg) (*Recopilacion*, 1681).

The royal quint was taken at this point, 20% of all silver and gold mined in Spanish America was taxed for the use of the Spanish Crown. Un-quinted bullion was illegal both in the Americas and on board outward-bound treasure ships. Coining un-quinted bullion was punishable by death (*Recopilacion*, 1681).

Each piece of gold and silver that went through a royal assay office was marked with a unique identifying number, its weight, fineness, date of assay, indication that the royal quint had been paid and the monogram of the owner (de Ulloa, 1792) (Figure 2.6).

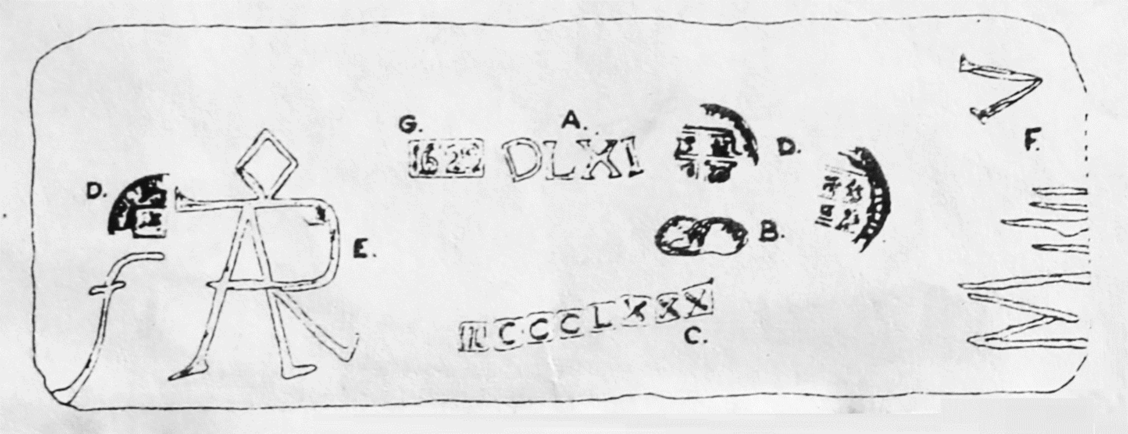


Figure 2.6 – The markings required for bullion cast in Spanish America. A) serial number B) assayer's "bite" to test the purity C) "Ley" or fineness (maximum fineness was 2400) D) "Quinto" indicating that the royal quint has been paid E) the monogram of the owner or shipper F) other marks recording transactions of the bar by various handlers G) the year of assay. (Mel Fisher's Treasures Certificate of Authenticity)

Of the silver produced in Spanish America between 1550 and 1800, on average 62% was shipped to Europe, of which 20% was shipped around Africa to Asia. Of the remaining Spanish American silver; 16% went directly to Asia from Acapulco, and 22% remained in the Americas (Walton, 2002) (Figure 2.7).

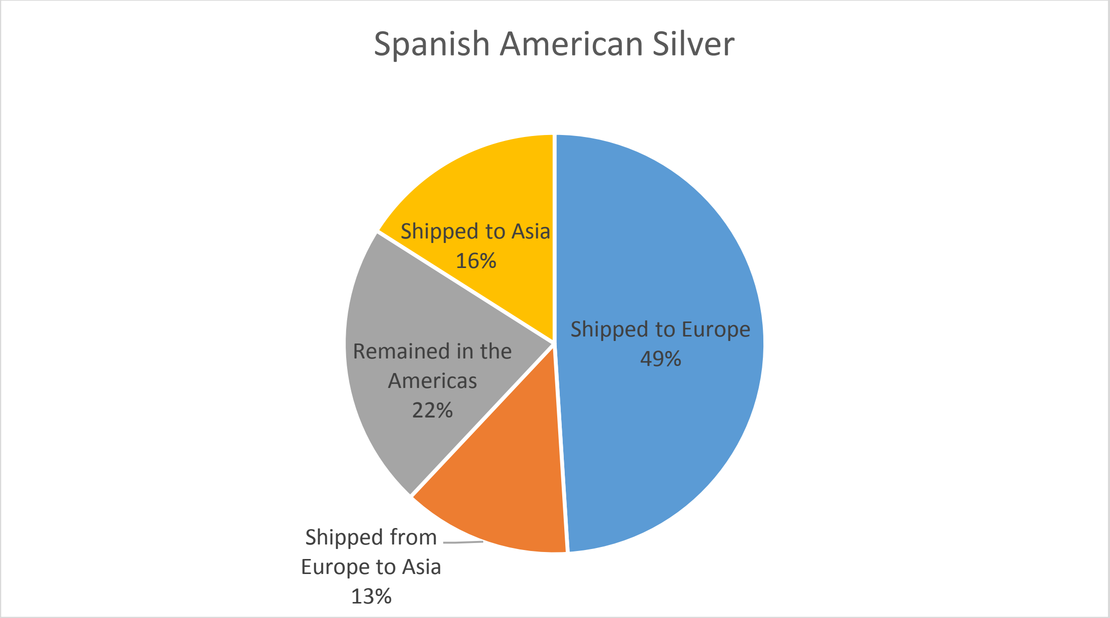


Figure 2.7 – Disbursal of Spanish American silver

2.2.2 Silver movement from the Americas east

It is estimated that between a third (Chaunu, 1966) and half (Wakeman, 1985) of all silver mined in the Americas would eventually flow to the Far East. It has estimated that between 16% and 20% of American silver was shipped directly across the Pacific to Manila rather than being traded via Europe (Wakeman, 1985).

2.2.3 Silver retained in the Americas

Initially, all silver mined for the Spanish in the Americas was intended for shipment to Spain in the form of assayed ingots or ‘cobs’ (assayed silver in the shape of a coin). The majority of this silver was melted down and recoined upon arrival in Spain while some cobs did go directly into domestic circulation.

Prior to European colonisation, Native Americans predominantly used a barter system for trade, or exchanged labour for goods. Immediately after European colonisation, domestic trade was conducted using account books of credits and debits (Attman, 1986). Attempts were also made by colonists to assign a nominal value to rare European items, in order to use them in place of money. This was attempted with iron nails, metal items such as cutlery, and later textiles. However with fluctuating access to these items with the arrival of different shipments from Europe, this system was a failure (Attman, 1986). The colonists in the Americas soon identified a need for a domestic currency, and so mints were established at Mexico in 1535, Lima in 1565, and Potosí in 1572, in order to mint coins to be used domestically, and also shipped to Spain.

Silver which was retained in the Americas for domestic use was traded amongst the native workforce, spent on local produce, invested into public works and donated to churches. Silver was also retained to continue the Spanish colonisation of the Americas (Vilar, 1976), and put towards establishing war treasuries, in particular to quash native rebellion (Attman, 1986, Hamilton, 1934).

In any case, considering the high volume of production of silver in the Americas the amount retained there was low. It has been posited that this was due to the simple fact the silver was worth more elsewhere which encouraged the drain of silver away from the Americas (Attman, 1986).

2.2.4 Silver movement from the Americas to Spain

The majority of silver mined in Spanish America was transported overland to the ports of Vera Cruz in the Gulf of Mexico, and Portobelo on the northern part of the Panama isthmus, and then shipped to Spain via Havana. Peruvian precious metals were shipped from Callao to Panama before being shipped onward to Spain. All Spanish treasure ships from the Americas were required to sail to the port of Seville, and from 1679, to the port of Cadiz (Hamilton, 1934; Attman, 1986). The penalty for the captain of a treasure ship which did not return to Seville was death, as stated in a pragmatic of 1529 (Colmeiro, 1863).

From 1565, fleets of ships carrying American gold and silver to Spain were accompanied by Spanish war ships to protect against pirates and foreign powers (*Recopilacion*, 1681). This arrangement was evidently effective, as it was infrequent that significant amounts of precious metals were seized by foreign ships. In 1628, the United Netherlands took an entire returning fleet of Spanish ships, and in 1656 the English took most of another Spanish fleet (Hamilton, 1934). It is worth noting that both of these attacks took place during the reign of Philip IV of Spain under whom the armaments on Spanish war ships had markedly declined (Hamilton, 1934). Arguably the catalyst for the Spanish Armada was an act of piracy by Francis Drake, who in 1577 captured two Spanish treasure ships off the coast of Lima and returning to England with 25,000 pesos and 36kg of gold, 13 chests of *reales* and 26 tons of silver, for which he was knighted (Vilar, 1969).

An estimate of the silver (in *reales*), arriving in Spain from the Americas is given in Figure 2.8. (Eight *reales*, also known as a *peso de a ocho, peso duro, peso fuerte, piaster, duro* or piece of eight, weighed about 25.98g and contained between 24.25g and 25.56g of silver, depending on the year of minting). These estimates are taken from various scholars, who used different sources to come to their conclusions. Estimates are derived from figures from the Seville House of Trade (Hamilton, 1934), the registration of mining royalties in the Americas (Soetbeer, 1879), tax and mintage records (Te Paske, 1983), mercury consumption in the Americas (as mercury was used to refine silver) (Brading & Cross, 1972), French consulate reports (Everaert, 1973) and contemporary newspaper reports (Morineau, 1968; Morineau, 1985). Morineau (1985) found fault with the largely accepted figures put forward by Hamilton (1965) based on Hamilton's reliance on the records at the *Casa de Contratacion* in Seville as the only source for his data. Morineau goes so far as to suggest a conspiracy as the reason that no other scholars had yet acknowledged the perceived flaws in Hamilton's work. Morineau used newspaper accounts from the Low Countries as his source of data on the influx of American treasure, which would indicate the imports of treasure increased in the 17th century, rather than decreased. Attman (1986) argues that the figures provided by Hamilton have underestimated silver imports into Spain as Hamilton has failed to consider that there are no reliable sources for the amount of silver imported privately, and that from 1640 a growing number of receipts of treasure were held at Cadiz, not Seville, where Hamilton conducted his research. Attman considers Morineau's estimates to be high, and considers Everaert's to be the most accurate.

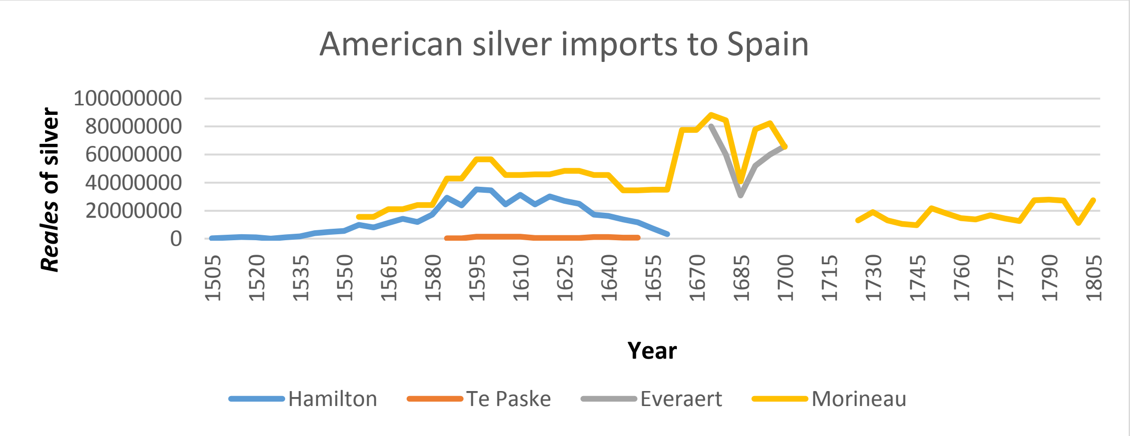


Figure 2.8 – Estimates of American silver imports into Spain in *reales*, from 1500 to 1805. (Blue – Hamilton, 1965, orange – Te Paske, 1983, grey – Everaert, 1973, yellow – Morineau, 1985)

By order of the Spanish Council of the Treasury, all gold and silver treasure arriving in Spain from Spanish America whether owned privately or by the Crown, was to pass through the House of Trade (*Casa de Contratacion*) in Seville upon its arrival in Spain. The House of Trade was a government bureau that had been established in 1503 particularly for the purpose of managing imports of American treasure after the discovery of the sea route to the Americas (Attman, 1986), and to oversee the enforcement of relevant decrees, manage the logistics of the treasure fleets, control travel and the postal service to and from the Americas, and develop and promote navigation and geography (Hamilton, 1934). The House of Trade was administered by the Spanish Council for the Indies, and was controlled by a factor, a treasurer and a comptroller (Merriman, 1925) and after 1579, also a president (Haring, 1918).

Based on the records of the House of Trade, initially the majority of silver imported into Spain was privately owned; between 1503 and 1660, 74% of treasure imported to Spain was privately owned (Hamilton, 1934). Public treasure from the Americas consisted of the Royal quint, fees charged for the smelting, assaying and marking of private treasure, and also tributes from American tribes, sales of papal indulgences, fines, and profits on goods sold in the Americas (Hamilton, 1934). Between 1680 and 1699, that percentage had dropped to 16% (Hamilton, 1934). Rarely, the Spanish Crown would seize privately owned treasure when under pressure from debtors, in the form of forced loans in exchange for a bond to the value of the seized treasure (Vilar, 1969).

On arrival at the House of Trade, precious metals were weighed by a *balanzario* (official weigher) and stored in chests (de Veitia Linaje, 1672). The treasure chests had triple locks, as did the doors to the treasure chambers and each of the three officials of the House of Trade carried a key. Windows of treasure chambers were protected with double iron bars. Occasionally night-guards would be employed to further protect the treasure (*Patronato*).

All bullion was then required by Royal order to be coined within six months of arrival; a certificate from the mint to prove that the bullion had been coined was to be presented to the House of Trade (Hamilton, 1934). However the Spanish Crown was known to pay their creditors with bullion at times (Hamilton, 1934). The right to coin Crown bullion was bought at auction by middle-men known as silver merchants, who were then responsible for delivering the bullion to a mint to be coined (*Contratacion*, 1531). Silver merchants were also responsible for facilitating the coining of the majority of private bullion, although this was not a legal requirement (Carranza 1629). Concerned with lost profits, the Council of the Indies repeatedly argued that the House of Trade could coin Crown bullion without silver merchants. The House of Trade attempted to coin Crown bullion without the assistance of silver merchants in 1621, the results were unsuccessful, and the House of Trade never attempted this again (de Veitia Linaje, 1672).

From 1471, with a pragmatic issued by Henry IV, Crown mints were heavily regulated in Spain (*Cortes*, 1861). Under penalty of death, mint employees were not to have unauthorised bullion at their workspace, must return all equipment to a guard at the end of the day, and not coin before sunrise or after sunset (*Cortes*, 1861). However these regulations were not enforced, and coining of bullion was known to take place illegally outside of Crown mints (*Cortes*, 1861).

Smuggling of precious metals from the Americas into Spain also occurred. Several initiatives were put in place to limit smuggling and to encourage others to turn in would-be smugglers. In 1634 the Spanish penalty for smuggling was confiscation, exile from Spanish America, and a ban on any trade between Spain and the Americas, while men of low status would instead be sentenced to ten years in the galleys (de Veitia Linage, 1672). Anyone who turned in a smuggler would receive between one sixth and one third of the value of the smuggled goods, as well as an additional reward decided by a judge (*Recopilacion*, 1681). While at sea Spanish treasure ships were not permitted to tie on to any other vessel, or to send a boat to any vessels in distress without the presence of someone who was deemed trustworthy by the captain general (*Recopilacion*, 1681). When approaching land, the penalty for sailing a boat from the ship to land was two hundred lashes and ten years in the galleys (*Recopilacion*, 1681). Firing salutes or sending out messenger ships at the arrival of a treasure ship was forbidden from 1614, to avoid unnecessarily notifying other ships and boats in port of their arrival (*Recopilacion*, 1681). Upon reaching port, the Captain General of a treasure ship was to notify the Spanish Council of the Indies and the House of Trade of arrival, and a judge-official of the House of Trade, with a sheriff, an attorney, and guards, would inspect the ship within a day of receiving notice. In that time, no one was permitted to leave the ship. While the inspection was taking place, foreign vessels in port were to leave the vicinity of the treasure ship. Every individual on board would declare under oath whether they knew of any smuggling on board (*Recopilacion*, 1681).

However, these extensive measures were evidently not as effective as the Spanish Crown had hoped, since amnesties were declared in years when it was suspected that significant amounts of smuggled gold and silver had reached Spain. During an amnesty pardons were granted to those who admitted to smuggling and they had to pay the *averia*, a convoy tax specific to goods being carried to and from the Americas (*Contratacion*, 1594).

After Cadiz took over as the main port for Spanish treasure ships, treasure was registered at the House of Trade at Seville less and less (Attman, 1986), which has had some effect on the ability of historians to accurately quantify silver and gold imports into Spain after the 1640s, particularly in the seminal work of Hamilton (1965) (Morineau, 1968; Everaert, 1973). The House of Trade was eventually moved to Cadiz in 1717 by the Bourbon regime, and even after 1764, when other Spanish ports were opened to trade from the Americas, Cadiz retained the largest share of that trade until the 19th century (Girard, 1932; Morineau, 1985).

2.2.5 Silver movement from Spain to disburse through Europe

Spanish silver during the 17th to 19th centuries was a trusted currency, considered to be of generally good weight and fineness by the rest of Europe and other parts of the world. Spanish *reales* were trusted trade coins in their original form either as denominations of one, two, four and most commonly eight *reales*, or as the counter-stamped or reminted currency of other countries. Other European nations, including the Portuguese, who had their own imports of precious metals coming from Brazil and West Africa, often found it preferable to export and trade with silver in the form of *real* coins, and only supplemented these with different silver currency if *reales* were not plentiful enough (Attman, 1981).

Despite concerted efforts by the Spanish to retain as much Spanish American gold and silver as possible in Spain much of the Spanish American treasure was lost to the rest of Europe. The reasons for this loss of currency are due to a combination of paying off royal debt, funding warfare, and trade. It became increasingly clear to the Spanish that laws against exporting metals could not be maintained when an increasing trade deficit existed with other nations. As such, it was necessary to pay for foreign goods with precious metals (Vilar, 1969).

It should be noted that American precious metals were not the only ones flowing into Western Europe. During the period 1550-1800, American precious metals were supplemented by a small but steady supply of silver and gold produced in Africa and

Europe, at an average of 2.16 million *reales* per year (Morineau, 1985). As American precious metal production increased however, this amount quickly became relatively insignificant. In the 1780s for example, precious metals from Africa and Europe made up only 10% of the precious metals in Western Europe (Morineau, 1985).

Of the 11 million publicly owned *reales* that arrived in Spain from Spanish America in 1590, 2 million went to France for imports, 6 million to Italy for imports and military expenses (of which 2.5 went up the Spanish Road, a military supply and trade route to the Netherlands and Belgium), and 1 million to the Ottoman Empire. In 1665, the debts of the Spanish Crown were 30 million *reales* short-term and 300 million long-term. (Walton, 2002).

During the 17th century, Spain imported approximately 10 million *reales* per year. These figures do not include precious metals from the "Royal quint", which the Spanish Crown used to pay off royal debts, particularly to Italian, German and Portuguese financiers (Attman, 1986). This figure takes into account a decline of approximately 8-9 million *reales* per year, from 1600-1650, followed by an increase to approximately 11-12 million *reales* for the rest of the century (Attman, 1986). During the latter part of the 17th century, Spain exported a total of approximately 6-7 million *reales* per year to the United Netherlands, directly and indirectly. Spain also exported approximately 2-4 million *reales* per year to France.

In the 18th century, imports of American precious metals into Spain rose steadily from 10 to 20 million *reales* over the course of the century due to increasing productivity in the Americas, particularly in Mexico. Spanish exports of precious metals to the United Netherlands during the 18th century totalled at least 6-8 million *reales* per year, to France approximately 4-6 million *reales* per year, and to England approximately 1-2 million *reales* per year (Attman, 1986).

The drain of precious metals from Spain is apparent in the following example: on 23rd May 1590, the Spanish Cortes complained that by the middle of the year, despite the amount of treasure being brought to Spain from Spanish America, there was no money except *vellon* (copper currency of small denominations) to be found anywhere in Spain and little *vellon* at that (Hamilton, 1934, p.62). The drain of precious metals was to continue unabated. In 1617 the Spanish Cortes noted that, upon arriving in Spain

American silver "… immediately goes to foreign kingdoms, leaving this one in extreme poverty" (*Actas de las Cortes de Castilla XXXVII,* 1617).

The Netherlands in particular were known to use foreign coins, especially Spanish *reales*, as local currency. In 1626 the Netherlands Parliament published a coin tariff catalogue, detailing the large range of foreign coins circulating in the Netherlands, and how much they were worth in Netherlands guilders. The Spanish seemed to have little control over silver imported from the Americas and further, were aware and concerned that they were unable to retain sufficient quantities of precious metals for domestic use. In the same report quoted above from 1617, the Spanish Cortes asserted that Castile "…serves as a bridge over which the products of our mines pass to foreign hands at time even to our worst enemies." (*Actas de las Cortes de Castilla XXXVII*).

While trade with the Spanish American colonies was mostly legally limited to Spain (Walton, 2002), in some cases American silver circumvented the Spanish House of Trade altogether, mostly through smuggling. Non-Spanish European merchants would use Spanish agents, or '*cargadores'* to enable them to participate in Spanish imports and exports while avoiding Spanish control (Gonzalez and Guadalupe, 1997). At other times, foreigners were allowed to obtain licenses to export Spanish currency legally (Vilar, 1969).

2.2.6 Silver movement from Europe to the Far East

The majority of precious metals exported from Spain to other European countries were in turn re-exported to the Far East. The flow east saw a steady increase over the course of the 16th to 19th centuries (Figure 2.9)

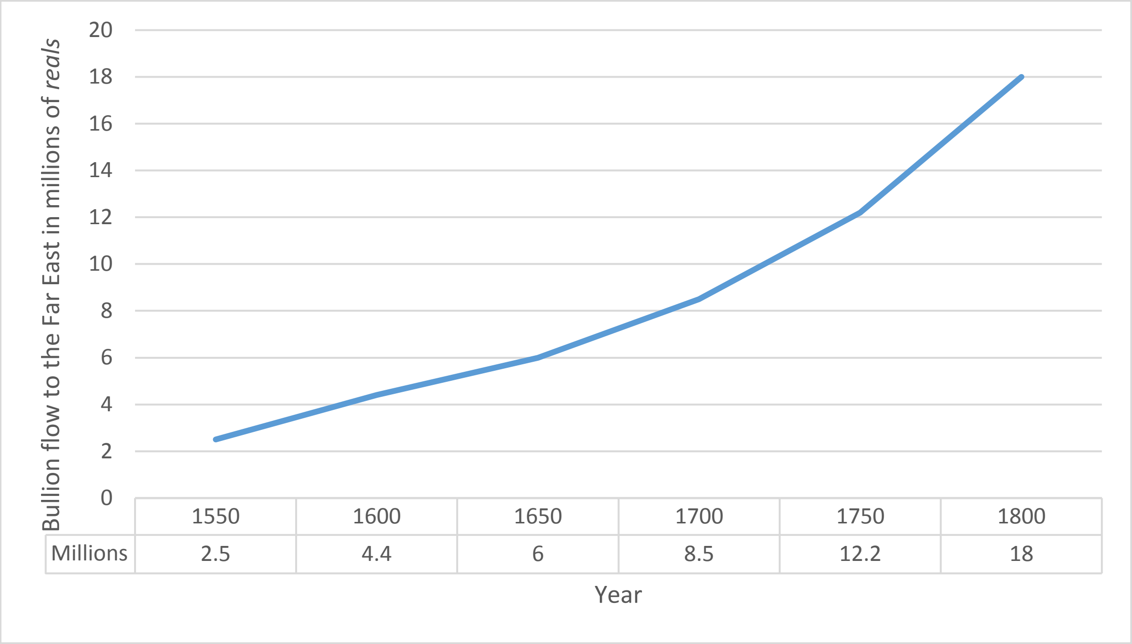


Figure 2.9 – Total bullion flow from Europe to the Far East in millions of *reales* (Morineau, 1985)

In the early 17th century, the great European maritime empires were formed. The *Verenigde Oostindische Compagnie* (VOC) (United Dutch East India Company) was formed to increase the efficiency of existing maritime trade between the Dutch and the Far East in 1602 (Attman, 1981). Prior to the VOC, small fleets of Dutch ships would sail via the Cape of Good Hope to Asia and then sail around Asia accumulating enough Asian goods in exchange for precious metals to facilitate trade and bartering within Asia. Further, the VOC ships were able to return to the Netherlands with enough Asian goods to make a profit in the market there (Parthesius, 2010). The VOC was established with the goal of attaining a monopoly on particular Asian goods, which required a Dutch stronghold in Asia where goods could be acquired and stored (Parthesius, 2010).

European nations did not succeed in exchanging European goods for Eastern goods while trading with the Far East. Rather, demand dictated that European nations exchanged silver and gold for Eastern goods, in particular spices, tea coffee, textiles etc. (Attman, 1981). At the time, it was also known that bimetallic ratios between Europe and the East differed so significantly that a large profit could be made by exchanging silver for gold in the East. From the mid-16th to mid-17th centuries in China the bimetallic ratio was 6:1, that is, 6oz of silver could buy 1oz of gold. At the same time, the bimetallic ratio in Europe was 12:1, which meant that gold bought with silver in China could be sold for twice the amount of silver in Europe (Flynn, 2012). As such, it was generally accepted that silver should be exported East in favour of gold.

An attempt by the United Dutch East India Company (VOC) to interest the Indies in Dutch-made goods and to facilitate access to trade can be seen in the speculative silverware which was on board the *Batavia.* In 1627, Francisco Pelsaert, later the Commander of the *Batavia,* presented the governing body of the VOC, the *Heeren XVII* (Gentlemen Seventeen), with his *Remonstratie* (Report) suggesting new avenues of trade to explore in the Dutch East Indies. As Pelsaert saw it, meeting the Eastern demand for precious metals in the form of already manufactured items would provide a compromise to try to correct the demand imbalance by sparking an interest in European manufactured goods. Manufactured items would also attract a higher price than the equivalent amount of silver in ingots or coins. In the *Remonstratie,* Pelsaert suggests manufacturing precious metals into objects already in use in the Dutch East Indies rather than trading them in coin or ingot form (Pelsaert, 1627). As Pelsaert details from the point of view of Dutch merchants in the Dutch East Indies

“Many of the great men express surprise that we do not have the gold and silver (coined and uncoined), which we import in large quantities, manufactured by us into articles which are here in common use. Provided the workmanship is good, half the silver might be paid for manufacture, which would give ample payment for Dutch work; or in any case manufactured goods would yield quite as much profit as *reales* or Holland dollars, and could meet the taste of the nobles everywhere without loss to us.” (Pelsaert, 1627 p.27).

The Gentlemen Seventeen immediately commissioned several silver items to be manufactured for speculative trade in the Dutch East Indies, to be shipped with Francisco Pelsaert on the *Batavia*.

Of the 2 million *reales* reaching the Dutch Republic in 1590, 75% went to the Baltic for naval stores, while 25% went to Asia (Walton, 2002). Compared to the value of VOC imports of Asian goods, they exported a large proportion of precious metals to pay for them, demonstrating the trade imbalance present (Figure 2.10) (Gaastra, 1976).

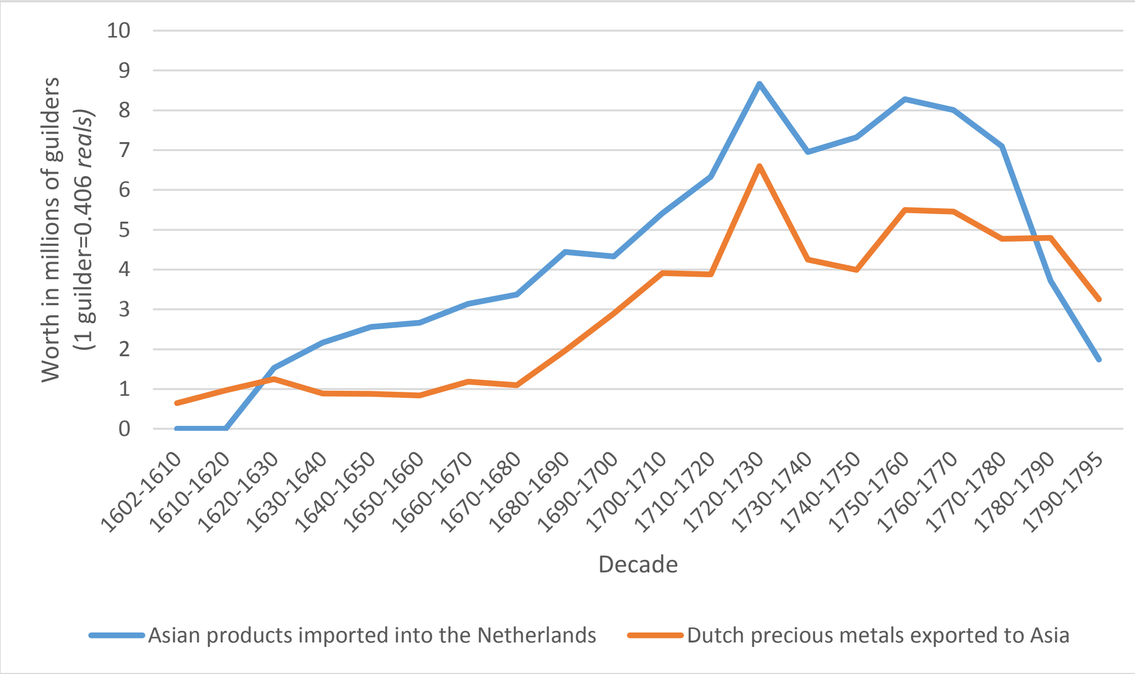


Figure 2.10 – VOC imports of Asian goods compared to exports of precious metals (Gaastra, 1976).

Conversely, there was also some movement of Asian precious metals within Asia facilitated by European trade. Between 1630 and 1680, the VOC supplemented their supply of precious metals for trade in Asia with silver and gold from the Japanese bullion market (Attman, 1981). Alternatively, European traders in Asia also occasionally had trade access to precious metals which had been shipped by the Spanish direct from the Americas to Manila in the Philippines (Attman, 1986).

2.2.7 Summary

The discovery of the sea route around the Cape of Good Hope and the colonisation of the Americas had an enormous impact on world economies. Unprecedented production of precious metals, particularly silver, in the Americas lead to an influx of wealth into Spain to be disbursed through Europe. At the same time, the world's first true corporations, the maritime empires of the Dutch and the English, (and also the Spanish and Portuguese, although this trade was government-run), were founded to facilitate trade with the Far East. A trade imbalance between European demand for Asian goods, and Asian demand for precious metals meant that much of the silver in Europe quickly drained east.

The significance of this information is that the coins which form the basis of the present study came to be wrecked off the coast of Western Australia carried on board trading ships from the United Netherlands, Portugal and the United States of America. An understanding of world silver movement at the time of these ships’ voyages assists in an understanding of the assemblages of silver coins found in association with these wrecks. Further analysis of the coins, with historical information in mind, can provide a more holistic understanding of the journey of these coins from their mine and mint of origin as well as a better, broader understanding of world silver trade and movement in the 17th to 19th centuries.

Further, the use of novel analytical techniques on legacy data such as the coins of this study, can be appraised and applied to other artefacts and assemblages.

2.3 Mints represented

Twenty-two mints are represented in this study, with the majority of coins originating from Spanish or Spanish American mints. Based on the movement of silver at the time, it can be concluded that the majority of silver used in European mints outside of Spain would have originated in the silver mines of the Americas.

The method of manufacture of coins at each mint is important to know in order to understand the microstructural traits exhibited by a coin, as well as to use those traits to identify unidentified coins. The understanding of the location of the mint in proximity to a silver mine, or where a mint procured its silver from if not from a nearby mine, is important in understanding a coin’s trace elemental composition. Further, having knowledge of events in a mint’s history, for example legal and illegal debasement of coinage, or counter stamping of coinage, is also important to developing an understanding of changing coinage composition through time, from a particular mint.

2.3.1 Mineralogy and compositional variability between silver sources

Fingerprinting of archaeological metals relies on the principle that the unique mineralising event that creates an ore will create an ore with a unique elemental composition. It then follows that metals refined from particular ores will retain a trace elemental composition unique to the ore of origin.

Silver is principally extracted from three types of sources:

1. Silver ores, in which the value of the silver present in the ore is higher than that of any other component in the ore;
2. Native alloys of gold and silver;
3. Lead or copper ores;

and any amount of native gold, or any amount of lead ore, almost certainly contains some silver (Phillips, 1867).

Figure 2.11 – Location of world silver sources c.1500-1800.

Silver is found most commonly occurring with;

- lead (argentiferous galena (PbS, freislebenite ($AgPbSbS_3$)),
- copper (tennantite ($Cu_6[Cu_4(Fe,Zn)_2]As_4S_{13}$)),
- zinc (blende (ZnS)), and
- iron (spathic iron ($FeCO_3$), haematite (FeO_3), pyrite (FeS_2), sternbergite ($AgFe_2S_3$)).

Silver also occurs in its native state commonly in combination with;

- gold (electrum (Au,Ag)),
- copper (argentiferous copper-glance (Ag_2S,Cu_2S), stromeyerite (AgCuS))
- and platinum, as well as
- sulphur (silver-glance (Ag_2S)),

- chlorine (argentic chloride ($AgCl$)),
- bromine (bromargyrite ($AgBr$), bromian chlorargyrite ($Ag(Cl,Br)$)),
- iodine (iodargyrite (AgI)) and
- selenium (naumannite (Ag_2Se), eucairite ($CuAgSe$)),

and also with other metals such as;

- arsenic (xanthoconite (Ag_3AsS_3), proustite ($3Ag_2S,As_2S_3$), polybasite ($[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$)),
- antimony (antimonial silver (Ag,Sb), miargyrite ($AgSbS_2$), stephanite (Ag_5SbS_4), dyscrasite (Ag_3Sb), pyrargyrite ($3Ag_2S,Sb_2S_3$), Freibergite ($4Ag_2S,Sb_2S_3$), brittle silver-glance ($5Ag_2S,Sb_2S_3$)),
- magnesium (selbite ($Ag_2S,CaMg(CO_3)_2,Ag$)),
- tellurium (hessite (Ag_2Te)) and
- mercury (amalgam (Ag_xHg))

(Greenwood, 1875; Phillips, 1867; mindat.org, 2017).

The mines where these minerals are found are detailed in Table 2.1. The locations of these mines are mapped in Figure 2.11.

Table 2.1 – Silver containing minerals found at Old and New World silver mines (Greenwood, 1875; Phillips, 1867; mindat.org; Wilson and Petrov, 1999).

Country	Mine	Silver-bearing Minerals	Formula
Mexico	Guanajuato (since 1548)	Native silver	Ag,Fe
		Silver-glance	Ag_2S
		Brittle silver glance	$5Ag_2S,Sb_2S_3$
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Proustite	$3Ag_2S,As_2S_3$
		Chlorargyrite	$AgCl$
		Bromargyrite	$AgBr$
		Bromian chlorargyrite	$Ag(Cl,Br)$
		Iodargyrite	AgI
		Acanthite	Ag_2S
		Aguilarite	Ag_4SeS
		Andorite	$AgPbSb_3S_6$
		Argyrodite	Ag_8GeS_6
		Fischesserite	Ag_3AuSe_2
		Jalpaite	Ag_3CuS_2
		Naumannite	Ag_2Se
		Pearceite	$[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Stephanite	Ag_5SbS_4
Peru	Cerro de Pasco (since 1630)	Native silver	Ag,Fe and Ag,Cu
		Silver-glance	Ag_2S
		Brittle silver glance	$5Ag_2S,Sb_2S_3$
		Antimonial silver	Ag,Sb
		Proustite	$3Ag_2S,As_2S_3$
		Chlorargyrite	$AgCl$
Guatemala	Alotepec mountains (since c.1750s)	Acanthite	Ag_2S
		Electrum	Au,Ag
		Jalpaite	Ag_3CuS_2
		Stromeyerite	$AgCuS$

Bolivia	Cerro Rico de Potosi (since 1545)	Native silver	Ag
		Acanthite	Ag_2S
		Andorite	$PbAgSb_3S_6$
		Chlorargyrite	$AgCl$
		Matildite	$AgBiS_2$
		Miargyrite	$AgSbS_2$
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Tetrahedrite	$[(Ag,Cu,Fe,Zn)_{12}Sb_4S_{13}]$
Norway	Kongsberg (1624-1960)	Native silver	Ag,Cu
		Silver-glance	Ag_2S
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Chlorargyrite	$AgCl$
		Acanthite	Ag_2S
		Argentopentlandite	$Ag(Fe,Ni)_8S_8$
		Argentopyrite	$AgFe_2S_3$
		Chlorargyrite	$AgCl$
		Dyscrasite	Ag_3Sb
		Eucairite	$AgCuSe$
		Jalpaite	Ag_3CuS_2
		Miargyrite	$AgSbS_2$
		Naumannite	Ag_2Se
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Stephanite	Ag_5SbS_4
		Sternbergite	$AgFe_2S_3$
Germany	Harz mountains (10th Century – 1930)	Native silver	Ag,Cu
		Silver-glance	Ag_2S
		Brittle silver-glance	$5Ag_2S,Sb_2S_3$
		Antimonial silver	Ag,Sb
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Chlorargyrite	$AgCl$
		Naumannite	Ag_2Se
		Acanthite	Ag_2S
		Argentopyrite	$AgFe_2S_3$
		Bohdanowiczite	$AgBiSe_2$
		Dyscrasite	Ag_3Sb
		Eucairite	$AgCuSe$
		Miargyrite	$AgSbS_2$
		Naumannite	Ag_2Se
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Proustite	$3Ag_2S,As_2S_3$
		Pyrostilpnite	Ag_3SbS_3
		Samsonite	$Ag_4MnSb_2S_6$
		Stephanite	Ag_5SbS_4
		Sternbergite	$AgFe_2S_3$
		Xanthoconite	Ag_3AsS_3
	Erzgebirge (on present day border between Germany and the Czech Republic) (2500 BCE – 1970s)	Native silver	Ag,Cu
		Silver-glance	Ag_2S
		Miargyrite	$AgSbS_2$
		Stephanite	Ag_5SbS_4
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{13x}$
		Brittle silver-glance	$5Ag_2S,Sb_2S_3$
		Proustite	$3Ag_2S,As_2S_3$
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Freislebenite	$AgPbSbS_3$
		Chlorargyrite	$AgCl$
		Sternbergite	$AgFe_2S_3$
		Acanthite	Ag_2S
		Argentopentlandite	$Ag(Fe,Ni)_8S_8$
		Argentopyrite	$AgFe_2S_3$
		Diaphorite	$Ag_3Pb_2Sb_3S_8$

		Eucairite	$AgCuSe$
		Friesite	$Ag_2Fe_5S_8$
		Pearceite	$[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$
		Pyrostilpnite	Ag_3SbS_3
		Stephanite	Ag_5SbS_4
		Stromeyerite	$AgCuS$
		Xanthoconite	Ag_3AsS_3
	Baden-Württemberg (11th Century – 1794)	Silver-glance	Ag_2S
		Proustite	$3Ag_2S,As_2S_3$
		Antimonial silver	Ag,Sb
		Dyscrasite	Ag_3Sb
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Selbite	$Ag_2S,CaMg(CO_3)_2,Ag$
		Acanthite	Ag_2S
		Benjaminite	$Ag_3Bi_7S_{12}$
		Berryite	$Cu_3Ag_2Pb_3Bi_7S_{16}$
		Billingsleyite	Ag_7AsS_6
		Bohdanowiczite	$AgBiSe_2$
		Bromargyrite	$AgBr$
		Chlorargyrite	$AgCl$
		Cuprobismutite	$Cu_8AgBi_{13}S_{24}$
		Gustavite	$AgPbBi_3S_6$
		Iodargyrite	AgI
		Jalpaite	Ag_3CuS_2
		Matildite	$AgBiS_2$
		Naumannite	Ag_2Se
		Pavonite	$AgBi_3S_5$
		Pearceite	$[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$
		Proustite	$3Ag_2S,As_2S_3$
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Pyrostilpnite	Ag_3SbS_3
		Stromeyerite	$AgCuS$
Hungary	Schemnitz (in present day Slovakia) (3rd Century BCE – 1850s)	Silver-glance	Ag_2S
		Brittle silver-glance	$5Ag_2S,Sb_2S_3$
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Amalgam	Ag_xHg
		Acanthite	Ag_2S
		Arcubisite	Ag_6CuBiS_4
		Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$
		Matildite	$AgBiS_2$
		Miargyrite	$AgSbS_2$
		Ourayite	$Ag_3Pb_4Bi_5S_{13}$
		Pearceite	$[Ag_9CuS_4][(Ag,Cu)_6(As,Sb)_2S_7]$
		Proustite	$3Ag_2S,As_2S_3$
		Pyrostilpnite	Ag_3SbS_3
		Stephanite	Ag_5SbS_4
		Xanthoconite	Ag_3AsS_3
Russia	Ural mountains (since 1720s)	Native silver	Ag,Cu
		Acanthite	Ag_2S
		Chlorargyrite	$AgCl$
		Hessite	Ag_2Te
		Krennerite	Au_3AgTe_8
		Matildite	$AgBiS_2$
		Muthmannite	$AuAgTe_2$
		Naumannite	Ag_2Se
		Perroudite	$Hg_5Ag_4S_5(I,Br)_2Cl_2$
		Petrovskaite	$AuAg(S,Se)$
		Petzite	Ag_3AuTe_2
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Stromeyerite	$AgCuS$

		Stützite	Ag_7Te_4
		Sylvanite	$(Au,Ag)_2Te_4$
		Uytenbogaardtite	Ag_3AuS_2
		Volynskite	$AgBiTe_2$
	Siberia (since 1720s)	Silver-glance	Ag_2S
		Stromeyerite	$AgCuS$
		Hessite	Ag_2Te
		Acanthite	Ag_2S
		Diaphorite	$Ag_3Pb_2Sb_3S_8$
		Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$
		Hocartite	$Ag_2(Fe^{2+},Zn)SnS_4$
		Naumannite	Ag_2Se
		Petzite	Ag_3AuTe_2
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Sylvanite	$(Au,Ag)_2Te_4$
		Volynskite	$AgBiTe_2$
France	Allemont (17th Century)	Antimonial silver	Ag,Sb
		Proustite	$3Ag_2S,As_2S_3$
		Amalgam	Ag_xHg
		Acanthite	Ag_2S
		Argentojarosite	$AgFe^{3+}{}_3(SO_4)_2(OH)_6$
		Chlorargyrite	$AgCl$
		Dyscrasite	Ag_3Sb
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
	Huelgoat (Roman era – 19th Century)	Native silver	Ag
		Bromargyrite	$AgBr$
		Canfieldite	Ag_8SnS_6
		Chlorargyrite	$AgCl$
		Dyscrasite	Ag_3Sb
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Pyrargyrite	$3Ag_2S,Sb_2S_3$
England	Cornwall (1292 – 1880s)	Pyrargyrite	$3Ag_2S,Sb_2S_3$
		Polybasite	$[(Ag,Cu)_6(Sb,As)_2S_7][Ag_9CuS_4]$
		Chlorargyrite	$AgCl$
		Acanthite	Ag_2S
		Argentojarosite	$AgFe^{3+}{}_3(SO_4)_2(OH)_6$
		Boleite	$KPb_{26}Ag_9Cu_{24}(OH)_{48}Cl_{62}$
		Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$
		Pyrostilpnite	Ag_3SbS_3
		Stephanite	Ag_5SbS_4
Sweden	Sala (15th Century – 1950)	Native silver	Ag
		Eucairite	$CuAgSe$
		Amalgam	Ag_xHg
		Acanthite	Ag_2S
		Diaphorite	$Ag_3Pb_2Sb_3S_8$
		Dyscrasite	Ag_3Sb
		Freibergite	$Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$
		Freieslebenite	$AgPbSbS_3$
		Hessite	Ag_2Te
		Miargyrite	$AgSbS_2$
		Proustite	Ag_3AsS_3
		Pyrargyrite	Ag_3SbS_3

Mexican silver ore contains an average of 0.25% silver, while an ore of 0.5% silver is considered to be rich. In Europe, silver ore in the Harz Mountains contains 0.098% silver, and only 0.05% in Frieberg ores. The richest silver ores in Europe, at Joachimsthal in the Erzgebirge Mountains, contain between 2 and 3% silver. Even with such small percentages of silver in these ores, the high value of silver meant it was still profitable to extract the silver from the ore (Greenwood, 1875).

Silver extracted in Great Britain and Ireland is recovered exclusively from argentiferous lead ore as a product of lead mining. Cornish lead ores are the richest in silver (with the exception of lead ore on the Isle of Man), producing an average of 850g of silver per tonne (Phillips, 1867).

A relatively small amount of silver is extracted from the Norwegian mines of Kongsberg, discovered in 1623. Norwegian silver ore exists in gneiss and crystalline slate, in fahlbands that principally contain sulphides of iron, copper and zinc, and occasionally sulphides of lead, cobalt and silver (Phillips, 1867).

Silver produced in France is sourced from mines in the Alpine region, and Brittany. The Huelgoat mine in Brittany produces silver almost exclusively from argentiferous galena. Silver from the Allemont mine is extracted from copper pyrites and argentiferous fahlerz (Phillips, 1867).

The ore at the Swedish silver mine of Sala is highly argentiferous galena. The mine itself has been mined since antiquity, and silver production there had seen a steady decline into the 18th and 19th centuries. The Schemnitz district in Hungary (present day Slovakia) is in a formation of porphyry associated with syenite, granite and gneiss, located in a group of mountains composed of trachytes. It is estimated that silver has been worked at Schemnitz for the past thousand years. Silver is found mostly in sulphides of silver and argentiferous galena (Phillips, 1867).

Germany was a major producer of silver before the discovery of silver deposits in the Americas, and many mines remained profitable enough to continue being mined through the 18th and 19th centuries. Silver mined in Germany is found principally in the Erzgebirge and Harz Mountains, as well as in Baden-Württemberg. The Erzgebirge Mountains form part of the border between present-day Germany and the Czech Republic, and have been mined for silver since as early as the 10th Century. Veins of silver producing ores in the Erzgebirge Mountains are enclosed in gneissoid rocks, and contain iron pyrites, carbonates and oxides, arsenopyrites, blende, and galena. Silver mines of the Harz Mountains have been utilised since the 1520s, with silver being principally extracted from argentiferous galena. Silver from Baden-Württemberg and other smaller Alpine mines was extracted from copper pyrites and argentiferous fahlerz (Phillips, 1867).

In general, Mexican silver is extracted from syenite and porphyry. The silver-containing ores are generally compounds of silver sulphides, which have decomposed into native silver towards the surface. There are many silver mines in Mexico, of which two were especially significant for their continued and consistent silver output: Guanajuato, Zacatecas, and Real del Monte. Guanajuato ores consist of native silver, silver antimony sulphides, and small amounts of proustite, pyrargyrite, iron pyrites and galena. Zacatecas ores consist of native silver, and silver chlorides above water level, as well as silver sulphides, blende, galena and iron pyrites below water level (Phillips, 1867).

Guatemalan silver mostly originates from the Alotepec Mountain region. Silver is found in veins surrounded by porphyritic rocks, with lead and copper, and also as silver sulphides and chlorides. Silver being worked in Guatemala originates from argentiferous iron oxides, in very similar conditions to those found in Mexico (Phillips, 1867).

Production of silver from the Cerro Rico ('Rich Mountain') de Potosi in present-day Bolivia, quickly eclipsed the production from any previous silver mine, and remains the largest silver deposit in the world. The deposit consists of veins of cassiterite, wolframite, bismuthinite, and arsenopyrite surrounded by the minerals sphalerite, galena, lead sulphosalt, and native silver (Cunningham *et al.*, 1996).

Analysis on Roman coins has shown that there is an identifiable trace elemental composition between ore, slag, lead bullion and silver coins from the same mine (Schnieder, 1994: Rehren et al., 1999). In many cases coinage metals are recycled and recoined, in this 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).

Based on the different mineralogy of European and American silver mines, a cursory investigation into silver-bearing minerals may indicate those elements that could be considered characteristic of specific silver mines. For example, copper may be expected to be more prevalent in silver sourced from Mexico, Guatemala, Chile, Norway, and Germany, while tellurium would be expected to be retained in silver sourced from Chile and Russia. This geological information is used to inform the trace elemental analysis of silver coins presented in this study.

2.3.1 Development of minting technology

2.3.1.1 Casting

Coins are known to have been cast in China from around 350BCE (Hartill, 2005). Casting was employed to make coins, in which about a dozen cavities with the coin designs in relief were connected by channels in a two-part mould made of stone, bronze, clay or sand (Figure 2.12). Once cast, the coins would require manual touching up to clarify details in the coins' design (Cooper, 1988).

Figure 2.12 – Coin tree of brass, 1905 Guangxu zhongbao coins (© The Trustees of the British Museum, 2005)

Casting was also used in India to make coins, using a slightly different technique which facilitated casting coins in a stack rather than a tree around 100BCE (Cooper, 1988).

Due to the inevitable roughness of the finished coin this method was rarely employed in the Western world, and only for coins of low value and quality.

2.3.1.2 Hammering

From the invention of coinage in Lydia in the first millennium BCE until the adoption of advanced minting machinery during the 17th century, the vast majority of coinage, certainly in the Western world, has been created by hammering the desired metal flat, and then hammering between two dies to achieve the desired designs on the obverse and reverse of the coin (Cooper, 1988).

After the fall of the Western Roman Empire in 476CE, centralised standardisation of coinage was not maintained, and coinage became crude both in design and quality. In the

10th century European coinage became more standardised, and minting practices improved (Cooper, 1988).

The initial preparation of the coin blank, flan, or planchet varied somewhat from mint to mint, but in general, ingots were cast, and then hammered to approximately the desired thickness, before being annealed and hammered again to the precise thickness. Squares would be cut from the sheet of metal, and then cut again to make octagons of a specified weight, at this point metal would be wedged and hammered into the flan, or clipped from the edges to ensure the weight was correct. The flans would then be hammered into a circular shape and placed between a die which had been mounted in a bolster of wood, and another die, to be struck with a heavy hammer to impress the design onto the coin (Figure 2.13) (Cooper, 1988).

Figure 2.13 – Hans Burgkmair the Older and Leonhard Beck, *Maximilian at the Mint in Hall-in-Tirol*, 1510. On the left is a furnace for smelting the metal. In the centre, the metal is being hammered into a sheet (in reality this would have been a strip rather than a rectangle). In the front left, coin blanks are being cut. In the front right, the coins are being struck.

It is worth noting here the manufacture of 'cob' coins. With increasing demand for precious metal exports from the Americas to Spain creating 'cobs' was found to be a more efficient, if less sophisticated, method of manufacturing coinage. Rather than being hammered or rolled to a specified thickness and being cut into coin blanks, cobs were instead simply cut into chunks of a specified weight prior to being stamped with their final designs. This method created crude, thick and often disfigured coins which frequently did not have an entire legible design stamped onto them. Despite this, cobs served their purpose as easily transportable coinage between the Americas and Spain. However, cobs were also more prone to debasement and clipping given their irregular shapes (Sedwick, 1995).

A demand for larger coins of higher value meant that hammering was no longer an effective method of making coins. A heavier hammer with a dedicated operator was required, and the iron dies would not withstand the force of the hammer blows for long. As such, the rolling mill and screw press were widely adopted from the 16th century. Further, to prevent counterfeiting and clipping or filing of coinage, a perfectly circular coin was more difficult to counterfeit or clip, while a coin with official markings around the edge, even more so. With this in mind, minting technology continued to develop (Cooper, 1988).

2.3.1.3 Rolling mill

By 1550, the mint in Augsburg, Germany, was using a roller to prepare sheets of metal to a consistent thickness to be cut into flans, rather than hammering the metal flat (Figure 2.14). The process spread through France and England (Fantom, 2011).

Figure 2.14 – A 1764 rolling mill from the Augsburg mint in Germany (www.segoviamint.org)

At the same time, the Hall mint in Tirol, Germany, had developed a roller press, which was used exclusively for minting there by 1567. The roller press used two cylindrical dies, which rolled bullion between them and produced sheets of metal with the printed obverse and reverse of coins (Figure 2.15). The coins were then cut from the sheet (Fantom, 2011).

Figure 2.15 – A roller die from the Augsburg mint in Germany (www.segoviamint.org)

2.3.1.4 Screw press

A screw press was developed by Donato Bramante to create lead medals in 1506. A screw press capable of minting coins from less malleable gold and silver was not developed until approximately 1530 by Benvenuto Cellini, who minted coins for Pope Clement VII (Cellini, 1571). The screw press multiplies manual effort with a lever attached to a screw. The press produced a significant impact to the coin blank between two dies, by swinging the weighted lever and allowing the screw to run down its thread until impact (Figures, 2.16 and 2.17).

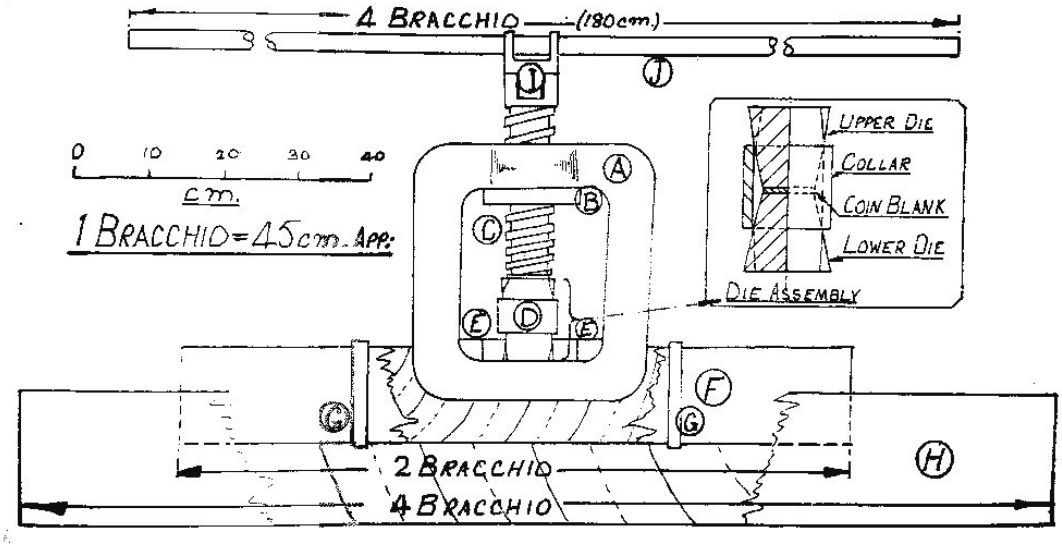


Figure 2.16 – An interpretation of the Cellini press. A- Wrought iron frame. B- The nut carrying the main screw. C- The main screw. D- Die assembly. E- Wedges fixing the bottom die. F- Beam the frame is recessed into. G- Iron straps fixing beam F into the foundation beam. H- Foundation beam. I- Bracket holding the lever arm to the head of the screw. J- Lever arm. (Cooper, 1988).

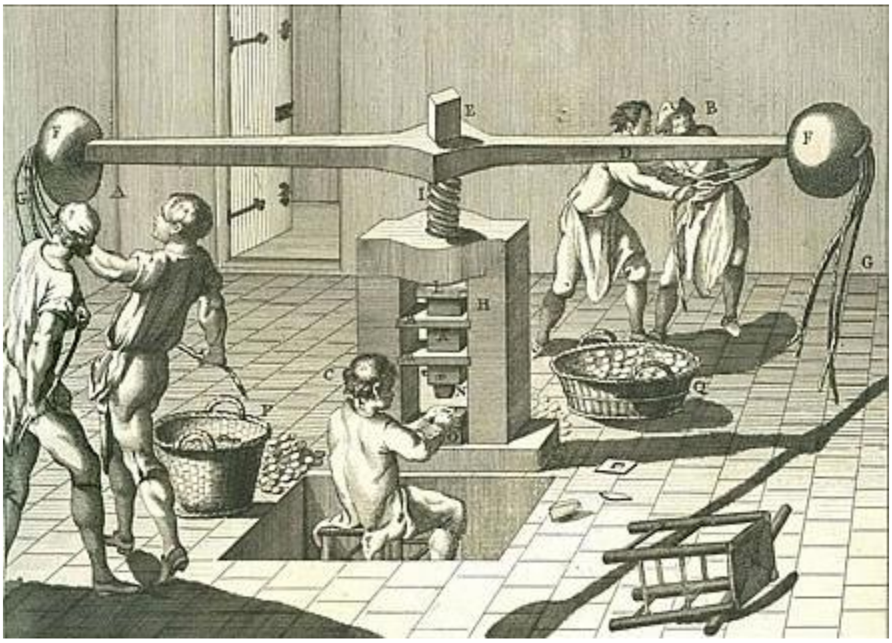


Figure 2.17 – Diderot and d'Alembert. *Monnoyage – Balancier*. 1772. Depiction of a screw press in use to make coins.

Minting machinery by and large was not embraced by moneyers, who claimed the machinery was less efficient than a skilled moneyer, and feared the loss of their jobs. However with technical improvements and a push for minting machinery by sovereigns, the screw press came into widespread use in Europe in the 17th century (Cooper, 1988).

For some time, the screw press was used in conjunction with the roller mill, the roller mill being used to create coin blanks and the screw press being used to strike them (imprinting a design on both sides of the coin simultaneously). However by the late 18th century, the screw press was developed to be able to shear a circular coin from a sheet of metal, as well as imprinting it (Cooper, 1988).

2.3.2 Spain

Gold and silver treasure arriving in Spain from Spanish America, whether owned privately or by the Crown, was to pass through the House of Trade in Seville upon its arrival in Spain (Hamilton, 1965). All treasure was then required by Royal order to be coined within six months of arrival. A certificate from the mint to prove that the bullion had been coined was to be presented to the House of Trade (Hamilton, 1965). Four Spanish mints are represented in this study. They are Cadiz, Madrid, Segovia, and Seville.

2.3.2.1 Cadiz

From 1680 the port city of Cadiz had held a monopoly on silver and gold brought to Spain from Spanish America as the primary port at which it was delivered and processed (Bernal, 2006). In 1717 the Board of Trade and Commerce officially relocated from Seville to Cadiz, marking the beginning of the decline of Seville as a centre for trade (Woodward, 2006). The mint in Cadiz was founded in 1809 as a provisional mint by the Spanish during the French invasion of Spain (Fantom, 2003). Due to these difficult conditions, workers and machinery were taken from the mints at Segovia, Madrid, and Seville to create the Cadiz mint. The first coin was struck at Cadiz in 1810. The mint was dismantled in 1815 when the French army abandoned Spain (Fantom, 2003).

2.3.2.2 Madrid

The Madrid mint was established in 1615 and is still functioning today. During this time, four different mints had been operational in Madrid; Segovia Street (1615-1861), Puerta de Alcala (1661-1664), Plaza de Colón (1861-1964) and Dr. Esquerdo Street (1964-) (Fantom, 2003). The Puerta de Alcala mint boasted several large buildings and horse drawn roller mills. The Plaza de Colón mint, a large steam powered mint, replaced the old Segovia Street mint in 1861 (Hamilton, 1965). The coinage minted in Madrid made up a very small proportion of coins minted in 17th century Spain although of the coins minted in Madrid, an unusually high proportion of them were gold (Hamilton, 1965). Today, the Madrid mint along with the Burgos mint operate as two different plants of the *Fábrica Nacional de Moneda y Timbre – Real Casa de la Moneda* or the National Coinage and Stamp Factory – Royal Mint.

2.3.2.3 Segovia

Segovia is a historic mint town, minting coins as early as Roman times. The mint mark for Segovia is its famous Roman aqueduct which is still standing today (Green, 1977).

In 1583 Felipe II chose Segovia to be the site of a new mechanised mint to house machinery imported from Austria, as the site stood by the river Eresma which was used to power the mint’s two waterwheels. One was used to power two rolling mills to prepare strips of metal, the other to power two Walzenwerk mills for coining, in which strips of metal could be coined, rather than individual blanks (Cooper, 1988).

The first coin was minted on a roller mill in 1586, and this practise continued until 1756. The use of minting machinery in Spain was exclusive to the Segovia mint for many decades, while other mints in Spain run by the National Treasury continued to hammer their coins (Fantom, 2011).

In 1597 Felipe II issued a royal privilege to Juan Castellón to coin copper *vellon*, small petty cash, at the Segovian mint (Hamilton, 1965). The influx of *vellon* as well as the simultaneous debasement of silver coinage lead to inflation, severely affecting the economy of Castile at the time (Hamilton, 1965). The mint was closed in 1869 and converted into a flour mill (Fantom, 2011).

2.3.2.4 Seville

The Seville mint operated between 1497 and 1869 (Fantom, 2003). The House of Trade, particularly in the early years of Spanish American treasure fleets, would supervise the coining of the received treasure mostly in the mint at Seville (Ericson and Earle, 1982). As an example of the dominance of the Seville mint over other mints in Spain between 1585 and 1595 55%, and in 1620 52% of private bullion shipped from Spanish America was coined at Seville (Hamilton, 1965). The Seville mint was closed in 1868 (Fantom, 2003).

2.3.3 Americas

Following the Spanish conquests of Mexico, Peru and New Granada, Carlos I ordered the establishment of mints in Mexico City, Lima, and Santa Fe de Bogotá on May 11, 1535 (Aiton and Wheeler, 1931). In 1545 a temporary mint was also established at Potosí until a permanent mint was built there in 1572 (TePaske, 2008). Prior to the creation of the Spanish American mints, gold and silver in Spanish America was shipped to Spain to be coined. Circulating currency in Spanish America having been shipped back from Spain was overvalued and scarce. For example a silver real, worth 34 maravedis in Spain, was valued at 44 maravedis in Spanish America (Vilar, 1976). Settlers in Spanish America resorted to using gold and silver slugs or dust as currency, valuing them by weight (Aiton and Wheeler, 1931). It was under these conditions that it was decided that minting coinage in Spanish America would be beneficial. The mints were established in locations conveniently close to silver mines. Each mint produced coinage exclusively from nearby mines.

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. The Viceroyalty of Peru consisted of all Spanish American territories south of Panama except Venezuela. Peruvian mints represented in this study are Lima, Potosí, and Santa Fe.

2.3.3.1 Guatemala

During his reign (1621-1665) Phillip V transformed the mint system in Spanish America to create a smoothly functioning network of mints. One of the new mints ordered by the King was the Guatemala mint, opened in 1733. The mint continued to function until Guatemalan independence in 1821 (TePaske, 2008).

2.3.3.2 Mexico

The mint in Mexico City was established in 1535. The first coin was minted there in 1537 (Vilar, 1976). All coins minted in Mexico for the first few decades of the mint's operation were of the "cob" type, crude hammer struck coins of varying shape, but constant weight and fineness. The first dated coin was minted in Mexico in 1600 (Green, 1977). The mint has continued to operate through the struggle for Mexican independence in the early 19th century and on to the present day (TePaske, 2008).

2.3.3.5 Lima

The Lima mint in Peru began minting coins in 1565. It was closed in 1588, and reopened in 1684. The mint was finally closed permanently in 1822. The mint suffered damage during earthquakes in 1687 and 1747 (Vilar, 1976).

2.3.3.6 Potosí

The Potosí mint in modern day Bolivia was opened in 1572, to process the enormous amount of silver being mined from Cerro Rico, a silver mine nearby (Vilar, 1976). The mint machinery was powered by horse-gins (Cooper, 1988).

In 1650 it was discovered that coins in circulation in Castile, minted at Potosí, had been illegally debased. Such was the gravity of the scandal that Potosí minted coins were banned from circulating in Navarre, Aragon, and Valencia. In Italy and Flanders, the coins were only accepted based on their weight and fineness, like bullion, rather than on their face value. The Spanish Crown attempted to have all defective coins called out of circulation and reminted in Spain but the scandal had already created a significant distrust throughout Europe for coins minted in Potosí. In 1653 the mint underwent significant reformation, and on September 23rd of that year a royal order was released in Spain assuring the kingdom that coins minted in Potosí were of acceptable quality (Hamilton, 1965). The mint closed in 1825 when Bolivia gained independence from Spain (Hamilton, 1965).

2.3.3.7 Santa Fe de Bogotá

The mint of Santa Fe de Bogotá in Colombia began producing coinage in 1620. The mint was located close to a productive gold mine and was allowed by Felipe IV to produce gold as well as silver coins. Other Spanish American mints were initially permitted to only mint silver coins. The few silver coins struck at Santa Fe de Bogotá were made from the silver removed as an impurity from local gold (Green, 1977). Coins were made using a bronze press made of melted down cannons captured in battle (Cooper, 1988).

2.3.4 The United Netherlands and the Spanish Netherlands

Until centralisation in 1806, when a single, national mint was set up in Utrecht, every Dutch province had its own mint which operated relatively autonomously, having begun operating in the Middle Ages or earlier (Hart *et al.*, 1997). Information on Dutch mints, when they were active, and how the coins were minted is for the most part lost in Dutch archives. Province mints represented in this study are: Friesland, Gelderland, Holland, Overijsel, Utrecht, West Friesland, and Zeeland.

The Middleburg mint in the province of Zeeland was powered by horse-gin. The horse-gin powered three rolling mills and one spur wheel (Cooper, 1988).

2.3.5 Germany

As with mints and minting practices in the Netherlands, few details on the years of operation and minting processes are readily available on German mints. The German mints represented in this study are: Cologne, Holstein Gottorp, Lubeck, Nuremberg, and Saxony

The mint at Cologne minted both gold and silver coins from 1340 (Spufford, 1988).

From 1340, the Lubeck mint was the only German mint outside of the valleys of the Rhine and Main to be allowed to strike gold coins as well as silver. The gold used was purchased in Flanders (Spufford, 1988).Strip rolling mills were first used and developed at the Nuremberg mint between 1530 and 1540. Over the next decade, at various mints around Germany, the strip rolling mill was further developed to emboss coins onto strips of metal. The mint at Nuremberg also boasted what was probably the largest and most powerful screw press of its time (Cooper, 1988).

2.3.6 Summary

The majority of the coins used in this study would have been hammered, with the remainder the products of the rolling mill or screw press. This information is important for interpretation of the microstructure of coins, and it can be expected that evidence for significant cold working will be present within these microstructures.

2.4 Wrecks represented

Shipwrecks represent a unique archaeological opportunity to research an assemblage ‘frozen in time’. With a single catastrophic deposition event, one has the opportunity to study all the material remains from a specific time and place, and what they represent in terms of the people involved.

In this study, coins have been studied from the wrecks of five trading ships, providing an opportunity to understand aspects of world trade at the time of the great maritime empires, with representative assemblages of artefacts that hold implications for our understanding of the mechanics of trade at the time.

The ships represented sailed from the Netherlands, the USA, and Portugal, and were wrecked en-route to Indonesia and China. To facilitate trade with the East, due to the imbalance between Eastern demand for European goods and European demand for Eastern goods, a large portion of the cargo on all of the ships was silver; in coins, ingots or bullion. Chests of silver were also doubled as ballast in the ships’ holds.

2.4.1 The *Batavia*

The *Batavia* commanded by Francisco Pelsaert, was wrecked on the 27th of October, 1628 in the Houtman Abrolhos Islands, while en-route from Texel in the Netherlands, to Batavia (Jakarta). The ship had gone off-course and ran aground on Morning Reef about two hours before day-break, the surf which had been seen on the reef by the skipper, Ariaen Jacobsz, had been mistaken for the reflection of the full moon on the water (Pelsaert, 1629).

Pelsaert and 46 other passengers and crew then sailed to Batavia for help in one of the ship's longboats. He returned two months later on the ship *Sardam* to discover that a mutiny and the murder of over 100 of the shipwreck survivors had taken place under Jeronimus Cornelisz. The mutineers and murderers were tried and sentenced on the island, and the survivors were rescued and taken to Batavia. The exact location of the wreck was subsequently lost. In 1840, during a survey of the Western Australian coast, Lieutenant Lort Stokes and Commander J. Wickham on the HMS *Beagle* correctly identified another VOC wreck in the Abrolhos, the *Zeewijk*, however they incorrectly identified the southern end of the Abrolhos as the location of the *Batavia* wreck (Green, 1989). It wasn't until 1955, after a detailed examination of Pelsaert's journals that the site of the wreck was correctly suggested by historian Henrietta Drake-Brockman, and subsequently discovered in 1963 (Drake -Brockman, 1955).

A number of expeditions were made to the site in the 1960s, with the recovery of artefacts such as cannons, astrolabes, coins and ceramics. Also during the 1960s, the Western Australian State Government set about enacting legislation to ensure the protection of underwater cultural heritage material with the view to protecting the *Batavia* and other historic wrecks off the WA coast. In the *Maritime Archaeology Act* (1973) the Western Australian Museum is named as the body responsible for the excavation and study of these sites.

The *Batavia* was excavated by the Western Australian Museum between 1972 and 1975 by a team lead by Jeremy Green. Initially excavation was focussed on determining if there was any hull structure remaining of the wreck. The entire wreck was in a stable condition, loosely concreted with coralline algae. Excavation was carried out by gradually levelling areas of interest by removing coral and artefacts rather than excavating in trenches, which would have been impossible in the conditions. Conditions on site were near impossible to predict from day to day, and it was estimated that only one in three days were suitable for diving and excavation (Green, 1989).

The first artefacts to be recovered from the site were 128 sandstone blocks which were to form a portico in the walls of the Batavia Castle (Green, 1989). The constructed portico is now on display at the Geraldton Museum. A large section of the hull of the ship was removed and conserved, and is on display at the Western Australian Maritime Museum in Fremantle, along with a copy in plaster of the portico.

Coins on the site were recovered in large concretions and brought to the field station on Beacon Island for initial examination (Green, 1989).

2.4.2 The Vergulde Draeck

The *Vergulde Draeck* ('Gilt Dragon') left Texel, the Netherlands, on the 4th of October, 1655, bound for Batavia, Indonesia under the captaincy of Pieter Albertsz. Due to a miscalculation of longitude, the *Vergulde Draeck* was wrecked just south of what is now Ledge Point in Western Australia on the 28th of April, 1656. Only 75 of the original 193 people on board made it to shore alive, at which point seven were sent in a small boat to Batavia to seek help. They arrived in Batavia on the 7th of May, 1656, at which point the VOC sent two ships to search for the survivors and any salvageable goods from the *Vergulde Draeck*. Bad weather made this search impossible, and the ships returned having lost eleven of their own men. Two more ships were sent from Batavia to search for the *Vergulde Draeck*, again finding no sign of the wreck or survivors, and returning to Batavia having lost a further ten men. Salvage attempts were then abandoned by the VOC.

In 1931, a young boy found 40 silver coins dating between 1619 and 1655 in sand hills near Cape Leschenault. Due to the dates on the coins it was strongly suspected that the discovery was associated with the wreck of the *Vergulde Draeck* (Green, 1973). The wreck itself was discovered in 1963 by five spearfishermen, John Cowen, Jim, Alan and Graeme Henderson, and Alan Robinson.

After reports of the use of explosives on the wrecksite in 1963, the State Government of Western Australia declared all wrecks prior to 1900 State property, to be excavated by the Western Australian Museum in the *WA Museum Act* (1964), a precursor to the *Maritime Archaeology Act.*

The wreck was excavated in 1972 by a team lead by Jeremy Green of the Western Australian Museum. The wreck is exposed to the Indian Ocean swell and is 10m deep at its maximum. It is very difficult to discern wreck material from the limestone reef. Excavation took place mostly under good environmental conditions, allowing divers to spend as much as eight hours per day excavating (Green, 1973; 1977).

Priority during excavation was given to excavating the highly disturbed surface from the wreck, and to investigate if the wreck below had any remaining structure. Little structure was found due to what has been interpreted as a violent wrecking event, and so only significant finds were recorded on a plan of the site.

Artefacts recovered from the wreck include ivory tusks, ‘beardman’ jugs and an astrolabe. Two cannon were raised in order to research methods of conserving corroded iron. Animal remains also represent an opportunity to research an assemblage of the remains of pre-breeding revolution cow and pig (Green, 1977).

Coins were concentrated in a gulley on the wrecksite, the concentration of coins indicates that the eight chests of silver the ship had been carrying remained intact. Some preliminary electrolysis on the coins was performed on site, while the majority of the coin conservation took place at the Western Australian Museum. The coins were subsequently catalogued and identified by Western Australian Museum numismatist Stan Wilson (Green, 1977).

2.4.3 The *Zuytdorp*

The *Zuytdorp* (‘South Town’) sailed on her final voyage on the 1st of August 1711, from Texel, the Netherlands bound for Batavia, Indonesia under the captaincy of Marinus Wijsvliet. Most likely due to a miscalculation of longitude, the *Zuytdorp* was wrecked on cliffs just south of Shark Bay, now known as the *Zuytdorp* cliffs. No survivors reached Batavia to alert the VOC of the wrecking, and so it is not known exactly when the wreck occurred. Perhaps due to the expense and loss of life caused by previous salvage attempts by the VOC, no ships were sent south from Batavia to search for the *Zuytdorp* when it became apparent she had been lost. Terrestrial archaeological evidence indicates that some survivors made it to shore alive and camped there for a time, but what became of them is unknown. It has been speculated that they were accepted into local Aboriginal tribes (Dash, 2002).

In 1834 local Aboriginals informed a farmer of wreck material in the area. The material was assumed to be from a recent wreck and a search for survivors proved fruitless. In 1927 more wreck material was seen at the bottom of the cliffs. Expeditions to the wrecksite of the *Zuytdorp* were made in 1941, sponsored by *The Sunday Times* newspaper, and in 1954 and 1958, sponsored by the *Daily News* newspaper (Playford, 1959). In 1964 a team of divers lead by Mr Tom Brady successfully located the wreck and were able to dive on it (McCarthy, 1990). The Western Australian Museum became responsible for the site in 1969 and excavated at the site in 1971, 1978, 1986, 1987, 1988, 1992, 1993 and 1996 (McCarthy, 1990; Playford, 1998).

Excavations on the wreck of the *Zuytdorp* have been limited, as conditions at the site make diving difficult. On the limited occasions that excavation was possible, it was noted that significant looting of the site had taken place. After an assessment of the site in 1978, it was estimated that 90% of the silver cargo was intact on the site. The next time the Museum was able to dive on the site in 1986, only patches of coins in potholes and crevices remained (Playford, 1998). It is suspected that whoever was responsible for the looting was likely also responsible for burning down the caravan that a watch keeper, installed by the Museum to protect the wreck, had been living in (Playford, 1998). Priority was given to the recovery of silver coins, in order to make the site less attractive to looters (McCarthy, 1990). Other recovered artefacts included several swivel guns in varying conditions of preservation.

As there were no contemporary salvage attempts of the *Zuytdorp*, the entire cargo of coins had remained on the wreck site, including a special minting of *paymenten* ‘small change’ coins. It was this special minting that allowed the wreck to be conclusively identified as that of the *Zuytdorp*, as the only other ship carrying coins from this minting, the *Belvliet*, reached Batavia safely (Playford, 1959). In total 21,539 silver coins were recovered from the wreck and conserved at the Western Australian Museum (McCarthy, 1990).

2.4.4 The *Rapid*

The *Rapid* departed Boston, USA on the 28th of September, 1810 bound for Canton, China under the captaincy of Henry Dorr. She was carrying a cargo comprised of almost eight tonnes of silver coins, and eight guns which may have been mounted on the deck to protect the coins. Due most likely to a miscalculation of longitude the ship was wrecked on the reef at Point Cloates in Western Australia on the 7th of January, 1811. All on board survived, and the day after the wrecking the crew set fire to what remained of the ship, so as not to attract the attention of passing vessels before the coins had been salvaged. The entire crew then sailed to Batavia where six weeks later many of them boarded the *General Greene* and sailed with it to Philadelphia, arriving on the 27th of July, 1811. From Philadelphia a ship was sent to inspect the wreck, and in the following months most of the coins were salvaged, with only 19,000 unaccounted for.

The site was rediscovered in 1978 by spearfishermen, who surrendered 600 silver coins as well as other ceramic, glass and copper artefacts to the Western Australian Museum. The *Rapid* wrecksite was excavated shortly after the discovery, to protect the wreck from looters after the fishermen reported seeing a large mound of exposed silver on the wrecksite. Excavation took place over three field seasons by the Western Australian Museum in 1978, 1980 and 1982. The wreck was identified based on the dates on the coins, and a barrel of salt beef labelled ‘BOSTON MASS. MESS BEEF’, indicating that the ship’s origin was Boston. After archival research in Boston, the wreck was identified as that of the *Rapid* (Henderson, 1983).

The site is protected from swells by a reef and is under less than 5m of water. The wreck itself and many concretions were examined and preserved *in situ* by being buried in sand and coral, to protect from cyclone damage. The ship’s bell, anchors, guns and fastenings were all raised and conserved by the Western Australian Museum, while concreted artefacts were returned to the wrecksite for *in situ* conservation (Henderson, 1979, Garratt, 1983). The majority of the 19,000 coins known to at the site were recovered, conserved and are stored or displayed at the Western Australian Museum (Garratt, 1993). The *Rapid* remains a significant find as it is the only American China trader to have been studied in an archaeological context.

2.4.5 The Correio da Azia

The *Correio da Azia* (“Asian Mail Ship”), an advice ship, left Lisbon, Portugal in 1816 bound for Macau, China. As the name of the ship suggests, the *Correio da Azia* was carrying mail, and also miscellaneous cargo such as coinage, tea, chinaware, and porcelain (Berry and Baker, 2008). She sailed under the captaincy of Joao Joaquim de Freitas. She was wrecked on Ningaloo reef on the 26th of November, 1816 due to several mishaps on board, such as a fire in the binnacle which severely affected the crew’s ability to navigate. The survivors left Australia in the ship’s boat bound for Batavia but were intercepted and picked up by the American ship *Caledonia*. When they reached Macau, a party was sent back to try to salvage the wreck, but no trace of it could be found (Green and McCarthy, 1997).

The wreck of the *Correio de Azia* was found in 2003 by Jeremy Green of the Western Australian Museum using an airborne magnetometer survey provided pro bono by Fugro Airborne, together with contemporary accounts of its location from the Captain of both the *Correio da Azia* and the *Emillia* that was sent to chart Point Cloates. The wreck is in a thick reef, approximately 10m deep, in very difficult conditions for diving, which prevented previous Museum expeditions from locating it (Green, 2003).

Limited excavation was conducted on the wreck of the *Correio da Azia* in 2004. Visible, loose items, especially coins, were removed from the site by the Western Australian Museum in order to deter looters (Souter, 2004). Few coins were recovered from the site individually; some coins were contained in concretions of 2-10 coins, while the majority were recovered in a large concretion of approximately 700 coins. The coins were subsequently removed from concretion, conserved and are stored or on display at the Western Australian Museum.

2.4.6 Summary

The ships represented in this study were largely wrecked due to errors in navigation. The ability to accurately calculate longitude, or the distance the ship had travelled east on the Roaring Forties trade winds from Africa was impossible to calculate with any degree of accuracy. It wasn't until the 19th century that the marine chronometer was introduced, allowing longitude to be calculated at sea.

The cargo of the *Batavia* was salvaged by the VOC, and a trial and punishment for the mutineers was held whilst on Beacon Island. When the *Vergulde Draeck* was lost, the VOC sent two further ships to find the wreck and salvage the cargo, to no avail. Interestingly, when the *Zuytdorp* was lost, the VOC made no attempts to locate the wreck. This decision was probably made considering the losses suffered by the VOC in attempts to locate the *Vergulde Draeck.* Survivors of the *Vergulde Draeck* wreck had been available to help locate the wreck and yet still never found it, and so an attempt to find the *Zuytdorp* without the assistance of wreck survivors may have been deemed too costly and risky an exercise for the VOC to undertake. The cargo of the *Rapid* was salvaged very successfully by an expedition sent from Philadelphia under instructions from the *Rapid*'s crew members. After survivors of the *Correio da Azia* wreck reached Macau, the wreck was lost until 2004.

With the exception of the *Correio da Azia*, the wrecks represented in this study were discovered in the 1960s and 1970s. The *Batavia* and the *Zuytdorp* were discovered by expeditions with the express purpose of locating those wrecks. The *Vergulde Draeck* and the *Rapid* were discovered by spearfishermen. It was the quick succession of discoveries combined with concern for the safety of the wrecks from looters that drove the efforts of the Western Australian Museum and the Western Australian State Government to put forward legislation to protect the wrecks for the public and future study. This legislation helped to set up the Western Australian Museum's maritime archaeology department as a world-leader in underwater cultural heritage management, as well as providing the impetus for federal legislation and a framework for international underwater cultural heritage protection and management.

It should be noted that there are also many other coins from the same shipwrecks held in private collections. Since 1976 federal legislation in the form of the *Historic Shipwrecks Act* (1976) prohibits the disturbance or removal of items associated with historic shipwrecks. However, it is legal to privately purchase and sell shipwreck coins if they have a registration certificate and a permit for their transfer. Since 1976 if a private individual discovers a wreck or item associated with a wreck in Western Australia they are legally obligated to inform the Western Australian Museum, and to refrain from disturbing the site. However three of the five wrecks represented in this study were discovered prior to 1976 by private individuals. According to the *Navigation Act* (1912), anything removed from a shipwreck was to be declared to a Commonwealth appointed Receiver of Wrecks, however this legislation was rarely enforced. As such a significant amount of wreck material was removed in 1963, the year the *Batavia* and *Vergulde Draeck* were discovered, by private individuals prior to the implementation of the Museum Act (1964), Western Australian state legislation which was found to be invalid when it came to wrecks in Commonwealth waters, and the *Historic Shipwrecks Act* (1976), Commonwealth legislation that does protect wrecks in Commonwealth waters (Rodrigues, 2011). A Commonwealth Historic Shipwrecks Amnesty was declared in 1993-1994 during which time individuals who were in possession of items associated with wrecks that were older than 75 years declared items to the relevant State or Territory agency to be recorded. Items were returned to the individuals with a registration number and a permit, and were to be held by the individual in accordance with the *Historic Shipwrecks Act*. Some 20,000 artefacts were declared nation-wide including approximately 4,000 coins, as well as 30 previously unknown shipwrecks in Queensland, Victoria and Tasmania (Rodrigues, 2011). Since the amnesty, shipwreck material held illegally in private hands can be seized by police and given to the relevant State or Territory agency or museum.

As the body responsible for the excavation, preservation, study and display of these shipwrecks, the Western Australian Museum developed, in many cases through trial and error whilst on site, many excavation, recording, and conservation techniques now taken as standard practice in the field of maritime archaeology.

2.5 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 were submerged in seawater for between 168 years (for coins aboard the *Rapid*) to 335 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 sub-tropical waters, with a mean temperature of approximately 24°C. The sites of the wrecks vary somewhat in the turbulence they are subjected to (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). The issue of copper precipitation and silver surface enrichment is further investigated and discussed in sections 5.1, 6.1, and 7.1.

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, 1979).

The corrosion layer on the coins used in the present study was consolidated using the sodium dithionite method (MacLeod and North, 1979). Electron probe microanalysis (detailed in section 6.1) has been used to determine the depth from the surface of the coins that is affected by corrosion processes, and this information has been used to inform further analyses on the coins.

2.6 Coin conservation and identification

Coins from the wrecks detailed above are frequently delivered to the Western Australian Museum in large concretions. In order to both study and display the coins, they must first be excavated from concretion and conserved. Further, damage on the surface of the coins due to corrosion is prevalent, and so visual identification can be limited. However, to an experienced numismatist, partial identification based on physical aspects of each coin is often possible, with the ability to extrapolate further information from there.

2.5.1 Conservation

Conservation of coins recovered from historic shipwrecks off the Western Australian coast is carried out by the Department of Maritime Archaeology and the Department of Materials Conservation of the Western Australian Museum. For Dutch wrecks, this work is undertaken under the authority of the Australian Netherlands Committee on Old Dutch Shipwrecks, who also oversee the distribution of shipwreck material between Australia and the Netherlands.

The majority of coins from the wrecks mentioned were conserved using the sodium dithionite method, which is detailed in MacLeod and North (1979). This method was developed after the rediscoveries, in quick succession in the 1960s and 1970s, of the *Batavia, Vergulde Draeck, Zuytdorp* and *Rapid,* at which time the Western Australian Museum found themselves with several thousand corroded coins to be conserved.

Initially, electrolysis was used to treat the corrosion on the coins. However, a decision was then made to preserve the corrosion layer on the coins in order to also preserve inscriptions and die stamps on the faces of the coins. Electrolysis was found to frequently disintegrate the corrosion layer, destroying any identifying features on the coin due to the evolution of hydrogen during the process (MacLeod & North, 1979).

Coins from the *Zuytdorp* concretion were placed in 30% hydrochloric acid before being immersed in a 5% alkaline dithionite solution. The coins were then washed in running deionised water for a day to remove excess caustic. Finally, the individual coins were fibreglass brushed, rinsed, dried, and coated in to layers of Incralac (Digwood, 1989).

Coins from the *Correio da Azia* concretion were removed from concretion using 10% hydrochloric acid over several days, which dissolved calcareous concretion and copper corrosion products from the surface of the coins. Initial mechanical cleaning of coins was performed using wooden skewers, brushes or scalpels under a microscope. To consolidate the corrosion layer on the coins the sodium dithionite method was used, and in some cases a 25% ammonia solution was used to soak the coins for four hours, followed by immersion in silver dip (1% sulphuric acid / 5% thiourea), before the sodium dithionite method (Nystrom Godfrey, 2005).

When conserved, soaked in deionised water and air dried, coins were given a final polish using a soft Dremmel brush and some were coated with a broad spectrum vapour phase inhibitor (Senson) to determine if this would prevent tarnishing (Nystrom Godfrey, 2005).

A silver chloride patina on the surface of some coins has been noted to have developed following storage, and is assumed to be due to chlorine in the PVC bags used for storage reacting with finely divided silver on the coins' surfaces. The patina was of minor concern and no further treatment was required. Small paper envelopes have been used for further storage to prevent reactions with the coins (Nystrom Godfrey, 2005).

In terms of the present study, understanding how the coins were treated following their excavation is important to be able to apply appropriate analytical techniques and to take the potential effects of conservation into account when interpreting results. In this case, it is known that the corrosion layer of the coins was consolidated with conservation, and so research has been conducted in this study to determine how deep this layer is, and if it can be considered to be representative of the composition of the entire coin.

2.5.2 Identification

The visual identification of the coins in the collection used in this study consists of the identification of as many of the following features as possible: country, province, ruler, date, mint, denomination. These features are identified based on markings printed onto the faces of the coin including mint mark, assayer mark, coat of arms, sovereign portrait, and other decorative symbolic devices such as crosses or shields. In addition, the shape and weight of the coin can be used to estimate identifying features such as mint and date.

In the case of heavily corroded and damaged coins, when only some of these features can be identified, it is possible, based on the numismatist's knowledge and experience, to extrapolate further information from what is immediately identifiable. For example, the identification of the sovereign on a coin will necessarily narrow down the possible years of minting of that coin to the years of the sovereign's reign, and the place of minting to mints under the control of the sovereign.

Historical records and modern databases of the features on many types of coinage are available for study. Aspects of a coin's decorative design can be indicative of the year and mint it was produced in as small variations are known to exist between mints over time in the dies used to strike coins. Further, an understanding of technology changes at different mints over time, and their manufacturing processes, lends itself to the identification of coins based on their general size and shape. For example, Spanish American coins with especially irregular shapes are known to be most likely from the Mexican mint.

The work presented in this thesis complements the work done by the numismatists who identified the coins used in this study. Research into the composition and structure of these coins has enabled confirmation of visual identifications, as well as the estimation of aspects of a coin's identity that were impossible to identify visually.

2.6 Museum coin collections; deaccession of duplicates

Museums cannot be expected to retain all items in collections for perpetuity. Ethical guidelines, policies of museums, and in some cases legislation dictate the appropriate methods of acquisition and deaccession and disposal of museum collection items. A common justification for the declination of donated items, and also for the deaccession and disposal of items, is that they represent a duplicate of another item already held by the museum. Disposal will most often involve sale, exchange, donation or destruction. While this can be seen as an appropriate response for many items in the collections of museums, it can become problematic when dealing with items which are inherently numerous and similar, such as coins and stamps. With adherence to museum policy charters and relevant legislation, many museums are within their rights to dispose of duplicate coins through return to the donor, auction, or exchange with other museums for different items. This would theoretically enable breaking up large assemblages and hoards of coins where a coin is found to be identical in mint and year of minting to another coin in the assemblage or already in the museum's possession. This thesis demonstrates the importance of retaining whole assemblages for the purposes of further research. The legacy data provided by the foresight of the Western Australian Museum in this case has proved invaluable for the creation of a database of compositional and structural analysis of hundreds of silver coins.

The National Standards for Australian Museums and Galleries (2016), are a collection of standards and guidelines produced collaboratively by a number of Australian museums and galleries. These standards are incorporated into museum and gallery development and accreditation programs nation-wide. One of the standards states "The museum develops its collection to reflect its unique purpose and the significant stories and interests of its diverse and changing communities" (Museums Australia, 2016, p.16). Included in this standard is the requirement for museums to have a deaccession policy. Such a policy should include the procedure for the deaccession and disposal of an object. In order of preference after a predefined cooling off period, an object should be returned to its donor or their family; transferred to an appropriate community organisation; kept as an interpretive/educational tool or prop; sold; or destroyed.

The Western Australian Museum Collections Policy and Procedures (2015) contains a specific No Duplication principle, which states "As a general principle, the Museum must avoid the duplication of items already held in the Collection and there is a presumption against acquiring items that are identical to another item already in the Collection. Indiscriminate duplication with other collecting institutions should be avoided" (Western Australian Museum, 2015, p.11). In order to deaccession an item in the collection of the museum, the item is expected to meet one or more of the following criteria: The item is to be repatriated; exchanged; it is damaged beyond repair; legal title cannot be established; it is fake; or if the item would be more useful to advancing knowledge through destructive analysis or as a service material. Further, an item may be deaccessioned if its continued conservation outweigh its significance to the museum's collection; would be better performed by a different public institution; or pose an occupational health and safety risk. If the item is sold, it is not permitted to be bought by museum staff, their families or close associates. Profits from sold items are to be used for the benefit of the collections. In terms of coins, the Collections Policy and Procedures allows the Western Australian Museum to dispose of coins, or to not accept coins into their collection if they are duplicates of other coins in the collection. However while this option is available to the Museum, coins have not been deaccessioned.

The Royal Australian Mint maintains the National Coin Collection. The National Coin Collection Preservation Policy (2016) states that in order to develop and maintain the collection, disposal of coins may be necessary. A coin being considered for disposal is expected to meet one or more of the following criteria: duplicates; insignificance; inferiority; lack of documentation or provenance; deterioration, assets management; legal and moral obligations or impediments; ethical considerations; copies; and fakes. The disposal of items must demonstrably benefit the National Collection. The method of disposal varies with each coin however destruction is to be considered a last resort.

The Museums Association provides codes of ethics, standards for excellence and policy for museums in the United Kingdom. The Museum Association's Disposal Toolkit (2014) provides guidelines for museums regarding the deaccession and disposal of items in museum collections. The Toolkit states that an item should only be disposed of if it meets one or more of the following criteria: the item falls outside the museum's core collection; is a duplicate; is underused; can no longer be cared for is damaged beyond repair; if the provenance of the item cannot be determined; or if the item poses a risk to occupational health and safety. In the case of duplicates, it is noted that this is not automatically significant justification to dispose of an item. It is recommended to consider whether a duplicate has a unique history, or if there is cultural value in retaining more than one of an item. The Disposal Toolkit also outlines circumstances in which it is unacceptable to dispose of a museum item: for financial reasons; on an ad hoc basis; without the advice of a specialist; if the pubic reputation of the museum would be adversely affected; if the disposal is not in the long-term public interest; or the disposal of items outside the public domain. Items to be disposed of should be donated; transferred; exchanged; sold to another museum or another public institution; returned to the donor; recycled; or destroyed. In exceptional circumstances it may be appropriate to sell or donate an item outside the public domain. The Museum Association's Disposal Toolkit indicates that only in circumstances in which a duplicate coin could be demonstrated as not adding any more cultural value than its duplicate, could a coin be disposed of.

According to the *Treasure Act* (1996), the British Museum is responsible for processing treasure finds from England and Wales, defined as two or more coins in the same hoard of at least 300 years old, or 10 or more coins when the silver or gold content is less than 10%. The Museum then has the option to acquire treasure for their collection. *The British Museum Act* (1963) states that the British Museum is forbidden to dispose of its holdings, with exceptions made in certain circumstances. An object in the museum's collection may be disposed of if it satisfies one or more of the following criteria: it is a duplicate; was made after 1850 and consists of printed matter which can be copied in a photograph or similar; or can be disposed of without detriment to the interest of students. In these cases an object can be sold; exchanged; or donated. If the object has become useless for the museum's purposes through damage to the object, it may also be destroyed. However, no action can be taken that contradicts any conditions that were attached to an object at its acquisition by the museum. Any money gained through the sale of objects from the British Museum's collection must be used to purchase other objects to add to the collection. According to *The British Museum Act*, one of the few types of objects which can be disposed of by the British Museum would be duplicate coins.

The Association of Art Museum Directors communicates standards of excellence in museum practice for art museums throughout North America. Their policy on deaccessioning (2010) states that for an item to be deaccessioned and disposed of it should meet one of the following criteria: the item is of poor quality; a duplicate with no value as part of a series; was stolen or illegally imported; fake; damaged beyond repair; does not meet the collection goals of the museum; or can no longer be adequately cared for. Items should be disposed of according to the terms stated at their acquisition, in order of preference: exchanged with another pubic institution; sold at auction; or sold through a dealer. No person associated with a museum should acquire a deaccessioned item. It is interesting to note that according to this policy, a duplicate object must also be demonstrated to have no value as part of a series. In this case, it can be presumed that duplicate coins which are part of a hoard or assemblage may be considered to be of enough value as a part of a series so as to prevent them from being deaccessioned.

It can be seen that in many museums, the deaccession policy regarding coins means that there is no requirement to keep assemblages, collections or hoards of coins together when there are duplicates of the same coin. However, as this thesis will demonstrate, there is enormous value in retaining entire collections of coins rather than representative samples. This value lies in the opportunity for analysis of large collections of coins in order to answer research questions regarding both individual coins and groups of coins, as well as larger enquiries into trade and economy in the past.

Chapter conclusion

An accurate interpretation of results from the present research is reliant upon an understanding of those factors which will affect the coins in question. The method of manufacture, from mining to minting, will affect both the microstructure and composition of a coin. The movement of silver from mine to mint and onwards, will likewise affect the composition of a coin whether coins are minted from silver sourced exclusively from one nearby mine, from a combination, or further counter stamped or recoined. The coins used in this study have all been affected by corrosion processes due to their deposition underwater. An understanding of the environment the coins were in, how they were excavated and conserved is of importance to understanding the relationship between the corroded surface and the intact bulk of a coin both in terms of composition and microstructure. The methods of identifying coins visually are important to understand in order to effectively tailor further research questions towards confirming or denying such identifications, and using these identifications as the foundation for research into identifying unidentified coins. Finally, the policies and guidelines regarding coin collections in museums has been explored, with regards to the ability to break up coin collections, hoards or assemblages. The foresight of the Western Australian Museum in keeping their collection of shipwreck coins together has provided the unique opportunity to study this legacy data some decades after the discovery of the coins.

Chapter 3 – Literature Review and Methodology

Chapter introduction

This chapter details research that the present study relates to, specifically the application of scientific analysis to the study of numismatics and archaeological metals. Further, a review of ICP-MS and electron microscopy in numismatic studies, previous research on the collection of coins used in this study, and an explanation of the justification behind the choice of analytical techniques utilised in this study.

The purpose of this chapter is to justify both the use of each individual method of analysis in this study, and also the complementary use of the combination of techniques used. Individually, each analytical method used on the sample coins in this study has answered one of the research questions posed in the introduction to this thesis. In combination, different analytical methods are able to corroborate, complement, and gain a deeper understanding of the results of other methods.

3.1 Scientific Methods of Analysing Coins

Scientific analysis of coins generally has had an emphasis on the investigation of coinage standards and metallurgy, specifically through the determination of their composition. This is because much interest is placed in the fineness of currency of a State, as it is a reflection on the condition of the economy at the time (Casey, 1986).

Knowledge of a coin’s major elemental composition, when combined with its year of minting, if known, may be able to shed light on the utilisation of resources in a State, the differences in minting processes over space and time, differences in minting processes between rulers from the same State over time, or between contemporary States. This is possible through the understanding of the fineness of issues of coins at different times and places, when combined with other available information of the social and political context surrounding their manufacture. A detailed knowledge of a coin’s minor or trace elemental composition may also help in determining which mine or mines were being used as the source of silver for the coins and identifying any possible debasement of currency over time. This is due to the trace elemental composition of silver ore from the unique mineralising event when it was created being retained through refining and manufacture.

Quantitative analysis on Roman silver coins was performed by both Claude Bouteroue and Petri Chacon in the 17th Century. This analysis consisted of testing the fineness of Roman silver coinage, with the aim of determining the level of technology possessed by the Ancient Romans in making their coinage (Butcher and Ponting, 2015). The first quantitative analysis of archaeological coins was conducted by Martin Klaproth in 1815 with the aim of determining their alloy composition. Klaproth (1815) displaced individual metals from the alloy by dissolving each coin in various acids, and precipitating the different component metals, alongside identical experiments of pure metals used as a control (Caley, 1949). Results were reported in actual weights of component metals present in the original coin and then converted into percentages. Further research has shown that the results for major elemental composition is relatively accurate, even though Klaproth failed to account for or identify impurities, or minor and trace metals (Caley, 1949).

Methods to determine the composition of a coin vary widely in effectiveness and are limited by ideally doing as little damage as possible to the coin itself, as an object of cultural heritage significance. Exceptions are generally made on a case-by-case basis, when the benefits of destructive analysis outweigh the loss of the coin. A simple method to determine bimetallic ratios of coins is the specific gravity method. The method was used at Sutton Hoo to determine the fineness of 37 coins found in association with a 7th century ship burial (Kent, 1975). Thirty-seven coins were analysed, as well as 750 other examples of the same coinage from various European collections. The coins were weighed in air and in liquid to determine their specific gravity, from which it is possible to determine their bimetallic ratios of either silver to gold, or gold to copper. It was found that the bimetallic ratios of the coins at Sutton Hoo correspond to those of roughly 625 CE (Kent, 1975). This information was crucial in determining the date of the ship burial.

From the very inception of neutron activation analysis (NAA) in the 1950s, the technique has been used on coins (Kraay, 1958). In a preliminary study, Greek Athenian coins were analysed to determine whether or not coins minted in Croton had been struck from silver sourced from Sicily. Initial results were inconclusive, but the technique had been proved to be valid in its application to both coins and ceramics (Kraay, 1958). From this point until the 1980s, NAA was the predominant form of multi-elemental analysis used on archaeological materials (Pollard and Heron, 2008).

Fast neutron activation analysis (FNAA) has been used more recently, for example, to determine if silver coins in the Phoenician city of Tyre had been devalued when the neighbouring Sidonian coinage was devalued in 365BCE (Elayi *et al.*, 2008). Thirty-nine Tyrian silver coins were analysed using FNAA to determine their bulk composition. A continuous decline in the silver content of Tyrian coins was found between 395BCE and 358BCE (Elayi *et al.*, 2008). These results have also been used to establish a chronology of Tyrian coins based on their silver fineness, and to create a system of classification of Tyrian coinage.

Non-destructive elemental analysis has been used to great effect in numismatic studies. For example, 115 Roman silver *denarii*, minted between 119CE and 194CE were analysed using both scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) and prompt gamma activation analysis (PGAA) for non-destructive analysis (Kasztovszky *et al.*, 2005). The aim of the study was to trace debasement of silver coins over time by determining their composition. It was found that SEM-EDS analysis did not penetrate far enough into the sample to determine bulk composition, while PGAA did (Kasztovszky *et al.*, 2005). The two techniques were used to complement each other, to investigate both the surface and bulk composition of the coins. Results indicated that copper content of the coins increased over time due to debasement, and the study also detected some contemporary forgeries.

Using destructive methods to analyse the composition of coins in their entirety provides very accurate quantitative results. Samples of coins from the Gallic Empire (258-273BCE) discovered in a hoard of 130 coins in Piercebridge, Durham were analysed destructively to determine their composition (Casey and Coult, 1977). As it was known that consistent debasement of silver in the coins of the Gallic Empire had taken place, it was possible to use the results of chemical analysis to determine whether the coins were minted early or late in the reign of Postumus (260-269BCE). The coins were dissolved in nitric acid and then the resulting precipitate analysed. Of the hoard, all but two coins fell between 235BCE and 262BCE; the two outliers had been dated to 268BCE by numismatists (Casey and Coult, 1977). This six year gap was the impetus for further research. It was found that the silver content of the two outlier coins was relatively high, which allowed Casey and Coult (1977) to confidently date them as having been minted early in Postumus' reign, rather than in 268BCE.

X-ray fluorescence (XRF) analysis has also been used to non-destructively determine the composition of coins. The technique is straightforward to perform and interpret, however does not boast the sensitivity of other techniques described here, and is limited to surface analyses. Five bronze Egyptian coins from Antinoopolis, dating to the 6th and 7th centuries BCE were studied using XRF analysis to determine their composition, and hence their provenance (Torrisi *et al.,* 2010). With so few samples, the study was also focussed on testing the validity of the technique used for future research on the same coins. The results from the five coins have been interpreted to indicate the possibility of a local mint in Antinoopolis, further supported by the number of distinctly inferior imitation Alexandrian coins found *in situ* in Antinoopolis (Torrisi *et al.*, 2010).

Micro x-ray fluorescence (µ-XRF) was used together with SEM-EDS to analyse 65 silver coins from the reign of the Roman Emperor Trajan (98-117CE) (Rodrigues *et al.*, 2011). The aim of the study was to determine if a change of ore source was reflected in the coins' composition using µ-XRF. SEM-EDS was used to document the cross-section of coins, to investigate the surface compared to the bulk. A possible change in ore source was indicated by significant differences in gold, bismuth and lead concentrations. Cross-section analysis revealed silver surface enrichment due to corrosion, 100-200µm thick (Rodrigues *et al.,* 2011). The study provides a foundation for further research into the development of the silver alloy used during Trajan's reign.

Proton induced X-ray emission (PIXE) analysis was used to compare the elemental make-up of ancient Indian coins to the ore of various mines in India to determine ancient Indian silver and copper sources (Hajivaliei *et al.,* 1999). Fifteen coins were analysed, all minted during the Hindu Shahis Dynasty of Kabul (990-1015AD). The coins were discovered in various districts in Panjab state in India. It was found that there is a strong positive correlation between lead and zinc, and a strong negative correlation between silver and copper (Hajivaliei *et al.,* 1999). Antimony was present in all but one coin which the authors attribute to primitive smelting techniques. It was concluded that the primary source for copper ore was Khetri and Singhana in Rajasthan and that the silver came from Afghanistan (Hajivaliei *et al.,* 1999).

3.1.1 Destructive, semi-destructive, and non-destructive analyses in numismatic research

As discussed, destructive analyses of cultural heritage materials, in particular sampling by removing part of an artefact for further analysis, and/or digesting or dissolving the sample for analysis, is not an ideal solution for most archaeological artefacts. By their very nature, archaeological artefacts tend to be unique or irreplaceable, and the value of the information that can be gleaned from destructive analysis does not always outweigh the inherent value of keeping the artefact intact. When the value of information that can be gained from destructive analysis does outweigh the value of the artefact remaining intact, destructive, semi-destructive, or "constructive" (Golfomitsou *et al.,* 2016) analysis can be justified. In the present study, some destructive sampling in order to analyse the cross-sections of coins has been permitted by the Western Australian Museum, as the information that can be gained has been deemed more valuable than keeping the sample coins intact.

Entirely non-destructive techniques, such as SEM-EDS or XRF/XRD analysis are not suited to every type of artefact. Limitations exist on the size and material of an artefact to be studied by such techniques. The processes any artefact goes through in terms of manufacture, use-wear, deposition, and degradation will generally mean that the artefact is inhomogenous, and non-destructive surface analyses may not be representative of the entire artefact. This has been demonstrated on the consistent overestimation of silver content in Roman coins that had been artificially silvered, by Walker (1976) when analysed by non-destructive surface analysis (Ponting, 2009). In the present study, destructive techniques have been used on a subset of coins in order to assess how representative non-destructive surface analyses will be.

A further option for sampling of items of cultural heritage significance would be semi-destructive. Semi-destructive analysis will generally consist of taking a small amount of sample from an artefact, which will not detract from the overall aesthetic or integrity of the artefact. Depending on the artefact and the conditions of analysis, LA-ICP-MS may be considered to be semi-destructive, as a certain amount of material is removed from the sample, though it is generally invisible to the naked eye. In terms of coin analysis, many researchers have drilled into the side of coins and analysed the drillings (Schmitt-Korte and Cowell, 1989; Gitler and Ponting, 2003; Gitler *et al.,* 2008; Ponting, 2009).

The type of analysis chosen for a given artefact should be chosen on a case-by-case basis, with the value of the information that can be gained by potentially destructive analysis weighed against the inherent value of the artefact if it remains intact. While the solution may seem to be to limit artefacts to entirely non-destructive analysis, this is also not always an appropriate course of action. The analytical techniques chosen for this study are mostly non-destructive, while a subset of samples have been allowed for destructive analysis, in order to test the effectiveness of the non-destructive analyses used.

3.1.2 Summary

This section has detailed numerous methods used to analyse coins, with examples of research performed, the aims of the research and the results gained from the methods chosen. Of the methods described, NAA has the highest sensitivity, able to detect elements in the range of parts per billion, however NAA has the drawback of requiring a small amount of the object in question to be sampled, although this can be as little as 50mg. The same kind of sampling of an object is required for PGAA, and it is not as sensitive as NAA with a sensitivity of parts per million. Very little sample preparation, if any, is required of PIXE or XRF, however the techniques have limited sensitivities, at best detecting elements at parts per million. With this knowledge it is possible to make an informed evaluation of the methods chosen for the present study, to be detailed further over the rest of chapter 3.

3.2 ICP-MS in numismatic studies

Unlike PIXE, x-ray microanalysis, and XRF analyses, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technology can detect elements that are present in the range of parts-per-million to parts-per-billion (Skoog *et al.*, 2007). LA-ICP-MS can generate data for almost any element, with the noteworthy exceptions of the gaseous elements and the majority of the halogens. The atoms making up the sample are ionised using a high temperature plasma which allows them to be separated and detected by their mass to charge ratio (Skoog *et al.,* 2007).

Until laser ablation was used as a sample introduction technique in the 1970s (Abercrombie *et al.,* 1978) and coupled to an ICP mass spectrometer in the 1980s (Gray, 1985), it was necessary for samples to be digested using acid dissolution. The advantages of using laser ablation for sample introduction include minimal damage to the sample (especially in comparison to using acid dissolution), minimal sample preparation and fast and easy generation of data (Skoog *et al.,* 2007). Coupling a laser ablation unit to an ICP mass spectrometer allows for an extremely sensitive analysis, data gained having been demonstrated to be comparable to data determined using techniques such as NAA, XRF, and solution ICP-MS (Speakman and Neff, 2005).

3.2.1 Trace elemental analysis for provenance determination

A method of chemical "fingerprinting" using LA-ICP-MS was initially developed by Watling et al. (1994) to determine the provenance of gold ores in Western Australia. The aims of this research were to enable the provenance of gold to be determined based on the premise that gold ores have unique trace element fingerprints based on the individual mineralising events in which they were created. It was found that both processed and unprocessed gold could be traced back to mine of origin (Watling *et al.,* 1994). This approach was found to have beneficial applications in investigating criminal activities in the forging, smuggling and theft of gold, as well as archaeological applications for gold artefacts (Watling, 1999, Watling *et al.*, 1994, Watling *et al.,* 1999, Watling *et al.*, 2005).

Guerra *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. Determining the provenance of ores using trace elements or lead isotope ratios is often difficult (or impossible) without damaging the sample. ICP-MS has the potential to allow several trace elements to be determined in a small sample with minimal destruction. Importantly, this makes provenancing of ores of precious metals possible in an archaeological context (Guerra *et al.,* 1999).

In one example of the application of this technology, a Viking gold torque was analysed and compared to a Viking gold ring, both found in the same field in Cambridgeshire, United Kingdom (Watling, 1999). It was found that the torque was most likely created from a single piece of gold in a single manufacturing process, whereas the ring was found to be made from seven different interwoven strands of gold. It was concluded that construction of strands of gold was more time consuming to make than a torque; as each strand was made and set aside, the molten alloy from which they were being created would have been progressively losing lead to the atmosphere, resulting in each strand having a different fingerprint (Watling, 1999).

The circulation of gold and silver in 17th Century Brazil has been investigated using a combination of LA-ICP-MS, NAA and proton activation analysis (PAA) (Guerra, 2004). A selection of gold and silver coins minted in Mexico, Peru, Guatemala and Chile were analysed and results compared to the composition of a selection of coins minted in Brazil. It was found that coins circulating in Brazil in the 17th Century were made from a mixture of precious metals from South and Central American sources outside of Brazil. The study also found that gold from different sources can be characterised by the platinum group elements, while silver from different sources is characterised by gold, indium and tin (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). This phenomenon can be caused by cooling and hammering of coin blanks as well as preferential copper corrosion from a silver/copper alloy. Sarah *et al.* (2007) argued that popular non-destructive analytical techniques such as XRF and FNAA can give unreliable results, XRF only being capable of determining the elemental composition of the outer surface of a coin and FNAA becoming unreliable when a coin has corroded and is particularly thin (<300µm). Alternatively, LA-ICP-MS can be used to analyse specific locations on the surface of the coin avoiding visible inclusions (Sarah *et al.,* 2007). LA-ICP-MS was also used in the study by to determine the concentration of silver and copper through depth profiles of ancient silver coins (Sarah *et al.,* 2007).

Ancient Chinese gold foil fragments were subjected to LA-ICP-MS in an attempt to determine “fingerprints” from very small samples, which can then help establish and support theories on historical, technical and stylistic relationships between objects (Brostoff *et al.,* 2008). The results of the research supported the theorised relationships and enabled the matching of corresponding fragments of gold foil to each other based on the “fingerprints” discovered

Celtic gold coins from the Middle Rhine and Moselle regions in Germany were analysed using LA-ICP-MS to determine the elemental composition of the alloy in order to trace changes in gold sources over time (Bendall *et al.,* 2009). LA-ICP-MS was used to identify those trace elements that showed the most variation (in this case: nickel, antimony and platinum). Isotopic data has confirmed that the amount of gold in the alloy used in Celtic coins can be determined, and that this information can be used to further differentiate between possible gold sources (Bendall *et al.,* 2009). These results indicated that possible sources for the gold used in Celtic gold coins include eastern Mediterranean and Alpine regions.

Analysis of Athenian style tetradrachms discovered in Israel using ICP-atomic emission spectrometry (AES) and ICP-MS was conducted by Ponting *et al.*(2011; Gitler *et al.,* 2009). The study aimed to determine whether the tetradrachms originated in Athens, or if they were imitations, by comparing the trace elemental composition of the 20 coins in question with the composition of Philistian coinage of the Persian period. It is concluded that the source of the silver used in the coins is Greek, most likely from the silver mines at Laurion in Attica, and that the coins are authentic Athenian tetradrachms, disagreeing with the visual assessment and identification of some of the coins as imitations (Gitler *et al.,* 2009; Ponting *et al.,* 2011).

3.2.2 Isotope ratios for provenance determination

A lead isotope database of various ore deposits with relevance to archaeological materials was created in by Stos-Gale *et al.* (1995). Lead isotope data had already been shown to be a successful indicator of provenance for archaeological artefacts of metal, glaze and glass, however lead isotope data in the geological literature had proved to have significant limitations when used for provenance determination of archaeological artefacts, as it was most often concerned with large, currently exploited ore deposits rather than smaller deposits that are no longer exploited. The aim of the study was to compile a comprehensive database of lead isotope ratios of a number of ores that were relevant to archaeological metal, glaze and glass. Ore samples were collected from a number of different sites and characterised using thermal ionisation mass spectrometry (TIMS) to create the database, which has since been expanded and can now be found online (Stos-Gale *et al.,* 1995; oxalid.arch.ox.ac.uk).

Laser ablation multi collector (LA-MC) ICP-MS was used on 14 Roman coins of known origin to create lead isotope signatures of particular Roman mints and workshops (Ponting *et al.,* 2003; Butcher and Ponting, 1997). The study aimed to use lead isotope signatures as a complementary tool to trace elemental analysis, as lead isotope analysis is capable of distinguishing between different sources of individual elements, where trace elemental fingerprints can become indistinct in the case of mixing or reuse of coins. The study found that lead isotope analysis on silver coins could provide a unique isotopic signature for individual mints (Ponting *et al.,* 2003; Butcher and Ponting, 1997).

Seventy-eight silver Roman *denarii* were analysed using both SEM-EDS with a subset also subjected to lead isotope analysis (Butcher and Ponting, 2005). The authors of the paper suggest that previous compositional studies on Roman coins (Walker, 1976) were flawed due to the non-destructive surface analyses employed being considered to be representative of the fineness of the entire coin. Butcher and Ponting argue that Roman silver coins have an artificially produced surface layer of silver created during manufacture, and so identify the need to re-analyse some of the same coins analysed by Walker (1976) with new analytical techniques in order to identify the source mints of silver coinage under the Judio-Claudian emperors. Through the combination of SEM-EDS and lead isotope analysis, it is found that a single mint, Lugdunum, minted *denarii* between c. 12 B.C. and 54 A.D. (Butcher and Ponting, 2005).

Provenance determination of Spanish, American, and European silver coins was conducted by Desaulty *et al.*, (2011) to determine if the isotopic abundances of silver could be added to the use of lead and copper isotopic ratios for provenance determination. By using multi-collector ICP-MS on samples in solution, Desaulty *et al.* (2011), determined the abundance of the isotopes of silver, copper, and lead of 91 antique, medieval and 16th to 18th century European silver coins. It was found that populations of coins from different origins and times can be separated from each other based on their isotopic abundances, and that the influx of American silver into Spain can be traced through isotopic data (Desaulty *et al.*, 2011). The conclusion of this study was that silver isotopes can be used to trace the provenance of coinage.

ICP-MS has been used in numerous archaeological studies, most frequently for trace elemental composition to determine the provenance of artefacts. While trace elemental analysis is reliant on the principle that refined and manufactured metals will retain a trace elemental fingerprint unique to the ore from which the metal is sourced, problems can arise when metals are mixed and reused. In some cases it has been shown that the elemental fingerprint of re-smelted metals becomes homogenous and identifying the origin of the ore using trace elemental composition is no longer possible. It should be noted that when metals are mixed and reused to such an extent that their trace elemental composition becomes homogenous, that this homogeneity will be limited to the time and place of the mixing and reuse. For example, the Spanish mints represented in this study minted silver from a combination of mines in the Americas, and so necessarily will have produced coins with a mixed trace elemental signature from those mines. However, this mixed trace elemental signature, while being unidentifiable in terms of mine of origin, will be unique to the Spanish mint where the coins were produced.

Trace elemental analysis can be effectively supplemented with isotopic information. In the case of silver, as silver is frequently found in lead ores and/or refined with lead, the abundance of the different isotopes of lead can be indicative of the origin of the silver, even when the trace elemental composition has been blurred through mixing and reuse of the metal. ICP-MS has been used to determine isotopic abundance in order to provenance artefacts, and to avoid problems in analysing inhomogeneous artefacts by only analysing specific parts of the surface of the artefact.

3.3 Electron microscopy in numismatic studies

Scanning electron microscopy is another non-destructive analytical technique, with minimal sample preparation for a conductive sample such as a coin. While scanning electron microscopy energy dispersive spectroscopy (SEM-EDS), with a detection limit of approximately one atomic per cent, is not as sensitive as LA-ICP-MS, it is capable of imaging the surface of a sample to a resolution of nanometres, and of mapping the elemental distribution on the surface of a sample.

Metallographic analysis of 128 late Roman coins using SEM-EDS has been used to investigate the method used to plate debased Roman coinage with silver (Vlachou, 2002). SEM-EDS was used to provide a metallographic analysis of the surface of the coins, revealing that the silver plating survived in only 43 of the sample coins. It was also found that the manufacturing process of these coins did not rely on surface enrichment of coins which already contained silver, but rather that the silver plated layer was an addition during manufacture (Vlachou, 2002). Based on this information, and the observed thickness of the layer, the more sensitive analytical technique LA-ICP-MS was chosen to further examine the silver plating. It was concluded that the method of manufacture of the silver plating observed on these coins was the application of silver amalgam, demonstrated through the presence of mercury in the coins (Vlachou, 2002). It was also found that precise preparation of the amalgam was necessary for the success of the silver plating, to give the coins a silver colour, while having very little if no silver at all, in the bulk of the coin (Vlachou, 2002). However these findings are not universally accepted, due in part to the small sample size in this study (Pappalardo *et al.*, 2012).

SEM-EDS was used to characterise forgeries of modern New Taiwan dollars, to enable identification of forged coins (Meng, 2002). It was found that separating genuine from forged coins was impossible with the naked eye, not even when the size and weight were taken into account. Secondary electron images were used to inspect fine details on the coins, detecting blurred and incomplete details in forged coins invisible to the naked eye, as well as circular tool marks on forged coins that were absent in genuine coins. Backscattered electron images were used to analyse the elemental distribution on the surface of the coins, indicating that forged coins can be identified based on small particles of lead and slightly higher ratios of copper than the genuine coins (Meng, 2002).

SEM-EDS, EDXRF and PIXE have been used to characterise medieval silver coins (Linke *et al.*, 2004). The research aimed to identify the provenance mint of silver coins from the Friesacher and Tiroler mints in Vienna. A total of 221 coins were analysed using EDXRF, SEM-EDS and PIXE, and it was found that based on trace elemental composition, they could be successfully assigned to their mint of origin. Linke *et al.* (2004) also outline the advantages and disadvantages of the three techniques used, namely that corrosion and high copper content affected results from SEM-EDS and EDXRF, with large differences observed between results of silver content from the two techniques, while PIXE trace elemental analysis was more successful.

A study of seven Spanish silver coins from the wreck of the *San Pedro de Alcantara* (1786) was conducted with the aim of characterising the corrosion mineralogy and metallurgy of those coins in their unique depositional environment (MacLeod, 2004). Using mosaics of backscattered electron images from SEM-EDS it was determined that the main corrosion product was bromian chlorargyrite (Ag(Cl,Br)), which correlated with studies conducted on the *in situ* corrosion conditions (MacLeod, 2004). It was also found that the abrasion of and damage to the surface of the coins was a result of the erosion and corrosion at the site along with impact with other artefacts (MacLeod, 2004).Five fragments of western Greek incuse coins were characterised using XRF, XRD, SEM, and optical microscopy (Giovannelli *et al.*, 2005). The aims of the study were to investigate the source of metal, the manufacturing process and corrosion of the coins. The metal came from at least two different ore sources, as evidenced by two distinctly different morphologies observed in the sample coins. Iron oxide inclusions in the coins would indicate that the metal was re-melted under a strong blast of air (Giovannelli *et al.*, 2005), a method which cannot be described as cupellation, which has been described in modern texts. Stress corrosion cracking along grain boundaries and non-metallic inclusions were indicative of corrosion of a metal that has been extremely work-hardened (Giovannelli *et al.*, 2005).

An investigation into the manufacturing technique of Roman Republic silver serrati (Figure 3.1) was undertaken using a number of analytical techniques (Kraft *et al.*, 2006a).

Figure 3.1 – Three of the investigated *serrati* (Kraft *et al.*, 2006a).

SEM was used to create backscattered electron image montages of the notches found around the perimeter of the coin. These micrographs were used to identify firstly, contemporary forgeries based on the thickness of the silver in the notches, and secondly, the method of production of both the genuine and forged coins. This information has led to an interpretation of the function of the notches on these coins as an attempt to prevent forgery (Kraft *et al.*, 2006a), a subject of considerable debate.

Imaging of British gold coins at the British Museum, including a gold mancus coin using SEM revealed some of the manufacturing procedures used to create the dies which were then used to strike the coin (Williams, 2009). The gold mancus coin from the 1st century CE was found in near mint condition, and when imaged using secondary electron imaging it was found that the coin had been die-struck. In addition to this, the coin was in such good condition that it was possible to see the inverse of die marks, which were indicative of the method of manufacture of the die itself (Williams, 2009). This information was confirmed by stylistic and historic analysis, indicating that the die was consistent with those made by a die cutter who normally produced dies for Canterbury (Williams, 2009).

Twelve Roman coins were analysed and characterised using a combination of energy dispersive x-ray fluorescence (EDXRF), time-of-flight neutron diffraction (ToF-ND) and SEM-EDS to determine if EDXRF data could be considered to be representative of a whole coin (Canovaro, 2013). It was found that due to changes in the surface over time, EDXRF results could not be considered representative of the bulk of the coin. Rather it was found that ToF-ND would be the most appropriate method for determining the composition of the bulk of the coin. This finding was supported by SEM-EDS analysis. Cross-section analysis using secondary electron and backscatter electron imaging showed the microstructure of the coins, indicating their original casting followed by some plastic deformation (Canovaro, 2013). This information was interpreted as representative of the use of a mould to solidify the metal into an appropriate shape, followed by the flan being hammered to the desired thickness, and finally heated and coined (Canovaro, 2013).

In order to investigate the applicability of SEM-EDS for characterisation of a modern silver piece, Papp and Kovacs (2013) analysed a 2006 special issue Serbian commemorative silver coin. It was found that some surface defects could be located and identified, and that the patterns of elemental distribution on the surface of the coin indicated that silver-rich and copper-rich areas were interdependent. Several micrographs were also taken of the coin's surface, showing small holes that are a result of the manufacturing process (Papp and Kovacs, 2013).

An investigation of the comparability of data obtained using SEM-EDS and XRF was conducted by Buccolieri (2014), using Greek silver coins from between the 5th and 3rd centuries BCE, to determine the reliability and how representative XRF surface analyses are of the whole sample, when that sample has corroded and possibly been affected by preferential copper corrosion at the surface leading to silver surface enrichment. The study found that these silver coins which had corroded in soil have a corrosion layer of less than 25µm, and suffer from silver surface enrichment of less than 1wt%, leading to the conclusion that in this case, XRF analyses of the surface of the coins will be indicative also of their bulk composition. It was also found that silver coinage in Greece had been debased from 97% silver to 80% silver over the time period studied, which corresponds to social changes during this time (Buccolieri, 2014).

Scanning electron microscopy has been used to both image and gain compositional information on coins in a number of studies. As can be seen in this section, the various capabilities of SEM are often employed together, such as backscatter and secondary electron imaging, as well as EDS elemental mapping. This enables a coin to be both imaged in very high resolution and compositional information to be gained along with spatial information. As detailed in the following section, SEM is also frequently used in combination with other analytical techniques such as LA-ICP-MS, EDXRF, PIXE, and ToF-ND. In these cases, SEM has been used to compare, confirm and complement results from other analytical techniques on the same sample coins. SEM is of particular use in determining provenance, method of manufacture and the effects of corrosion on coins, through both imaging and determination of composition.

3.4 Electron backscatter diffraction in numismatic studies

Electron backscatter diffraction (EBSD) is frequently used in metallographic studies to determine the method of manufacture of a metal. EBSD detects the crystal structure and orientation of a sample, and this information is indicative of how a metal has been worked.

EBSD was used by Wanhll *et al.* (2003) to determine the correlation between a silver object's antiquity, and it's embrittlement due to discontinuous precipitation of copper. The embrittlement of ancient silver has long been held to be indicative of an object's antiquity (Schweizer and Meyers, 1978). Wanhill *et al.* (2003) aimed to determine if silver embrittlement is indeed a marker of an object's antiquity, by using EBSD and SEM to analyse samples from the silver Gundestrup Cauldron, known to have been created during the Iron Age. It was found that discontinuous precipitation of copper from silver-copper alloys is less significant for embrittlement than remanent deformation caused during the manufacture of the object, and so is not necessarily a reliable indicator of a silver object's age (Wanhill *et al.,* 2003).

Two silver 15th century CE Timurid coins, one silver 9-10th century CE Samanid coin and one homogenous 95% silver, 5% copper sample were subjected by Northover and Northover (2012) to EBSD analysis in order to determine the method of manufacture of the coins. When investigated using optical microscopy, the coins' structures appeared to be that of an annealed metal. However, EBSD results showed deformation in the grains, indicative of cold striking (Northover and Northover, 2012). The study also investigated the question of discontinuous copper precipitation at grain boundaries as a marker of a metal's antiquity, but with no definitive conclusions given the small sample size.

A 1964 USA silver Kennedy Half Dollar coin was analysed using both EBSD and SEM-EDS by Chan *et al.* (2013) in order to demonstrate the benefits of simultaneous EBSD and EDS collection. EDS was used to map the elemental composition of the coin's cross-section, while EBSD was used to determine the grain size and crystallographic orientation. It was found that the crystallographic structures could only be differentiated when EDS and EBSD were performed simultaneously, rather than separately (Chan *et al.,* 2013).

The microstructure of cast silver has been investigated by Northover and Northover (2014) using optical microscopy, SEM, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), EDX and EBSD. The study aimed to characterise the microstructure of both ancient and modern cast silver-copper alloys, and to determine whether some microstructural features observed using optical microscopy such as twin-like structures and surface oxidation layers are a result of the manufacturing process or later exposure to heat. The study found that microstructures of cast silver-copper alloys are characterised by silver-rich dendrites with copper-rich areas due to intergranular precipitation (Northover and Northover, 2014). A wider range of microstructures was found in the ancient silver objects, supporting but not confirming the theory that such microstructural changes are due to time in the same way as has been proposed for wrought and annealed silver objects.

EBSD is used in numismatic studies principally for the investigation of microstructural grain size and orientation. This information is indicative of a coin's method of manufacture.

3.5 Electron probe microanalysis in numismatic studies

Electron probe microanalysis (EPMA) allows for quantitative elemental distribution mapping on a polished surface. In terms of numismatic studies EPMA is especially applicable to determining the surface and bulk composition of a coin, when the cross-section of the coin is analysed. The understanding of differences between the surface and the bulk of the coin can be used to assess the reliability of surface analytical techniques, to assess the level of corrosion, or to investigate manufacturing techniques that affect only the surface of a coin.

Six rare 'XI' and 'IA' Roman *radiates* coins from the reign of Tacitus (275-276CE) were analysed to determine their silver content (Esty *et al*., 1993). The coins were subjected to EPMA, Rutherford backscattering analysis (RBA), or EDX at the copper core of the coin. The core was exposed using a knife to avoid the silvered surface of the coins. EPMA analysis on two of the six coins revealed silver content comparable to results of RBA, but higher than that reported using EDX (Esty *et al.,* 1993). The study concludes that silver content in the copper core of similar coins is highly variable, which could be due to a number of reasons, including sample preparation and analytical technique used.

The production and use of ancient Roman forged silver coins was investigated using EPMA by Kraft *et al.* (2004), in combination with SEM and secondary ion mass spectrometry (SIMS). Four ancient Roman coins, dating between 200BCE to 200CE, known to be contemporary forgeries, were analysed. By quantitatively imaging the cross-section of the four coins, it was found that the counterfeit coins consisted of a base metal core, and had been plated with silver. The silver plated layer was found to be 100µm thick, and to overlap in places, indicative of foil silvering (Kraft *et al.,* 2004).

EPMA was further used by Kraft *et al.* (2006b) to map the elemental distribution of the entire surface of the four coins investigated in Kraft *et al.* (2004). It was found that it is possible to characterise even highly degraded coin surfaces in order to determine if they have been silvered, even when the majority of the silver surface has corroded. Silver residue was detected on the surfaces of the coins by using large 40µm step wise mapping (Kraft *et al.*, 2006b). The results give an indication of the method of manufacture of forged Roman coins, as well as a precise indication of areas on the coins' surface to be further investigated by other techniques.

Over 700 Tyrian shekels (tetradrachms) and half-shekels (didrachms) from the Isfiya and Qumran coin hoards, found in Israel, were analysed using XRF by Notis *et al.* (2007). The study aimed to produce results from a large number of coins in order to trace their silver content over time in terms of the social and economic context at the time. EPMA was used on four of the sample coins to verify that XRF analyses were representative of the entire coin (Notis *et al.*, 2007). The results of the study indicate that interactions between King Herod of Judea and Roman Emperor Augustus may be reflected in the silver content of the coins.

It can be seen that EPMA analysis on coins is mostly used to verify the reliability of other techniques, particularly techniques which are simpler, faster, or non-destructive. Also, EPMA has been used to provide quantitative elemental distribution maps of both the surface and the cross-section of coins in order to further understand the manufacture, use and corrosion of coins. EPMA is used in this study to provide quantitative elemental distribution information on the cross-sections of coins, in order to investigate the applicability of surface techniques to coins that have been corroded and may display silver surface enrichment.

3.6 Previous research on the Western Australian Museum's coin collection

The Western Australian Museum holds a collection of approximately 68,000 coins associated with ships wrecked off the Western Australian coast. As well as coins from the wrecks of the *Batavia* (1629), the *Vergulde Draeck* (1656), the *Zuytdorp* (1712), the *Rapid* (1811) and the *Correio da Azia* (1816), which are represented in this study, the museum also holds a small number of coins from the wrecks of the *Zeewijk* (1727), the *Belinda* (1824) and the *Elizabeth* (1839). The large collection of coins held by the Western Australian Museum provides a unique opportunity to create a database for comparison of individual coins to populations of coins representing different mints or different years of minting.

Research on the sample coins used in this study has mostly been limited to identification by Mr Stan Wilson† and Prof. Walter Bloom, numismatists at the Western Australian Museum.

Coins from the *Batavia* were identified and a detailed historical analysis was conducted (Wilson, 1989). In particular, the entire assemblage of identified coins was investigated in terms of its contribution to our understanding of the economy of the Holy Roman Empire, as well as how the relationship between the United Netherlands and Spain effected silver imports into the United Netherlands. The coins from the *Batavia* were compared with collections from other Dutch wrecks in order to investigate changes in the composition of coin cargoes over time in terms of country of minting.

Coins from the *Vergulde Draeck* were identified and described in detail in their historical context (Green, 1977). This included a brief history of minting technologies in Spain and the Spanish Americas the imagery on the coins, and the movement of silver from the Spanish Americas to Spain and on to the rest of the world as a trusted trade coin. Following this history is a comprehensive list of coins recovered from the *Vergulde Draeck* accompanied by photographs of each individual coin (Green, 1977). No further archaeological or numismatic analysis is entered into.

Numismatic evidence provided by coins from the wreck of the *Zuytdorp* was critical in identifying the wreck. Research by Stan Wilson of the Western Australian Museum and Dr Philip Playford, former Director of the Geological Survey of WA, found that the *Zuytdorp* and the *Belvliet*, which sailed with the *Zuytdorp* but reached Batavia safely, were carrying a special minting of 100,000 guilders worth of *paymenten*, or ‘small change’ coins ordered by the Zeeland chamber of the VOC on February 16th, 1711 (Playford, 1959). The presence of these coins in association with the remains of the ship was the strongest evidence when identifying the wreck (Wilson, 1985). As these coins were from a special minting, it was also possible to study the variation in dies used in the minting process over a single minting run. The deterioration of a single die, seen in several coins with successively larger imperfections caused by a growing crack in the die over time, was also traced (Wilson, 1985).

Lead ingots found with the *Zuytdorp* were subjected to isotopic analysis using multicollector (MC) ICP-MS to complement other analyses of form, weight and markings (van Duivenvoorde *et al.*, 2013). The study aimed to determine the provenance and manufacturing technique of the ingots in the context of 17th and 18th century metallurgical studies, with a particular focus on European trade of lead with Asia. By comparing the lead isotope composition of the ingots to the Oxford Archaeological Lead Isotope Database (OXALID) it was found that the ingots were consistent with lead originating from the north of England, specifically the Derbyshire, Cheshire and North Yorkshire lead mines (van Duivenvoorde *et al.,* 2013). These findings support historical records of well-established maritime trade between the VOC and England in the 18th century.

Coins from the *Rapid* were also identified by Wilson (1979), who concluded that from a numismatic perspective, the coins found were interesting, representing a cross-section of bullion moved from Mexico along with a few other coins that were most likely in the personal possessions of the crew. However, as they are common and heavily corroded, the coins themselves are worth little more than their value as scrap silver, with the addition of their value specifically as shipwreck coins (Henderson, 1979).

Limited excavation and recovery of artefacts has been conducted on the *Correio da Azia*, which has been mostly limited to recovering items visible on the sea floor. Coins from the *Correio da Azia* were identified by Bloom, but no further research has been undertaken (Souter, 2004).

Preliminary conservation of silver coins in the Museum’s collection to remove the concretion layer and restore the corrosion layer beneath has had mixed success; a study on optimal conservation of silver artefacts was undertaken by the Museum’s conservator Dr Ian MacLeod using coins from the collection sampled for this study (MacLeod and

North, 1979). In the study, previous conservation methods that remove the corrosion layer were discussed. These methods were; treating the silver coins with ammonium thiosulphate, thiourea-formic acid mixtures and citric acid followed by concentrated ammonia. As most of the information inscribed on a coin is preserved in the corrosion layer, methods such as those mentioned above are entirely unsuitable, as they destroy that layer as well as any inscriptions or die stamps, revealing the metal underneath which has not yet corroded. Treatment of the coins with zinc in sodium hydroxide, which reduces the amount of oxidised silver in the corrosion layer without destroying the rest of the layer, and electrolysis of the coins were studied as potential conservation techniques. However, they were both found to be somewhat costly, inefficient and time consuming (MacLeod and North, 1979).

A simpler, cheaper and quicker conservation technique has been found in the alkaline-dithionite method, in which the concretion layer is removed by placing the coin in 10-12% v/v hydrochloric acid solution for anywhere between 12 hours to one week, depending on the amount of concretion. Any concretion which remains after this treatment can be carefully picked off with a dental pick (MacLeod, 1982; Henderson, 1979; MacLeod and North, 1979). Treatment of coins now involves reduction of the silver corrosion products, which can be achieved by dissolving 40g of sodium hydroxide per litre of water, adding 50g of sodium dithionite per litre of solution and agitating the coins in an airtight container for one week. The coins can then be washed in water and brushed to remove any powdery deposits of silver remaining (MacLeod and North, 1979; Henderson, 1979). This method has been the principal method of silver conservation employed at the Western Australian Museum since 1979.

Further studies on this collection of coins by MacLeod (1982: 1984), focussed on the detection of contemporary forgeries. One of the coins found in association with the *Rapid* wreck was observed to have corroded through the milled edges of the coin to reveal a pink copper core. Subsequent investigation, by dissolving a 24mg sample of the core of the coin in 10% v/v nitric and tartaric acid, and analysing this solution using atomic absorption spectroscopy showed that the core material was 94.5% copper and only 2.18% silver which was probably contamination (MacLeod, 1982). The surface of the coin was also analysed using scanning electron microscopy. This methodology confirmed that the alloy used to cover the predominantly copper core had a higher copper to silver ratio than similar genuine coins found on the site. This alloy was compared to a 92.5% silver alloy from the Perth Mint, to which it corresponded very closely (MacLeod, 1982; MacLeod, 1984).

A similar study was undertaken on a coin in the Museum's collection from the *Batavia* wreck. The corrosion products from the coin in question were analysed using x-ray diffraction and scanning electron microscopy. The corrosion products were then dissolved in 5% v/v, nitric acid solution, 2% v/v hydrochloric acid solution and 1% v/v tartaric acid solution and analysed using atomic absorption spectrophotometry. The results indicated that the core, which had created these corrosion products, consisted of 45.5% silver, 29.3% tin, 10.1% copper, 7.8% lead, 3.2% zinc and small percentages of other metals. These results led to the conclusion that the coin was a contemporary 17th century forgery (MacLeod, 1984). The reason for a relatively high concentration of silver, considering that this coin is a forgery, is because this alloy has a lower melting point than a similar alloy with less silver, and so it would be possible to cast a coin blank using a standard wood fire without needing access to a furnace. To create the silver coating, the coin blank would have been dipped in an etching solution such as tartaric acid, dissolving the tin, lead and copper closer to the surface. This silver surface would then have been stamped with an impression of a genuine coin (MacLeod, 1984).

Silver coins recovered from the *Batavia*, *Vergulde Draeck*, and the *Rapid* were analysed using XRD and SEM as part of a study to identify the corrosion products that resulted from being submerged in seawater (MacLeod, 1991). The main corrosion products identified in the silver coins were chlorargyrite ($AgCl$) and some bromianchlorargyrite ($Ag(Cl,Br)$). As copper was used as an alloy in the silver, the corrosion mechanisms of copper were also investigated. It was found that since copper is more readily soluble than silver in the aerobic conditions of the wreck sites, copper was often lost to the surrounding environment as $CuCl_2^-$ or precipitated on the surface of coins in the form of cuprite (Cu_2O) or a basic copper(II) chloride. It was also found that sulphide ions produced by sulphate reducing bacteria found in iron concretions or deep sand cover produced silver and copper sulphides as a corrosion product. This information was combined with SEM imaging of the cross section of the concreted corrosion products from coins, and was used to determine that many of the coins were alternately buried and exposed many times after the vessel was wrecked (MacLeod, 1991).

3.7 Summary of justification of use of analytical techniques

For artefact analysis it has been observed that ideally an analytical technique will maintain the physical integrity of the artefact in question, but that the optimum choice is often a technique which takes a minute amount of material from a sample (Rehren and Pernicka, 2008). Conversely, depending on the research question, it is also often justifiable to take a sacrificial sample for destructive analysis, or indeed to destroy the entire sample, as this will invariably result in more detailed analysis, and the benefits of the new knowledge obtained may outweigh the destruction of the sample.

Analytical techniques used in this study reflect the above considerations. Laser ablation ICP-MS, SEM-EDS, and FIB-SEM are all relatively non-destructive techniques with the possibility of minimal sample preparation, depending on the information required of the sample. Solution ICP-MS is a destructive technique, and has in this case been used to verify LA-ICP-MS data. EPMA and EBSD analysis are both non-destructive techniques, but require extensive polishing of the sample surface to be effective, and so in this case have been used on a small number of samples that were allowed to be damaged.

3.7.1 LA-ICP-MS

LA- ICP-MS has been used in the present study as a relatively non-destructive surface analytical technique to determine the trace elemental composition of 403 coins. With a high sensitivity the technique is able to determine the trace elemental composition of the samples with minimal sample preparation or destruction. Trace elemental composition can be used to determine the provenance of a sample, and this is a primary aim for the use of the technique in this study. Further, the possibility of trace elemental composition as indicative of the year of manufacture of a silver coin and the potential for this technique to be used to absolutely date other artefacts, is explored in this study.

Analysis of coins using LA-ICP-MS, solution ICP-MS, SEM imaging and EPMA has been done to investigate how representative surface LA-ICP-MS analyses will be of inhomogenous, corroded coins, and is detailed in chapters five, six, and seven.

3.7.2 Solution ICP-MS

Solution ICP-MS has been used in the present study to determine if data from surface analyses can be considered representative of the entire sample. In this case, 12 samples which were allowed to be destroyed have been analysed using both LA-ICP-MS and solution ICP-MS. The correlation between the two sets of data will indicate if LA-ICP-MS data from the surface of a sample can be used as representative of the bulk of the sample.

3.7.3 SEM-EDS

SEM-EDS has been chosen as a non-destructive technique in the present study to image the surface of coins, and to create quantitative maps of the elemental distribution on their surface. Standard optical microscopy with etching was not used for this study as copper and silver are optically isotropic and do not change much in colour using a polarised light microscope, and rarely provide new information outside of corrosion studies (Scott, 1991).

The elemental distribution of 30 coins has been determined in order to investigate the homogeneity of the coins, and further determine if LA-ICP-MS compositional data can be considered to be representative of the entire sample. The distribution of elements other than silver, in particular copper, has also been investigated to determine whether the morphology of the copper-rich phases is indicative of provenance or method of manufacture of a sample. This information would be lost with compositional analysis alone.

3.7.4 FIB-SEM

FIB-SEM has been chosen for this study as a relatively non-destructive analytical technique to further investigate the elemental distribution of one coin in three dimensions. The FIB-SEM allows an area of approximately 10μm^3 to be imaged and modelled, so that features such as copper-rich phases, surface porosity, silver grain size and stress and deformation on the surface of the coin can be observed. This information adds to the elemental distribution information gained from SEM-EDS analysis.

3.7.5 EPMA

EPMA has been used in the present study for five samples which were allowed to be destroyed to further the analysis undertaken using SEM-EDS, with lower detection limits and larger areas able to be mapped according to elemental distribution. Sample coins were prepared and analysed on their cross-sections in order to determine the effect corrosion and conservation has had on the surface of a coin compared to the bulk of the coin. In this way surface analysis for both elemental composition and elemental distribution can be appraised.

3.7.6 EBSD

EBSD was used to determine the crystal structure and orientation of seven samples in the present study, which in metallography is indicative of the way a metal has been manufactured. For this study, EBSD has been used to determine the manufacturing technology used to mint coins, to complement provenance and dating results.

Chapter conclusion

As demonstrated, while a single analytical technique certainly has its benefits as to what can be learnt from a sample, it is ideal to use complementary techniques to explore different aspects of an artefact’s manufacture and use, while also verifying and corroborating results from other analyses. It is also of importance to consider the value of information that can be gained from destructive, semi-destructive or non-destructive analysis. Ideally a combination may be used in order to gain the most information from a selection of artefacts.

In this study, while trace elemental compositional analysis would have successfully determined the provenance of coins of unknown origin further analytical techniques have been used to investigate the appropriateness of surface analyses, as well as compositional analyses, while also providing further information in terms of the manufacture of a coin.

Chapter 4 – Methods

Chapter introduction

This chapter details the analytical methodology used in analysis for this study. From centuries submerged under water, through to recovery, stabilisation and conservation, to scientific analysis for the present study, the silver in this study has been subjected to a number of processes which are significant to how the collection can be studied. Understanding the depositional environment, recovery and conservation of an artefact is integral to designing and implementing an effective research plan. In this case, the depositional environment resulted in many of the samples being heavily corroded, and so as well as research determining bulk, minor and trace elemental composition, and elemental distribution and microstructure, research has also been conducted to ascertain how representative non-destructive surface analyses will be on such samples.

4.1 LA-ICP-MS

4.1.1 Sample preparation

All coins were spot cleaned in order to remove surface contaminants before being analysed. Previous cleaning by the Western Australian Museum had consisted of 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 it being relatively clean and flat, which 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 for sample preparation removes the patina and may result in some visible damage to the coin. LA-ICP-MS analysis removes material from the sample coins which means that some damage to the coins is inevitable. A halo can be seen around the laser crater, consisting of debris of silver argide, and is easily wiped off the coin. Damage from the laser is almost invisible to the naked eye and consists only of the laser crater itself. The crater is approximately 50µm deep and 75µm in diameter (Figure 4.1).

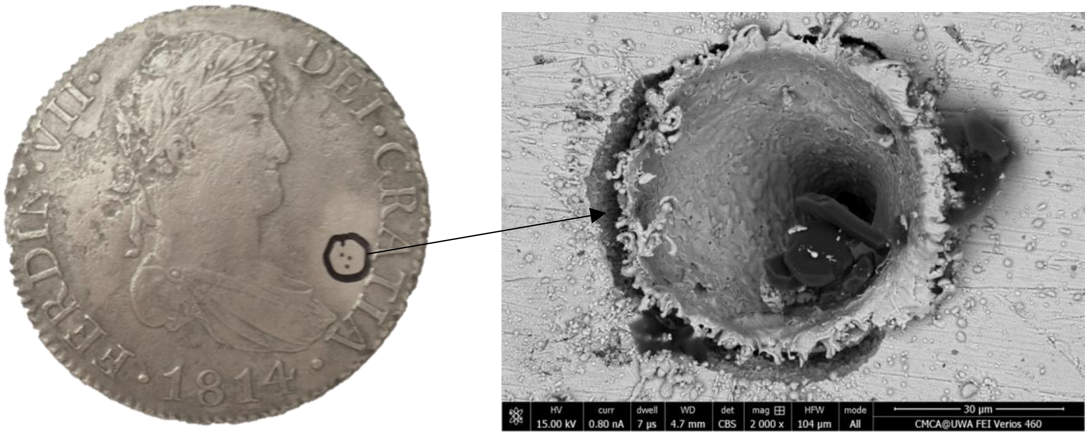


Figure 4.1 – Damage caused by LA-ICP-MS preparation and analysis

4.1.2 Instrumentation and parameters

LA-ICP-MS was undertaken using a New Wave Research Co. Ltd. (Cambridgeshire, England) UPI 213nm Nd:YAG laser system coupled with an Agilent Technologies (Tokyo, Japan) 7500cs inductively coupled plasma mass spectrometer. A generic set of conditions under which the laser ablation occurred are summarised in Table 4.1.

It should be noted that analytes consistently registering below 100 counts per second have not been included in the results. This count rate is approaching the detection limit of the instrumentation, a point where by definition the precision of the signal exceeds +/-50%. Consequently the exact values for signals in this region should only be used as indicative and not be included in the algorithms used to interpret data.

Table 4.1 - LA-ICP-MS Operating Conditions

Laser	213nm Nd:YAG
Spot Size	50µm
Pulse Rate	6Hz
Ablation Mode	Single spot
Laser Power	60%
Ablation Time	30 seconds

The isotopes used in this study are detailed in Table 4.2. These analytes were chosen as they are representative of the different trace elements present in the ore from which the silver was recovered. Factor analysis and discriminant analysis, detailed further in chapter five, confirm that these analytes are most indicative of separation between populations of coins from different mints of origin. Statistical analysis of analytical results has also been performed on subsets of these 38 analytes, based on the mineralogy of the relevant ores, the correlation between surface and bulk analyses, the reported accuracy and precision of LA-ICP-MS for each analyte, and factor analysis of the 38 analytes presented here.

Table 4.2 – Isotopes used in this study

^{9}Be	^{23}Na	^{24}Mg	^{27}Al	^{31}P	^{39}K	^{44}Ca
^{48}Ti	^{51}V	^{52}Cr	^{55}Mn	^{57}Fe	^{59}Co	^{60}Ni
^{64}Zn	^{65}Cu	^{75}As	^{82}Se	^{85}Rb	^{88}Sr	^{89}Y
^{90}Zr	^{93}Nb	^{98}Mo	^{103}Rh	^{108}Pd	^{111}Cd	^{115}In
^{120}Sn	^{123}Sb	^{126}Te	^{138}Ba	^{195}Pt	^{197}Au	^{202}Hg
^{208}Pb	^{209}Bi	^{238}U				

The accuracy and precision of LA-ICP-MS for determining concentrations of 48 elements has been investigated using six different certified reference materials (Bodnar and Fedele, 2012). NIST standard 610 was used as a reference to assess the accuracy and precision of LA-ICP-MS analysis. USGS standards BCR-2G, BHVO-2G, BIR-1G, NKT-1G and NIST standards NIST612 and NIST614 were analysed as “unknowns”. Accuracy was assessed by comparing the elemental abundances predicted by analyses with the “known” values. A summary of the accuracy (average percentage error) and precision (percentage relative standard deviation) of elements used in the present study that were reported by Bodnar and Fedele (2012) is given in Table 4.3.

Table 4.3 – Summary of the accuracy and precision of LA-ICP-MS analyses on analytes used in this study

Element	Precision RSD%		Accuracy x̄ error %	
Be	1.82	20.62	-24.18	14.37
Na	0.26	0.72	-5.20	3.11
Mg	0.30	4.77	-10.27	1.65
Al	0.35	4.41	6.48	13.2
K	0.34	1.17	-15.85	14.37
Ca	0.39	2.51	-6.91	5.25
Ti	0.38	7.23	-91.49	-329
V	0.18	6.47	-5.62	-1.16
Cr	0.27	4.65	-25.19	-2.06
Mn	0.24	4.12	-15.4	-0.58
Fe	0.29	1.39	-32.96	-4.67
Co	0.82	1.47	-2.34	8.72
Ni	2.44	16.75	-4.04	47.41
Cu	1.84	4.31	-14.06	11.06
As	0.14	25.71	-10.46	NA
Rb	0.61	18.71	-15.93	8.56
Sr	0.39	2.78	-8.56	6.97
Y	1.50	6.94	-20.49	10.41
Zr	1.02	4.06	-17.78	10.89
Nb	0.45	6.75	-12.28	-3.51
Sn	0.62	17.46	-65.51	-7.68
Sb	0.72	27.67	-73.53	4.85
Ba	0.58	1.32	-5.03	5.90
Au	3.88	67.86	-9.95	-2.59
Pb	1.05	3.07	-0.80	14.01
U	0.83	99.42	-3.09	66.78

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 via the instrumentation's camera and display prior to analysis for inclusions.

4.1.3 Data interrogation

The LA-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 ten samples a NIST 610 glass standard was analysed to facilitate retrospective normalisation of the data for instrumental drift. 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, unsuccessfully. Approximately ten seconds of instrumental gas blank were collected prior to each analytical run to allow for background correction.

Laser ablation ICP-MS results are presented in the form of counts per second. Using certified reference materials it is possible to quantify these results, however they can also be used in terms of comparison of inter-elemental ratios.

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

Subsets of analytes were chosen for further statistical analysis. These subsets were chosen based on mineralogy, a comparison of the surface and bulk of corroded silver, the accuracy and precision of LA-ICP-MS analysis, and factor analysis. Elements that are most indicative of a silver ore or mine were chosen based on information detailed in section 2.3.1. Elements were also chosen that have been found to be in consistent concentrations ($r>0.8$) from the surface to the bulk of corroded silver, as detailed in section 5.1, while those with little or no correlation ($r<0.2$) have been excluded. Finally, factor analysis on all of the analytes and relevant populations of coins has been taken into account, limiting elements chosen for further statistical analysis to those which are most indicative of separation between assigned populations.

Linear discriminant analysis (LDA) requires the user to assign the data to separate groups, in this case 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 maximise between-population to within-population differences using factor analysis. Factor analysis was used over 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 based on their entire elemental composition. Sample are plotted on the x and y axes by being “pulled” in the direction of the vectors which represent the different analytes that each sample is composed of. In order to identify the probability that the assigned groups of data are correct based on similarities in their elemental composition a number of validation samples per analysis is 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 based on their elemental composition, with a percentage confidence assigned to their belonging to any particular population.

4.2 Solution ICP-MS

4.2.1 Sample preparation

The Western Australian Museum allowed small (<0.5g) clippings of non-display quality silver artefacts to be taken and destructively analysed. The clippings were sealed in test tubes with 5mL of deionised water and 5mL of nitric acid. The test tubes were placed in a water bath on a hot plate until the silver dissolved, when the tubes were unsealed, to allow the solution to evaporate to a volume of 2-5mL. The solution was then diluted to a volume of 20mL with deionised water, 1.2mL of HCl was added to the solution to precipitate the silver from the solution as silver chloride, and 10mL of solution was then pipetted from the test tubes to use for solution ICP-MS analysis.

4.2.2 Instrumentation and parameters

Solution ICP-MS was undertaken using a Fisons Instruments (Ipswich, United Kingdom) PQIII Turbo Plus PlasmaQuad 3 ICP-MS system.

4.2.3 Data interrogation

Two ‘blanks’ were included in analysis to monitor the reliability of the results. These blanks were prepared with the samples, but no sample material was added during preparation.

Solution ICP-MS results are presented in the form of parts per billion or parts per million. Parts per million data were converted into parts per billion, to achieve uniformity. Where appropriate, solution ICP-MS data can be converted to percentage.

Solution ICP-MS data were compared to LA-ICP-MS data from the same samples to determine if a strong enough correlation exists between the two sets of data, and if results determined using LA-ICP-MS from the surface of a sample could be considered representative of the bulk of the sample. This was performed using the computer program Excel’s correlation coefficient capabilities.

4.3 SEM-EDS

4.3.1 Sample preparation

Coins were affixed directly to the sample stage inside the instrument using carbon tape.

For FIB-SEM, after the coin is inserted in the instrument, the remaining sample preparation is done using the instrument. Prior to analysis, samples were mounted in resin and polished to 1µm fineness, using Struers polishing LaboPol-5, with 10-1µm diamond paste and colloidal silica in suspension and ethanol in order to analyse the bulk of the sample. A second sample was analysed with no preparation in order to investigate the surface of the coin. Inside the instrument a layer of protective platinum is laid on the surface of the coin where analysis will take place, and trenches are created around the area of interest to contain debris. A platinum ‘x’ is also laid onto the surface of the coin to allow the instrument to correct for drift during analysis.

4.3.2 Instrumentation and parameters

Scanning electron microscopy was undertaken using a FEI (Oregon, USA) Verios XHR SEM equipped with an array of in-lens, in-column, and chamber detectors, bright field, dark field and high angle annular dark field STEM detectors, and an 80mm^2 Oxford Instruments (Oxfordshire, England) X-Max SDD EDX detector for microanalysis. The beam current for both imaging and mapping was 0.8nA with an accelerating voltage of 20kV. Working distance was 5.5mm. EDS mapping acquisition time was 10 minutes.

4.3.3 Data interrogation

Data from standards is stored in the Oxford Instruments computer program AZtec. This program is used to facilitate energy dispersive spectroscopic elemental distribution mapping of a sample. By comparing the spectra detected from the sample to those in the AZtec database, it is possible to quantify the results of analysis.

SEM BSE images are greyscale images, with lighter areas corresponding to elements with higher atomic numbers, and darker areas corresponding to elements with lower atomic numbers.

Having visually identified an area of interest using the SEM that is representative of the coin and free of visible contaminants, spot and area quantification can be conducted. Quantitative results are presented as percentage composition, and the AZtec software can display results, in atomic percentage, wt%, and normalised to 100%. Wt% was used for this research.

Elemental distribution is possible using energy dispersive spectroscopy. EDS results are presented in the form of X-ray spectra. Characteristic peaks on the spectra can be used to quantify the elemental composition of the area in question. Qualitative elemental distribution mapping is presented overlaid on BSE images in coloured maps representing different elements on the sample surface in this study.

Data normalisation was conducted using the computer program AZtec.

4.4 EBSD

4.4.1 Sample preparation

Seven scraps of coins of poor quality were allowed to be used for destructive analysis by the Western Australian Museum. All seven scraps were found in or around the *Vergulde*

Draeck shipwreck. They have been identified as scraps of eight *reales*, with one identified as originating in Mexico. The scraps were embedded in resin then ground and polished perpendicular to their surface in order to investigate their polished cross-sections. The samples were polished to 1µm fineness, using Struers polishing LaboPol-5, with 10-1µm diamond paste and colloidal silica in suspension and ethanol.

The same scraps were further prepared by precision cutting with a diamond saw, mechanical polishing down to 0.4µm fineness using colloidal silica and finally broad angle ion beam polishing by a Leica machine for 20 minutes with a 4 kV beam operating at ~10° glancing angle.

4.4.2 Instrumentation and parameters

Electron backscatter diffraction analysis was undertaken using a Tescan (Brno, Czech Republic) MIRA3 FESEM equipped with an Oxford ENSD. The instrument was operated at 20kV and 15nA. EBSD data were collected using an Oxford Nordlys system and optimized at 25ms per frame, and data were acquired using Oxford Instruments AZtec 3.0 software, and post-processed with Channel 5.12 software.

Samples were placed in the instrument at a 70° tilt, 19.9mm working distance, with a beam intensity of 20kV.

4.4.3 Data interrogation

Electron backscatter diffraction patterns are presented as coloured maps. Different colours represent different angles of orientation in the crystal structure of the sample. Data is detected in x, y and z planes, with a different image for each plane. A fourth image represents a combination of the crystallographic information from the x, y and z images. Data normalisation is conducted using the computer program AZtec.

4.5 FIB-SEM

4.5.1 Instrumentation and parameters

FIB milling and SEM imaging were performed on a FEI (Oregon, USA) Helios Nanolab G3 CX DualBeam^{TM} instrument using Auto Slice and View software. The milling and imaging parameters were optimised to suit the type of sample. Regions of interest were covered with a protective (about 1µm thick) platinum layer, then front and side trenches were milled with a 10nA Ga$_{+}$ ion beam. The front face of the region of interest was then cleaned and polished using a 2nA beam current. Imaging was performed at 2kV using the through lens detector in backscattered mode in order to minimize charging effects and maximize the contrast between metallic phases of differing masses. Sequential slices were milled with a 0.79nA Ga+ beam current, and the slice spacing was 10nm. Each newly milled face was imaged (4096×3536 pixels) with an image capture time of ~200nanoseconds with 16 line integration to obtain images of high enough quality for subsequent three dimensional reconstruction.

4.5.2 Data interrogation

The FIB-SEM instrument automatically acquires raw data using a built in program called Auto Slice and View, by milling and imaging continuous slices of material from the sample. The data set of images is presented in tag image file format (TIFF).

The TIFF images were imported into AVIZO 8.0 where the images were stacked, aligned, cropped and filtered (de-noised). The resulted volume was segmented allowing 3D models of the copper inclusions associated with the silver matrix to be produced. The models were visualized and rendered in AVIZO 8.0, and images were captured from multiple orientations in 3D space. Avizo enables visualisation of the series of images in three dimensional rendered models and animations.

4.6 TEM

4.6.1 Sample preparation

TEM specimens were prepared using a FEI Helios DualBeam™ instrument. Prior to FIB milling the thin sections were examined by SEM to gain an understanding of the distributions and morphologies and to select the most appropriate targets for detailed study. Thin specimens were, on average 15μm×8μm×100nm and were attached to Omniprobe® copper TEM grids.

TEM sample preparation was also performed using ultramicrotomy. Twenty nm thin sections of a coin were prepared using Leica EM FC7 microsystem with Diatome diamond knives and attached to holy carbon TEM grid. Prior to microtoming the thin sections were examined by light microscopy, to select the most appropriate targets for TEM sample preparation.

4.6.2 Instrumentation and parameters

TEM data were obtained using a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM elemental X-ray mapping technology operating at 200kV. Data included high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images, EDS (ChemiSTEM) maps, and electron diffraction for phase identification.

Crystallographic information can be obtained by TEM using selected area electron diffraction (SAED). In SAED the selected area aperture is used to select numerous randomly oriented grains/crystals to obtain their diffraction patterns. The diffraction pattern produced from polycrystalline material will consist of rings sampling all possible diffracting planes. It is possible to estimate the grain sizes by measuring the width of the rings and to also obtain information about texture (preferential orientation) in the sample. This technique can be used on samples with grain sizes in the range of 100nm-2µm.

4.6.3 Data interrogation

Standard data is similarly stored in the FIB-SEM instrument's computer program Auto Slice and View. This program allows automation of data acquisition and primary data.

4.7 EPMA

4.7.1 Sample preparation

The same seven scraps of coins that were used for EBSD analysis were also used for EPMA analysis. The scraps were embedded in resin then ground and polished perpendicular to their surface in order to investigate their polished cross-sections. The samples were polished to 1µm fineness, using Struers polishing LaboPol-5 with, 10-1µm diamond paste and colloidal silica in suspension and ethanol. The mounted samples were then carbon coated.

4.7.2 Instrumentation and parameters

EPMA compositional analyses were performed on a JEOL (Tokyo, Japan) 8530F Hyperprobe equipped with 5 tuneable wavelength dispersive spectrometers. The operating conditions were 40° take-off angle, and beam energy of 20kV. The beam current was 80nA and fully focussed.

The analysing crystals used to determine elements are detailed in Table 4.4.

Table 4.4 – Analysing crystals used and analytes determined in EPMA analysis

Analysing crystal	Analytes
LiF	Bi Lα, Au Lα, Pt Lα, Sb Lα, Te Lα
LiFH	Zn Kα, Cu Kα, Ni Kα, Fe Kα
PETJ	Ag Lα, Sn Lα, Pb Mα

The counting time was 30 seconds for Cu Kα, Ag Lα and Pb Mα, and 60 seconds for Zn Kα, Bi Lα, Ni Kα, Fe Kα, Sb Lα, Te Lα, Au Lα, Sn Lα, and Pt Lα.

Spot scans were performed on areas of interest, as well as spot scans traversing the cross-section of the coins at 10µm or 50µm intervals, in order to understand the varying composition.

For quantitative analysis and imaging, areas were scanned at different magnifications, 130×, 330×, 450×, 650× and 1000×. Areas chosen were deemed to be representative of the bulk of the sample in terms of visible ratios of silver to copper phases and the avoidance of significant inhomogeneities and other inclusions. Alternatively, when analysed at lower magnifications (130× and 330×), areas were chosen as representative of the corrosion layer and the bulk of the core of the sample, or as the cross-section of the sample.

Map acquisition utilised a 150nA beam current with a 0.5×0.5µm pixel dimension for smaller areas at higher magnification, and at, 1 µm ×1µm pixel dimension for larger areas at lower magnification, at 200msec dwell time per pixel.

4.7.3 Data interrogation

Certified primary standards were analysed alongside samples using EPMA, with total wt% of the standards being reported at 100%, giving an indication as to the reliability of the results of analysis of the coin scraps. The standards used are detailed in Table 4.5.

Table 4.5 – Standards used for EPMA analysis, and the analytes they were used to detect

Standard	Used to detect
Galena	Pb Mα
Silver	Ag Lα
Copper	Cu Kα
Nickel	Ni Kα
Bismuth	Bi Lα
Platinum	Pt Lα
Antimony	Sb Lα
Iron	Fe Kα
Cassiterite	Sn Lα
Zinc	Zn Kα
Gold	Au Lα
Te metal	Te Lα

EPMA results for spot and line scans are presented in both weight and atomic percentages in an Excel spreadsheet.

Five quantitative elemental maps are generated per imaged area. Four of the maps represent the wt% of a given analyte, in this case Cu, Ag, Pb, and Zn. The fifth map represents the total wt% data for the imaged area.
Mean atomic number background corrections were employed throughout (Donovan & Tingle, 1996). Unknown and standard intensities were corrected for dead time and the ZAF algorithm utilized for matrix absorption (Armstrong, 1988). On peak interference corrections were applied to Sn for interference by Ag, and to Pb for interference by Au, Fe, and Pt (Donovan *et al.*, 1993). Detection limits ranged from 0.004 wt% for Fe Kα, to .010 wt% for Cu Kα, to 0.010 wt% for Sn Lα, to 0.028 wt% for Te Lα, to 0.113 wt% for Bi Lα.

Quantitative chemical maps were acquired using the calibration set up described above for Cu, Ag, Pb, and Zn. Detection limit maps were acquired for these elements and applied as the minimum cut-off values for all maps.

Data were processed using CalcImage software package and output to Surfer® for further processing and enhancement.

The size and shape of copper-rich particles in samples were characterised using the ImageJ computer program. Images were adjusted for brightness and contrast to isolate the copper-rich phases, which were then measured and characterised using ImageJ's 'analyse particles' function.

Further, using results from area and line scans, the silver/copper ratio was determined across the cross-section of a sample and plotted, to determine if there exists any significant difference between the composition of the interior of a coin and its surface.

Chapter 5 – Results of ICP-MS

Chapter introduction

This chapter details results of analysis undertaken using ICP-MS methods. Firstly, solution ICP-MS and LA-ICP-MS analyses from the same selection of samples were compared to ascertain how representative surface LA-ICP-MS analyses could be considered of the composition of the bulk of a coin. Secondly, trace elemental analysis using LA-ICP-MS was used to determine the provenance of unidentified coins, and also a selection of silver artefacts from the *Batavia.* Lead isotope analysis has also been performed for provenance studies of silver coins in this study, to provide a comparison with a previously published paper by Desaulty *et al.,* (2011). Finally, a study into the use of trace elemental composition for absolute dating of silver coins is detailed.

5.1 Representability of LA-ICP-MS surface analysis of the bulk of an artefact, a comparison with solution ICP-MS

5.1.1 Aim

Non-destructive surface analysis of items of cultural heritage significance is generally preferable to destructive, more sensitive analyses, as the preservation of a historic object for future research is of utmost importance. In terms of this study, LA-ICP-MS was chosen as a technique to determine trace elemental composition of silver coins as it is relatively non-destructive. However, it was necessary to determine if LA-ICP-MS surface analyses could be considered to be representative of the entire artefact, in particular considering that the artefacts in question have been submerged in seawater for some centuries, and it is expected that their surface will have been affected by corrosion and the preferential leaching of some metals from the surface. This is a particular concern as it has been demonstrated that in silver/copper alloys copper will leach preferentially from the surface of the metal leading to silver surface enrichment (Beck *et al.,* 2004; Borges *et al.,* 2016). Silver surface enrichment occurs through both corrosion processes and as a deliberate manufacturing technique to increase the silver content on the surface of coins in the ancient (Butcher and Ponting, 1995) and medieval worlds (McLees, 1994). Based on accounts and records of minting procedures and technologies at the mints in question, it would seem unlikely that the coins in the present study were subjected to anthropogenic silver surface enrichment, and that any silver surface enrichment observed would be the result of corrosion processes.

A selection of artefacts was subjected to both LA-ICP-MS analysis and solution ICP-MS analysis in order to determine how representative the data from LA-ICP-MS, a technique which penetrates up to approximately 75µm into a sample's surface, is compared to solution ICP-MS, a technique which provides absolute elemental concentrations from a larger area of the sample (between 0.6g and 0.9g of each sample were put into a final solution of 10mL).

As quantitative data for LA-ICP-MS analyses were not necessary to carry out this study, determining the correlation coefficient for each analyte was chosen over a paired two sample t-test, which has been used to compare solution ICP-MS and LA-ICP-MS in other studies (Phung *et al.,* 2013; Ludsin *et al.,* 2006).

5.1.2 Results

Data for 37 analytes were taken from 18 silver artefacts using both LA-ICP-MS and solution ICP-MS. A scatter plot detailing the correlation for each analyte between LA-ICP-MS counts per second data and solution ICP-MS parts per billion data is given in Figure 5.1.

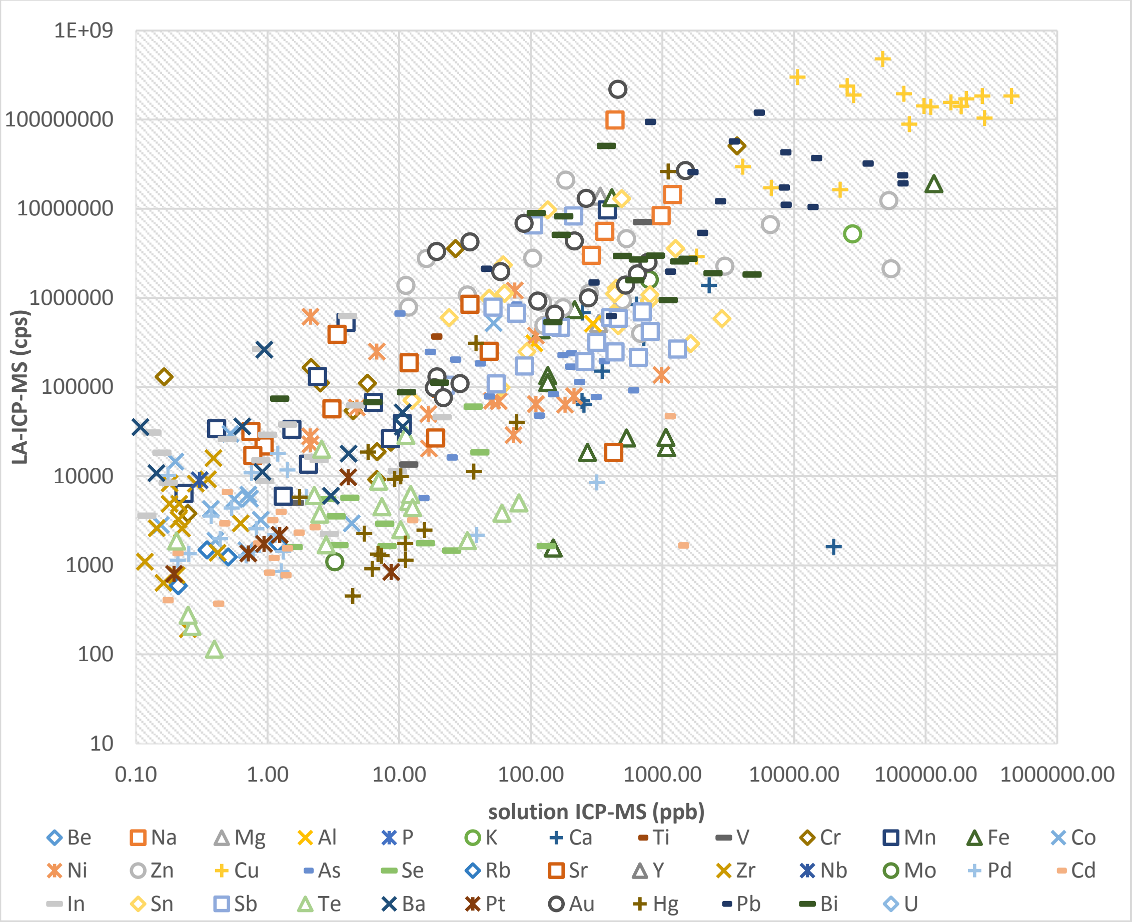


Figure 5.1 – Correlation between LA-ICP-MS and solution ICP-MS from 37 analytes for 18 samples.

Overall, a positive correlation between LA-ICP-MS and solution ICP-MS results can be seen, with a sample correlation coefficient r value of 0.54. At a 99% confidence level, 0.54 falls between the lower (0.483) and upper (0.584) values of r, to reject the null hypothesis.

H0: ρ=0 (that there is no correlation between LA-ICP-MS surface analyses and solution ICP-MS bulk analyses).

(With a sample size of 666, there are 664 degrees of freedom, the test statistic (t), $t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}} = \frac{0.54\sqrt{666-2}}{\sqrt{1-0.54^2}} = 16.53$. This gives a P-value of less than 0.0001, and so the null hypothesis is rejected.)

The correlation coefficient r value between LA-ICP-MS and solution ICP-MS results for individual analytes was also determined and is detailed in Figure 5.2.

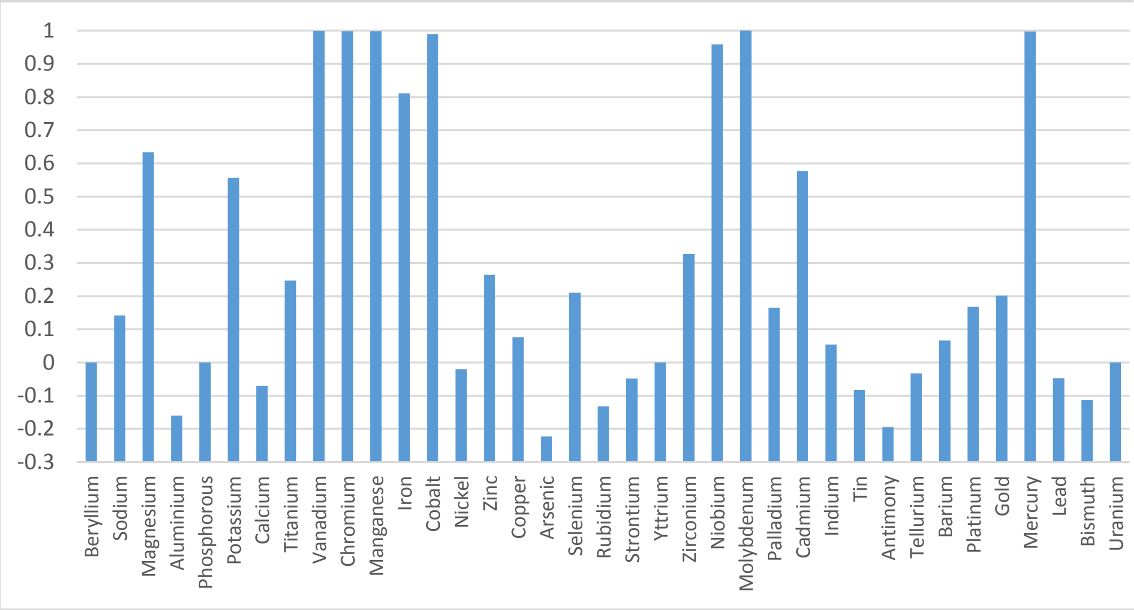


Figure 5.2 – Correlation coefficient r value for individual analytes.

Correlation coefficients above 0.8 were found between results for vanadium, chromium, manganese, iron, cobalt, niobium, molybdenum and mercury, while correlation coefficients below 0.2 have been found for beryllium, aluminium, calcium, nickel, copper, arsenic, rubidium, strontium, yttrium, indium, tin antimony, tellurium, lead, bismuth and uranium. It should be noted that copper, which has a relatively high content in comparison to the other elements, detected at approximately 1-4wt%, has low correlation reported between solution ICP-MS and LA-ICP-MS results, which may be indicative of a disparity between copper content at the surface of the samples and at the bulk. This may be due to preferential copper leaching at the surface of the samples, and may also explain some of the other analytes with low correlations.

5.1.3 Conclusion

A comparison of results of analysis conducted using LA-ICP-MS and solution ICP-MS has detailed that surface analysis using LA-ICP-MS on corroded silver coins can be considered to be representative of the bulk of the coin for a selection of analytes. Overall, statistical agreement between the two methods is good for vanadium, chromium, manganese, iron, cobalt, niobium, molybdenum and mercury. However, a number of analytes show poor correlation, which would be indicative of differences between the two techniques used, or of the difference between the surface and bulk composition of the coins. The differences between surface and bulk composition of the coins is detailed further in sections 6.1 and 7.1. This information is used to inform the choices of analytes used in subsequent analyses on the collection of coins.

5.2 Provenance determination of coins using trace elemental composition

5.2.1 Aim

The aims of this study were to apply a method of provenance determination for these coins using a method that has already been applied to similar archaeological materials. The method makes use of the inter-element association patterns of multi-element analytical data determined using LA-ICP-MS.

Most of the coins used had already been successfully identified by their mint markings by the Western Australian Museum numismatists. The data from LA-ICP-MS analyses of 399 coins, together with what is known about the coins through visual identification, were used to create a database to characterise the trace elemental composition of different mints. The trace elemental composition of coins that could not be visually identified could be compared to the database and their provenance mint identified.

The interpretation of the linear discriminant analysis (LDA) was used to identify the place of minting of coins which have previously not been identified. This was based on the statistical comparison of the trace elemental composition of unidentified coins against a database of the compositions of silver coins of known provenance.

5.2.2 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 which 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 that the coins are made up of. Pre-identified populations of coins, in terms of country or mint of origin, are plotted in such a way as to maximise separation between populations based on their elemental composition. It is worth noting that the vector a coin has plotted on, in relation to the centre of the plot, is what is particularly indicative of the population it belongs to, rather than its x,y coordinates. Coins of unidentified origin can then be included in the algorithm, and are plotted according to their composition. The algorithm will generate a prediction with a level of confidence as to which of the assigned populations that sample best fits into, with a 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.

5.2.2.1 Identification of Country of Origin

Results from all 399 samples were subjected to LDA analysis, detailed in Figure 5.3. In Figure 5.3 it can be seen that 79.85% of the variation between samples is described by the two components (F1 and F2); these components are made up of a combination of all 38 analytes. In order to be able to plot each sample in two dimensions, based on their entire trace elemental composition, each of the two components is represented on an axis in the plot further detailed in the lower right section of Figure 5.3. The samples are plotted with centroids representing the location of the means of the relevant subpopulations. In the lower left of the figures the unidentified coins are plotted with their associated predicted mint or country of origin. Factor analyses are related to the “predictions” LDAs.

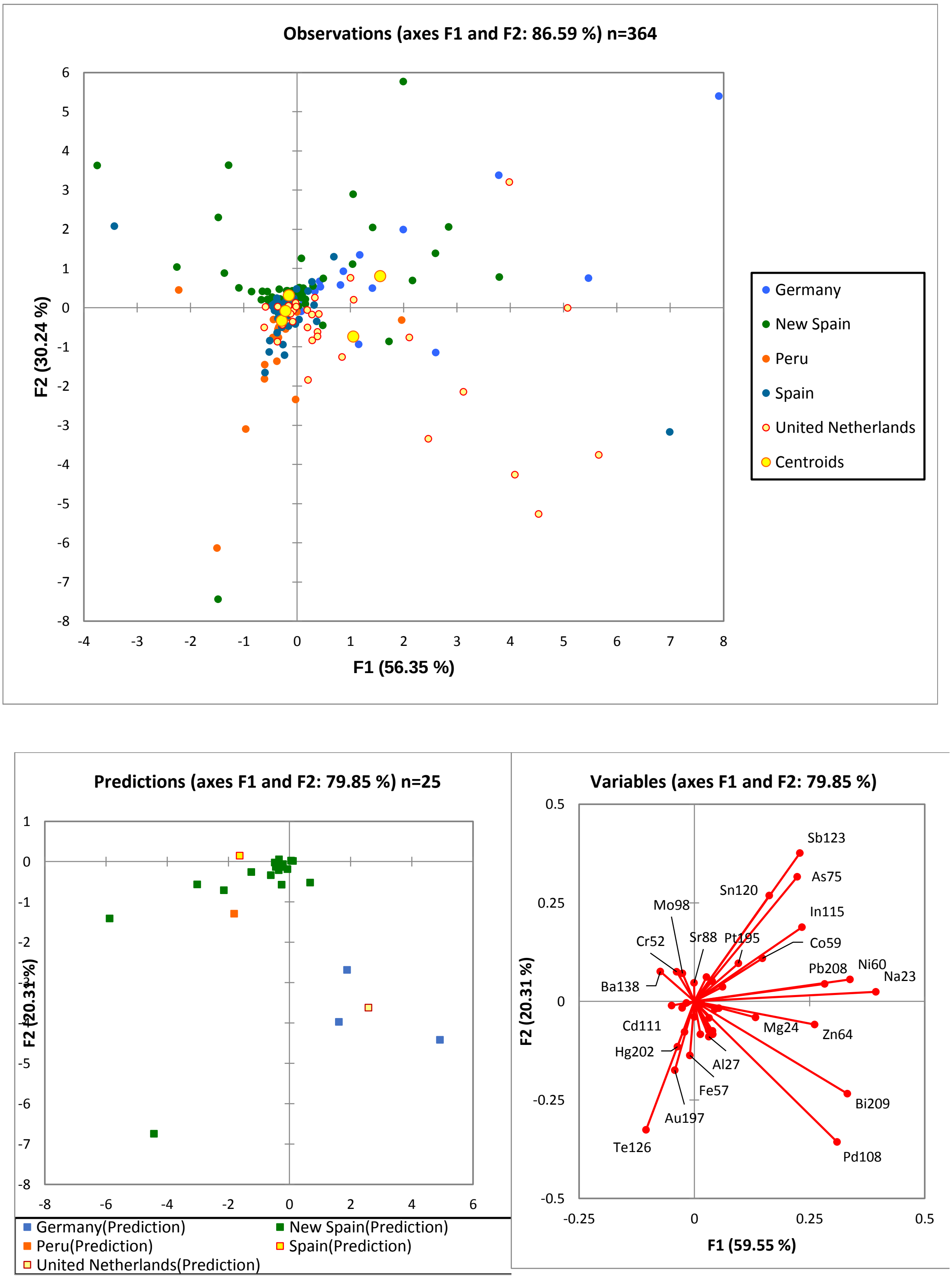


Figure 5.3 – LDA plot showing populations of coins based on their country of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis

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

German coins would appear to be relatively high in bismuth and sodium. Coins from New Spain are separated based on their relatively high tellurium content, while Peruvian and Spanish coins are characterised by their barium content.

When German and Dutch coins are removed from the LDA, clearer separation between Spanish populations can be established (Figure 5.4), which indicates that it is possible to distinguish between countries of origin of a coin based on its trace elemental composition.

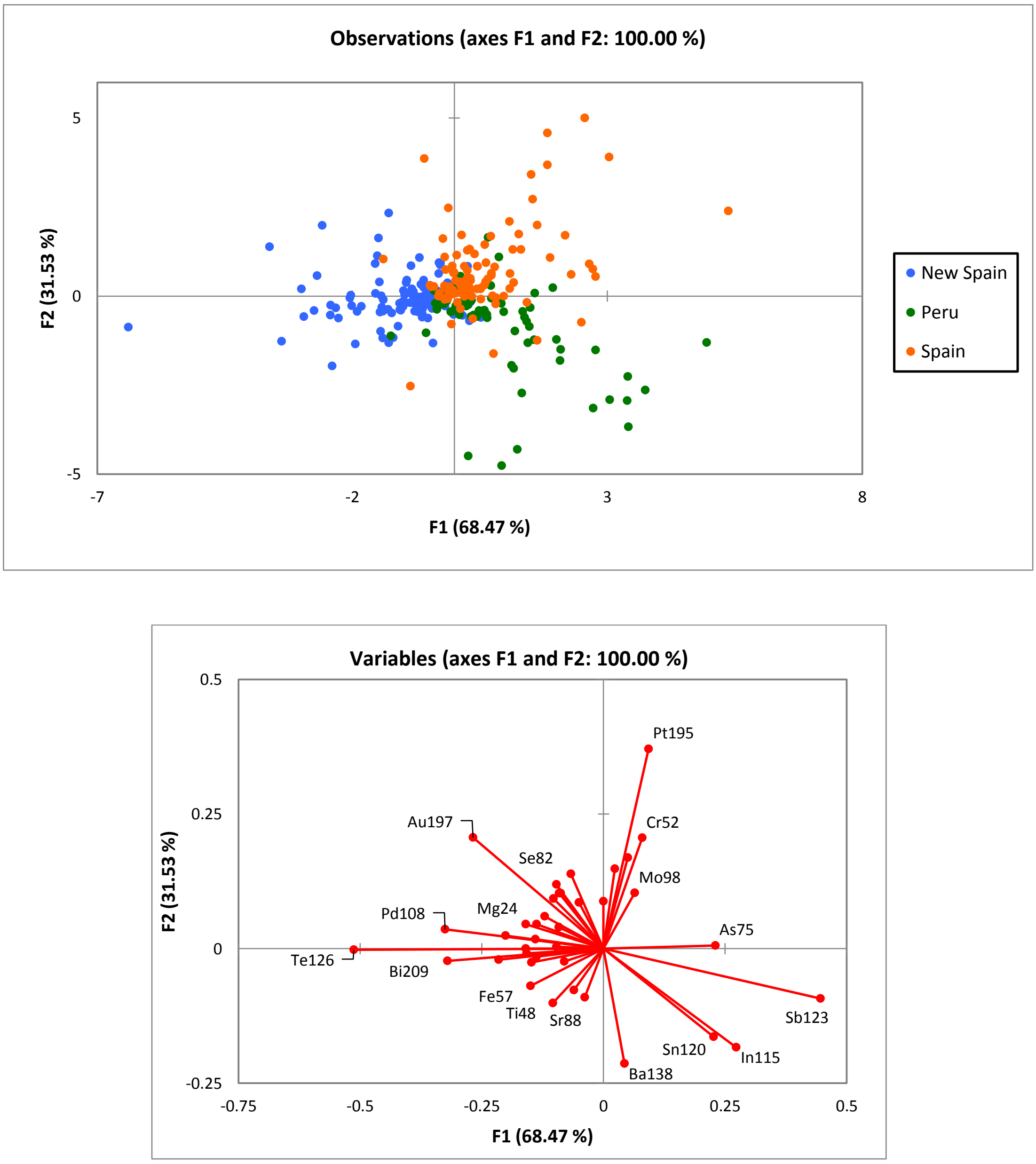
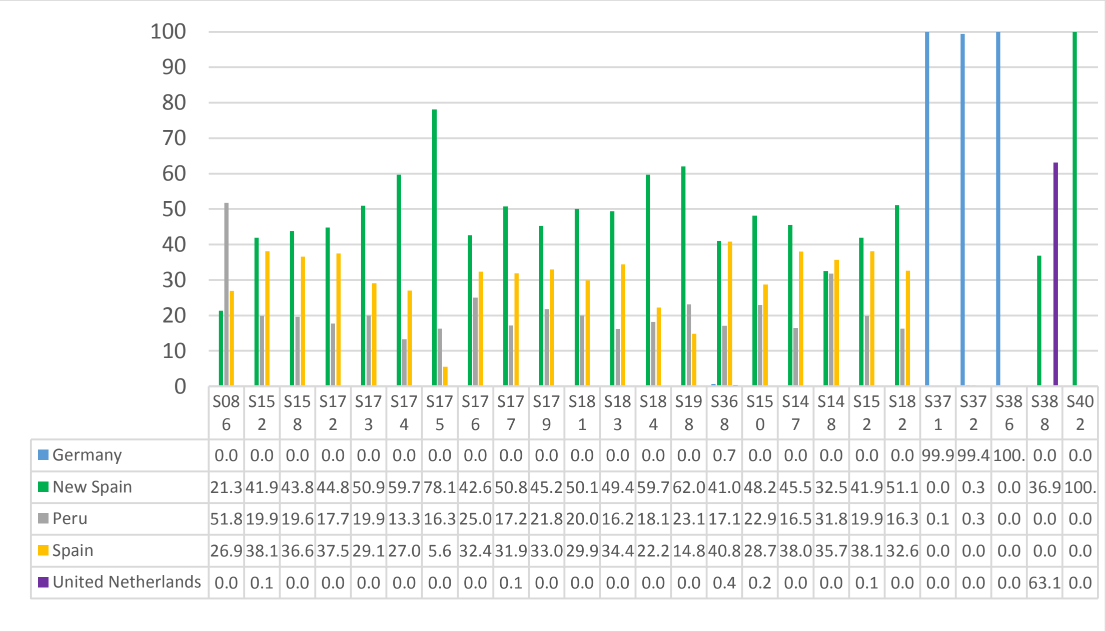


Figure 5.4 - LDA plot showing populations of coins based on their Spanish country or territory of origin. Below – factor analysis

In Figure 5.4 it can be seen that coins minted in New Spain are characteristically higher in tellurium, bismuth and palladium than those minted in Spain or Peru. Spanish coins are relatively high in platinum, chromium and molybdenum, while Peruvian coins are relatively high in barium, tin, indium and antimony. 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-five 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 composition. Results of the predictions are detailed in Figure 5.5. In order to identify the mint of origin of these 26 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 section 5.2.2.2.



	S086	S152	S158	S172	S173	S174	S175	S176	S177	S179	S181	S183	S184	S198	S368	S150	S147	S148	S152	S182	S371	S372	S386	S388	S402
Germany	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0	99.9	99.4	100.	0.0	0.0
New Spain	21.3	41.9	43.8	44.8	50.9	59.7	78.1	42.6	50.8	45.2	50.1	49.4	59.7	62.0	41.0	48.2	45.5	32.5	41.9	51.1	0.0	0.3	0.0	36.9	100.
Peru	51.8	19.9	19.6	17.7	19.9	13.3	16.3	25.0	17.2	21.8	20.0	16.2	18.1	23.1	17.1	22.9	16.5	31.8	19.9	16.3	0.1	0.3	0.0	0.0	0.0
Spain	26.9	38.1	36.6	37.5	29.1	27.0	5.6	32.4	31.9	33.0	29.9	34.4	22.2	14.8	40.8	28.7	38.0	35.7	38.1	32.6	0.0	0.0	0.0	0.0	0.0
United Netherlands	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.4	0.2	0.0	0.0	0.1	0.0	0.0	0.0	0.0	63.1	0.0

Figure 5.5 - Predicted country of origin with percentage confidence of prediction, of coins of unidentified country of origin.

5.2.2.2 Identification of Mint of Origin

5.2.2.2.1 United Netherlands

Figure 5.6 shows the distinct 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.

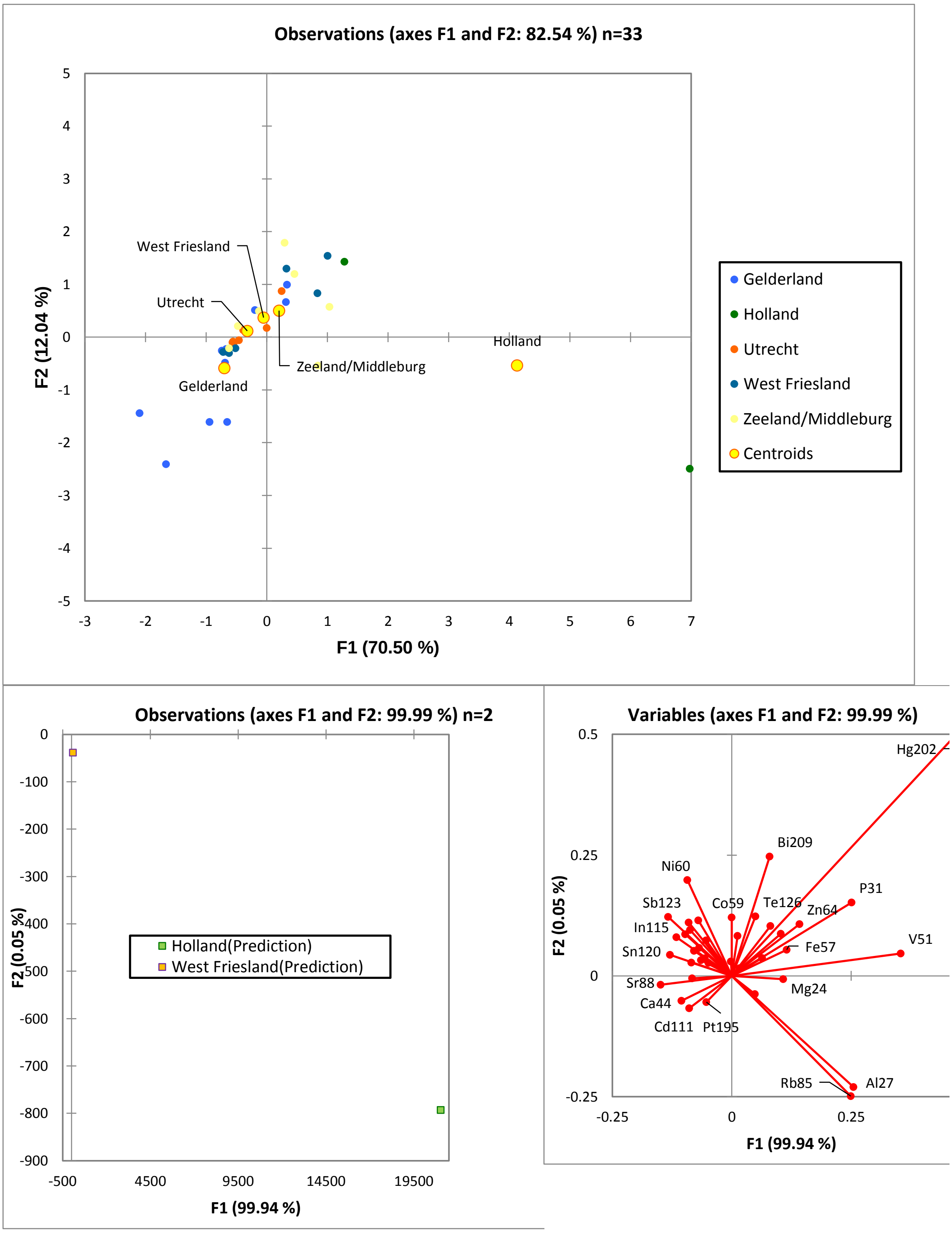


Figure 5.6 – LDA plot showing populations of United Netherlands coins based on their mint of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis.

Coins minted in Holland can be seen to be relatively high in mercury, while coins from Zeeland have a relatively high magnesium and nickel content. Coins minted in Gelderland are separated based on their high aluminium and rubidium contents.

5.2.2.2.2 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). Results of linear discriminant analysis of 132 samples identified to their provenance mint, as well as a further 19 unidentified samples known to be New Spanish are presented in Figure 5.7.

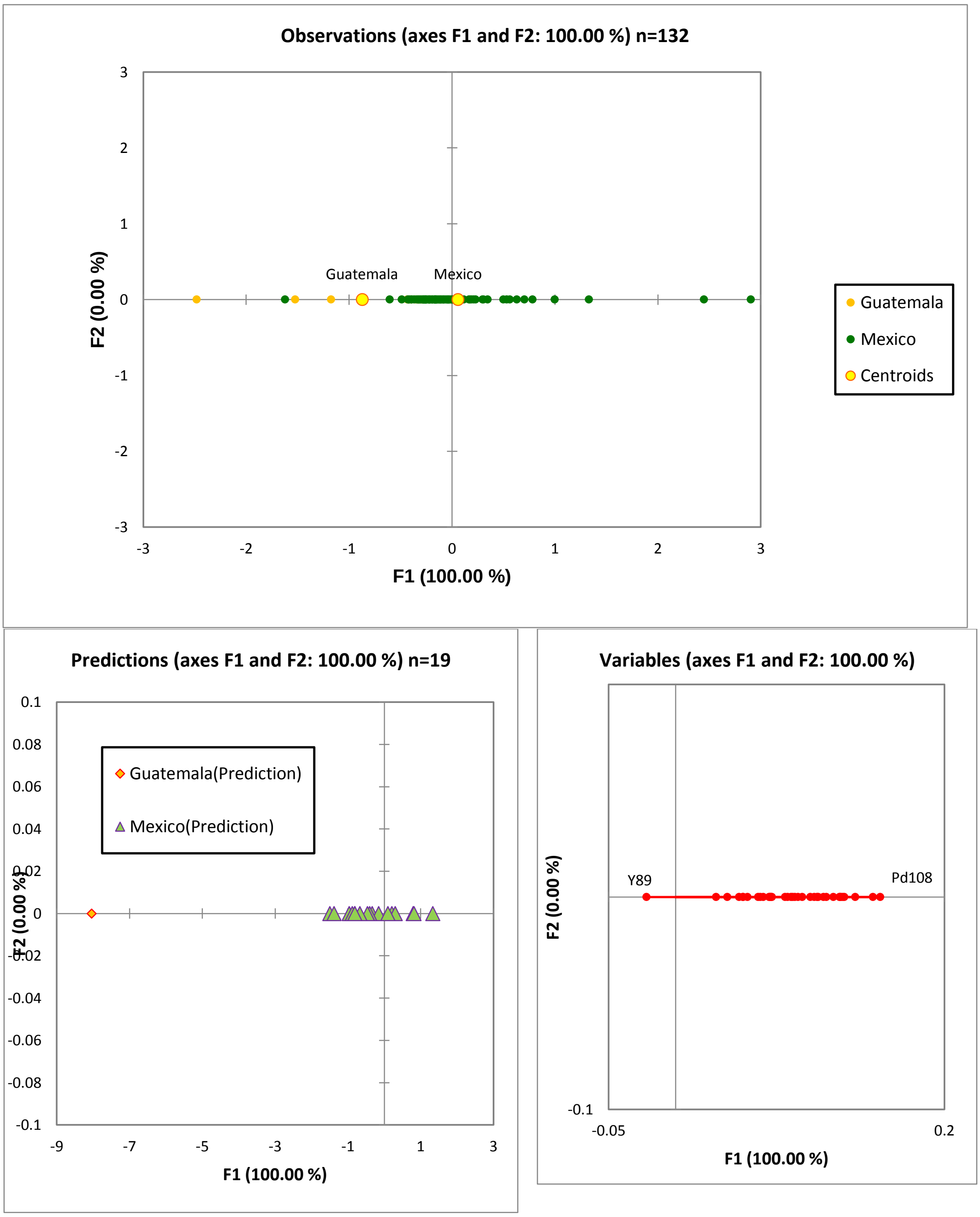


Figure 5.7 – LDA plot showing populations of coins based on their New Spanish mint of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis

Guatemalan silver is separated from Mexican silver based on its higher yttrium content. All but one of the 19 unidentified samples were predicted to be Mexican in origin with a confidence of at least 96%. Sample 368 was predicted to be Guatemalan.

5.2.2.2.3 Peru

The Viceroyalty of Peru consisted of all Spanish American territories south of Panama except Venezuela. 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 (Figure 5.3 and 5.5), has been included in the following LDA (Figure 5.8) in order to predict its mint of origin.

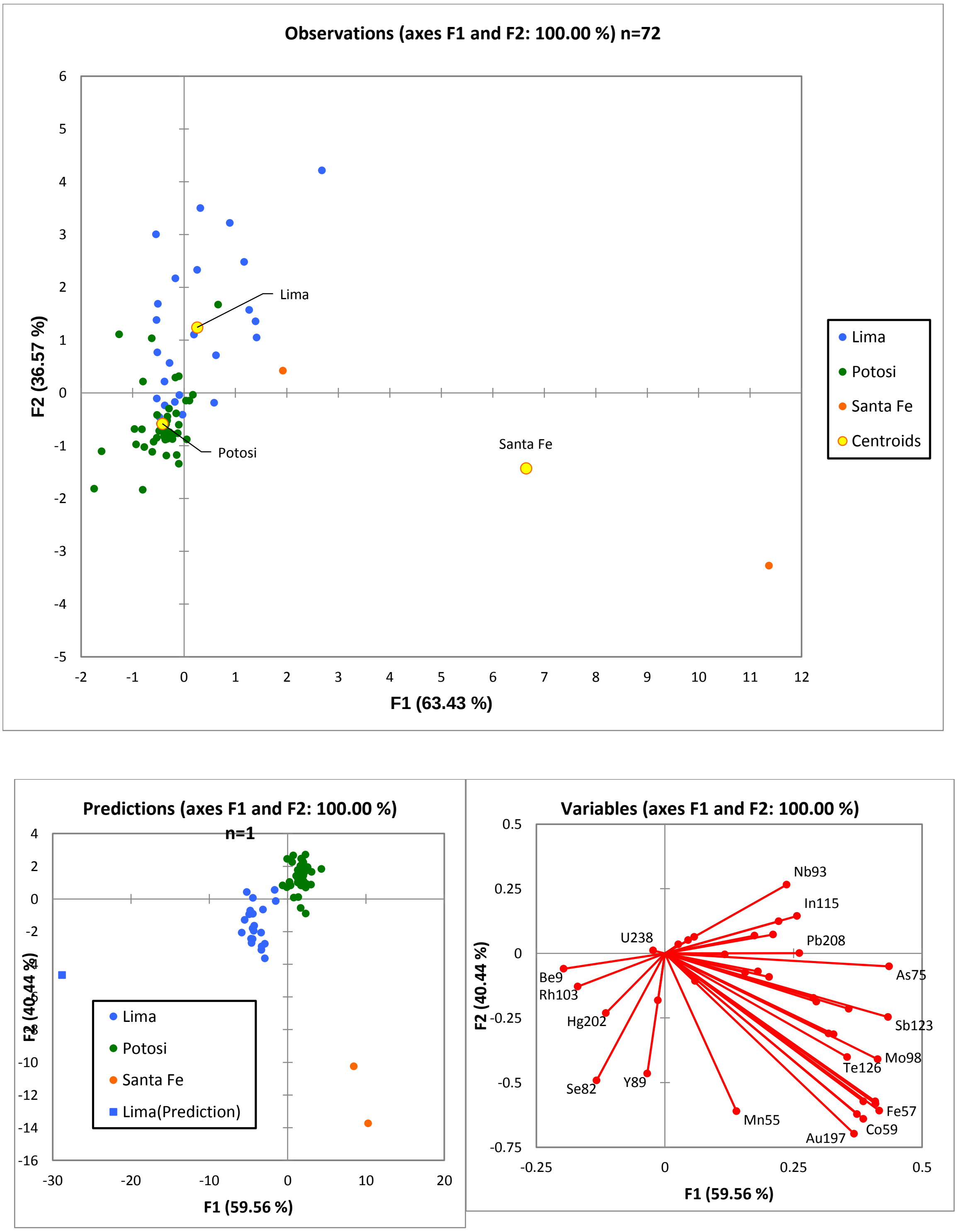


Figure 5.8 – LDA plot showing populations of coins based on their Peruvian mint of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis.

Coins minted in Lima are separated based on their relatively high beryllium and rhenium content, coins minted at Potosí are relatively high in niobium, while coins minted in Santa

Fe are distinguished by their relatively high gold, calcium, cobalt, strontium, sodium, iron and magnesium content.

5.2.2.2.4 Spain

A large group of coins were identified as having been minted in Spain at either Cadiz, Madrid, Segovia or Seville. Linear discriminant analysis of these 105 coins is detailed in Figure 5.9.

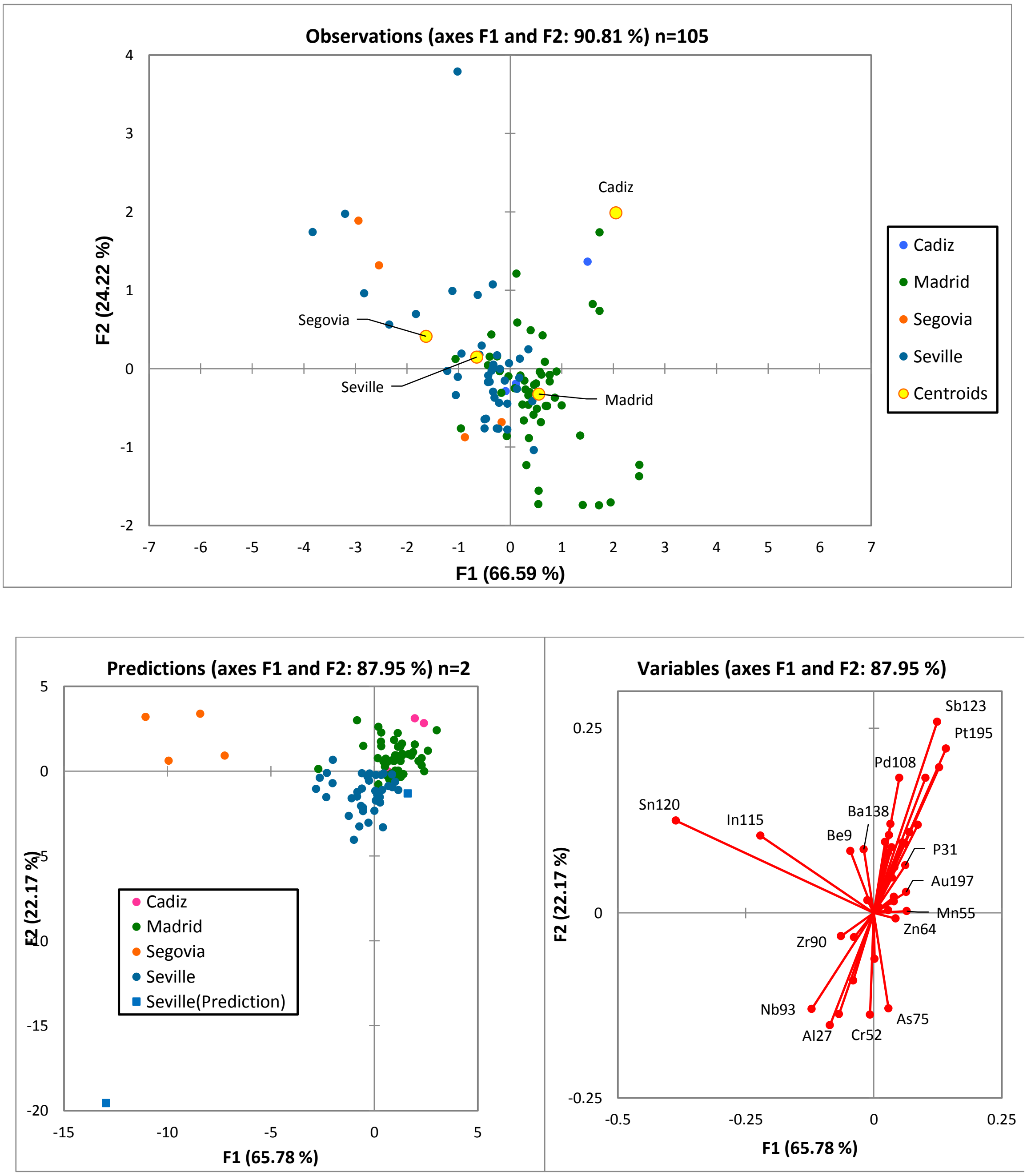


Figure 5.9 – LDA plot showing populations of coins based on their Spanish mint of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis.

Coins minted in Cadiz and to a lesser extent Madrid appear to be relatively high in platinum and antimony compared with coins minted elsewhere in Spain. Coins minted in Segovia are similarly high in tin and indium, and coins minted in Seville are distinguished by their relatively high niobium, aluminium, strontium and chromium content.

Two unidentified Spanish coins were predicted to have originated in Seville, with 68.25% and 63.04% confidence.

5.2.2.2.5 Germany

Twenty coins from three German mints were analysed, from Lubeck, Nuremberg or Sachsen. Results of LDA are detailed in Figure 5.10. Three previously unidentified coins were predicted to have been minted in Nuremberg.

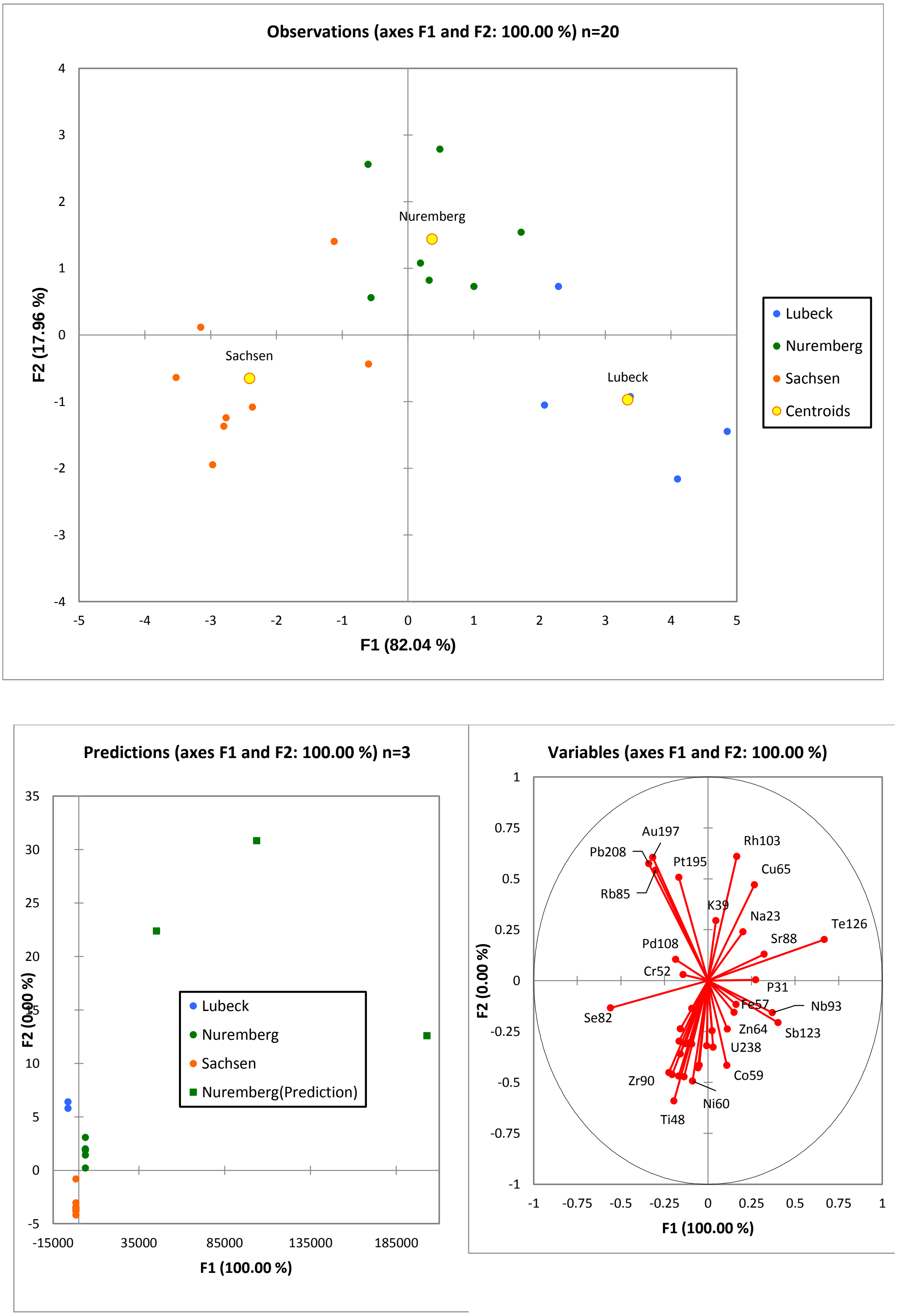


Figure 5.10 – LDA plot showing populations of coins based on their German mint of origin. Lower left – predicted origins of unidentified coins. Lower right – factor analysis.

Distinct separation can be seen between the three German mints. Coins from Lubeck would appear to be relatively high in lead and gold when compared to coins from the other two German mints, as well as rubidium and platinum. Sachsen coins are relatively high in selenium, while coins minted at Nuremberg are separated based on their relatively high concentration of tellurium.

5.2.2.3 Summary of predictions

A summary of the 26 previously unidentified coins and their predicted provenance mints is provided in Table 5.1. While for the majority of the coins the percentage confidence of the prediction is above 99%, it should be remembered that this is in terms of a limited sample size used to create the database, and this percentage will be over-estimated. With this in mind, with the exception of samples 148 and 168, the confidence of the predictions is very good. In terms of the LDA plots themselves, the samples which have been predicted will occasionally plot away from the subpopulation to which they have been assigned by the algorithm. It is worth remembering here that the vector, rather than x,y coordinates, that an unidentified sample and its predicted subpopulation plot on, is the best indicator of a correct prediction.

Table 5.1 – Summary of results of prediction of provenance mint

Sample #	Ship	Sovereign	Year	Predicted Mint
S086	*Vergulde Draeck*	Felipe IV	c.1650	Lima
S147	*Correia de Azia*	Unidentified	Unidentified	Mexico
S148	*Correia de Azia*	Unidentified	Unidentified	Seville/Segovia
S150	*Correia de Azia*	Fernando VII	Unidentified	Mexico
S152	*Correia de Azia*	Fernando VII	1815	Mexico
S158	*Correia de Azia*	Carlos III	1788	Mexico
S168	*Correia de Azia*	Joseph Napoleon	181x	Seville/Madrid
S172	*Correia de Azia*	Carlos III	Unidentified	Mexico
S173	*Correia de Azia*	Carlos IV	Unidentified	Mexico
S174	*Correia de Azia*	Unidentified	Unidentified	Mexico
S175	*Correia de Azia*	Unidentified	Unidentified	Mexico
S176	*Correia de Azia*	Unidentified	Unidentified	Mexico
S177	*Correia de Azia*	Carlos IV	Unidentified	Mexico
S179	*Correia de Azia*	Fernando VII	1815	Mexico
S181	*Correia de Azia*	Carlos IV	1806	Mexico
S182	*Correia de Azia*	Carlos IV	1806	Mexico
S183	*Correia de Azia*	Carlos IV	1804	Mexico
S184	*Correia de Azia*	Carlos IV	17xx	Mexico
S198	*Zuytdorp*	Unidentified	Unidentified	Mexico
S368	*Batavia*	Unidentified	c. 1620	Guatemala
S371	*Rapid*	Unidentified	Unidentified	Nuremberg
S372	*Vergulde Draeck*	Unidentified	Unidentified	Nuremberg
S374	*Zuytdorp*	Unidentified	166x	West Friesland
S386	*Zuytdorp*	Unidentified	Unidentified	Nuremberg
S388	*Zuytdorp*	Unidentified	Unidentified	Holland
S402	*Vergulde Draeck*	Unidentified	Unidentified	Mexico

5.2.3 Conclusion

This project 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 was subjected to chemical analysis, yielding results with implications that are able to go far beyond the scope of the initial project. The provenance mint of 26 previously unidentified silver coins was determined using trace elemental composition and linear discriminant analysis in a database of the trace elemental composition of coins of known provenance. The information adds to our knowledge of the cargoes of the ships represented, as well as the unique trace elemental composition of coins minted in different countries and mints. This method can be used on any artefact, given a large enough database of similar artefacts of known provenance.

5.3 Provenance determination of coins using lead isotope composition

5.3.1 Aim

Lead isotopes are an ideal tracer of silver objects that are derived from argentiferous ores (Stos-Gale *et al.*, 1995; Pernicka, 2014). Trace amounts of lead remaining in the refined silver will retain their isotopic ratio, indicative of their provenance ore, no matter how the silver is then manufactured. The coins in this study originate from argentiferous ores and were refined using the mercury amalgamation process. The use of lead isotopes for provenance determination of silver objects becomes more complex when silver objects are re-melted and mixed together, as potentially the lead will also be mixed with lead from other sources. The lead isotopic ratio of such mixed silver will necessarily be different from any of the source ores, and can be identified as having been mixed.

This study aims to take the abundances of the three lead isotopes, ^{206}Pb, ^{207}Pb and ^{208}Pb in 218 samples of silver coins and artefacts from the Western Australian Museum, as determined using LA-ICP-MS, and to combine them with data from 91 similar silver coins reported by Desaulty *et al.*, (2011). ^{204}Pb was not analysed, so as to avoid confounding results for ^{202}Hg for provenance determination using trace elemental analysis. Data have then been analysed to determine if the new data support the conclusions of provenance of Desaulty *et al.*, (2011), principally, if the influx of American silver into Spain and Europe is reflected in the lead isotope ratios of silver coins.

A quadrupole mass analyser has been found to have similar sensitivity, accuracy and precision to a multi-collector mass analyser when analysing lead isotopes (Barbaste *et al.*, 2001). The precision obtained for the ^{206}Pb/^{207}Pb and ^{208}Pb/^{206}Pb was 0.14–2.7% using the quadrupole mass analyser, and 0.01–0.12% using a multi-collector. The precision for ^{206}Pb/^{204}Pb was 0.44–5.29%, and 0.08–1.6%, respectively. The study concludes that the accuracy for each method (as well as ToF-ICP-MS) was satisfactory, while the precision for ^{206}Pb/^{204}Pb using a quadrupole was too poor to reliably use for provenance analysis (Barbaste *et al.*, 2001). As such, the use of a quadrupole system to compare results to those obtained using a multi-collector system is deemed appropriate, especially when ^{204}Pb is eliminated from the study.

5.3.2 Results

Lead isotope data is attached electronically as an appendix.

The 218 samples analysed were sorted into the six categories used by Desaulty *et al.*, (2011), 16th to 18th century German, 16th to 18th century Spain, 16th to 18th century United Netherlands, antique, Medieval Europe and Medieval Spain. A plot of ^{207}Pb/^{206}Pb versus, ^{208}Pb/^{206}Pb is detailed in Figure 5.11. Figure 5.12 details the section in Figure 5.10, indicated by the red rectangle.

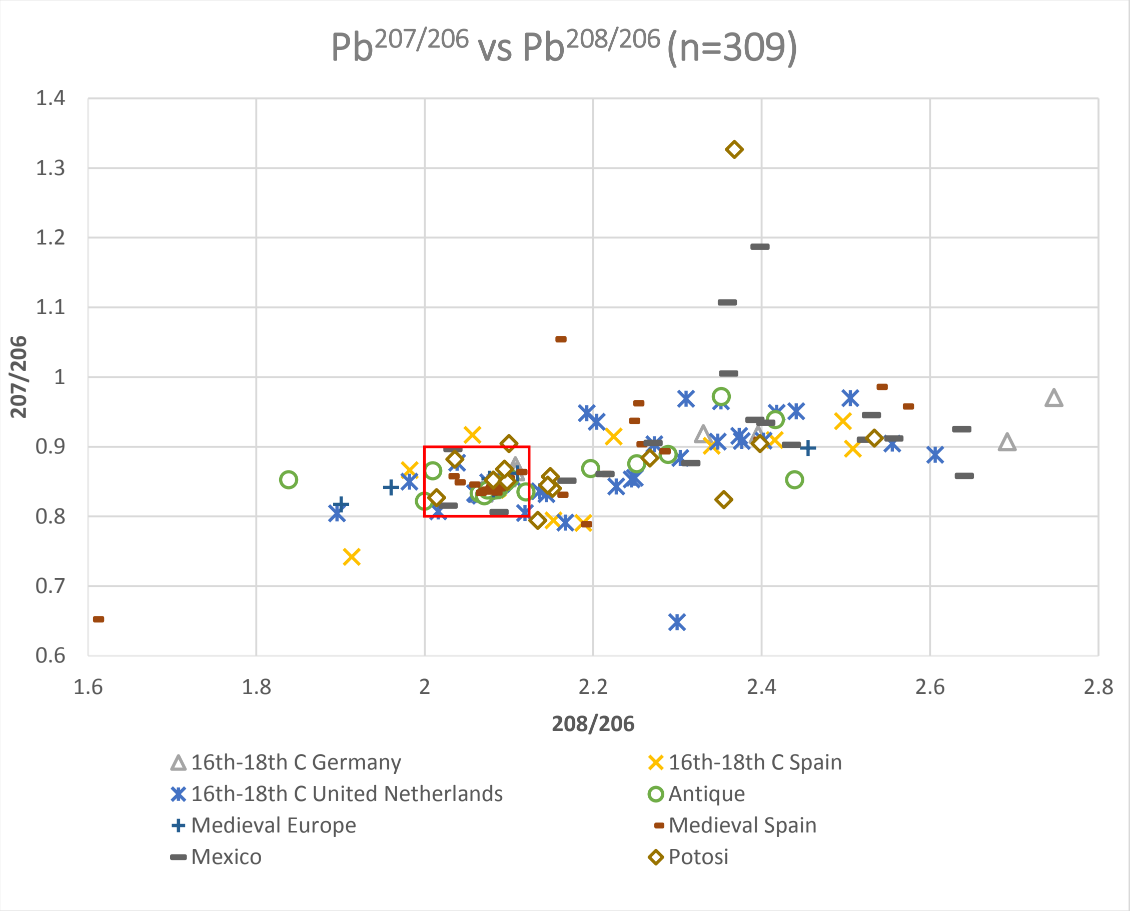


Figure 5.11 – Plot of ^{207}Pb/^{206}Pb versus ^{208}Pb/^{206}Pb isotopic composition of 218 Western Australian Museum silver coins, and 91 silver coins studied by Desaulty *et al.*

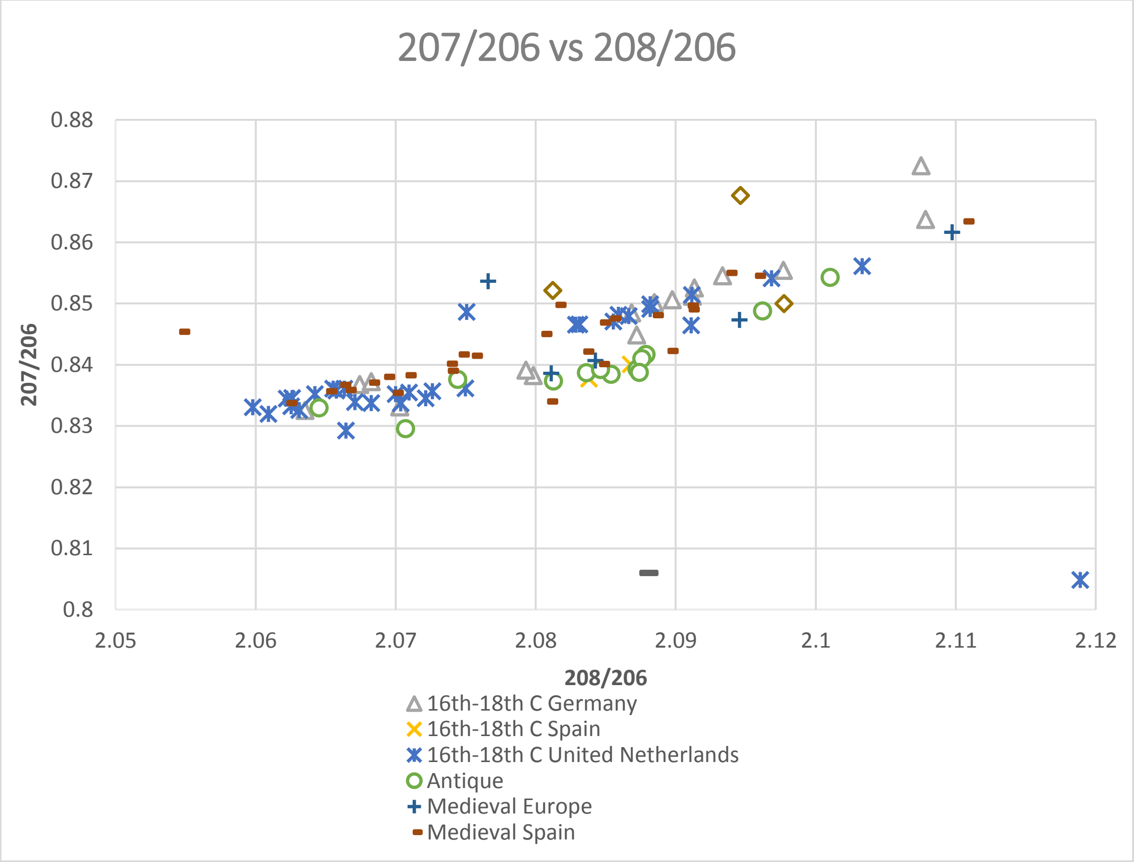


Figure 5.12 – Detail of section of Figure 5.11

5.3.3 Conclusion

The isotopic data of silver coin analyses from both Desaulty *et al.*, (2011) and the present study show that antique, medieval and American silver can be distinguished from one another based on lead isotope composition. Sixteenth to eighteenth century Spanish and Dutch silver can be seen to plot between Medieval European silver and American silver based on lead isotope composition.

This information would indicate that firstly, provenance determination of silver is possible based on its lead isotope composition. Secondly, mixing silver from different sources will create a new and distinct lead isotope composition, and this information can be used to identify silver from mixed sources. In this case, 16th-18th century Spanish silver in particular can be identified as having been mixed from more than one source of silver, which can be identified as the European source of medieval silver and American silver. Further investigation into the date ranges of 16th-18th century Spanish and European silver would indicate a trend over time of increasing utilisation of American over European silver in Spanish coinage.

5.4 Provenance determination of *Batavia* artefacts using trace elemental composition

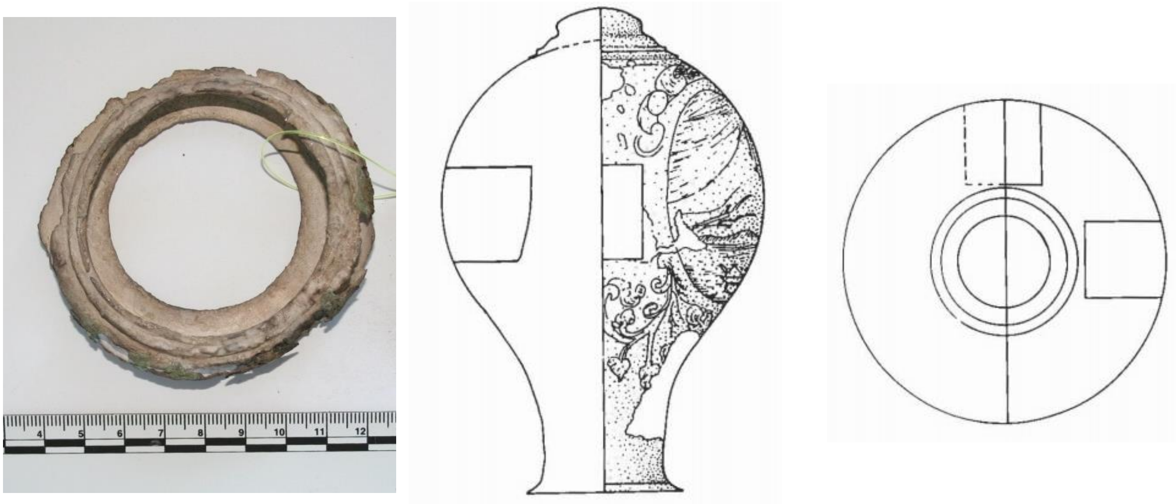
5.4.1 Aim

Silver artefacts from the shipwreck *Batavia* known to have been made on commission by the Dutch East India Company in 1627-1628 for trade in the Dutch East Indies, were analysed using LA-ICP-MS for trace elemental composition. The results were compared to a database of trace elemental compositions of Spanish, Spanish American and other European silver coins of known provenance. At the time Spain, which controlled the vast majority of world silver, was at war with the United Netherlands and was enforcing a trade embargo that severely limited the supplies of precious metals accessible by the Dutch. Based on their trace elemental composition, the *Batavia* silver artefacts were found to have been most similar to silver known to have originated in Germany as well as silver that reached the Dutch indirectly from Spain. These results shed light on the movement of silver as a commodity throughout the world during a unique time in history.

A brief description of the artefacts used can be found in Table 5.2, and Figure 5.13 shows images of the artefacts (artefact drawings are taken from *The Loss of the Verenigde Oostindische Compagnie retourschip* Batavia, *Western Australia 1629* (Green, 1989)).

Table 5.2 – Silver artefacts from the *Batavia* analysed for this study

Sample number	Museum number	Artefact description
S404	BAT3032	Part of an engraved bedpost
S405	BAT3563	An incomplete chalice, engraved with scroll and motif
S406	BAT3565	Unidentified engraved fragments, possibly from the foot rim of chalice. The underside displays zigzag contemporary assay tooling marks.
S407	BAT3568	Cherub section and fragments
S408	BAT3573	A copper coated ring. It appears to have a flat base as if part of a tubular object.
S409	BAT3605	An unidentified, worn object, possibly part of a sword hilt.
S410	BAT3626	A flat, engraved section of a plate.
S411	BAT3643	Candelabrum
S412	BAT3651	Bed post fragments engraved with scrolls and other designs.
S413	BAT3744	Unidentified object (3 fragments), possibly from a sword hilt.
S414	BAT3835	A screw top in two sections.



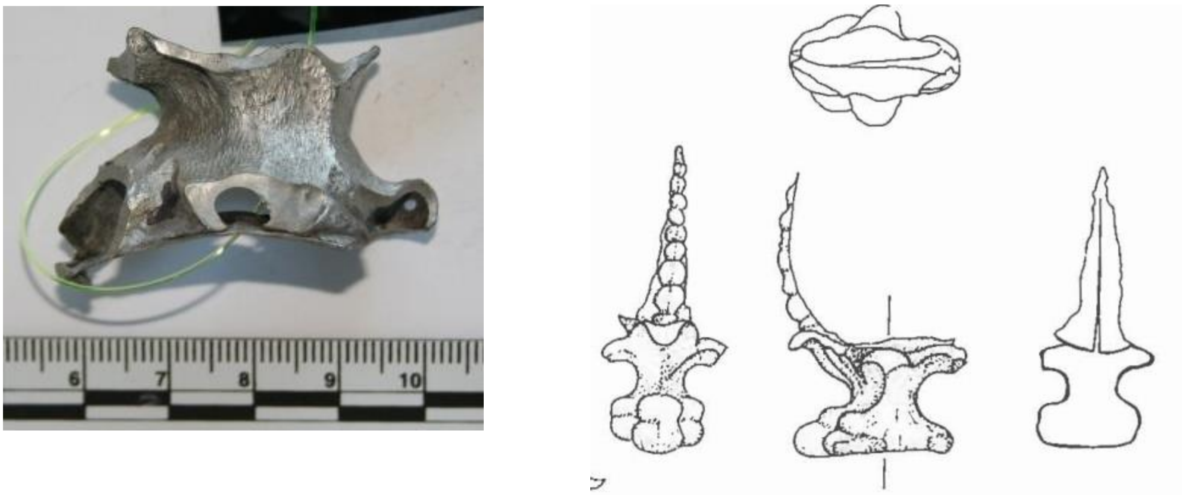
BAT3032 – Bedpost

BAT3563 – Bed foot or chalice.

BAT3565 – Foot rim of chalice

BAT3568 – Winged cherub with flute

BAT3573 – Tubular object

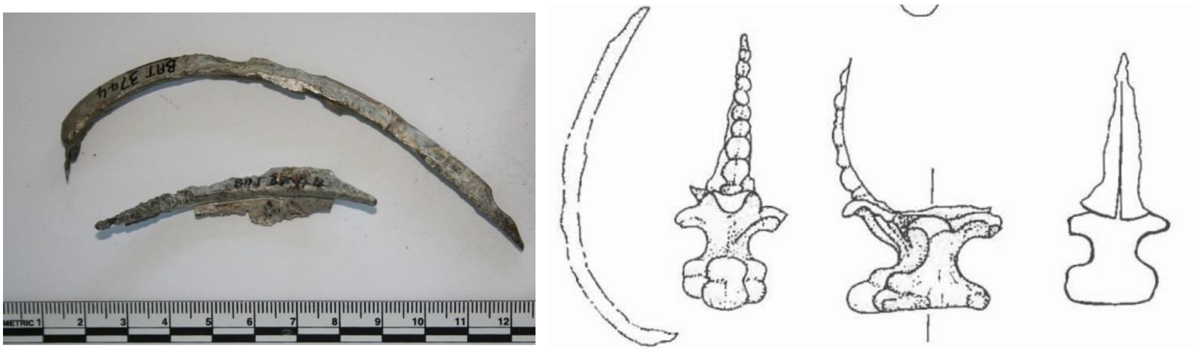


BAT3605 – Possible sword hilt

BAT3626 – Plate fragment

BAT3643 – Candelabrum fragment

BAT3651A – Bedpost fragments



BAT3744 – Sword hilt or stand/mount

BAT3835 – Screw top

Figure 5.13 – Artefacts from the wreck of the *Batavia* investigated in this study. Drawings from Green (1989).

5.4.2 Results

Table 5.3 shows that the silver items in general contain less silver than currency at the time, with a related increase in copper content. The cherub fragments, sample 407, is an outlier here, with a relatively high silver content of 97%.

Table 5.3 – Bulk elemental composition of *Batavia* artefacts determined using solution ICP-MS and LA-ICP-MS, and the mean bulk elemental composition of the database of silver coins used in this study determined using LA-ICP-MS.

(%)	Ag	Cu	Pb	Au
S404	92.2	6.3	0.8	0.2
S405	92.2	5.8	1.8	0.2
S406	89.9	9.4	0.6	0.0
S407	97.0	1.7	0.4	0.8
S408	91.8	6.8	0.7	0.2
S409	92.2	6.7	0.9	0.1
S410	92.2	6.9	0.9	0.0
S411	91.1	8.2	0.5	0.1
S412	92.4	5.6	1.0	0.8
S413	91.9	6.3	1.7	0.1
S414	91.0	7.8	1.0	0.1
Silver artefacts (x̄)	92.2	6.5	0.9	0.2
Silver coins (x̄)	94.9	4.9	0.1	0.2

The artefact data were compared to coins of known provenance country using discriminant analysis.

In Figure 5.14 it can be seen that 81.25% of the variation between samples is described by the two components (F1 and F2); these components are made up of a combination of all of the analytes. In order to be able to plot each sample in two dimensions, based on their entire trace elemental composition, each of the two components is represented on an axis in the plot. The samples are plotted with centroids representing the location of the means of the relevant subpopulations, as well as confidence ellipses for each subpopulation at a confidence of 0.95. Figure 5.15 details a factor analysis of the same data showing which analytes most discriminate between populations. The direction of the vector of the relevant analyte correlates with how an individual sample will be plotted in discriminant analysis, based on its relative composition of that analyte. In this way, samples of similar composition will necessarily plot in clusters, and subpopulations will become visually distinct groups of points.

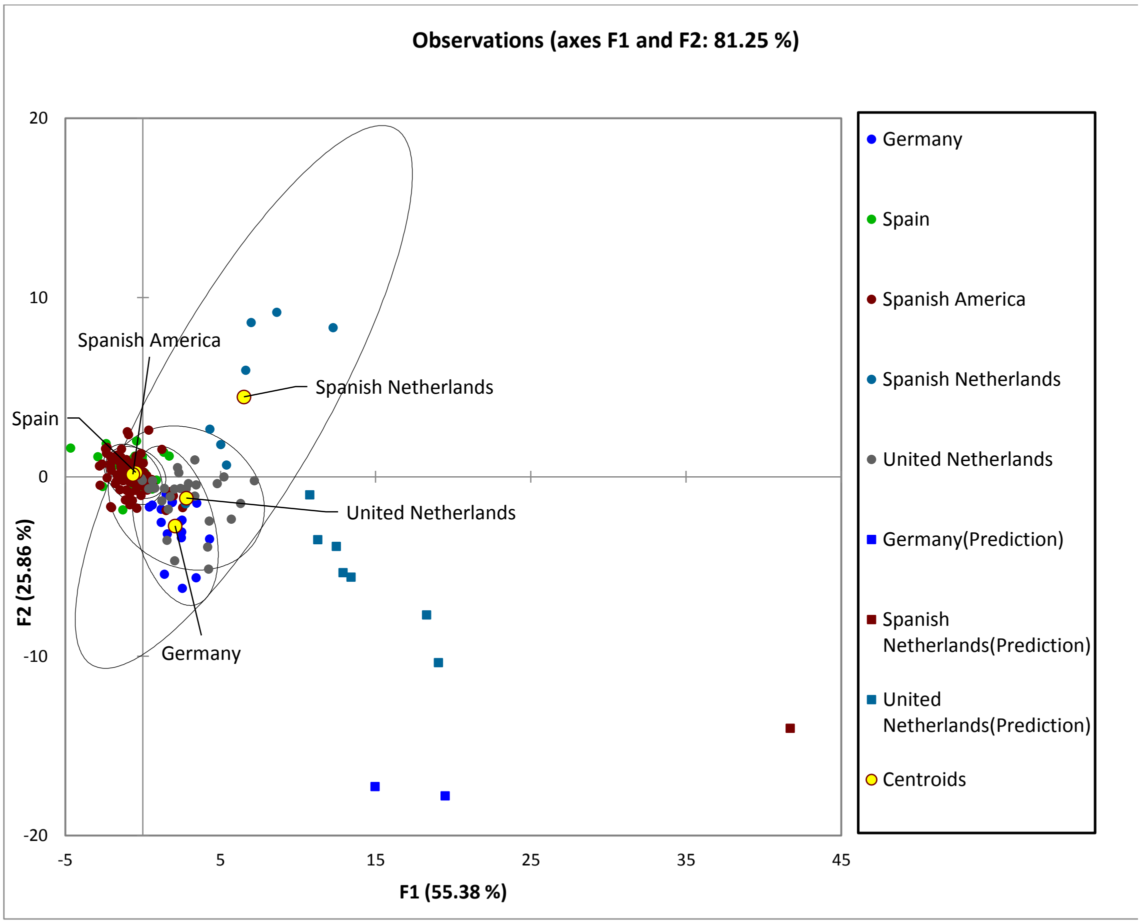


Figure 5.14 – Distribution of samples of known provenance country, and predictions of provenance of unknown *Batavia* artefacts.

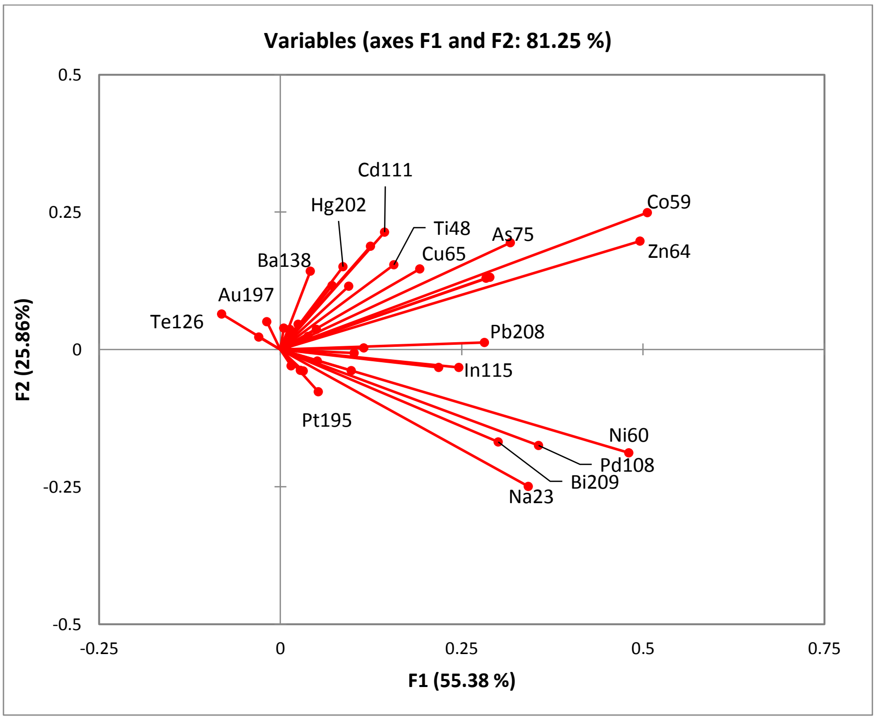


Figure 5.15 – Factor analysis detailing the analytes which most discriminate between populations.

Some overlap between populations can be seen in the plot (Figure 5.14), which is to be expected as the composition of samples in the database is necessarily very similar. Based on the factor analysis detailed in Figure 5.15, it would appear that the analytes most indicative of Spanish and Spanish American silver are tellurium and gold. Silver minted in the Spanish Netherlands is higher in cobalt, zinc and arsenic. Silver minted in the United Netherlands is higher in indium and antimony, while silver from Germany is higher in platinum.

The *Batavia* artefacts all plot in the lower right quadrant of Figure 5.14, outside any of the established subpopulation confidence ellipses. Based on factor analysis, they would appear to have a higher palladium, nickel, bismuth and sodium content than the silver coins. Since the artefacts are not coins, it is to be expected that they will not fit precisely into a subpopulation of coins, because while the artefacts are manufactured from silver from the same source, they are not manufactured under the same conditions. It is worth noting here that corrosion processes may also have had a part to play in the differences between trace elemental composition of silver coisn and artefacts. The silver coins, by and large, were held in chests when the ships were wrecked, and so corrosion processes have affected them differently to the silver artefacts, which would not have been protected by a large volume of other silver items in their depositional environment. Further, the silver artefacts are in most cases not as thick as the coins, and so it follows that corrosion, and particularly copper leaching, may affect the artefacts more than the coins. Of most interest in this plot is the distinction between the *Batavia* artefacts and the coins known to be from Spain and Spanish America.

There is significant overlap between Spain and Spanish America which is to be expected as Spanish silver was sourced almost exclusively from the Americas. It is also interesting to note that samples from the United Netherlands have some overlap with silver from Spanish sources, and more overlap with silver from Germany, which shows that United Netherlands silver had both German and Spanish origins, with an emphasis on the former. The unknown Batavia samples have been predicted to be from Germany, the United Netherlands and the Spanish Netherlands. These predictions are further detailed in Table 5.4. Note that none of the samples appears likely to have originated directly from Spain or Spanish America. It is also worth noting that the two fragments of sword hilt, which presumably belonged to the same sword, have both been identified as having been manufactured in the United Netherlands.

Table 5.4 – Predicted country of origin of *Batavia* artefacts

Object	#	Predicted country
Bedpost	S404	Germany
Chalice	S405	United Netherlands
Chalice	S406	United Netherlands
Cherub	S407	Spanish Netherlands
Tube	S408	Germany
Sword hilt	S409	United Netherlands
Plate	S410	United Netherlands
Candelabrum	S411	United Netherlands
Bedpost	S412	Germany
Sword hilt	S413	United Netherlands
Screw top	S414	United Netherlands

5.4.3 Conclusion

The samples used in this study represent a unique assemblage of silver artefacts, having been made in 1627 and 1628 in the United Netherlands specifically to support potential avenues of trade in the Dutch East Indies. This very narrow origin of the silver in question, both spatially and temporally, as well as the knowledge that the artefacts had yet to be used for their intended purpose as trade goods in the Indies, provides a rare opportunity to investigate Dutch silver sources in 1627 and 1628. Of particular interest at this time was the Spanish monopoly on world silver after colonisation of the Americas and the trade embargo in place between Spain and the United Netherlands in the midst of the Eighty Years' War. After several failed sieges on Dutch fortresses, the Spanish moved their military to a defensive position and instead besieged the entire United Netherlands by ceasing trade with them, in theory severely limiting their access to precious metals over which Spain had considerable control. However, precious metals drained rapidly out of Spain to the rest of Europe, and so the Dutch still had access to a (more limited) supply of Spanish silver via other European trading centres.

The significance of these findings is that the trace elemental composition of the Batavia artefacts has been shown to be indicative of Dutch silver sources at the time, confirming that the Spanish trade embargo with the United Netherlands as well as tensions between the two nations before the embargo diminished, but did not halt, the Dutch acquisition of Spanish silver. Future research into Dutch silver sources may involve further analysis of artefacts and the supplementation of the database of silver of known provenance with more samples. The methodology described in this study has applications to many materials other than silver or metals, and could be applied to any item of cultural heritage significance if there is an available database of samples of the same material of known provenance.

5.5 Absolute dating of coins using trace elemental composition

5.5.1 Aim

Trace elemental composition has been used widely in archaeological research in order to provenance artefacts, detailed in section 3.2. However, to the author’s knowledge, trace elemental composition has never been applied to determine the year or time period of manufacture of archaeological artefacts. This section details a new method of absolute dating for coins using their trace elemental composition. The method makes use of the inter-element association patterns of multi-element analytical data determined using LA-ICP-MS. The trace elemental composition of individual coins that are too damaged to identify were compared against a database of coins of known year of minting from the same country of origin. In this way it has been possible to demonstrate the potential of this technique for absolute dating of archaeological artefacts.

Most of the coins used had already been successfully identified by their mint markings. The data from LA-ICP-MS analyses, together with what is known about the coins through visual identification, were used to equate different mints, years of minting and sovereign issuers to the elemental fingerprint of the equivalent coins.

The interpretational statistical technique LDA was used to identify the year of minting of coins which have previously not been identified by other means, based on a statistical comparison against a database of compositional analysis of silver coins of known year of minting. The data produced have been used for absolute dating of an archaeological artefact based on its trace elemental composition.

5.5.2 Results

5.5.2.1 Germany

Twenty-five coins from Germany were analysed, of which five had not been identified visually in terms of year of manufacture. The 20 identified coins were minted in the 1560s, 1590s and 1620s. Linear discriminant analysis of these coins is detailed in Figure 5.16.

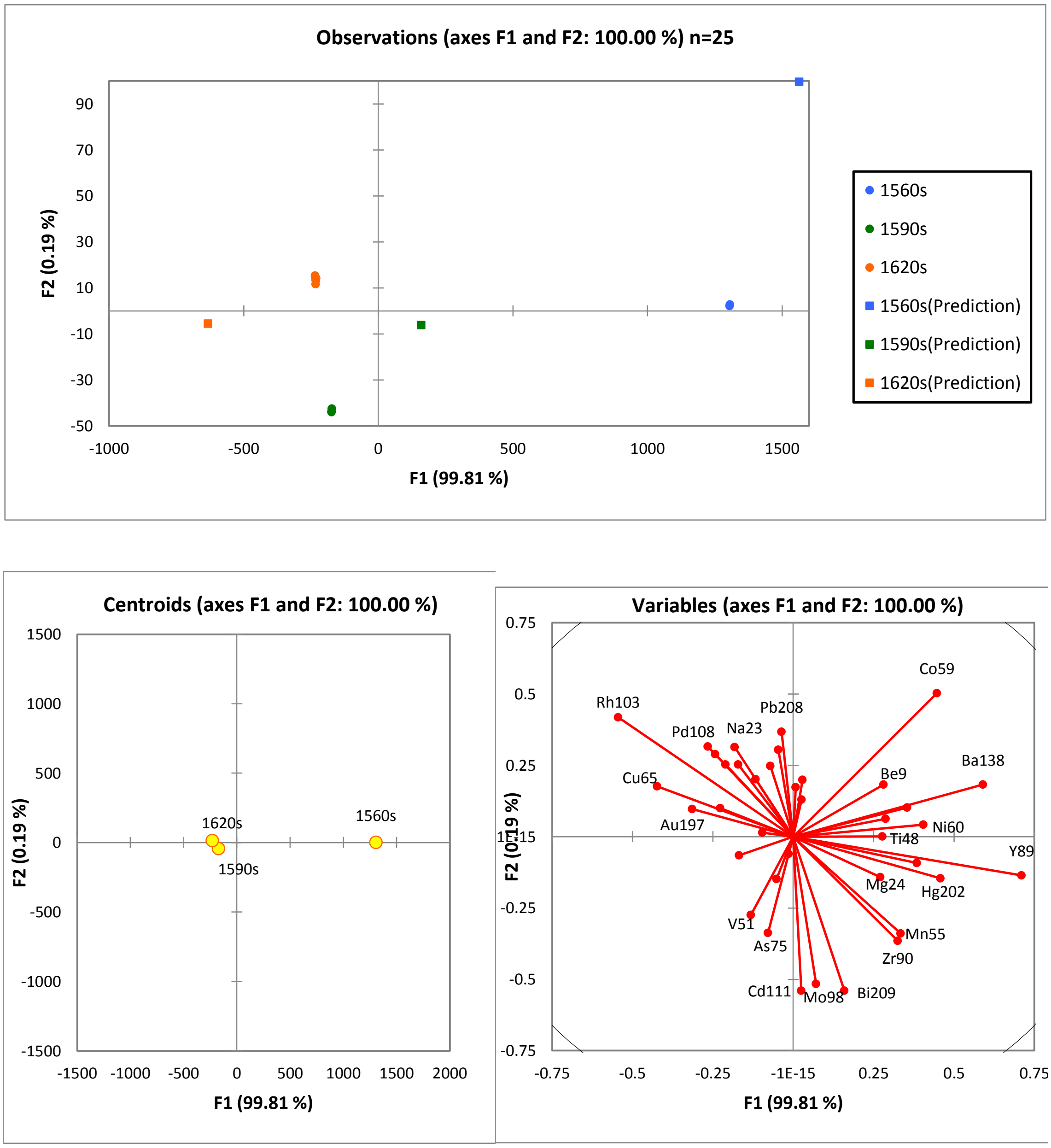


Figure 5.16 – LDA plot showing German coins in terms of their year of manufacture

Distinct separation is apparent between the three populations represented in Figure 5.17. Coins minted in the 1620s in Germany would appear to be characterised by relatively high rhenium content, coins minted in the 1560s are relatively high in barium and cobalt, and coins minted in the 1590s show relatively high arsenic and vanadium content.

5.5.2.2 New Spain

This study was of 145 coins minted in New Spain of which 73 had not been previously identified in terms of their year of minting. The identified coins were minted in the 1620s, 1640s, 1800s and 1810s. The sample contains enough coins minted in 1652, 1653, 1654, and 1708 to enable these years to be included in the analysis as individual populations. Linear discriminant analysis of these coins is detailed in Figure 5.17.

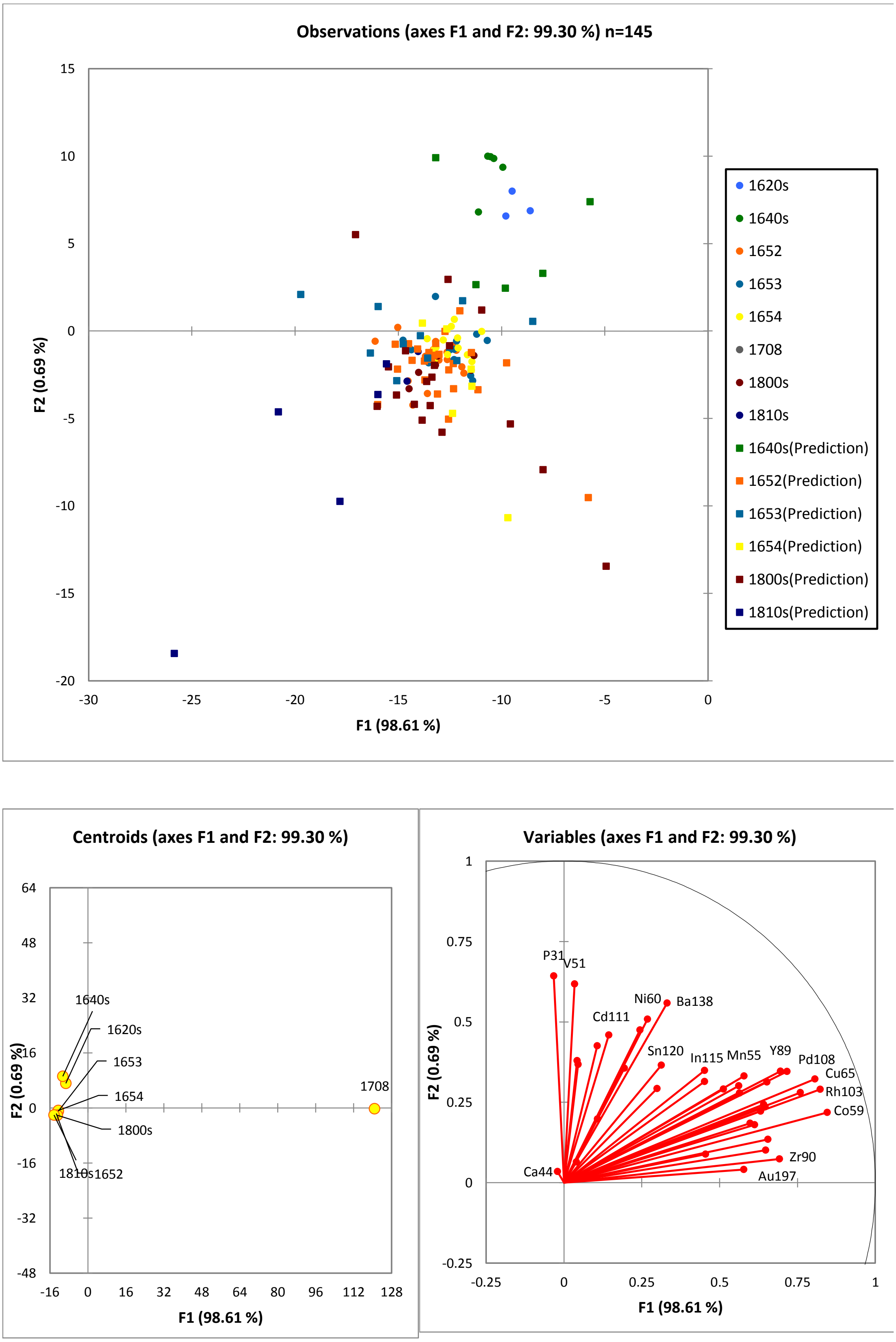


Figure 5.17 – LDA plot showing New Spanish coins in terms of their year of minting

Some overlap between populations is to be expected when some of the populations represent individual years rather than decades. The year 1708 is an outlier here, being the only year between 1654 and the 1800s for which it was possible to create population. It remains to be seen how a larger database with more representative populations from the 18th century would affect this analysis.

It would appear that coins minted in 1708 in New Spain are lower in calcium, and higher in gold and zinc than coins minted at other times.

5.5.2.3 Peru

This analysis used 73 coins minted in Peru, of which 24 had not had their year of minting identified. The coins that had been identified were minted in 1650, 1652 or 1653. Linear discriminant analysis of these coins is detailed in Figure 5.18. Good separation can be seen between the three populations represented by Peruvian coins. Coins minted in 1650 show as being relatively high in tellurium, phosphorous and aluminium, while those minted in 1652 are relatively high in arsenic and titanium. Coins minted in 1653 appear to be relatively higher in tin.

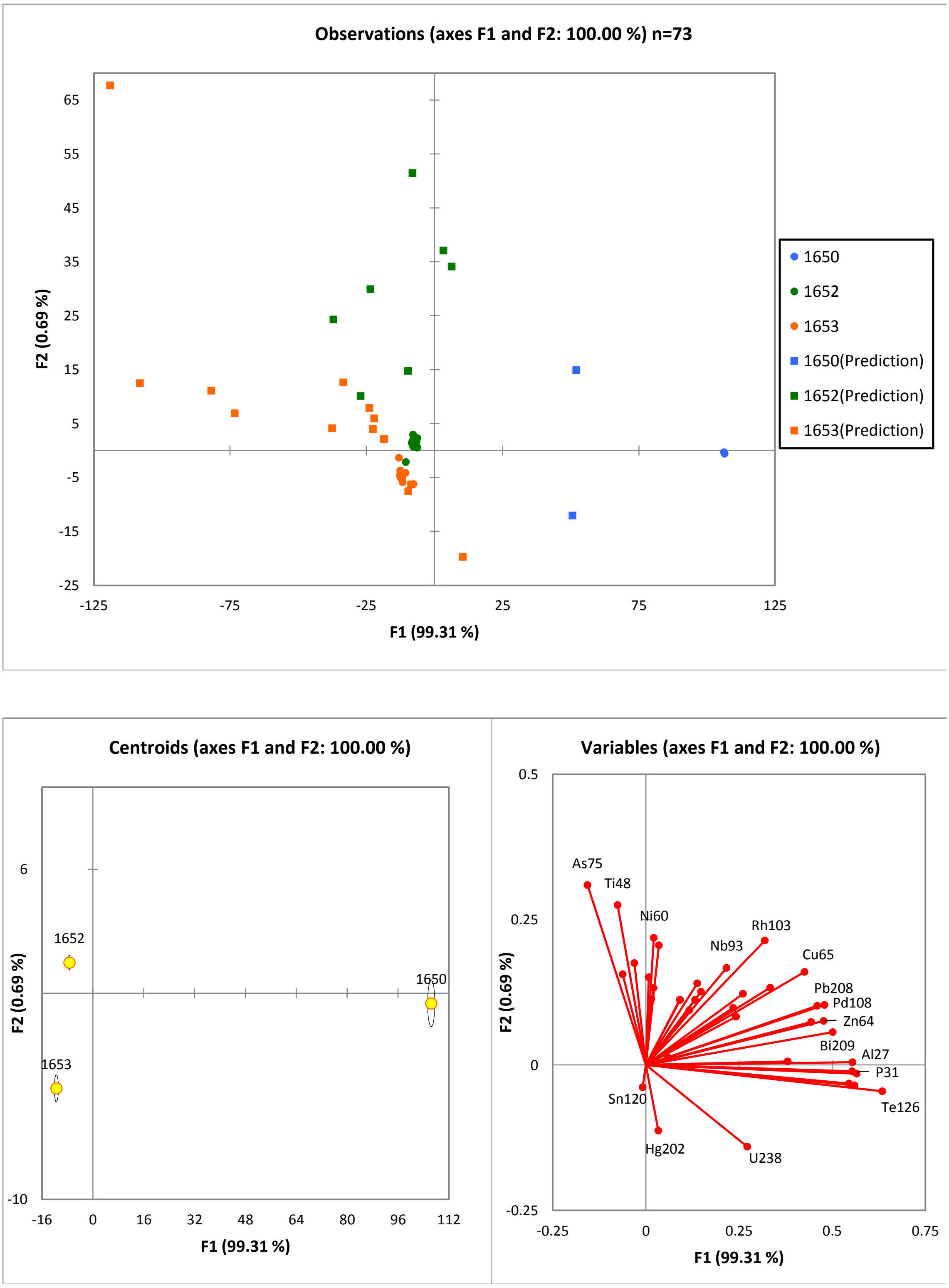


Figure 5.18 – LDA plot showing Peruvian coins in terms of their year of minting

5.5.2.4 Spain

This study used 103 coins minted in Spain. The coins were minted in the 1610s, 1800s and 1810s with enough coins minted in 1650 and 1651 to be able to separate those two years into two individual populations. Of the 103 Spanish coins, 48 had not been identified as to their year of minting. Linear discriminant analysis of these coins is detailed in Figure 5.19.

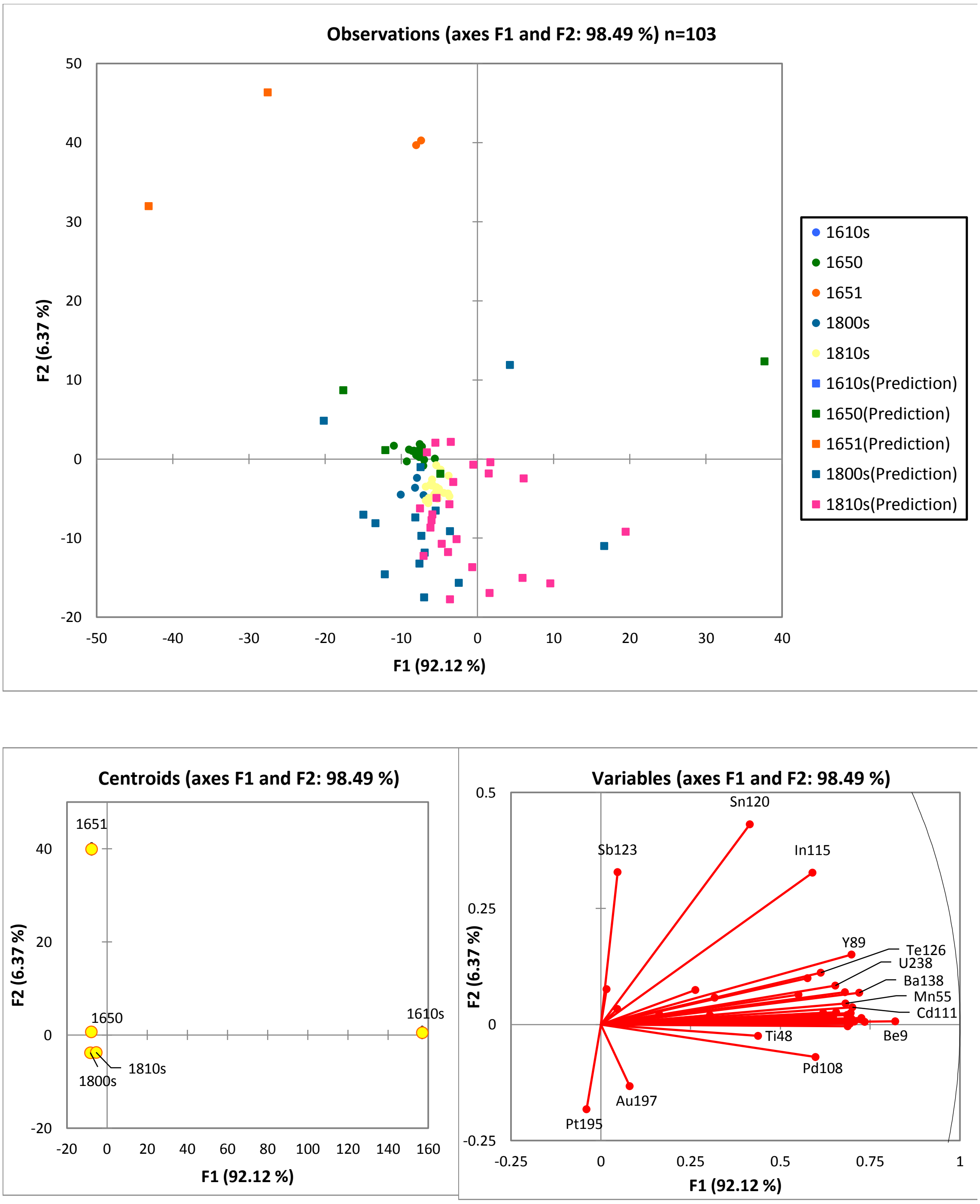
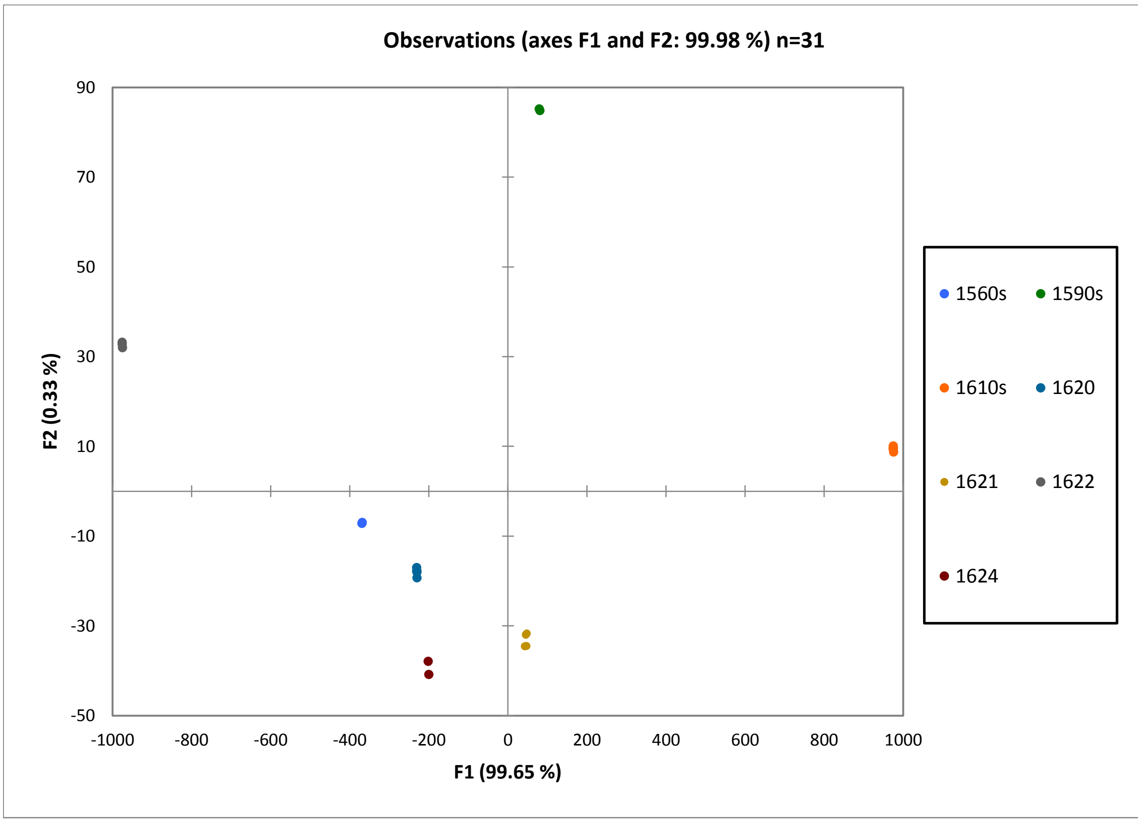


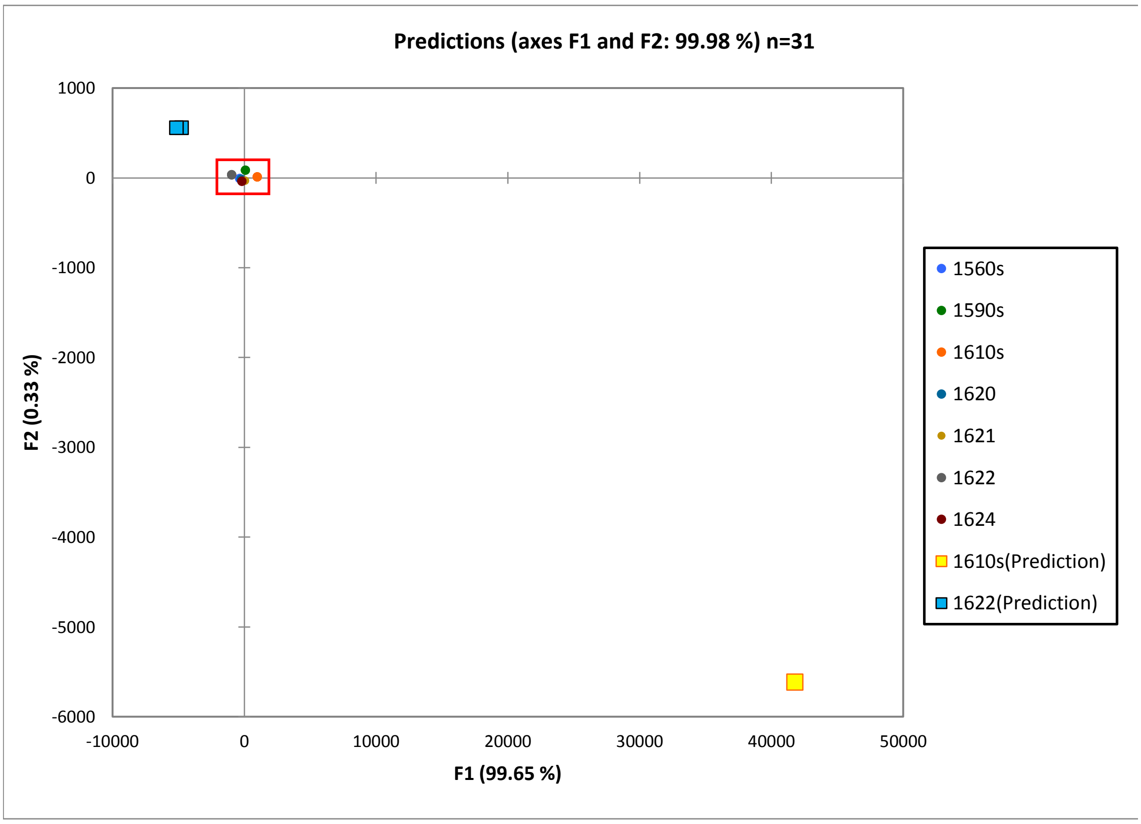
Figure 5.19 - LDA plot showing Spanish coins in terms of their year of minting

Generally good separation between populations can be observed in Figure 5.19, with some overlap between coins minted in the 1800s and 1810s. Coins minted in the 1610s are characterised by relatively high beryllium content, as well as titanium, cadmium and manganese. Those minted in 1651 would appear to be relatively high in antimony, while coins minted in the 1800s and 1810s are relatively high in platinum. Interestingly, no particular element would appear to separate coins minted in 1650 from other populations, but rather it is a lack of those elements which are significant in the other four populations.

5.5.2.5 United Netherlands

This study used 31 coins minted in the United Netherlands. The 28 coins that had been visually identified were minted in the 1560s and the 1610s, as well as a number of coins from each of 1620, 1621, 1622 and 1624. Linear discriminant analysis of these coins is detailed in Figure 5.20.


Observations (axes F1 and F2: 99.98 %) n=31
F2 (0.33 %)
90
70
50
30
10
-10
-30
-50
-1000
-800
-600
-400
-200
0
200
400
600
800
1000
F1 (99.65 %)
● 1560s
● 1590s
● 1610s
● 1620
● 1621
● 1622
● 1624


Predictions (axes F1 and F2: 99.98 %) n=31
F2 (0.33 %)
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-10000
0
10000
20000
30000
40000
50000
F1 (99.65 %)
● 1560s
● 1590s
● 1610s
● 1620
● 1621
● 1622
● 1624
□ 1610s(Prediction)
□ 1622(Prediction)

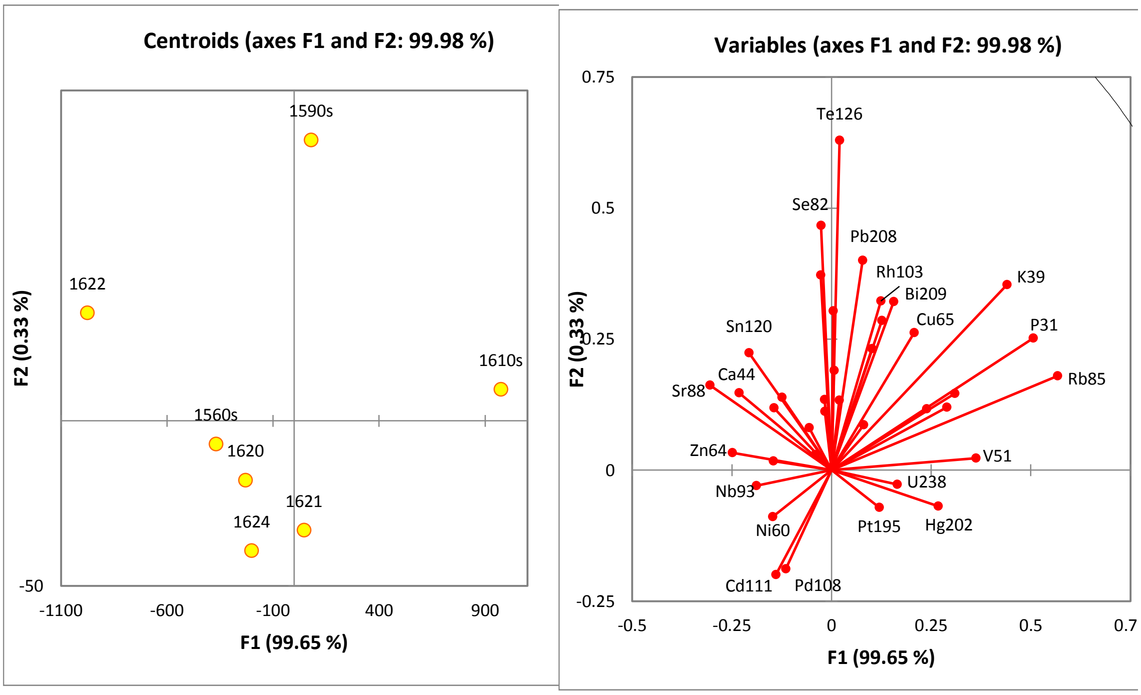


Figure 5.20 - LDA plot showing United Netherlands coins in terms of their year of minting. The top plot is the indicated inset from the following plot.

Due to fluctuating supply from a number of silver sources, as well as the relatively small sample size, coins from the United Netherlands separate well into subpopulations based on their year of minting.

Coins minted in the 1560s are characterised by relatively high niobium content, the 1590s are characterised by relatively high tellurium, the 1610s by vanadium, 1620 by nickel, 1621 by platinum and palladium, 1622 by strontium, calcium and tin and 1624 is characterised by relatively high cadmium content.

5.5.2.6 Summary of predictions

A summary of the 150 previously unidentified coins and their predicted year of minting is provided in Table 5.5. Predictions of year of minting generated by the LDA algorithm have been checked for accuracy by comparing them with the years the identified sovereign reigned, or the year the ship was wrecked. Errors in predicted year are marked in red, and the reason they have been determined to be errors, whether it is because they fall outside the reign of the sovereign on the coin or because they occur after the ship was wrecked, are similarly marked in red. The actual error in years, is detailed in the final column of Table 5.5.

Table 5.5 – Results of predicted of year of minting

Coin	*Ship*	Mint	Country	Sovereign	Predicted Year	Error (years)
S050	*Vergulde Draeck*	Mexico	New Spain	Unidentified	1652	0
S105	*Rapid*	Guatemala	New Spain	Carlos IV	1653	130
S106	*Rapid*	Guatemala	New Spain	Carlos IV	1640s	140
S107	*Rapid*	Madrid	Spain	Carlos IV	1651	130
S110	*Rapid*	Lima	Peru	Carlos IV	1650	130
S111	*Rapid*	Lima	Peru	Carlos IV	1653	130
S112	*Rapid*	Lima	Peru	Carlos IV	1652	130
S113	*Rapid*	Lima	Peru	Carlos IV	1650	130
S147	*Correia de Azia*	Unidentified	New Spain	Unidentified	1810s	0
S148	*Correia de Azia*	Unidentified	Spain	Unidentified	1810s	0
S149	*Correia de Azia*	Mexico	New Spain	Unidentified	1800s	0
S150	*Correia de Azia*	Unidentified	Peru	Fernando VII	1654	150
S172	*Correia de Azia*	Unidentified	Peru	Carlos III	1800s	15
S173	*Correia de Azia*	Unidentified	Peru	Carlos IV	1800s	0
S174	*Correia de Azia*	Unidentified	Peru	Unidentified	1653	0
S175	*Correia de Azia*	Unidentified	Peru	Unidentified	1654	0
S176	*Correia de Azia*	Unidentified	Peru	Unidentified	1810s	0
S177	*Correia de Azia*	Unidentified	Peru	Carlos IV	1800s	0
S184	*Zuytdorp*	Mexico	New Spain	Felipe V	1800s	80
S185	*Zuytdorp*	Mexico	New Spain	Felipe V	1652/1654	50
S186	*Zuytdorp*	Mexico	New Spain	Felipe V	1654	50
S187	*Zuytdorp*	Mexico	New Spain	Unidentified	1640s	0
S188	*Zuytdorp*	Mexico	New Spain	Carlos II	1800s	100
S189	*Zuytdorp*	Mexico	New Spain	Unidentified	1640s	0
S190	*Zuytdorp*	Mexico	New Spain	Felipe V	1800s	80
S191	*Zuytdorp*	Mexico	New Spain	Unidentified	1653	0
S192	*Zuytdorp*	Mexico	New Spain	Unidentified	1640s	0
S193	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S194	*Zuytdorp*	Mexico	New Spain	Felipe V	1653	50
S195	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	80
S196	*Zuytdorp*	Mexico	New Spain	Unidentified	1652	0
S197	*Zuytdorp*	Unidentified	Peru	Unidentified	1800s	80
S198	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	80
S199	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S200	*Zuytdorp*	Mexico	New Spain	Felipe V	1654	50
S201	*Zuytdorp*	Mexico	New Spain	Felipe V	1810s	80
S202	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	90

Coin	***Ship***	**Mint**	**Country**	**Sovereign**	**Predicted Year**	**Error (years)**
S203	*Zuytdorp*	Mexico	New Spain	Felipe V	1810s	90
S204	*Zuytdorp*	Mexico	New Spain	Felipe V	1800s	80
S205	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	90
S206	*Zuytdorp*	Mexico	New Spain	Felipe V	1800s	80
S207	*Rapid*	Madrid	Spain	Carlos IV	1652	130
S208	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S209	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S210	*Rapid*	Madrid	Spain	Carlos IV	1650	130
S211	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S212	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S213	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S214	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S215	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S216	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S217	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S218	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S219	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S220	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S221	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S222	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S223	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S224	*Rapid*	Madrid	Spain	Carlos IV	1651	130
S225	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S226	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S227	*Rapid*	Madrid	Spain	Carlos IV	1800s	0
S228	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S229	*Rapid*	Madrid	Spain	Carlos IV	1650	130
S230	*Rapid*	Madrid	Spain	Carlos IV	1810s	2
S231	*Rapid*	Guatemala	New Spain	Carlos IV	1810s	2
S232	*Rapid*	Guatemala	New Spain	Carlos IV	1652	130
S233	*Rapid*	Guatemala	New Spain	Carlos IV	1653	130
S234	*Rapid*	Guatemala	New Spain	Carlos IV	1800s	0
S235	*Rapid*	Guatemala	New Spain	Carlos IV	1654	130
S236	*Zuytdorp*	Mexico	New Spain	Felipe V	1640s	60
S237	*Zuytdorp*	Mexico	New Spain	Unidentified	1654	0
S238	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S239	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S240	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50

Coin	*Ship*	Mint	Country	Sovereign	Predicted Year	Error (years)
S241	*Zuytdorp*	Mexico	New Spain	Unidentified	1652	0
S242	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	80
S243	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S244	*Zuytdorp*	Mexico	New Spain	Unidentified	1810s	90
S245	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S247	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S248	*Zuytdorp*	Mexico	New Spain	Carlos II	1652	130
S249	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S250	*Zuytdorp*	Mexico	New Spain	Unidentified	1652	0
S251	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S252	*Zuytdorp*	Mexico	New Spain	Felipe V	1653	50
S253	*Zuytdorp*	Mexico	New Spain	Carlos II	1652	15
S254	*Zuytdorp*	Mexico	New Spain	Felipe V	1654	50
S255	*Zuytdorp*	Mexico	New Spain	Felipe V	1653	50
S256	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S257	*Zuytdorp*	Mexico	New Spain	Felipe V	1800s	80
S258	*Zuytdorp*	Mexico	New Spain	Felipe V	1653	50
S259	*Zuytdorp*	Mexico	New Spain	Unidentified	1653	0
S260	*Zuytdorp*	Mexico	New Spain	Felipe V	1653	50
S261	*Zuytdorp*	Mexico	New Spain	Unidentified	1800s	80
S262	*Zuytdorp*	Mexico	New Spain	Unidentified	1652	0
S263	*Zuytdorp*	Mexico	New Spain	Felipe V	1652	50
S264	*Rapid*	Seville	Spain	Carlos IV	1652	130
S265	*Rapid*	Seville	Spain	Carlos IV	1652	130
S266	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S267	*Rapid*	Seville	Spain	Carlos IV	1800s	0
S268	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S269	*Rapid*	Seville	Spain	Carlos IV	1800s	0
S270	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S271	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S272	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S273	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S274	*Rapid*	Seville	Spain	Carlos IV	1800s	0
S275	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S276	*Rapid*	Seville	Spain	Carlos IV	1650	160
S277	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S278	*Rapid*	Seville	Spain	Carlos IV	1800s	0
S279	*Rapid*	Seville	Spain	Carlos IV	1800s	0

Coin	*Ship*	Mint	Country	Sovereign	Predicted Year	Error (years)
S280	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S281	*Rapid*	Seville	Spain	Carlos IV	1800s	0
S282	*Rapid*	Seville	Spain	Carlos IV	1650	160
S283	*Rapid*	Seville	Spain	Carlos IV	1810s	2
S284	*Rapid*	Guatemala	New Spain	Carlos IV	1810s	2
S285	*Rapid*	Lima	Peru	Carlos IV	1810s	2
S286	*Rapid*	Lima	Peru	Carlos IV	1652	160
S287	*Rapid*	Lima	Peru	Carlos IV	1653	160
S288	*Rapid*	Lima	Peru	Carlos IV	1653	160
S289	*Rapid*	Lima	Peru	Carlos IV	1653	160
S290	*Rapid*	Lima	Peru	Carlos IV	1653	160
S291	*Rapid*	Lima	Peru	Carlos IV	1653	160
S292	*Rapid*	Lima	Peru	Carlos IV	1652	160
S293	*Rapid*	Lima	Peru	Carlos IV	1653	160
S294	*Rapid*	Lima	Peru	Carlos IV	1653	160
S295	*Rapid*	Lima	Peru	Carlos IV	1652	160
S296	*Rapid*	Lima	Peru	Carlos IV	1653	160
S297	*Rapid*	Lima	Peru	Carlos IV	1652	160
S298	*Rapid*	Lima	Peru	Carlos IV	1652	160
S299	*Rapid*	Lima	Peru	Carlos IV	1653	160
S300	*Rapid*	Lima	Peru	Carlos IV	1652	160
S301	*Rapid*	Lima	Peru	Carlos IV	1650	160
S302	*Rapid*	Lima	Peru	Carlos IV	1653	160
S303	*Rapid*	Lima	Peru	Carlos IV	1653	160
S304	*Rapid*	Lima	Peru	Carlos IV	1653	160
S305	*Rapid*	Unidentified	Peru	Unidentified	1652	0
S306	*Vergulde Draeck*	Unidentified	Peru	Unidentified	1653	0
S312	*Batavia*	Gelderland	United Netherlands	Unidentified	1620s	0
S321	*Batavia*	Holland	United Netherlands	Unidentified	1620s	0
S350	*Zuytdorp*	Brabant	Germany	Unidentified	1620s	0
S350	*Batavia*	Lubeck	Germany	Unidentified	1620s	0
S352	*Batavia*	Sachsen	Germany	Johann Georg II	1590s	65
S352	*Zuytdorp*	Brabant	Germany	Carlos II	1590s	75
S371	*Rapid*	Unidentified	Germany	Unidentified	1560s	0
S371	*Zuytdorp*	Brabant	Germany	Felipe IV	1560s	60
S372	*Vergulde Draeck*	Unidentified	Germany	Unidentified	1620s	0
S372	*Zuytdorp*	Unidentified	Germany	Unidentified	1620s	0
S386	*Zuytdorp*	Unidentified	Germany	Unidentified	1560s	0

Coin	***Ship***	**Mint**	**Country**	**Sovereign**	**Predicted Year**	**Error (years)**
S386	*Zuytdorp*	Mexico	New Spain	Unidentified	1560s	0
S387	*Zuytdorp*	Unidentified	Peru	Unidentified	1620s	0
S388	*Zuytdorp*	Unidentified	United Netherlands	Unidentified	1610s	0
S394	*Vergulde Draeck*	Seville	Spain	Unidentified	1610s	0
S395	*Vergulde Draeck*	Seville	Spain	Unidentified	1610s	0
S402	*Vergulde Draeck*	Unidentified	New Spain	Unidentified	1620s	0
S403	*Vergulde Draeck*	Mexico	New Spain	Unidentified	1620s	0

The error in populations of coins based on their country of minting is detailed further in Table 5.6. The rates of error for coins whose predicted year of minting is inconsistent with identified sovereign or the ship the coin was found associated with have been divided into three groups. The groups capture coins that have been predicted to have been minted 2-15 years outside of a range of years that would be consistent with identified coin features, 50-65 years, and 75 years and over. In total, approximately half of the coins were predicted to have been minted in a year which is consistent with, or within 15 years of what was already known about the coin. However, the other half were predicted to have been minted at least 50 years different to what would be consistent with known information about the coin.

Table 5.6 – The range of error in predicted years of minting of coins.

Country	Total coins predicted	% consistent	% error 2-15 years	% error 50-65 years	% error 75+ years
New Spain	63	26.98	4.76	34.92	33.33
Peru	35	22.86	5.71	0.00	71.43
Spain	48	37.50	43.75	0.00	18.75
United Netherlands	3	100.00	0.00	0.00	0.00
Germany	9	77.78	0.00	11.11	11.11
Total	158	33.54	16.46	14.56	35.44

Given the sample size from each of the countries studied, the United Netherlands, Germany and Spain show the least errors in prediction of year of minting. Over half of coins minted in New Spain and Peru, however, were predicted by this method to have been minted more than 50 years before or after other information would suggest they had been minted.

5.5.3 Conclusion

This research into trace elemental composition and absolute dating of artefacts, despite the discussed errors, has shown promising results for further research. While predictions of the year of minting of unidentified coins contained several errors which will be discussed further in chapter 7, the LDA process shows that of those coins of known year of minting separation between years or decades of minting is certainly possible.

Countries that relied upon imports for their silver supply, particularly Spain and the United Netherlands, and to a slightly lesser extent Germany, show greater separation between coins minted in different years or decades. This is due to fluctuations in imports of silver from different places necessarily altering the overall elemental fingerprint of imported silver on a larger scale than those countries with local silver supply (Peru and New Spain in this case). Given that mining activity in Peru and New Spain was not limited to a single mine with a unique trace elemental fingerprint, fluctuating output from different mines has the same effect but to a lesser extent, on the overall elemental fingerprint of Peruvian or New Spanish silver over time.

Given these results, it has been shown to be possible, given a large and comprehensive database, to determine the absolute date of an artefact based on its trace elemental composition.

Chapter conclusion

This chapter has demonstrated that based on ICP-MS analysis, the surface of a coin can be considered to be representative of the bulk of a coin. Following on from this confirmation, the present research has shown that trace elemental composition can be used for both provenance determination of the coins and artefacts in question, as well as a tool for absolute dating of archaeological artefacts. Further, lead isotope analysis confirms conclusions regarding European and New World silver provenance studies conducted by Desaulty *et al.* (2011).

Chapter 6 – Results of Electron Microscopy

Chapter introduction

Structural and morphological information about coins complements the compositional analysis of a coin detailed in chapter 5. In this chapter various electron microscopy techniques were employed to image the interior of coins, in order to investigate the structural and morphological differences which are indicative of effects on the surface of the coin from corrosion and method of manufacture. Compositional analysis alone cannot provide this information.

Firstly, the composition of the surface of coins in comparison to the bulk of each coin has been further investigated using EPMA and BSE imaging on polished cross-sections of coins. The aim of this study was to measure the amount of preferential copper leaching and silver surface enrichment on the silver/copper alloy's surface, in terms of the potential effect of silver surface enrichment on bulk compositional surface analyses. Secondly, the internal microstructure and morphology of the silver-rich and copper-rich phases of the coins was investigated and characterised using BSE imaging, FIB-SEM, and transmission electron microscopy (TEM). Finally, electron backscatter diffraction (EBSD) was used to investigate the internal microstructure of a selection of coins in order to determine their method of manufacture.

This chapter details analysis that was performed on the cross-section of a selection of coins, allowed by the Western Australian Museum for destructive analysis. Images of the coins prior to being clipped, mounted in resin and polished are shown in Figure 6.1.


372-1


372-2


372-3

372-B

372-F

372-H

372-J

025

050

072

395

Figure 6.1 – Images of coins (from left to right, top to bottom) 372-1, 372-2, 372-3, 372-B, 372-F, 372-H, 372-J, 025, 050, 072 and 395 prior to analysis

6.1 Measuring corrosion and silver surface enrichment on the surface of silver coins

6.1.1 Aim

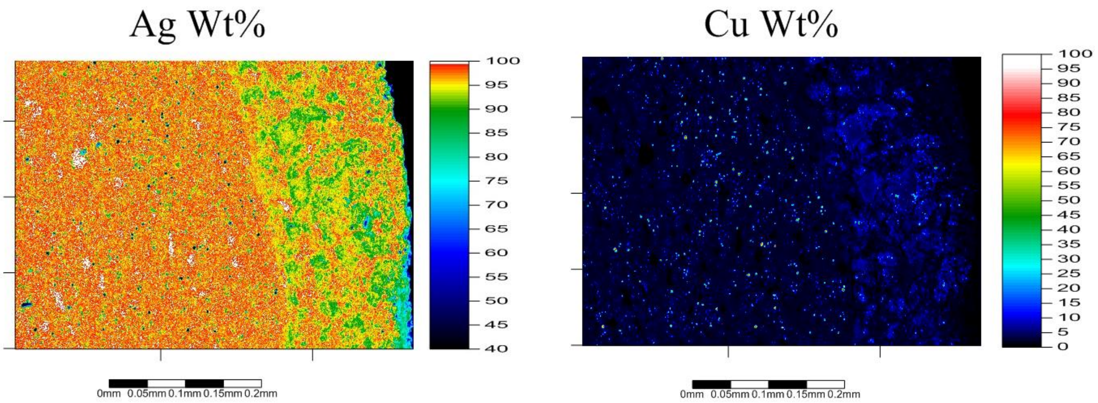
Surface corrosion of archaeological metal artefacts will often lead to a difference in composition between the surface of the artefact and the bulk. Analytical techniques commonly used to determine the elemental composition of metal artefacts are preferably non-destructive, including surface analytical techniques such as XRF, PIXE and SEM-EDS. In this case, the elemental composition of the degraded surface of a sample may not be indicative of the bulk of the sample. This study focuses on 17th century silver associated with the 1656 wreck of the *Vergulde Draeck* which the Western Australian Museum allowed to be destructively analysed. Preferential copper leaching from the surface of archaeological silver has been observed to lead to silver surface enrichment, and misleading results of silver/copper composition from surface analyses (Borges *et al.*, 2016). Here we study the composition of both the surface and the bulk of a selection of scrap coins.

6.1.2 Results

6.1.2.1 EPMA results

Coin scraps recovered from the *Vergulde Draeck* were subjected to EPMA analysis. The scraps had been mounted in resin polished and were quantitatively imaged in order to determine the silver and copper compositional distribution from the surface to the bulk, on a polished cross-section of the coin. EPMA results for five coins follow (Figures 6.2-6.6).

A note on how to interpret the EPMA images follows: The images represent the total wt% of a given analyte, in this case silver or copper, as indicated in the image, or the total wt% of the sample, as is the case for images which have been annotated for quantitative compositional analysis at the surface, the bulk, and across a line scan of the entire image. The hue of each pixel represents the wt% at that point, according to the legend to the right of the image. Where the hue would indicate lower silver content, the corresponding copper wt% image often shows a higher copper content at the same point. In terms of the total wt% images, anything lower than 100% total wt% can be interpreted as porosity. The line scans below the total wt% images represent the silver and copper content across the indicated line in the image, and have been used to quantitatively visualise both the relationship between silver and copper content in the coin and also to determine if the surface of a coin has a significantly different silver/copper content to the bulk of the coin and hence if surface analyses on the coin would be representative of the content of the entire coin. The white areas indicated on the total wt% images further investigate the differences between silver and copper content from the bulk to the surface of the coin with silver and copper content results detailed in the table following the figure


Ag Wt%

Cu Wt%

Figure 6.2 – Silver and copper elemental distributions on the polished cross-section of sample 372-H, identified as having originated from the Mexico mint.

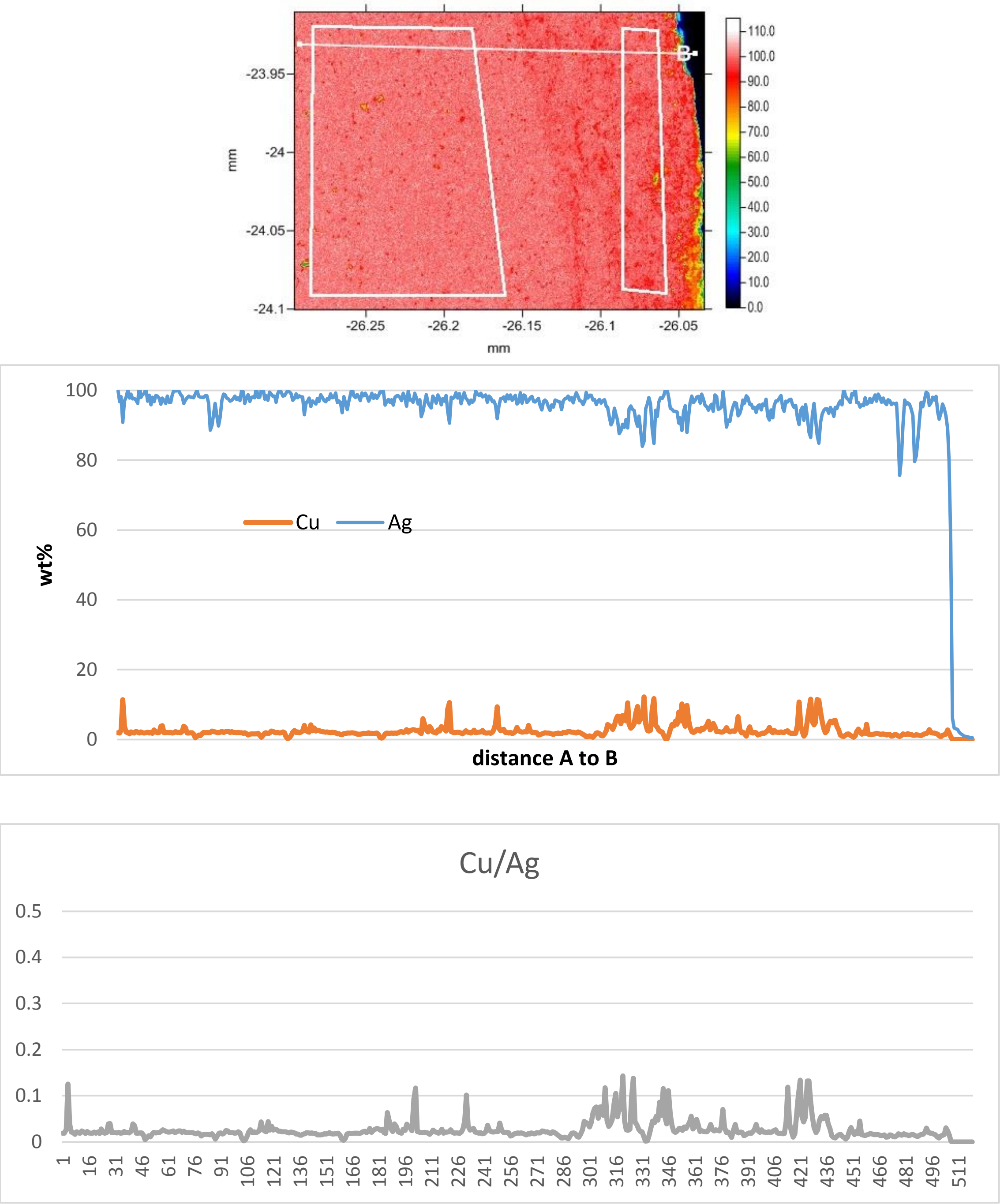


Figure 6.3 – Total wt% elemental distribution on sample 372-H, with indications (in white) of the locations of a quantitative line scan, and area scans representative of the bulk and surface of the coin. Below, the wt% distributions along the line scan of silver and copper, and the ratio of copper to silver along the line scan.

Table 6.1 – Silver and copper content of the bulk and surface areas identified in Figure 6.3

wt%	Ag wt%	Cu wt%
372-H bulk	97.0 (±4.67)	2.77 (±4.28)
372-H surface	94.1 (±4.75)	3.3 (±2.85)

A layer on the surface of 372-H, approximately 200µm thick, can be observed at the right of the images (Figure 6.2 & 6.3). The bulk of this coin can be characterised by variable copper-rich phases in a silver-rich matrix, while the surface is characterised by porosity, a decrease of 5-10% in silver content with an increase of 5-10% in copper content, and larger copper-rich phases. The total wt% image (Figure 6.3) shows increased porosity in the surface of the coin especially in the top 50µm. The accompanying profile graphs of silver and copper content in wt% should not be taken as absolute, particularly in terms of copper content, given the sensitivity and resolution limitations of EPMA which has an interaction volume in silver of approximately 1×1.2µm at 20kV. Investigation using other techniques detailed in section 6.2.2 demonstrated that copper-rich inclusions are close to 100% copper. However, the profiles do serve to detail the correlation between copper-rich phases and a decrease in silver content, the increase of porosity towards the surface of the coin reflected in more variable silver concentration towards the surface, and the relative decrease of copper towards the surface of the coin. In terms of the silver/copper ratio between the surface and the bulk of the coin, copper-rich phases can be seen to be larger and more numerous towards the surface of the coin. This accounts for the higher variation seen in the right of both the silver and copper wt% line scans, and is also reflected in the small increase in copper content and related decrease in silver content between the bulk and the surface of the coin (Table 6.1).

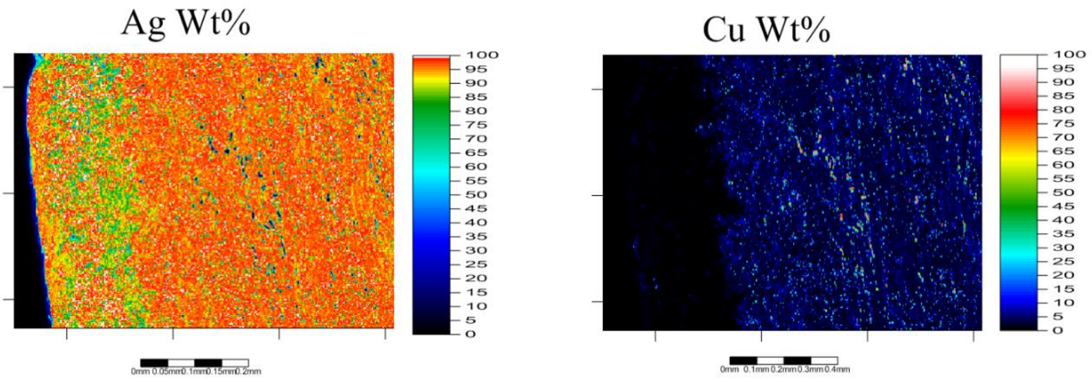


Figure 6.4 – Silver and copper elemental distributions on the polished cross-section of sample 372-3, an unidentified coin.

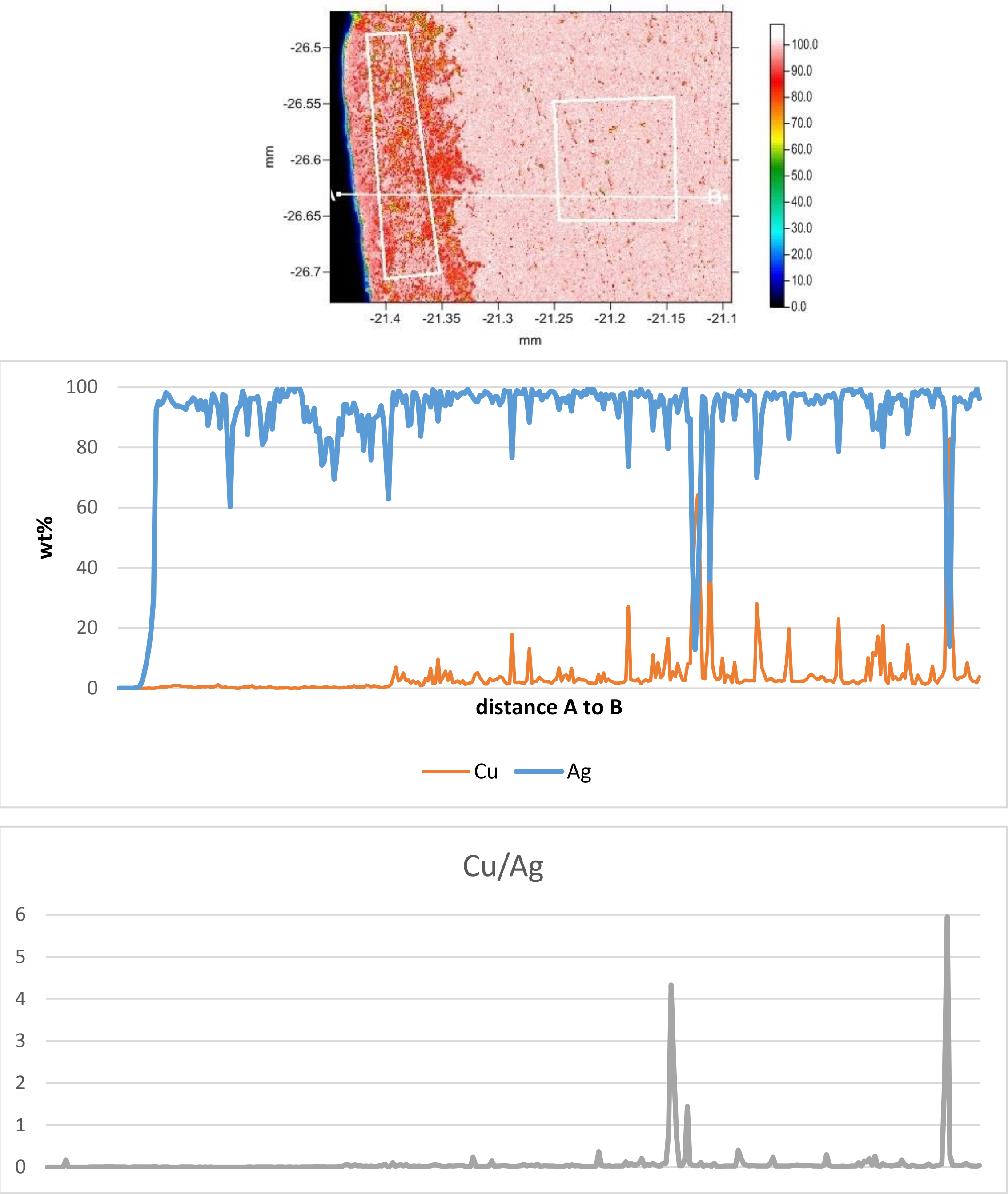


Figure 6.5 – Total wt% elemental distribution on sample 372-3, with indications (in white) of the locations of a quantitative line scan, and area scans representative of the bulk and surface of the coin. Below, the wt% distributions along the line scan of silver and copper and the ratio of copper to silver along the line scan.

Table 6.2 - Silver and copper content of the bulk and surface areas identified in Figure 6.5

Wt%	Ag wt%	Cu wt%
372-3 bulk	93.6 (±11.85)	5.72 (±10.13)
372-3 surface	92.21 (±8.69)	0.37 (±0.77)

Sample 372-3 also displays a distinct surface layer of approximately 200µm thick to the left of the images (Figure 6.4 & 6.5). The bulk of the coin is similarly characterised by consistent copper-rich phases in a silver-rich matrix, copper-rich phases correlate with areas of low silver content, as seen in the line scans of the coin. The surface layer of this coin displays an increase in porosity which can be seen in both the total wt% image, and increased variability of silver content in the surface region of the line scan, and almost no (<1wt%) copper content. This information is reflected in both the line scans and the silver and copper content of the surface compared to the bulk (Table 6.2).

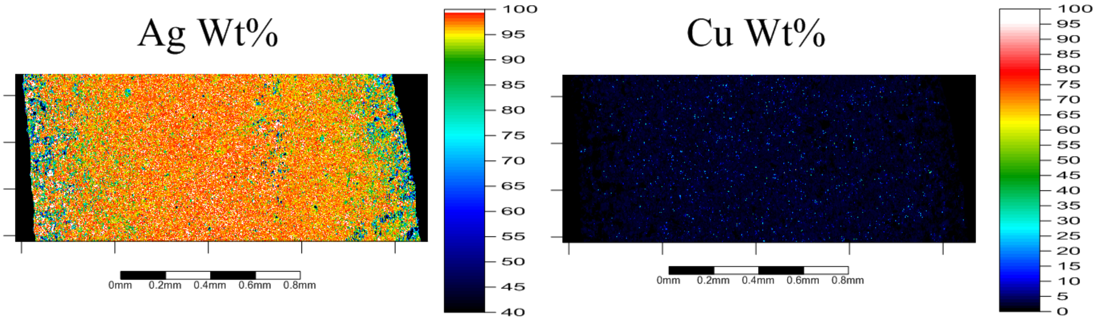


Figure 6.6 – Silver and copper elemental distributions on the polished cross-section of sample 372-1, an unidentified coin.

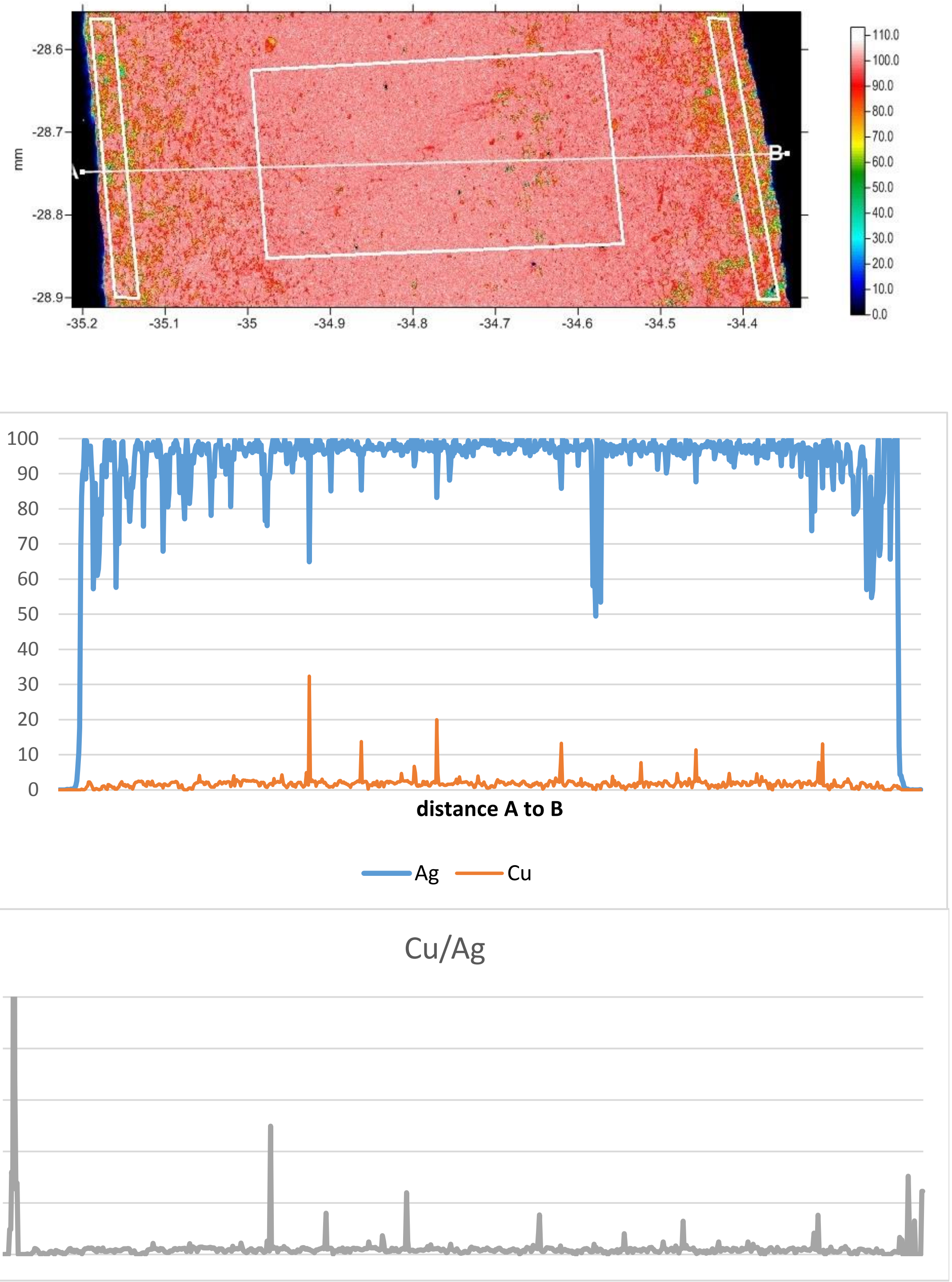


Figure 6.7 - Total wt% elemental distribution on sample 372-1, with indications (in white) of the locations of a quantitative line scan, and area scans representative of the bulk and surfaces of the coin. Below, the wt% distributions along the line scan of silver and copper and the ratio of copper to silver along the line scan.

Table 6.3 - Silver and copper content of the bulk and surface areas identified in Figure 6.7

Wt%	Ag wt%	Cu wt%
372-1 bulk	96.6 (±6.05)	2.08 (±2.59)
372-1 surface (left)	86.83 (±16.59)	0.8 (±1.54)
372-1 surface (right)	85.95 (±15.93)	1.04 (±1.42)

An image of the entire cross-section of sample 372-1 is shown (Figure 6.6 & 6.7). On both surfaces of the coin (designated as "left" and "right"), there is a visible surface layer of approximately 200µm. The bulk of the coin shows a silver-rich matrix with copper-rich phases, and a slightly more homogeneity between silver and copper-rich phases towards the centre of the coin. The surface layers of this coin are characterised by a decrease in both silver and copper content and an increase in porosity, as can be seen in both the line scans and the silver and copper composition of the bulk compared to the surfaces (Table 6.3).

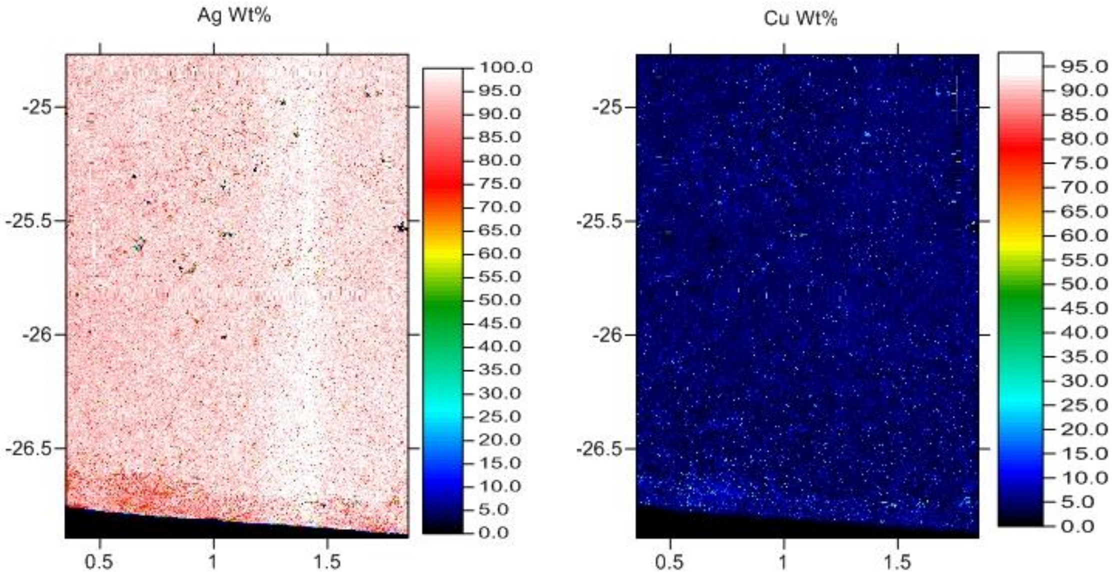


Figure 6.8 - Silver and copper elemental distributions on the polished cross-section of sample 025, an 8 *reale* piece minted in Mexico in 1653.

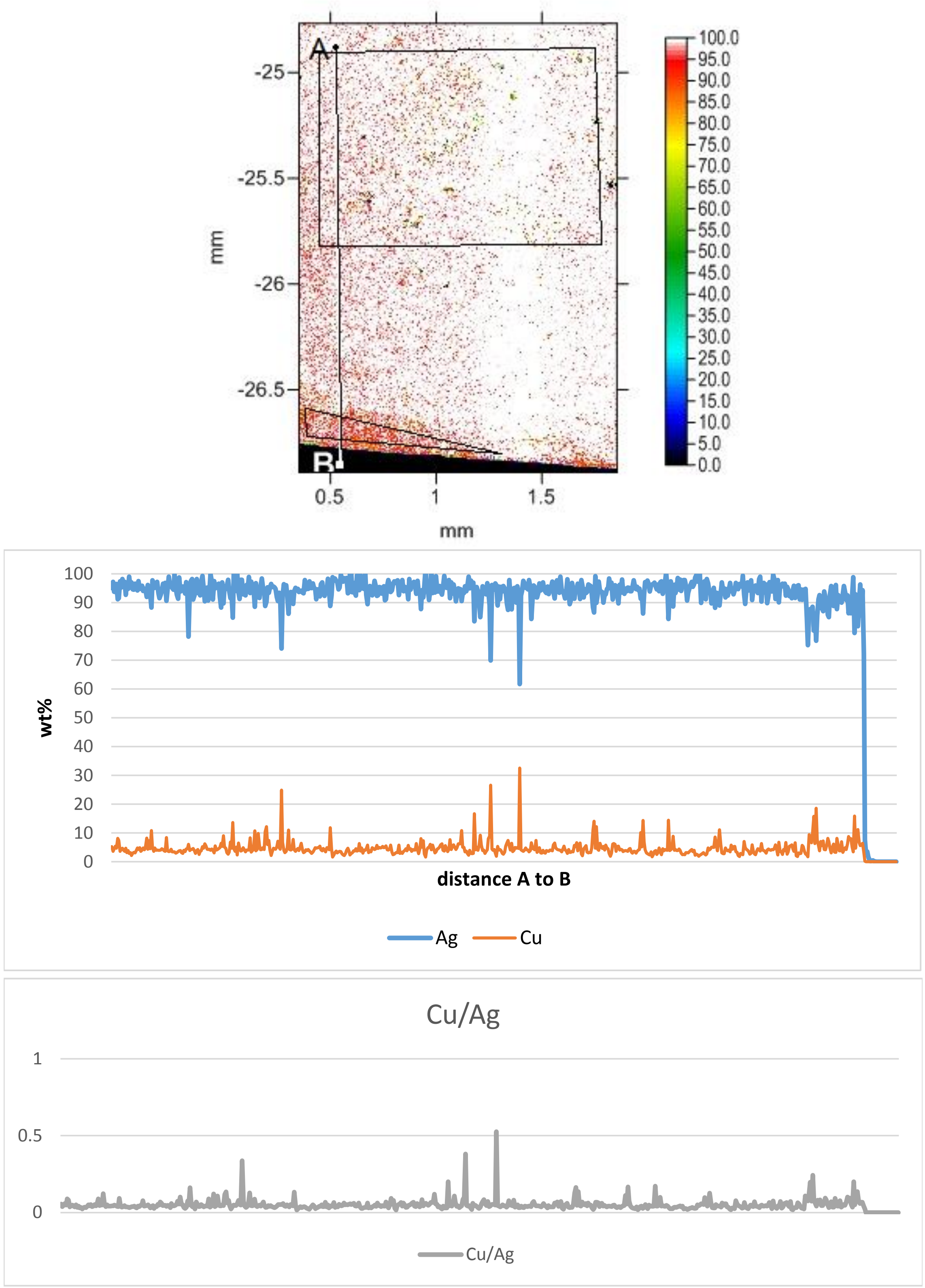


Figure 6.9 - Total wt% elemental distribution on sample 025, with indications (in black) of the locations of a quantitative line scan, and area scans representative of the bulk and surface of the coin. Below, the wt% distributions along the line scan of silver and copper and the ratio of copper to silver along the line scan.

Table 6.4 – Silver and copper content of the bulk and surface areas identified in Figure 6.9

Wt%	Ag Wt%	Cu Wt%
025 bulk	95.39 (±7.31)	4.81 (±3.16)
025 surface	88.84 (±8.72)	6.81 (±5.55)

A surface layer of approximately 200µm thick is visible at the bottom of the images in Figures 6.8 and 6.9. The bulk of the coin can be characterised by a consistent silver-rich matrix with some instances of copper-rich phases which correlate with a lower silver content, as detailed in the results of the line scan. The surface shows a decrease in silver and an increase in copper content, with no significant increase in porosity.

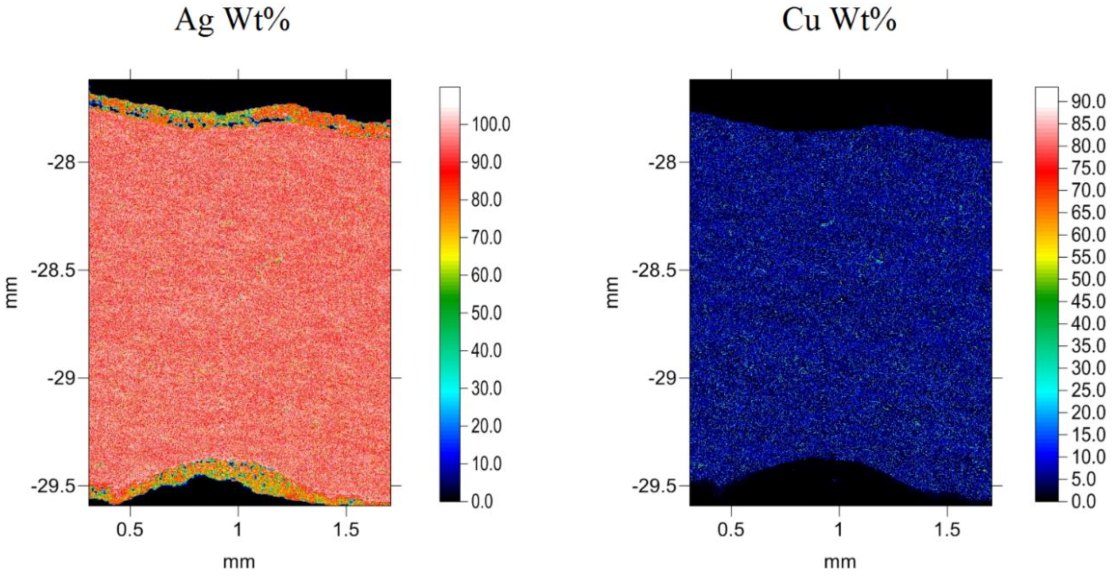


Figure 6.10 - Silver and copper elemental distributions on the polished cross-section of sample 072, an 8 *reale* piece minted in Potosí in 1653.

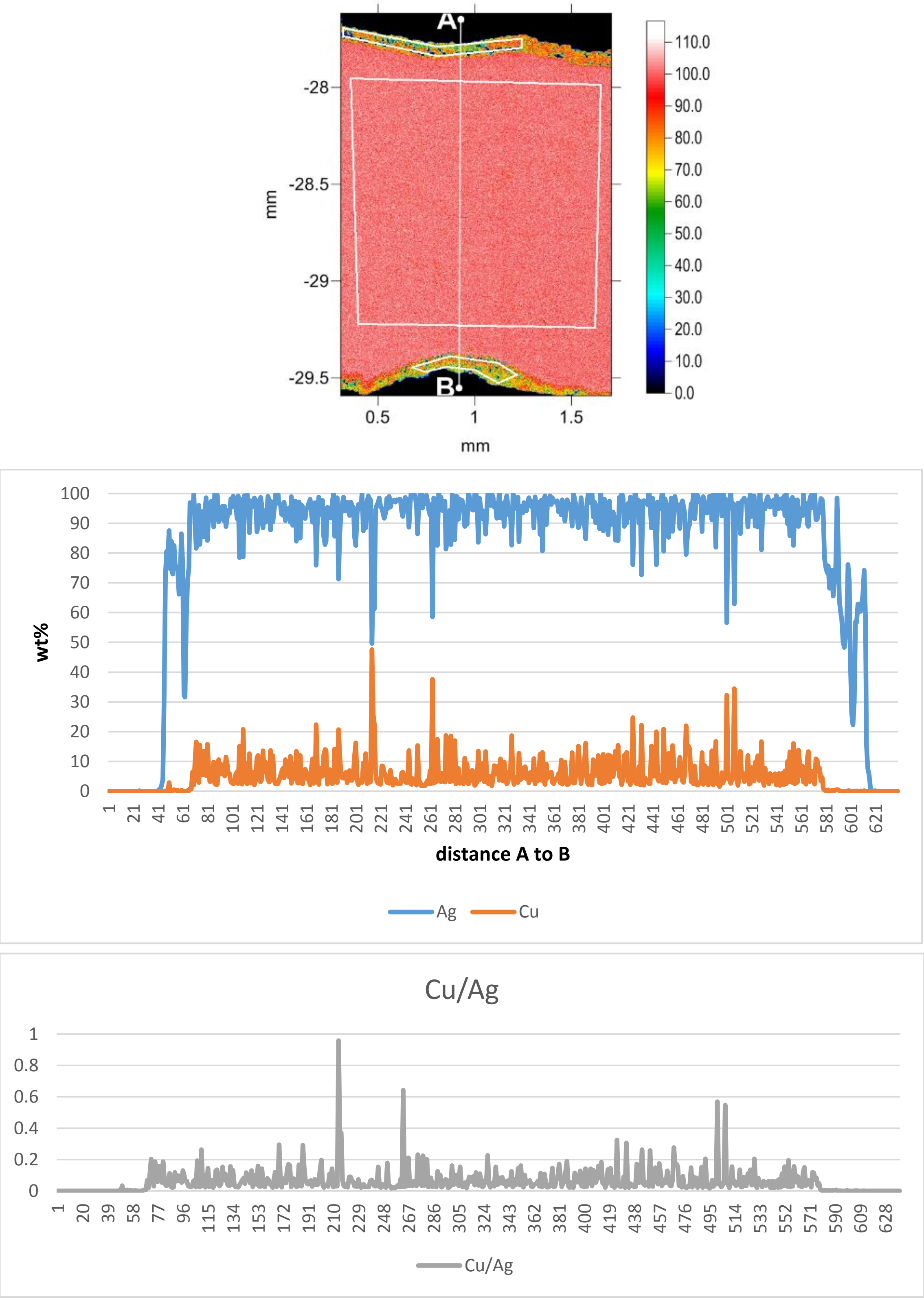


Figure 6.11 - Total wt% elemental distribution on sample 072, with indications (in white) of the locations of a quantitative line scan, and area scans representative of the bulk and surfaces of the coin. Below, the wt% distributions along the line scan of silver and copper and the ratio of copper to silver along the line scan.

Table 6.5 - Silver and copper content of the bulk and surface areas identified in Figure 6.11

Wt%	Ag Wt%	Cu Wt%
072 bulk	93.86 (±7.49)	6.62 (±6.27)
072 top surface	64.57 (±24.86)	0.2 (±0.44)
072 bottom surface	67.05 (±21.72)	0.25 (±0.43)

Surface layers of approximately 70µm thick can be observed at the top and bottom of the images in Figures 6.10 and 6.11. The bulk of the coin can be seen to be of relatively uniform composition, with copper-rich phases corresponding to a decrease in silver content, as reflected in the line scan results. The surfaces of this coin are porous, as can be seen in the total wt% image of the coin as well as in the line scan results, which show a decrease in both copper and silver content towards the surfaces of the coin.

Table 6.6 provides a summary of the quantified differences between silver and copper content from the three coins from their bulk to their surface. Coin 372-H can be seen to maintain a silver/copper ratio from bulk to surface, and indeed slightly increase copper content in the surface of the coin. Coin 372-3, observed to have close to zero copper content in the surface of the coin can be seen to have a significant percentage decrease in copper content from the bulk to the surface of the coin in contrast to coin 372-1, which also displays less than 1% copper content at the surface of the coin however the copper content in the bulk of the coin was also low. It is of interest to note that coin 372-3 has the lowest silver content of the three sampled, and as such can be expected to be most affected by preferential copper leaching and silver surface enrichment.

Table 6.6 – Summary of data gained from EPMA results of bulk and surface analyses of silver coins.

Wt%	**Ag wt%**	**Cu wt%**
372-H bulk	97.0 (±4.67)	2.77 (±4.28)
372-H surface	94.1 (±4.75)	3.3 (±2.85)
372-3 bulk	93.6 (±11.85)	5.72 (±10.13)
372-3 surface	92.21 (±8.69)	0.37 (±0.77)
372-1 bulk	96.6 (±6.05)	2.08 (±2.59)
372-1 surface ($\bar{x}$)	86.39 (±16.26)	0.92 (±2.96)
025 bulk	95.39 (±7.31)	4.81 (±3.16)
025 surface	88.84 (±8.72)	6.81 (±5.55)
072 bulk	93.86 (±7.49)	6.62 (±6.27)
072 surface ($\bar{x}$)	65.81 (±23.29)	0.23 (±0.44)

6.1.2.2 BSE imaging results

SEM BSE imaging was used to further investigate the surface layer of polished cross-sections of coins at a higher magnification than EPMA. Coin scraps from the wreck of the *Vergulde Draeck* were imaged using SEM BSE imaging. The results are detailed below (Figures 6.11-6.17). It is worth noting when interpreting these images, that they are a two dimensional representation of a three dimensional object. In particular, the copper rich phases that are oriented parallel to the coins' surface do not all appear this way in the BSE images. Three dimensional imaging confirms their orientation and is discussed further in figures 6.26-6.28 and in appendix 7.

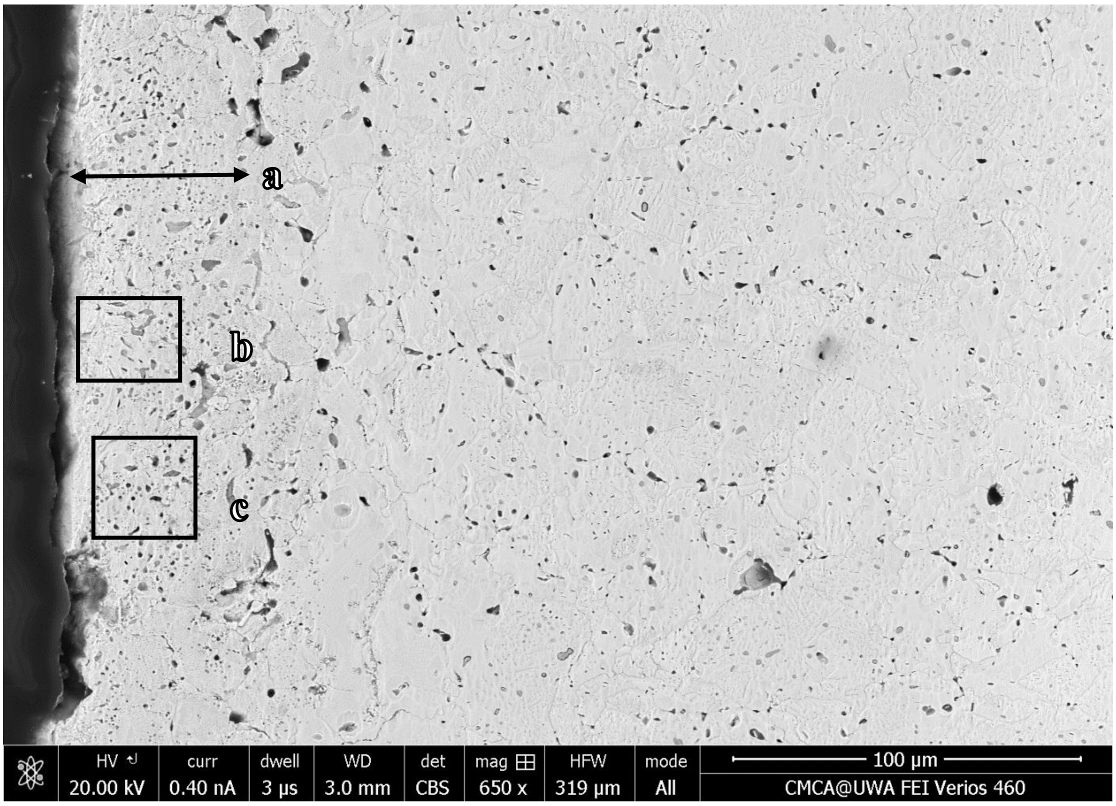


Figure 6.12 – BSE image of the cross-section of sample 372-B, an unidentified coin. a) the depth of the surface layer, b) an increase in copper-rich phases, c) an increase in porosity.

Sample 372-B (Figure 6.12) shows a surface layer approximately 50µm thick, indicated in the image. The surface layer is characterised by increased porosity and more frequent copper-rich phases than the bulk of the coin. Porosity can be identified in the image as grey sections, while the copper-rich phases are darker. Copper-rich phases can be seen throughout the rest of the coin however they are not as numerous as they appear in the surface.

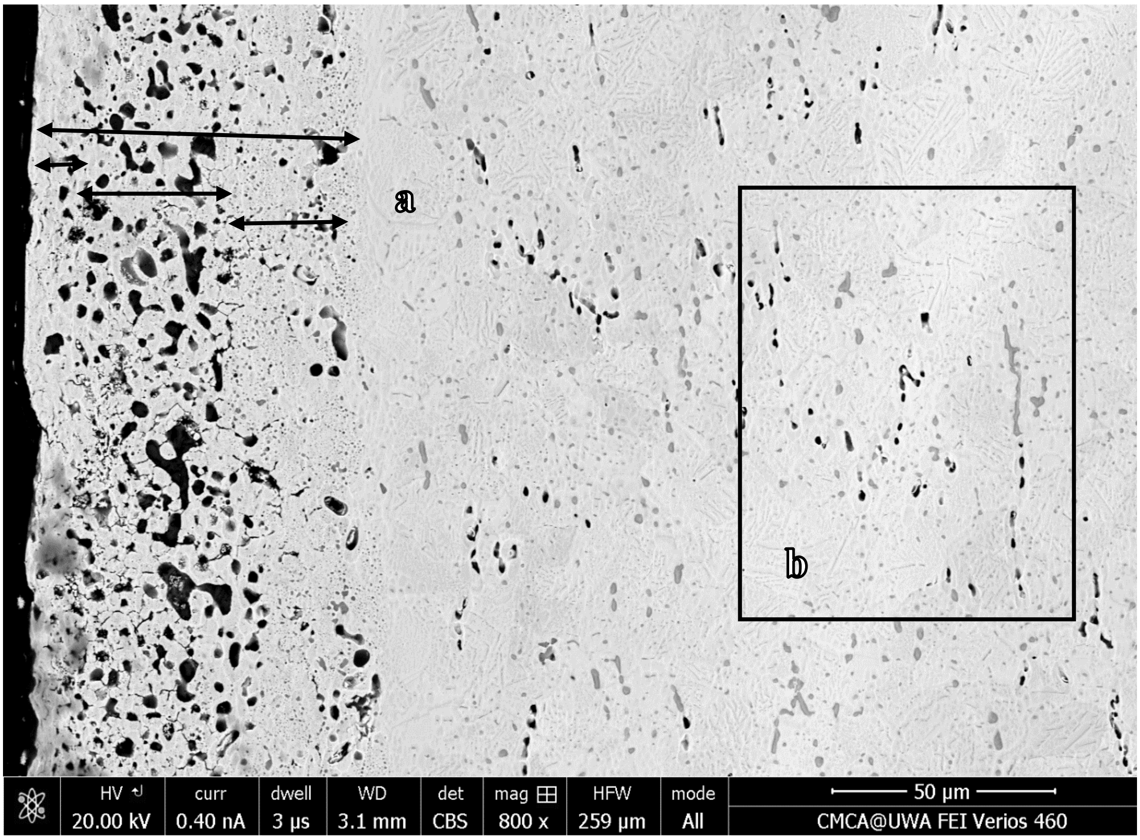


Figure 6.13 - BSE image of the cross-section of sample 372-F, an unidentified coin. a) surface layers, b) copper-rich phases in the interior of the coin running parallel to the surface

Sample 372-F shows a total surface layer of approximately 70µm thick (Figure 6.13). Within this layer, an immediate surface layer of consolidated metal with little porosity is visible for the first 10µm. Below this layer is a 40µm thick, extremely porous layer, followed by a 20µm thick layer demonstrating some porosity and smaller, more frequent copper-rich phases than the bulk of the coin. The copper-rich phases in the bulk of the coin can be seen to be orientated parallel to the surface of the coin.

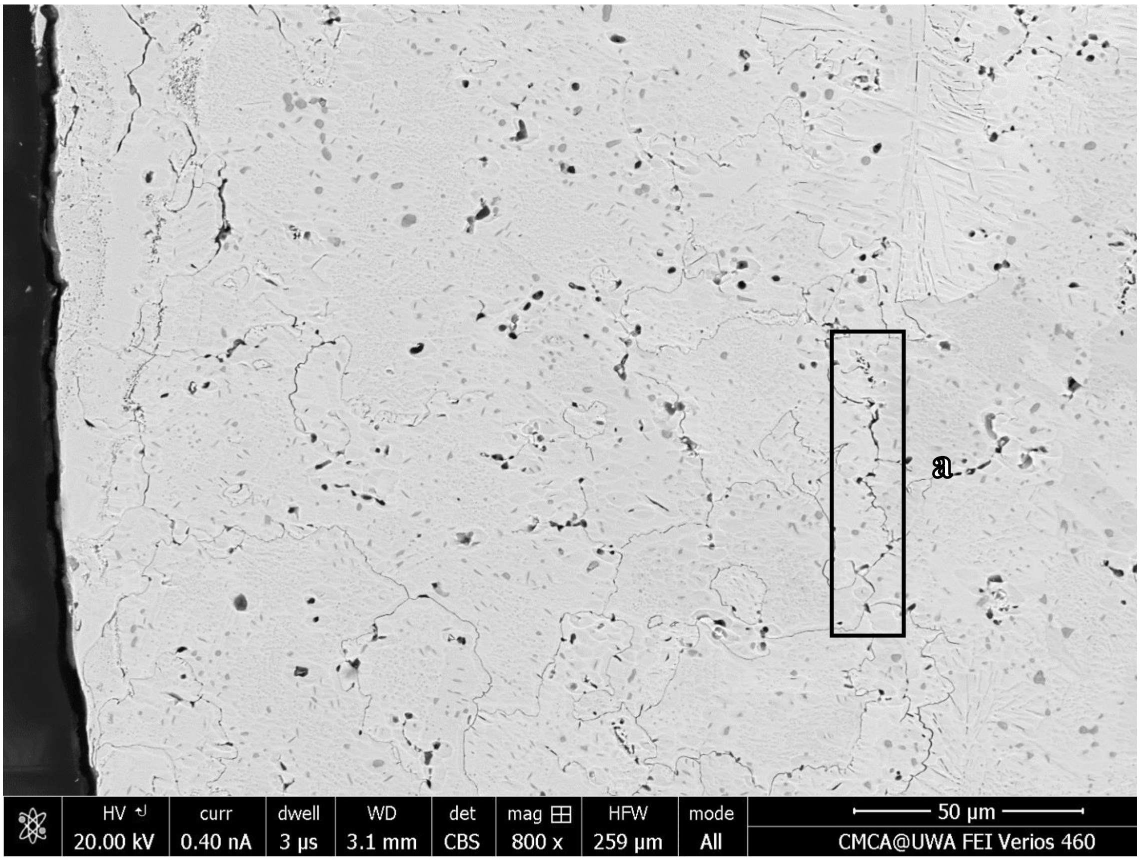


Figure 6.14 - BSE image of the cross-section of sample 372-J, an unidentified coin. a) cracks in the interior of the coin.

No identifiable surface layer is visible in sample 372-J (Figure 6.14). It is interesting to note that throughout the bulk of the coin cracks can be seen, which would indicate that the coin is embrittled. Cracks in the interior of the coin represent intergranular corrosion, which can be caused by trapped oxygen within the metal and making the coin embrittled and prone to corrosion.

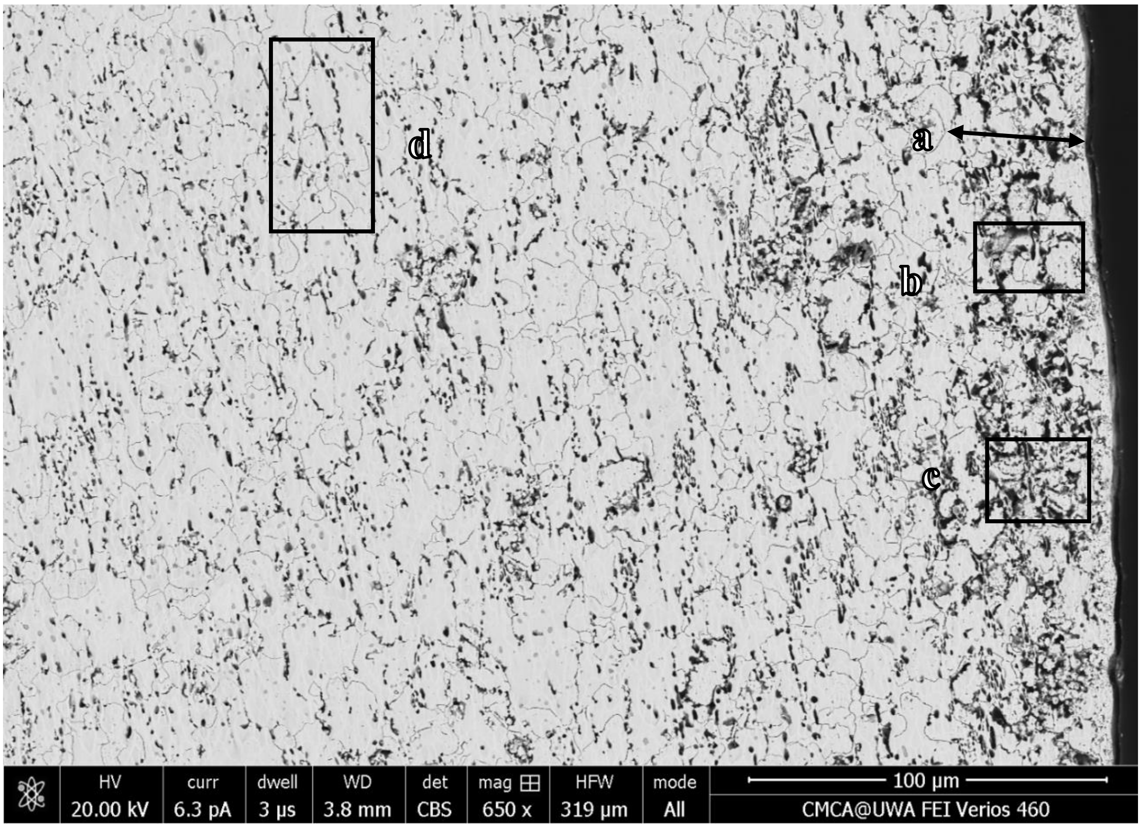


Figure 6.15 – BSE image of the cross-section of sample 372-1, an unidentified coin. a) the surface layer, b) increased porosity, c) larger copper-rich phases, d) copper-rich phases in the interior of the coin running parallel to the surface

A surface layer of approximately 50µm can be identified in sample 372-1 (Figure 6.15). This surface layer can be characterised by increased porosity and larger copper-rich inclusions than in the bulk of the coin. The copper-rich inclusions in the bulk of the coin are orientated in strings that run parallel to the surface of the coin.

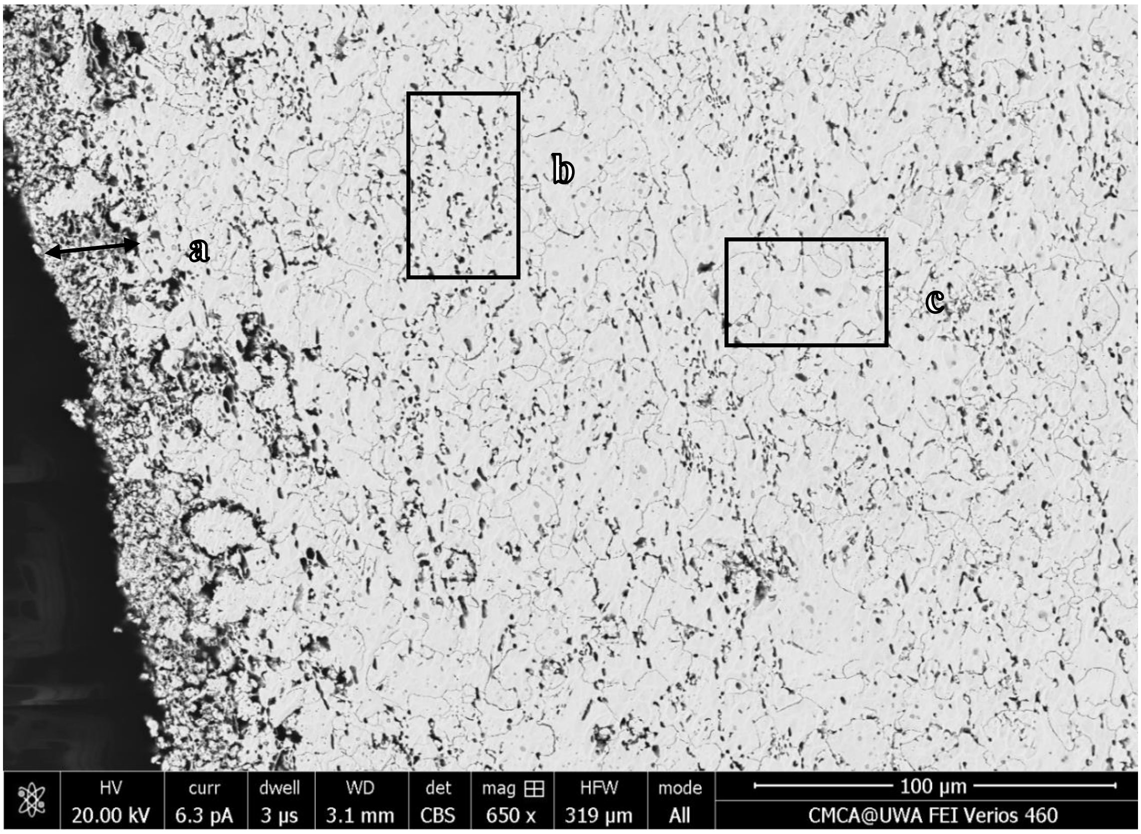


Figure 6.16 - BSE image of the cross-section of sample 372-2, an unidentified coin. a) the surface layer, b) copper-rich phases parallel to the surface of the coin c) cracks

Figure 6.16 details the surface, in cross-section, of sample 372-2. A surface layer of approximately 30µm can be seen, which displays increased porosity when compared to the bulk of the coin. Also of note, the copper-rich phases in the interior of the coin again run parallel to the surface of the coin. Cracks are also visible throughout the bulk of the coin indicative of annealing.

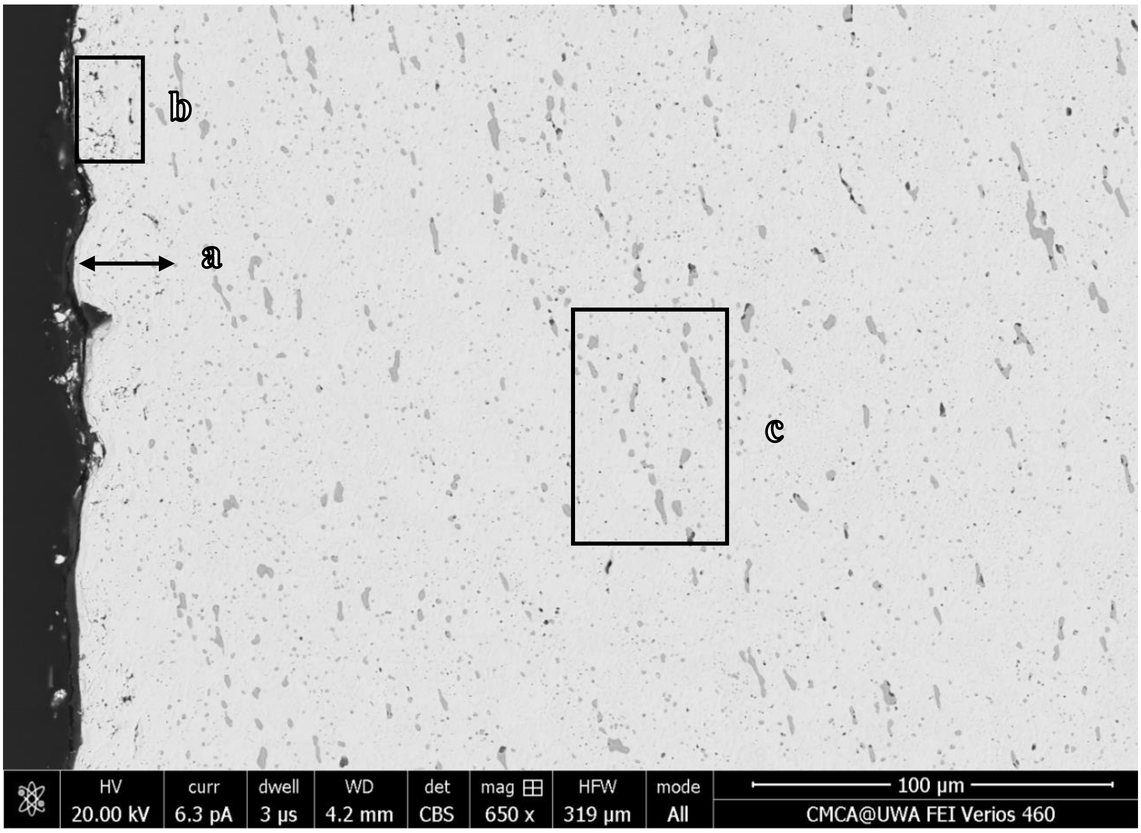


Figure 6.17 – BSE image of the cross-section of sample 372-3, an unidentified coin. a) the surface layer, b) porosity, c) copper-rich phases parallel to the surface of the coin.

Sample 372-3, as demonstrated using EPMA can be seen to have a surface layer which is lower in copper than the bulk of the coin (Figures 6.4 and 6.5). However, analysis on a different section of the coin’s surface reveals that the surface layer is considerably shallower, in Figure 6.17 this layer can be seen to be approximately 40µm thick. The surface layer has an increase in porosity and a decrease in copper-rich phases. In the interior of the coin the copper-rich phases can be seen to run parallel to the surface of the coin.

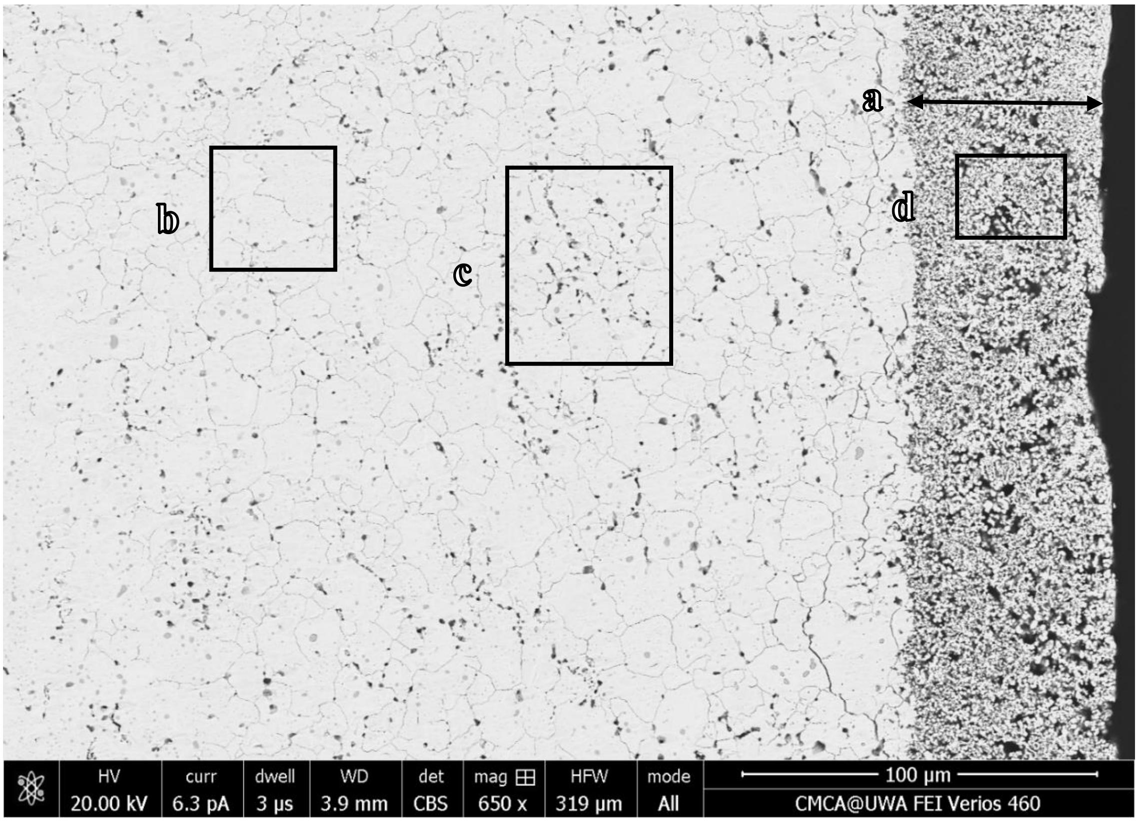


Figure 6.18 - BSE image of the cross-section of sample 372-H, minted in Mexico. a) the surface layer, b) cracks, c) copper-rich phases running parallel to the coin's surface, d) porosity.

Sample 372-H can be seen to have a very distinct surface layer of approximately 60µm thick (Figure 6.18). This surface layer can be characterised by a significant increase in porosity as compared to the bulk of the coin. The bulk of the coin displays both cracks due to intergranular, as well as copper-rich phases that are orientated parallel to the surface of the coin.

6.1.3 Conclusion

It has been found that while the surface of the samples is visibly more porous than the bulk due to corrosion, EPMA line scan results indicate that the silver/copper ratio remains constant in coins of high silver concentration (>95%). It has been concluded that silver/copper alloys with high (>95%) silver content, such as the majority of coins in this study, do not exhibit significant silver surface enrichment, and that the ratio between the major elemental components remains constant from the bulk to the surface of the coin. However, silver surface enrichment can be seen to significantly affect coins with <95% silver content, as can be seen in the EPMA results for coin 372-3. The implications of these findings is that surface analyses of these coins, indeed surface analyses of any archaeological silver/copper alloy with a high silver content, will be representative of the artefact as a whole, as the artefact will not have been affected by silver surface enrichment. However, surface analysis of artefacts of silver/copper alloys with a silver content of less than 95% may not be representative of the bulk of the artefact, this can be taken into account by carefully selecting the area of analysis, as the surface layer varies across the artefact, and setting instrumental parameters to mitigate the effect of silver surface enrichment on results.

6.2 The structure and morphology of copper-rich phases in silver coins

6.2.1 Aim

Copper-rich phases exist within silver/copper alloys. The structure and morphology of these copper-rich phases in relation to the silver-rich grains can be indicative of the way the alloy was manufactured, the temperature reached during manufacture, and stressors placed on the metal during manufacture and use (Scott, 1991). This study uses a combination of elemental distribution imaging and mapping, complementary to the determination of trace elemental composition, on the polished cross-sections of coins, in order to further understand the structure and morphology of the copper-rich phases in archaeological artefacts of silver/copper alloys.

6.2.2 Results

SEM-EDS and EPMA was used to confirm that the different phases visible in BSE images of coins are indeed silver-rich and copper-rich phases. This was conducted as a preliminary confirmation of the major elemental composition of the coin and also to confirm that the copper in the coins is not in solution within the silver matrix, but rather has formed copper-rich phases throughout the alloy. The importance of understanding both the composition and the elemental distribution lies in the interpretation of the composition, which can be limited if the distribution is not also understood. Following this confirmation of the major elemental distribution, the structure and morphology of different types of copper-rich phases is discussed in terms of the manufacture of the coins.

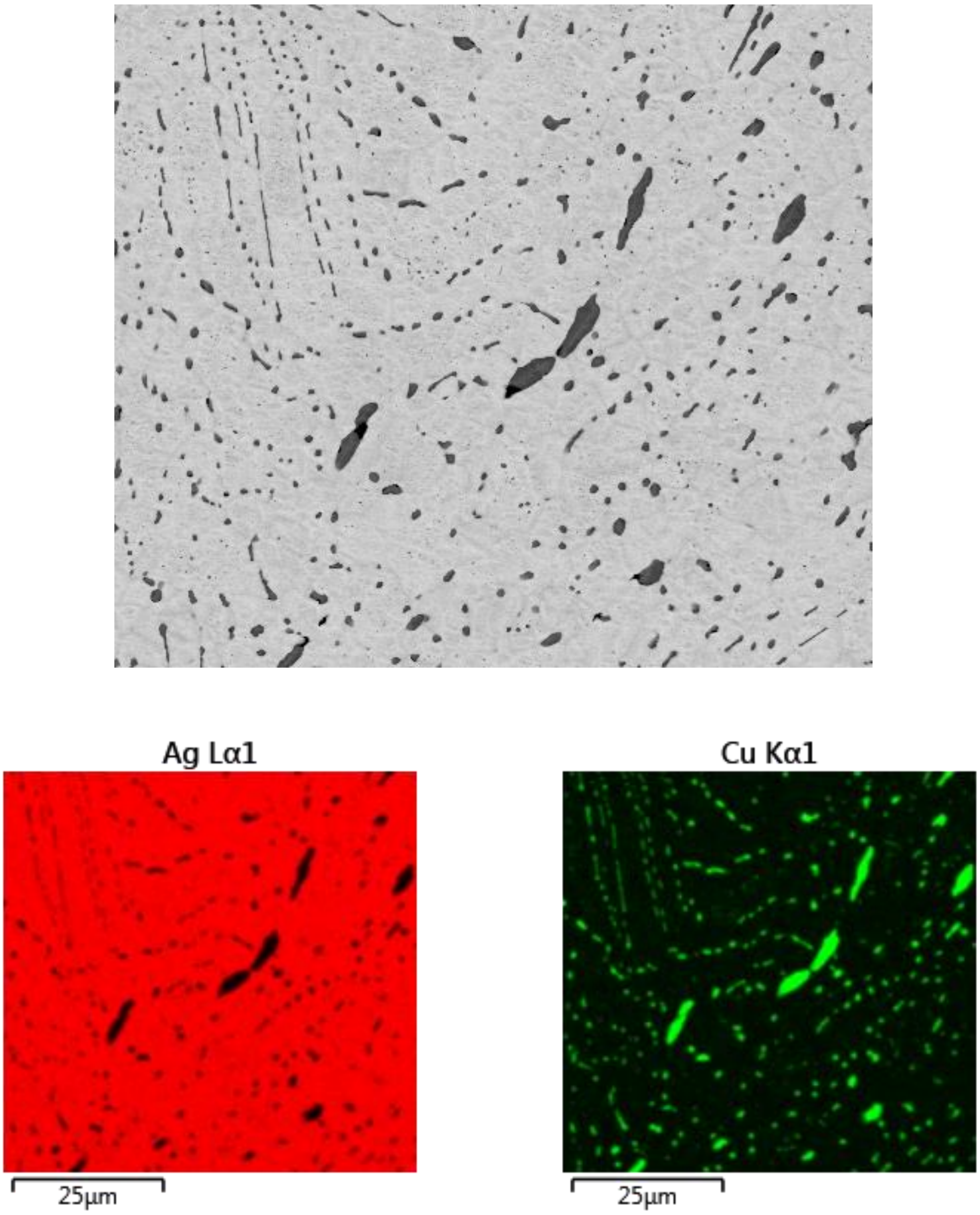


Figure 6.19 – SEM images of the polished cross-section of sample 072, an 8 *reale* coin minted at Potosí in 1653. Top: BSE image. Bottom left: EDS map of silver distribution. Bottom right: EDS map of copper distribution.

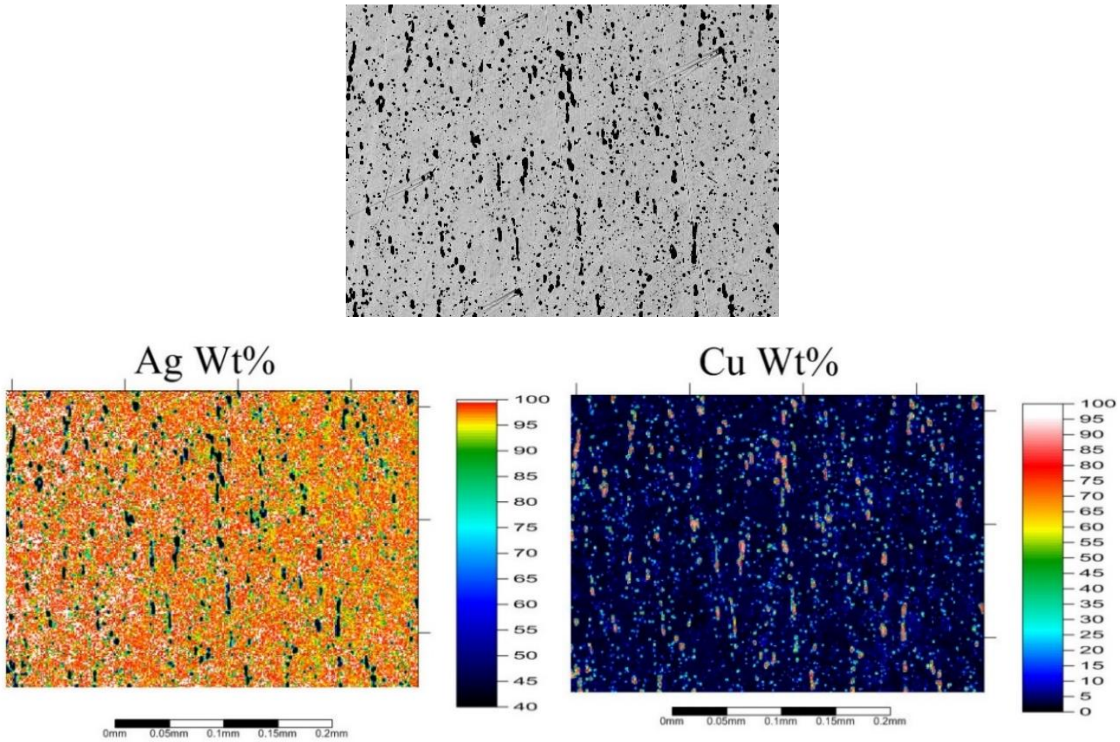


Figure 6.20 - EPMA images of polished cross-section of sample 372-3. Top: BSE image. Bottom left: EPMA map of silver distribution. Bottom right: EPMA map of copper distribution.

Figures 6.19 and 6.20 confirm that the darker areas in the BSE images of the coins are copper-rich phases in a silver-rich matrix.

Two different morphologies of copper-rich inclusions were observed. Elongated copper phases are found within silver-rich, equi-axed grains, orientated parallel to the surface of the coin and more circular copper-rich phases can be associated with the discontinuous precipitation of copper that can be seen between silver grains.

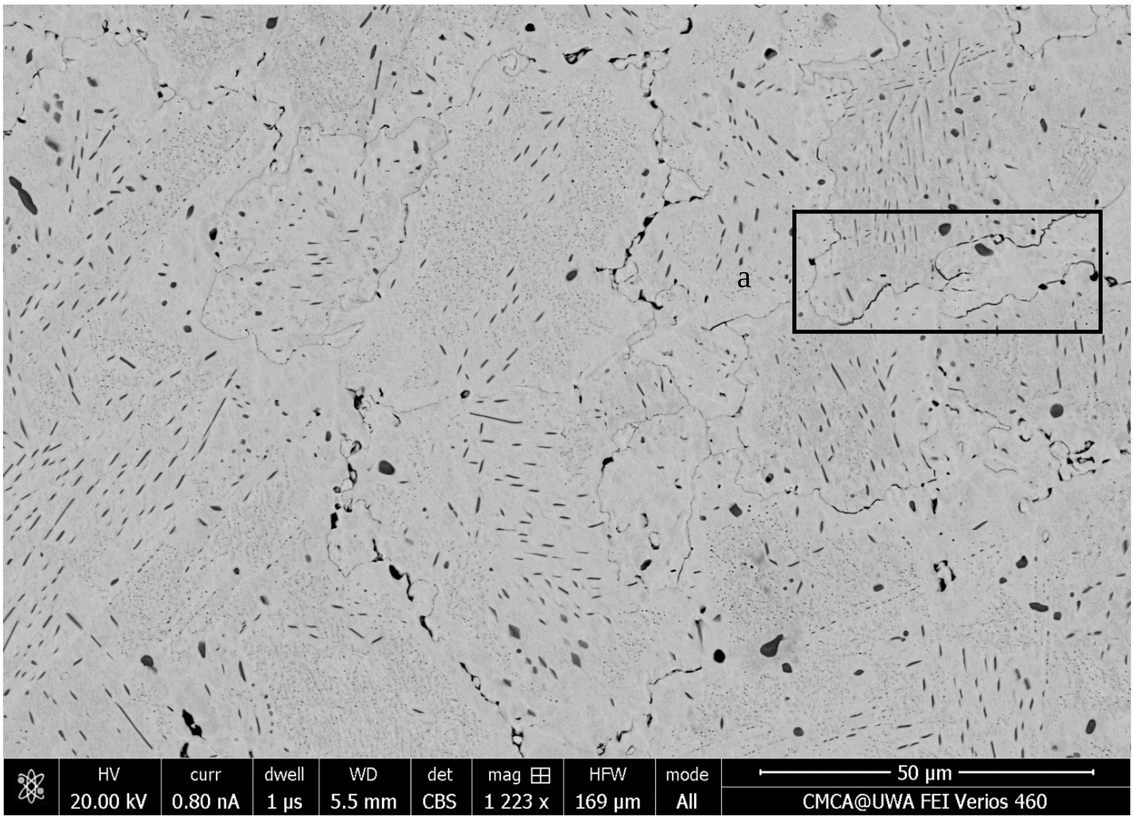


Figure 6.21 – BSE image of the cross-section of sample 025, a Mexican 8 reale coin showing a) intergranular corrosion outlining the individual silver grains

Flattened silver-rich grains with elongated copper-rich phases orientated approximately parallel to each other within individual metal grains can be observed in Figure 6.21. Microscopic cracks between grains, indicative of some embrittlement, can also be seen. These cracks are due to oxygen being introduced into the metal during manufacture of the metal object.

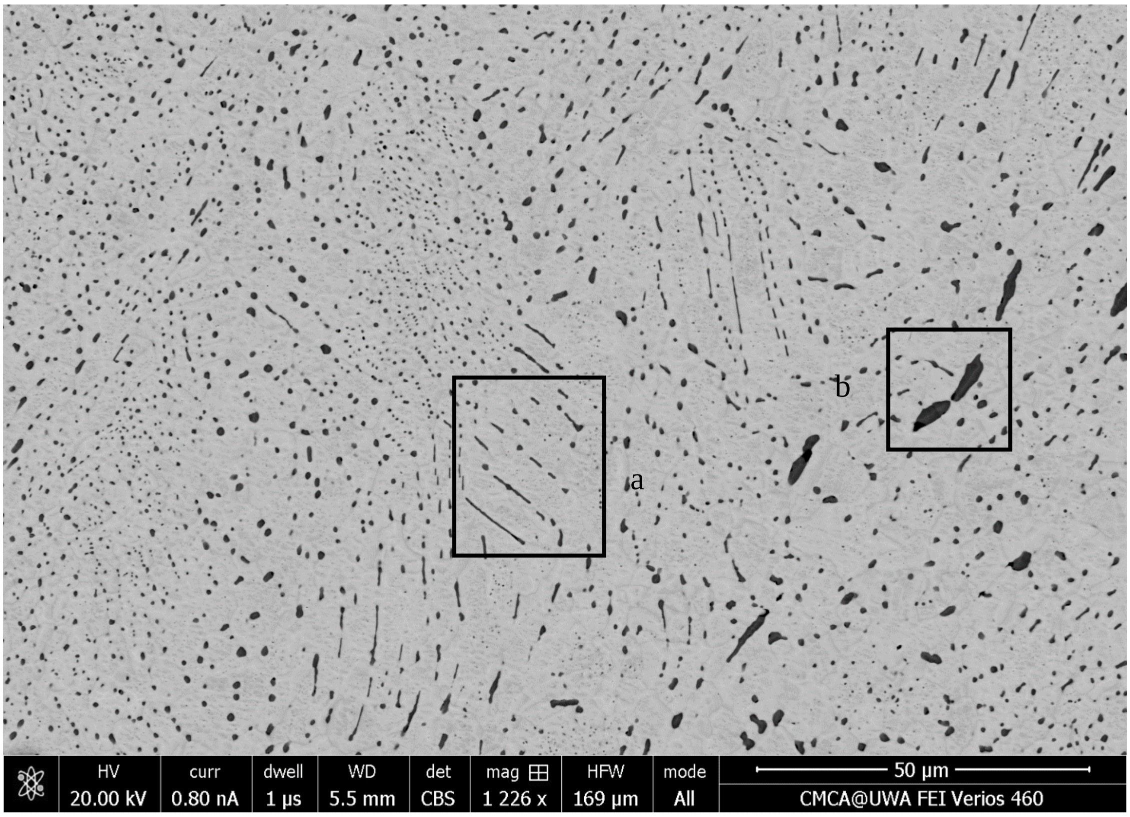


Figure 6.22 – BSE image of the cross-section of sample 072 an 8 *reale* coin from Potosí. a) parallel copper-rich phases, b) larger copper-rich phases

Figure 6.22 shows very well preserved structure without corrosion, with the two distinct morphologies of copper-rich phases visible in the image. The elongated copper-rich phases orientated approximately parallel to each other are indicative of how the metal has been worked. The small equi-axed and non-equi-axed large copper phases are the result of precipitation of copper over time after the object has been manufactured.

A summary of the morphology of copper-rich phases observed in imaging of the polished cross-sections of coins using EPMA is detailed in Table 6.7. This analysis was undertaken using the image processing and analysis software ImageJ, using the threshold feature to isolate the copper rich phases, and the ‘analyse particles’ function to characterise them. Feret measurements correspond to the distance between two parallel planes restricting an irregular object at its minimum and maximum, and can be used to provide the dimensions of irregular two-dimensional shapes, in this case, the copper-rich phases in the silver matrix of coins. It must be taken into account here that the inherent limitation in characterising the copper-rich phases in this way is that they are in two dimensions, while they exist within the coins in three dimensions and so their three dimensional morphology has not been characterised here. However, this two dimensional characterisation provides an opportunity for an initial appraisal and comparison of the typical microstructure of different coins.

Table 6.7 – Morphology of copper-rich phases

Coin	Surface layer depth (μm)	Copper-rich phases in the bulk of the coin			
		$\bar{x}$ area (μm)	Max feret (μm)	Min feret (μm)	% of total area
372-B	50	2.97	2.43	1.42	3.99
372-F	70	16.37	6.07	3.39	10.59
372-J	0	13.23	5.37	3.08	4.93
372-1	50	2.95	2.49	1.42	8.81
372-2	30	10.32	1.25	0.65	7.39
372-3	40	2.71	2.55	1.39	11.48
372-H	60	11.38	4.85	2.90	5.66
025	200	0.15	10.40	0.26	3.78
072	70	0.31	11.25	0.44	4.23

The ferret measurements of copper-rich phases detailed in Table 6.7 allow for the characterisation of these phases. It can be seen that copper-rich phases in historical silver coins are generally approximately 5.18μm×1.66μm in size. The percentage of the total area taken up by copper-rich phases correlates to the percentage of copper content detected in the samples.

Transmission electron microscopy (TEM) was employed to further investigate the structure of silver-rich and copper-rich phases in the sample coins. TEM enables imaging of a sample to the atomic level, and in this case has been used to investigate the crystal structure of copper rich phases in the coins when compared to the silver rich phases. The electron diffraction pattern (Figure 6.23) confirms the polycrystalline nature of both copper and silver phases. Electron diffraction patterns from interfaces between silver and copper grains revealed cube on cube crystallographic relationships between the two phases.

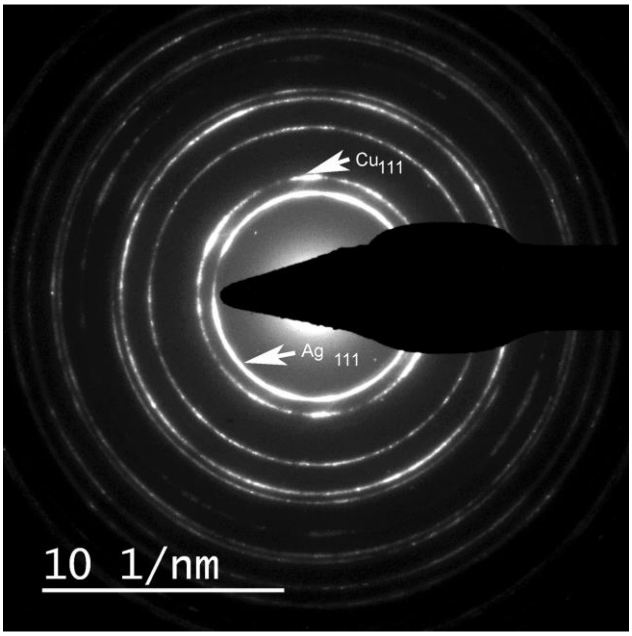


Figure 6.23 – Electron diffraction pattern of sample 050, an 8 *reale* coin minted in Mexico. The diffraction pattern is a ring diffraction pattern from polycrystalline face centred cubic (fcc) silver and copper. Selected area diffraction measurements revealed an orientation relationship between copper and silver phases: <110> Ag // <110> Cu and {111} Ag // {111} Cu

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used to image the structure of sample 050, with an EDS map overlaid (Figure 6.24).

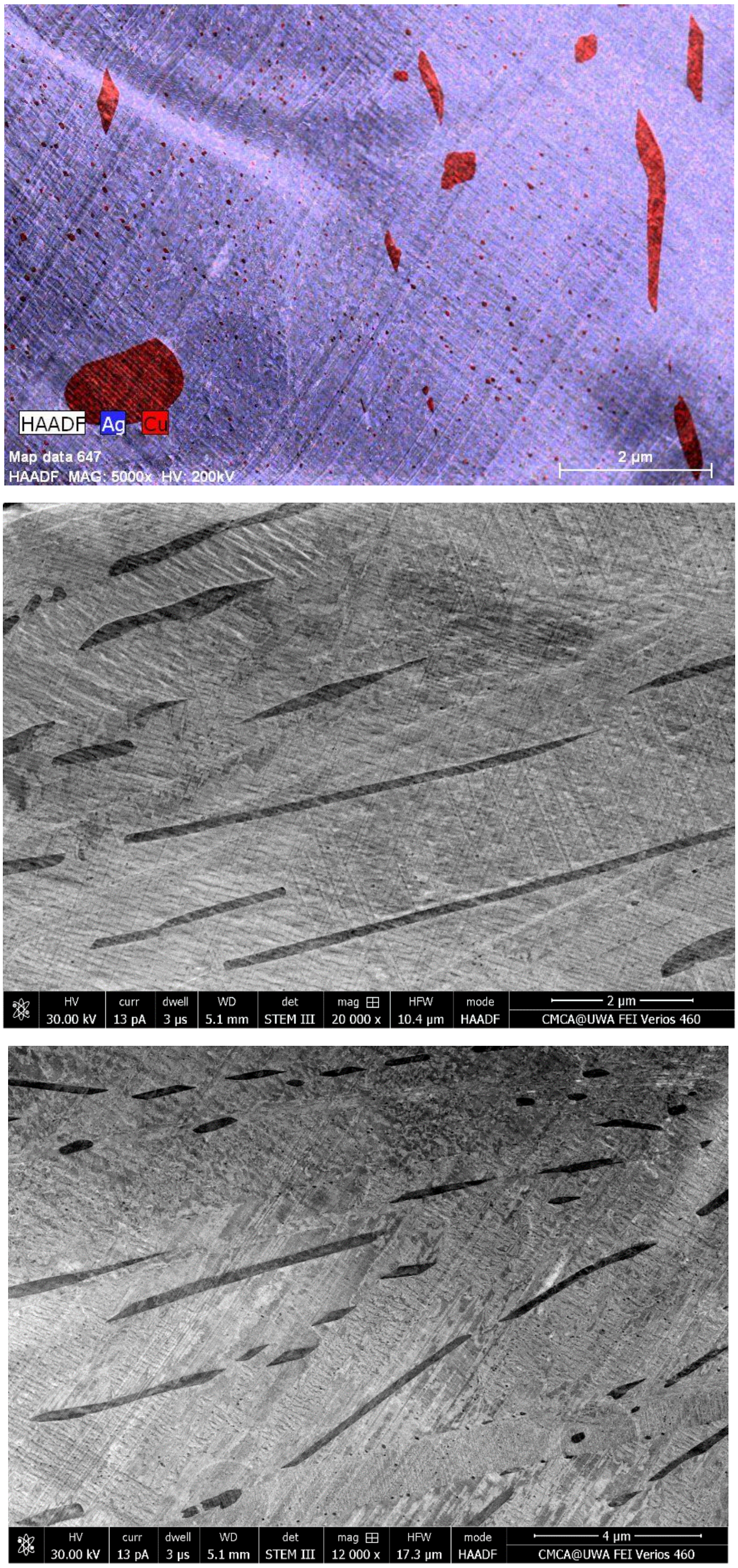


Figure 6.24 – HAADF-STEM images of three regions of sample 050, an 8 *reale* coin from Mexico (a) overlaid with an EDS map of silver (blue) and copper (red) distribution (b) two images without EDS

Figure 6.24 details the distribution of copper-rich phases, both elongated and equi-axed. It can be seen in the top image that the copper-rich phases, both elongated and equi-axed, are surrounded by much smaller copper-rich phases throughout the silver matrix. The face centred cubic structure of the lattice can also be determined, based on the regular arrangement of the lattice through all three images.

A phase diagram of silver/copper alloys (Figure 6.25) can be used to determine the temperature at which the alloys in this study were manufactured. The area in the diagram most pertaining to the coins in this study is highlighted. From the phase diagram it can be seen that no more than 8% by weight of solid silver can dissolve in solid copper, while no more than 8.8% by weight of solid copper can dissolve in solid silver. The solid silver/copper alloy thus consists of a mixture of two solid phases, one consisting of a copper-rich solid (alpha α-phase) that can dissolve in a maximum of 8 wt% silver at 779.1ºC (more at higher temperature), and one consisting of a silver-rich (beta β-phase) that can dissolve in a maximum of 8.8 wt% copper at 779.1ºC (more at higher temperature). The solvus line indicates the temperature below which particular concentrations of silver and copper will not form a homogenous mixture in the liquid state. This information shows that for alloys with a silver content above 91.2%, with increasing silver content, higher temperatures are required to achieve a homogenous liquid, from 779.1ºC up to 961.8ºC, the melting point of pure silver. The coins in this study will fall within this range, and can be seen to go through three microstructural phases from liquid to solid. When a relatively pure alloy is cooled quickly, dendritic structures will result. When cooled slowly, grains of silver will form surrounded by films of copper, as is observed in the microstructures of the coins in this study. It can be concluded that the coins in this study would have had to be heated to over approximately 900 ºC for any of the copper to dissolve into the silver, and that the metal was not quenched prior to being worked, but was rather allowed to cool slowly. Slow cooling is advantageous in coin manufacture as quenching, like annealing, will allow oxygen to be introduced to the interior of the metal, which can be associated with intergranular corrosion and embrittlement of coins.

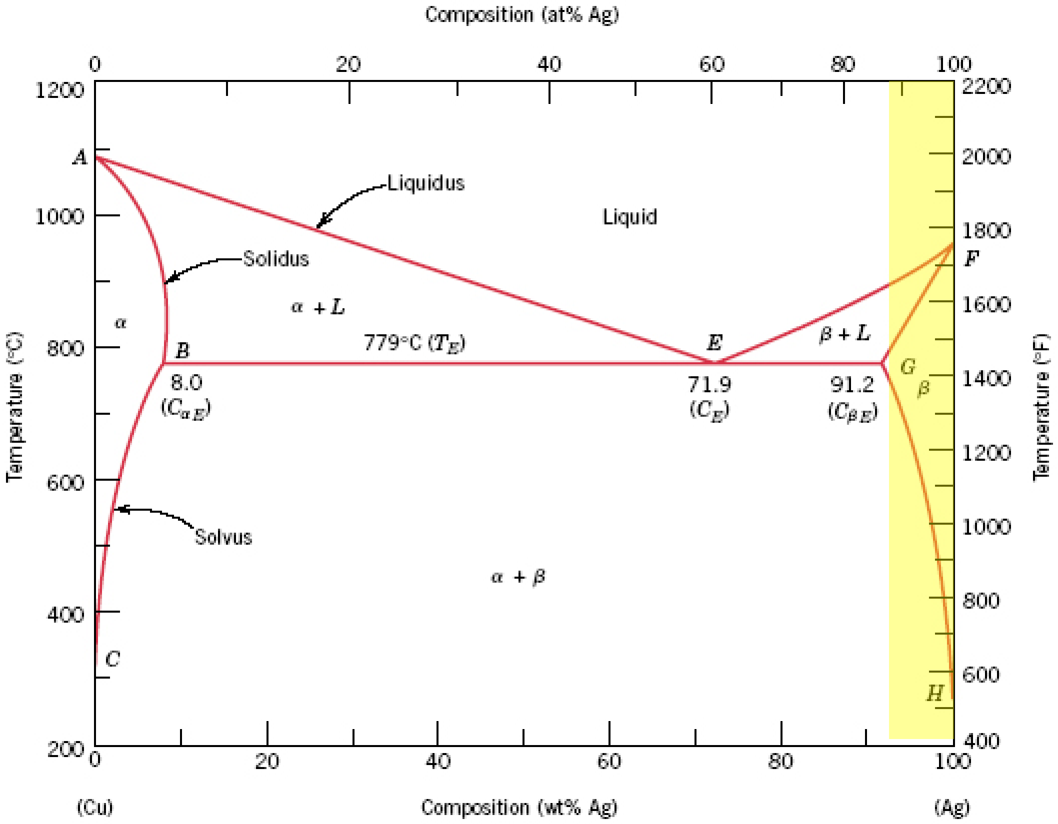


Figure 6.25 – Phase diagram for silver/copper alloys

Finally, FIB-SEM was used to three dimensionally image the copper-rich phases within the silver-copper alloy. Figure 6.26 shows a still from a video file supplied in the appendices, of the volume of the coin being milled, the field of view is 15µm horizontally). Indicated in white are areas of interest which can be seen progressing through the volume of the coin.

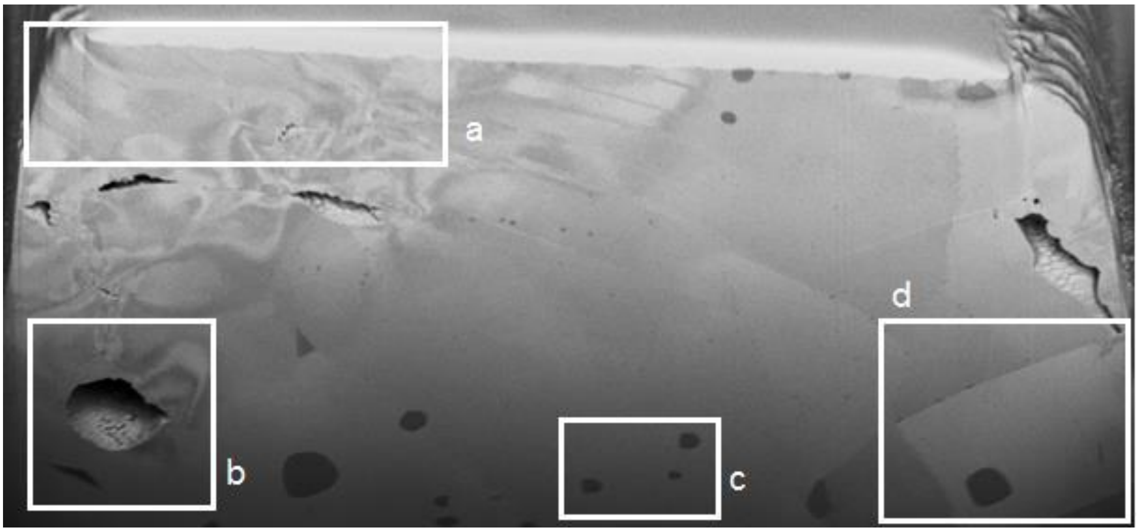


Figure 6.26 – The milled surface of the interior of coin 395, an 8 *reale* piece from the wreck of the *Vergulde Draeck* using FIB-SEM.

a) Stress can be seen to have affected the surface of the coin b) porosity, c) copper-rich phases and d) individual silver grains with some copper precipitation at the grain boundaries.

Figure 6.27 shows a volume rendered reconstruction of the BSE images of 10nm thick slices of the sample. The three dimensional image (Figure 6.28) details the copper-rich phases within the volume.

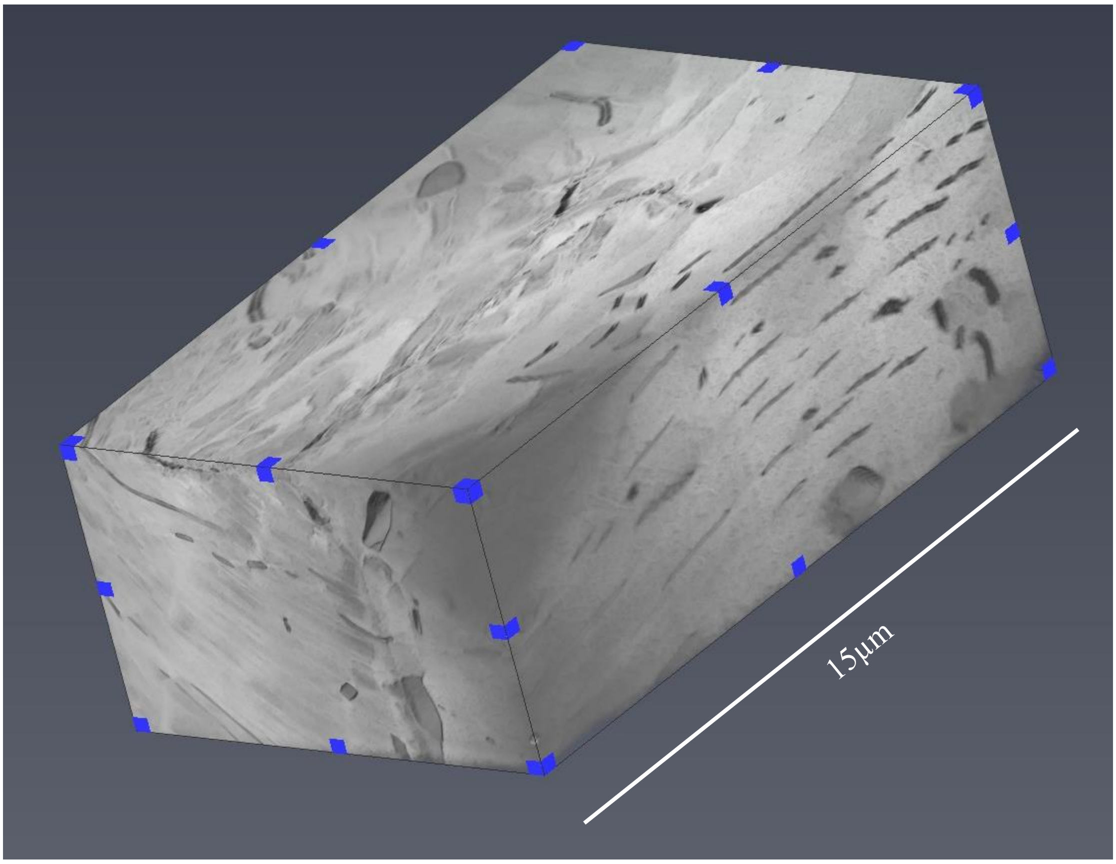
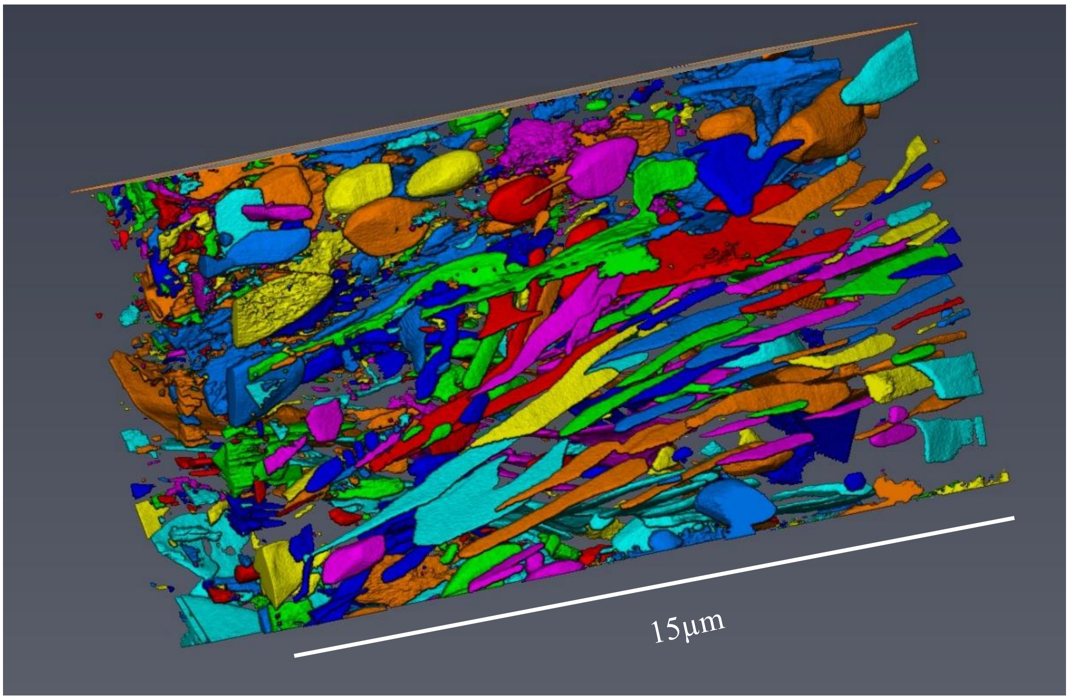


Figure 6.27 – FIB-SEM volume rendered image of BSE imaging of sample 395, an 8 *reale* coin from the wreck of the *Vergulde Draeck*.



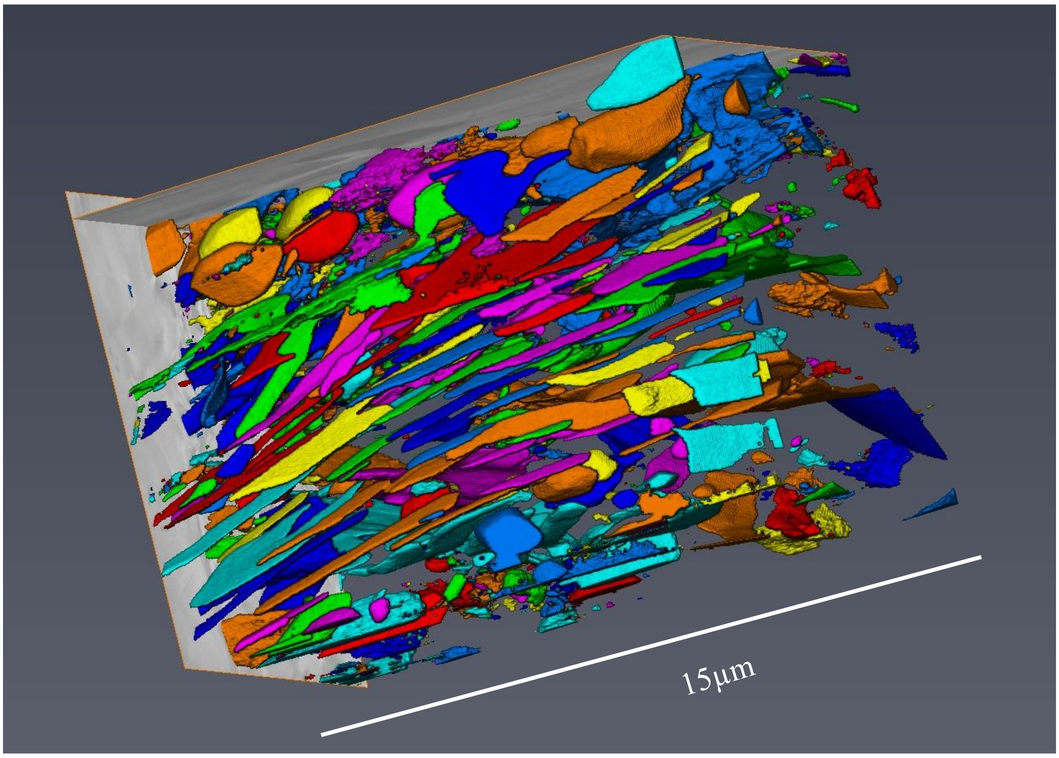


Figure 6.28 – Volume rendering of copper phases within sample 395, an 8 *reale* coin from the wreck of the *Vergulde Draeck*

Three dimensional volume rendering of copper-rich phases within a coin reveals that what appeared to be rod-like structures in two dimensional investigations in the coins are in fact sheets of copper. These sheets are orientated parallel to the surfaces of the coin indicating that the manufacturing process of the coin has had an identifiable effect on the microstructure of the coin.

6.2.3 Conclusion

EDS and EPMA imaging of the cross-section of a selection of coins confirms that the structure visible in BSE images are indeed copper-rich phases in a silver-rich matrix.

BSE imaging shows structures indicative of significant cold-working, i.e. hammering, on the surface of the coin as the elongation of the phases runs parallel to the surface of the coin.

BSE imaging also shows discontinuous copper precipitation at silver grain boundaries, which has been argued to be indicative of age, as the copper precipitates at a regular rate post-manufacture in the solid state. Discontinuous precipitation of copper is also thought to contribute to embrittlement and silver surface enrichment when the metal is also corroded.

TEM imaging and electron diffraction analysis showed that the silver and copper phases are polycrystalline. TEM imaging also confirms that the copper-rich phases are copper inclusions, with approximately 100% copper content, in an otherwise silver matrix.

FIB SEM shows the copper-rich phases, both the elongated, lenticular, rhomboidal and equi-axes type morphologies, in three-dimensions, furthering our understanding of the types of copper-rich phases, and our interpretation of what they are indicative of in this context.

The 3D reconstruction and visualization of the copper inclusions reveals additional features that are essentially hidden in 2D images.

Three-dimensional FIB-SEM data reveal further complexities to the microstructure and additional insights into copper distribution in silver matrix. These data demonstrate several morphologies of the inclusions: lenticular shaped and banded shaped/filaments. The filaments morphology changes quite significantly over spatial scales of only a few micrometres along the length of a filament. In some FIB slices, their filamentous nature is clear, and sheets of copper crystals appear neatly stacked, whereas in other slices the filaments are seen to branch or suddenly thicken. Furthermore, SEM highlights a number of nano-cracks within the silver matrix; these often feed right into the filaments.

6.3 Determining the method of manufacture of coins using electron backscatter diffraction (EBSD)

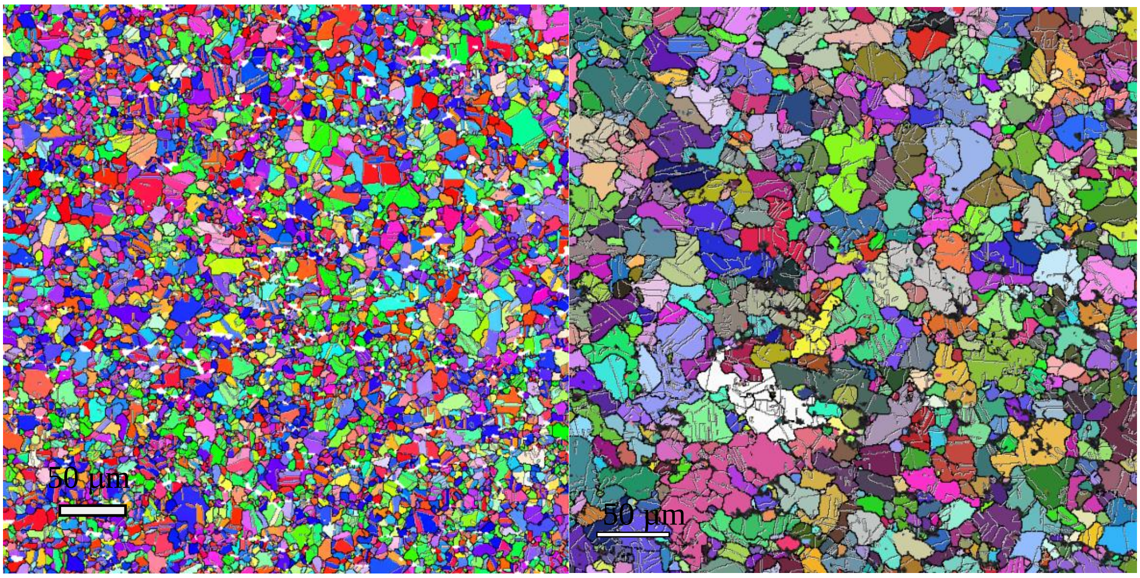
6.3.1 Aim

EBSD can be used to detect the crystal structure of the cross-section of a sample, this structure has been found to differ in metals based on their method of manufacture, and to retain traits that are indicative of reworking. The microstructure of a worked metal has been found to be indicative of the manufacturing history of the metal, with particular characteristics being indicative of different methods of working, at different stages of heating, cooling or annealing (Scott, 1991). EBSD was used on a selection of coins with the aim of determining their method of manufacture, and to investigate possible evidence for reworking.

6.3.2 Results

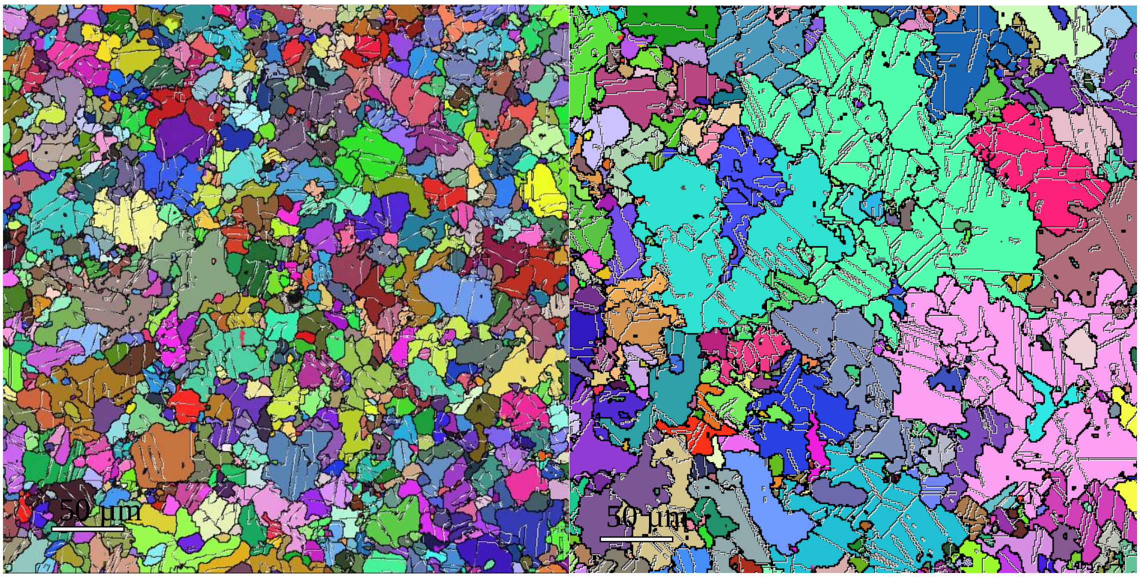
EBSD analysis revealed individual grain boundaries (>15° difference in orientation), as well as grain orientation, of silver-rich grains. No significant difference in grain orientation or texture was observed between coins of different origin or year, indicating a similar method of manufacture for all analysed coins.

Figure 6.29 shows EBSD measured orientation maps of sample 372-B 372-F, 372-J, 372-H (known to have originated in Mexico), 372-3, 025 (known to have originated in Potosí) and 072 (known to have originated in Mexico) respectively. The measurements were conducted in the cross-sectional area of each sample. The vertical directions in the maps are along the normal directions of the coin disk. The black lines represent high angle boundaries *i.e.* the orientation differences between the pixels across the black lines are over 10°. Therefore an area enclosed by black lines is considered a grain. The grains are colour coded according to the plot in the inverse pole figure in the inset, representative of the crystal orientation of the individual grains. In a metal such as the silver under consideration, the overall random colour distribution in the grains gives an impression that the grains do not have a preferential orientation *i.e.* they are not crystallographically textured. The grains in sample 372-J and 025 are noticeably bigger than the relatively uniform grain size in the other five samples.



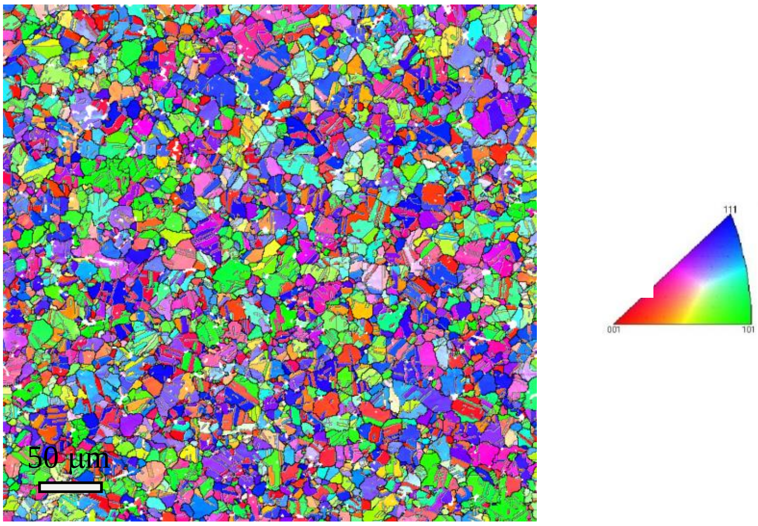
372-B

372-F

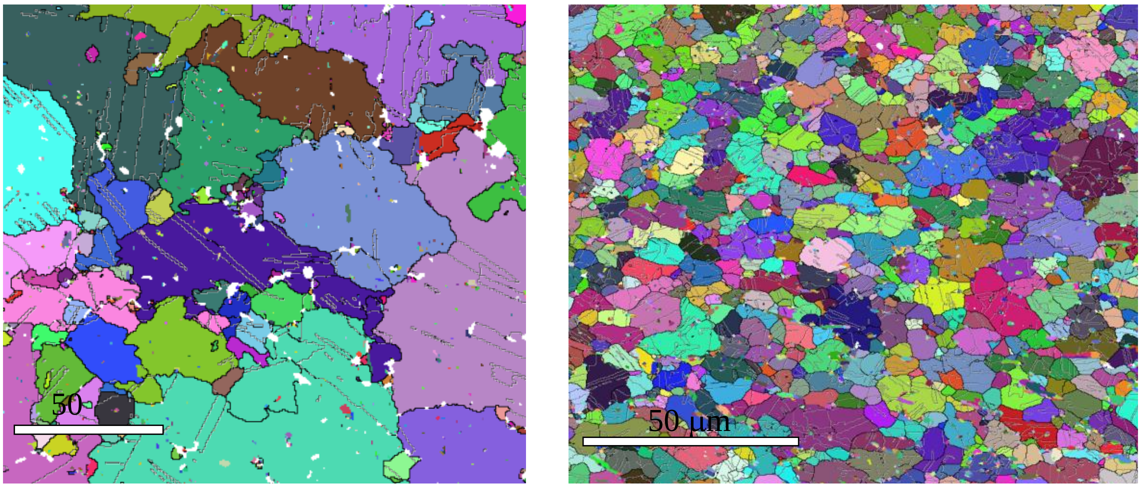


372-H

372-J



372-3



025

072

Figure 6.29 - EBSD measured orientation maps showing the silver grains in the cross-sections of coins 372-B, 372-F, 372-H, 372-J, 372-3, 025 and 072. The horizontal directions are parallel with the normal direction of the coin discs.

Figure 6.29 gives an overall impression of the grain size, however for the statistical grain size distributions in Figure 6.30, grains are measured from large scan maps and the data are shown as plots of accumulative area fraction occupied by varying grain sizes in µm^2. A given point on the curve represents the fraction of the scanned area occupied by the grains of that size and below. In sample 372-J in Figure 6.29, the largest grain is 20876 µm^2, whereas in the 372-B and 372-F the largest grains are of 2256 and 3755 µm^2 sizes. These curves also indicate that the size range of the grains in sample 372-J are much wider than that in the samples in 372-B and 372-F.

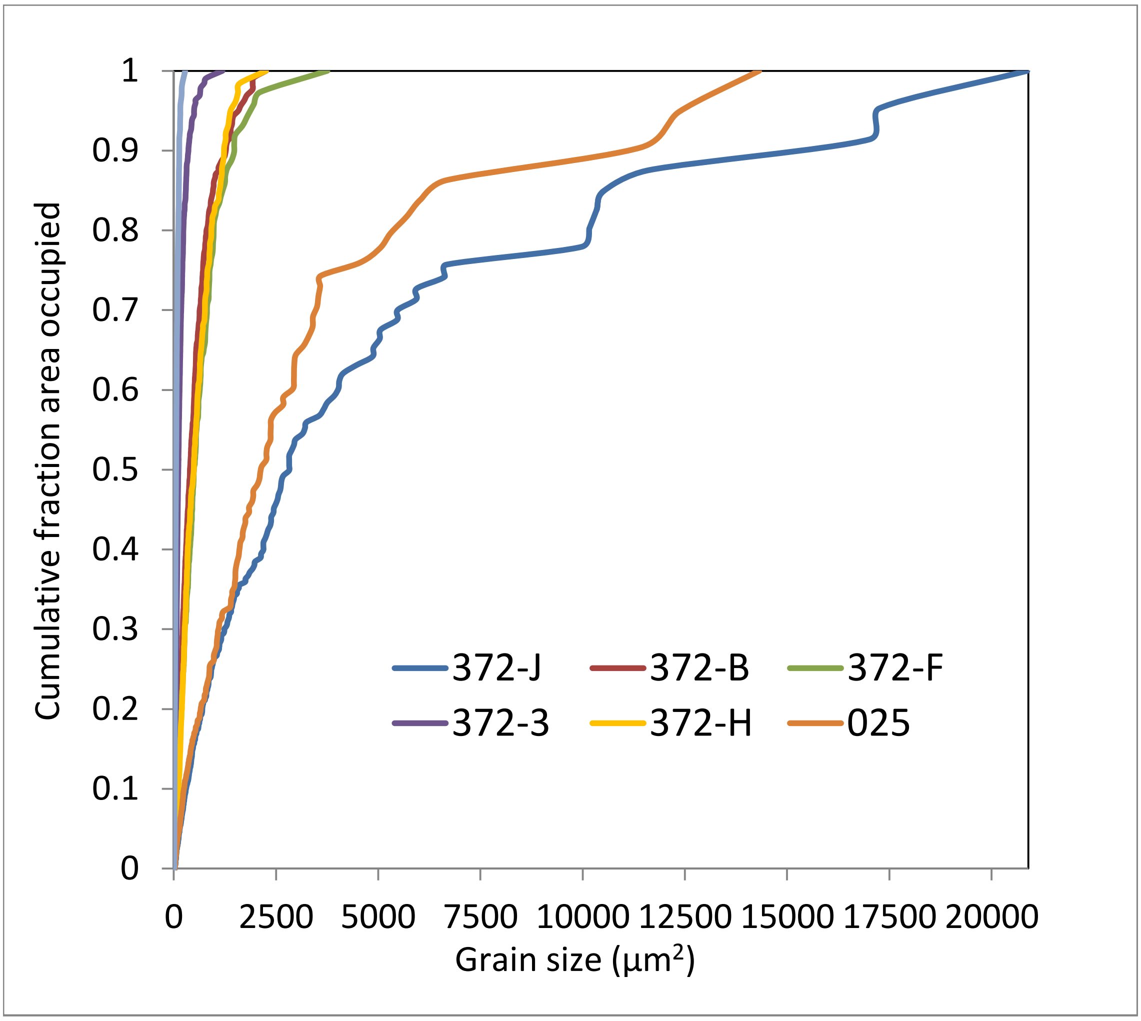


Figure 6.30 - Cumulative fraction of scanned area occupied as a function of grain sizes.

There is a clear difference in both Figures 6.29 and 6.30, between the larger grain sizes of coin 372-J and 025, and the smaller grain sizes of the other five coins studied. BSE images of 372-J and 025 also show a slightly different morphology of copper-rich phases (Figures 6.13 and 6.20) in comparison to the other coins imaged, specifically less elongate copper-rich phases, and also evidence for intergranular corrosion and embrittlement.

6.3.3 Conclusion

EBSD results show a relatively uniform, small grain size (<2500µm^2) for coins 372-B, 372-F, 372-H, 372-3, and coin 072. The grain size, in combination with the morphology of copper-rich phases in these coins as identified using BSE imaging, would indicate significant cold working on these coins in the form of hammering or pressing. Twins, or repeating grains identified in the EBSD images are indicative of annealing or hot-working. In this case, it would appear that the twin grains are caused by hammering followed by annealing. High deformation also indicates cold working in the form of hammering.

Coins 372-J and 025 show a much larger grain size (>5000µm^2), and evidence from BSE imaging shows that they both also exhibit intergranular corrosion and a lack of elongated copper-rich phases. These results suggest that these two coins have been annealed during the hammering of the coin blanks stage of their manufacture, while the other five coins were not.

The results of EBSD analysis are indicative of this type of minting, with twinning within grains indicative of the annealing, and significant deformation indicative of the many stages of hammering and striking involved in manufacturing a coin.

Chapter conclusion

This chapter has quantified the depth of the corroded surface layer of various coins, including how that surface layer has been affected by preferential copper leaching and silver surface enrichment. With this information further analyses can be appropriately planned and undertaken to compensate for potential differences between the surface and the bulk of a coin.

This chapter has also used elemental distribution mapping and backscattered electron imaging to measure and quantify the distribution of copper-rich phases within the silver matrix of the coins. This information has been used to determine the method of manufacture of the coins.

Chapter 7 – Discussion

Chapter introduction

This chapter discusses the results of analysis of silver coins and artefacts, in terms of the research aims detailed at the start of the thesis. Specifically, the thesis research was intended to address the aims: to identify the mint of origin of a coin; its year of minting; and how it was manufactured based on composition and microstructure alone.

Firstly, the applicability of non-destructive surface analyses is discussed, a pertinent issue in archaeological research, as destructive analyses of artefacts are often not an option. This discussion details research performed comparing surface and bulk analyses of silver coins, in order to determine how representative results from surface analyses are of the whole coin. This is of particular importance when examining archaeological metals, with significant changes to the surface of a metal due to manufacture, use and corrosion.

Secondly, the results of provenance determination of previously unidentified coins and also silver artefacts is discussed in both an historical context and in terms of the applicability of the techniques used for this research, as well as the potential for similar analysis on other archaeological artefacts.

Third, the potential for dating coins based on their trace elemental composition is discussed. Trace elemental composition of archaeological artefacts has not been used in this way before and while the results to date are not definitive, the potential for this method can be demonstrated, and the predicted dates of minting of previously unidentified coins is discussed.

Fourth, the structure and morphology of the coins is discussed in terms of their method of manufacture, in the context of historical accounts of minting technologies.

Finally, the importance of the use of complementary analytical techniques in the analysis of archaeological artefacts is discussed in terms of the results of this study.

7.1 Suitability of non-destructive surface analytical techniques as representative of the bulk of metal artefacts

It is of utmost importance to appraise the suitability of surface analytical techniques as representative of the whole sample, particularly in an archaeological context.

Archaeological artefacts, as items of cultural heritage significance, ideally will not be damaged or destroyed in the process of scientific research to gain more information than is possible through visual identification alone. Of particular concern is how representative the results of surface compositional analysis can be considered of the whole artefact, particularly when depositional processes affecting the surface of an item such as corrosion are taken into account.

Results of non-destructive surface analytical techniques were compared to destructive, more sensitive analytical techniques on a selection of archaeological silver coins. LA-ICP-MS surface analysis was compared to results of solution ICP-MS analysis of digested samples from the same artefacts. Further, SEM BSE imaging and EPMA were used to image and quantify the cross-section of a number of silver coins, to enable the surface layer to be characterised in direct comparison with the bulk of the coin.

7.1.1 LA-ICP-MS surface analysis compared to solution ICP-MS bulk analysis

Silver surface enrichment is a studied phenomenon (Beck *et al.*, 2004) that particularly affects silver/copper alloys with a high silver content (Borges *et al.*, 2016). While comparisons of LA-ICP-MS and solution ICP-MS in tooth enamel have found good agreement between the two methods in terms of copper content (Dolphin *et al.*, 2012), the present study did not find any such agreement in copper content. It may be that this was due to silver surface enrichment and preferential leaching of copper from the surface of the sample, necessarily leading to a lower copper content in the surface of the sample. Conversely, correlation results using LA-ICP-MS will be somewhat confounded due to the fact that the study aimed to compare both surface and bulk composition, as well as the two different analytical techniques. Whether disagreements between results for particular analytes are due to inhomogeneities in the sample, or differences in the techniques, will be discussed below.

This study lacked a matrix-matched certified reference material for LA-ICP-MS analysis; NIST 610 and 612 glass certified reference materials were used. With this in mind, the agreement between solution ICP-MS and LA-ICP-MS is a particularly positive finding. The same was found by Dolphin *et al.* (2012) in a comparison of LA-ICP-MS and solution ICP-MS on trace elemental determination in human teeth. Dolphin *et al.* (2012) found that, despite not having a matrix-matched certified reference material for tooth enamel, agreement between LA-ICP-MS and solution ICP-MS data was good enough to conclude that LA-ICP-MS can adequately provide accurate concentrations for particular analytes.

Based on comparison between LA-ICP-MS and solution ICP-MS results from a selection of silver artefacts, it can be concluded that LA-ICP-MS trace elemental composition results for a selection of analytes from the surface of the samples can be considered to be representative of the bulk of the sample, despite the surface having been affected by corrosion processes. For other analytes this is not the case. Most significantly, corrosion processes have resulted in porosity at the surface of the coins, however the comparison between LA-ICP-MS and solution ICP-MS would indicate that in general, the inter-elemental ratios remain relatively constant from the bulk to the surface of the coin. It is important to note here that while LA-ICP-MS analysis of the surface of the coin may not always be used reliably as an indicator of the precise concentrations of analytes in the bulk of the coin, the use of LA-ICP-MS data as inter-elemental ratios has been demonstrated here to be very effective at characterising coins produced at different mints and during different years. This is a useful outcome and shows how important such studies are in illuminating the historical record.

7.1.2 Quantitative electron microscope imaging of the cross-section of coins

Electron microscopy results from the present study showed that while an identifiable corrosion layer on the surface of the coins is present up to a depth of approximately 200µm, the ratio between the major elements remains constant in silver/copper alloys where the silver content is over 95%. As discussed, in silver/copper alloys where the silver content is higher than 95%, silver surface enrichment is not always observed (Ager *et al.*, 2013). In fact very little has been published regarding the extent and the effects of silver surface enrichment on high silver alloys, specifically silver/copper alloys with a silver content higher than 91.2%, which corresponds to the maximum value of solid copper solubility in silver (Borges, 2017). As such it can be expected that the copper in the alloy will have gone into solution, and silver surface enrichment will not be displayed when the object corrodes. The surface corrosion layer is characterised not by silver surface enrichment or embrittlement, but rather by porosity. However, for silver/copper alloys with a silver content lower than 95%, this study has demonstrated that preferential leaching of copper and the resulting silver surface enrichment will affect the results of surface analysis, and copper will be underrepresented. For artefacts of lower silver content (<95%), it is essential to identify the most appropriate area for analysis based on a visual appraisal of the level of corrosion, and to set analytical parameters accordingly. For LA-ICP-MS analysis in this study, areas with minimal corrosion were identified for analysis, and ablation spot size set at 50µm with a depth of approximately 50-100µm in order to account for potential surface contaminants and differences.

The significance of these findings is that the degree of silver surface enrichment on historical silver/copper alloys has been measured. From these results, it can be concluded that non-destructive surface analyses of corroded silver will be representative of the entire object if the silver content of the alloy is higher than approximately 95%. For items with a silver content below 95% it will be necessary to investigate the depth of the surface layer in order to determine the best course of action for compositional analysis.

7.2 Provenance determination

7.2.1 Provenance determination using trace elemental composition

7.2.1.1 Provenance determination of silver coins

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

The significant overlap of elemental composition 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 composition 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 the price offered for bullion by its creditors was worth more than its minted value (Hamilton, 1965).

The significant similarities in composition 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 the few years prior 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. 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 IV ordered that all coins arriving from Peru be refined and recoined before being delivered to their owners. 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, 1934). It would appear that the close compositional 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 composition 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 utilisation 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.

In this study, coins minted in the Spanish Netherlands are represented by six coins known to have been minted in the Brabant mint between 1568 and 1679. With such a small sample size, it is difficult to extrapolate conclusions about the composition of these six coins, the characterisation of the Brabant mint, and coins minted in the Spanish Netherlands.

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*. 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.

A successful identification of provenance mint of 26 coins was made, based on trace elemental composition, and validation of known samples included in the algorithm as unknowns. This research has demonstrated that coins which are too heavily damaged for visual identification can still be identified based on their composition, and can further contribute to the understanding of the larger assemblage and context in question.

Of the 7,730 coins from the wreck of the *Batavia* in the Museum's collection, 15 were identified as *reales* of various multiples, originating in the Americas. Of those 15, those that had been identified originated from the Mexico and Potosí mints. Sample 368 in this study was recovered from the *Batavia* and was visually identified only as Spanish American. Having been confidently attributed as Guatemalan using LDA and trace elemental analysis, this sample represents the only evidence to date that coins minted in Guatemala were included in the cargo of the *Batavia*.

There are 989 coins from the wreck of the *Correio da Azia* in the Museum's collection. Of these, 824 were identified as Spanish American; 504 Mexican, 57 from Potosí, 101 from Lima and one Guatemalan coin. The rest could not be identified by mint. Also, 149 were identified as Spanish, 16 from the Seville mint, 104 from Madrid, 16 from Cadiz, and six from Segovia. The remainder were unidentified in terms of mint. The results of trace elemental analysis on 17 previously unidentified coins identified 15 as Mexican and two from Seville, which corresponds with the ratios of coins from different mints established by the visually identified coins.

Of the 17,630 coins recovered from the wreck of the *Rapid* in the Museum's collection, the vast majority originated in Spanish America (17,272). The remainder of the coins originated in the USA with only one or two coins each from China, France, Italy and

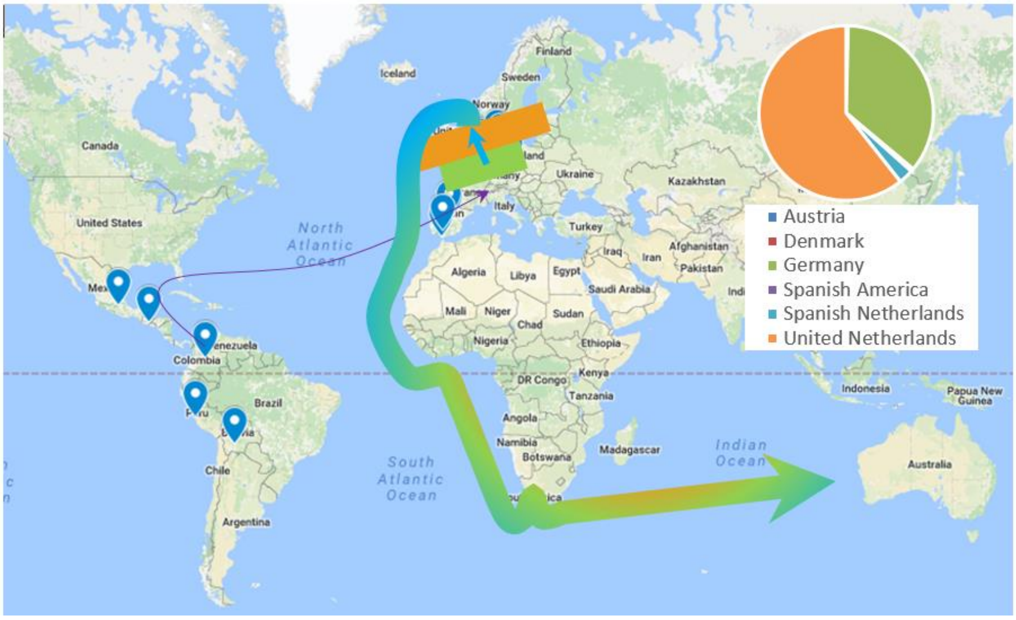
Portugal. Only five coins recovered from the wreck remained unidentified. One previously unidentified coin is represented in this study, and has been identified by trace elemental analysis and LDA as being German, from the Nuremberg mint. This finding represents the only known coin recovered from the *Rapid* originating in Germany. It may be that this coin was the private property of a crew member, which may have implications for our understanding of the makeup of the *Rapid's* crew. This sample may equally represent a larger assemblage of German coins as part of the *Rapid's* cargo, which has implications for our understanding of trade between the United States and Germany.

In the Museum's collection, 8,404 coins were recovered from the wreck of the *Vergulde Draeck.* Of those coins, the vast majority were identified as having originated in Mexico (7,026) with a further 467 of other Spanish American origin. Also recovered were three coins from the United Netherlands. Three coins in this study were recovered from the *Vergulde Draeck,* and had not been identified. Linear discriminant analysis found that those coins were likely from Lima, Mexico and Nuremberg. Of interest is the coin from the Nuremberg mint, the other two German coins recovered from the wreck originated in Wismar and Saxony. Also the coin which has now been identified as originating from Lima represents the only coin recovered from the *Vergulde Draeck* to have originated there.

A significant portion of the coins on board the *Zuytdorp* were *paymenten*, or small change, which have not been included in this study, as they represent currency intended not for trade but for domestic use by the Dutch within Batavia, and as such likely contain as much as twice the copper content as silver used for trade. Of the remainder, the *Zuytdorp* had a large number of Mexican coins on board. Of the 20,281 coins from the *Zuytdorp* in the Museum's collection, 1,331 are Spanish American, with 1,325 of those originating in Mexico and 18,844 coins from the United Netherlands. Four unidentified coins from the *Zuytdorp* were included in this study, and analysis has identified them originating in Mexico, West Friesland, Nuremberg and Holland. The Nuremberg coin would represent the only German coin recovered from the *Zuytdorp*, which may suggest that it was either the property of a crew member, or that it represents a larger cargo of German coins which were lost. There may be implications for our understanding of the make-up of the VOC *Zuytdorp's* cargo and crew.

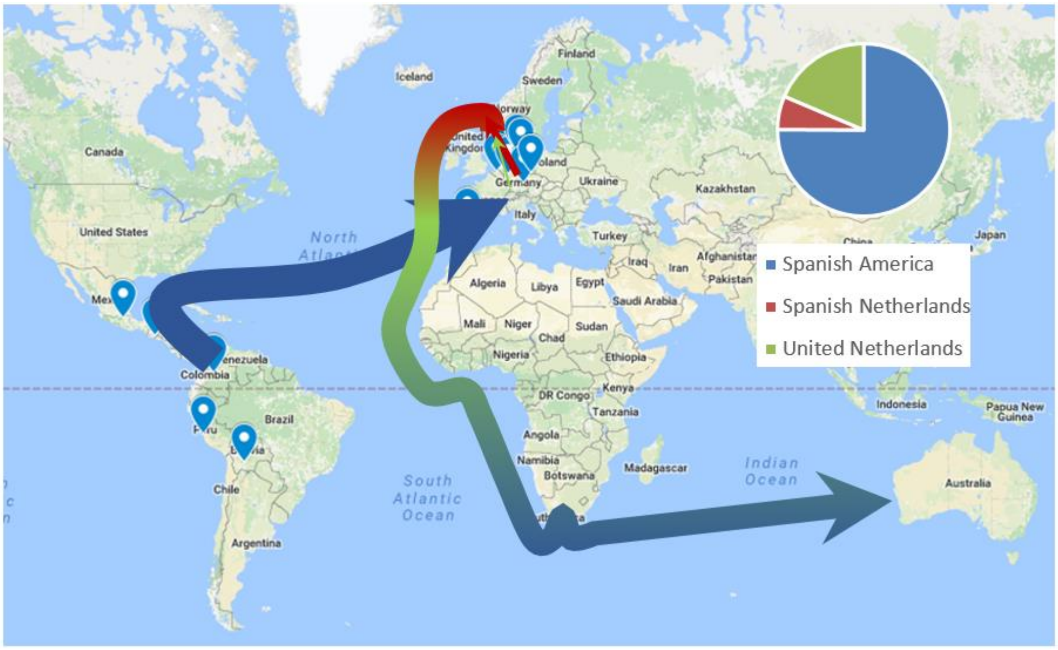
The analytes found to be most indicative of separation between populations of coins using factor analysis, would appear to have little correlation with the analytes expected to separate coins based on the mineralogy of relevant silver producing regions. It should be remembered that silver-bearing ores, while identifiably different in different geographical locations based on the minerals they are composed of, 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. Trace elemental analysis has shown that those elements that are most indicative of different silver sources are not always those that are mineralogically associated with silver. The reason for this is not clear from the present study, as there are a number of confounding factors from minting, corrosion, conservation and analytical processes that may or may not have an effect on these characterising trace elements.

Figure 7.1 shows maps of the sources of silver on board each ship in this study. In each map, an overview of the sources of silver is given in a pie chart, while a map of the world with the mints represented has been overlaid with the journey the silver took to be on board the ships in this study. The thickness of these lines correlates to the amount of silver from each source, while the final journey of each ship is depicted in different colours, their proportions within the line representing the amount of silver from that origin on board the ship.



Sources of silver on the *Batavia*

Sources of silver on the *Vergulde Draeck*



Sources of silver on the *Zuytdorp*

Sources of silver on the *Rapid*

Sources of silver on the *Correio da Azia*

Figure 7.1 – Maps showing the source of silver on each of the ship wrecks. The width of the lines corresponds to the amount of silver sourced from each country, detailed in the pie charts in the top right corner of each map, while the final journey shows a mixture of silver from each source.

7.2.1.2 Provenance determination of silver artefacts from the Batavia

It is known that all the items in this study were manufactured in the United Netherlands during 1627-1628, after Francisco Pelsaert's submission of the *Remonstratie* to the Gentlemen Seventeen and before the voyage of the *Batavia*. At the same time, Spain had introduced strict trade embargoes with the United Netherlands, in what has been interpreted as a siege on the Dutch economy, to weaken them militarily. The embargo was due to the Spanish military being over extended when on the offensive. After costly and ineffective sieges on Dutch fortresses, the Spanish reverted their military to a defensive position. The Spanish proceeded to wage their major attack on the Dutch by severely limiting trade and issuing in an economic depression; essentially attempting to besiege the United Netherlands from Spain.

A truce between Spain and the United Netherlands had been in place between 1609 and 1621, as both parties had suffered heavy financial losses in the years prior. However, due to Dutch mercantile skill during the truce, silver continued to drain steadily from Spain to the United Netherlands, and in 1621 the war and the trade embargo resumed (Israel, 1990). It follows that in 1628, when the *Batavia* commenced her voyage east, Spanish silver was certainly not reaching the United Netherlands directly.

The results of analysis clearly demonstrate that none of the samples in question is of Spanish or Spanish American provenance. This is not to say that some of the silver itself did not originate in Spanish America but rather that it has been mixed and remixed sufficiently to have taken on the trace elemental signatures representative of German or Dutch silver. It is worth remembering here that the trace elemental signature of worked silver is not necessarily equivalent to the trace elemental signature of a silver ore, although it will certainly retain those trace elements, albeit in different ratios with the addition of silver from different ores.

Prior to and during the Spanish utilisation 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 as discussed, it is also widely demonstrated that 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.

The key finding of this study is the demonstration that the source of the silver used in the trade items on board the *Batavia* is not from Spain or Spanish America. These results are significant as they provide evidence for the movement of silver from Spain, which held a monopoly on most of the silver in global circulation at the time. These results would indicate that Dutch silversmiths were working silver from a combination of sources.

Based on the results, Dutch silver would appear to have been sourced from both Spanish silver (from Spain, Spanish America and the Spanish Netherlands, likely through trade with other European countries) and silver from Germany, two nations that were producing silver from its source. Spanish and Spanish American silver is very similar in trace elemental composition, as the source mines were essentially identical and controlled by the Spanish Crown. These results support the theory that despite trade embargoes, the Dutch were still receiving some American silver through avenues other than direct trade with Spain while apparently supplementing this with silver from other sources, such as silver from Germany.

7.2.1.3 Provenance determination using lead isotopes

The addition of lead isotope data from a collection of 91 silver coins analysed by Desaulty *et al.*, (2011) has enabled a deeper interpretation of the mint of origin of 218 silver coins analysed from the present study for their lead isotope composition. The silver coins analysed by Desaulty *et al.*, represented 24 reference coins minted in the Ancient world (Greek, Hellenistic, Roman and Near Eastern), 16 medieval Spanish coins, seven Medieval European (non-Spanish) coins, 23 16th-18th century Spanish coins, two 16th-18th century European (non-Spanish) coins, 10 Potosí coins, one coin from Lima and eight Mexican coins.

The findings of Desaulty *et al.*, regarding lead isotope composition and provenance determination are that the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios are indicative of the geological age of the crustal volume that created specific ore bodies. Specifically, that the young (<130 million years old) ore bodies from the European Betic, Mexican and Andean districts can be distinguished from the old (250-450 million years old) ore bodies of Hercynian northern Spain and Western Europe. Further, the ancient and medieval coins were found to have mostly originated from the eastern Mediterranean. Mexican and Andean (Potosí and Lima) coins were found to originate from local silver ores. European and Spanish coins minted during the 16th-18th centuries were found to reflect changing silver sources over time, plotting between Medieval European silver and Mexican and Andean silver.

Provenance studies using lead isotopes were consistent with the findings of Desaulty *et al.,* (2011). Spanish American coins overlap with antique and precolonial European coins from the Aegean and Betic districts, 16th-18th century Spanish coinage is plotted between precolonial European and Mexican isotopic ratios, reflecting a shift in where Spain was sourcing silver, from European silver to American. European silver coins from the 16th to 18th centuries were also found to have variable lead isotope compositions, between the compositions of earlier European coinage and American. This reflects the process of American silver inundating the European currency market, and also the widespread recoining and refining of American silver using European lead. The lead isotope composition of Mexican coins was found to be consistent with the lead isotope composition of Mexican sulphide ores where the Spanish were conducting mining activities (Cumming *et al.,* 1979). The lead isotope composition of coins from the Potosí mint were found to be consistent with the lead isotope composition of nearby ore deposits, Cerro Rico, Oruro and Porco (Mamani *et al.,* 2008). Finally, based on the results of Desaulty *et al.,* (2011), the isotopic signature of European silver minted in Spain under Felipe III (1598-1621) had been entirely replaced by silver minted in the Americas by the reign of Felipe V (1700-1746).

This information, combined with results from the present study, confirms that Spanish American silver, which was being mined by the Spanish from 1498, and in earnest a few decades later (Garner, 1988), did not begin to reach Spain in significant enough amounts to affect the lead isotope ratio of Spanish coinage until the mid-17th century. It can be concluded that, until the mid-17th century, American silver was not being reminted in Spain. This would attest to the observation at the time that shipments of American silver moved out of Spain very quickly, most likely directly to the German bankers who secured Charles V's election as Holy Roman Emperor, and the Genoese bankers for other large loans to the Spanish Crown. It isn't until the 18th century and the Utrecht treaty that the isotopic signature of American silver can be seen in silver minted in Spain which coincides with a decrease in involvement in foreign wars by the Spanish. The lead isotope data of both Desaulty *et al.*, (2011) and the present study's analyses would indicate that American silver arriving in Spain was used predominantly to pay off royal debt and to fund foreign wars until the Utrecht treaty of 1713, with a significant decrease in Spain's involvement in foreign conflicts, American silver was retained in Spain to be reminted at such a volume that it all but replaced the European silver that previously formed Spanish currency.

7.3 Dating of coins using trace elemental analysis

This study has demonstrated that with a large database of coins of known year of minting, it is possible to identify the year or decade a coin was minted in by comparing the trace elemental composition of an unknown coin against a database of known coins. This method provides a new possibility for non-destructive, surface analytical absolute dating of archaeological artefacts, which can be integral to our further understanding of the artefacts themselves and other items they were found in association with.

It follows that with fluctuating sources of silver, whether within a single mine or from multiple source mines and trade, the elemental fingerprint associated with a mint will change somewhat over time. This has already been observed in some of the present sample of coins (Gentelli, 2012). Coins minted in Spanish American mints were observed to be more easily separated in space, rather than time, based on their trace elemental composition, while the opposite was found to be true of coins minted in Spain. This is due to a unique and constant source of silver for Spanish American mints, most frequently a nearby silver mine. The same can be extrapolated for coins minted in Germany, that their trace elemental composition will be more heavily dictated by the geographical location of the mint in proximity to a mine, rather than changing silver sources over time. Conversely, Spanish mints received their silver from the Americas in a combination which depended on the fluctuating output of individual mines and mints.

While most of the reported predictions are given with a high (>90%) level of confidence, when the dates predicted are compared to the visually identified sovereign on the coin (or when unavailable, the known date of wrecking of the ship carrying the coin), only 45 of the 150 predictions are consistent with visually identified features on the coin. Of the 105 incorrect predictions, 24 coins minted during the reign of Carlos IV were predicted to have been minted during the 1810s, while Carlos IV's reign ended in 1808; the error of these predictions is less than 12 years.

Another major inconsistency can be found in predictions for coins identified to have been minted during the reign of sovereigns who were on the throne during the 1700s. In the database of 399 coins used to make these predictions, only 10 were visually identified as having been minted in either 1708, 1711, 1788 or 1798. For the purposes of the LDA statistical analysis employed, the only population that could be used for these 18th century coins was “1708”. The 1708 population formed the only representative population between 1654 and 1800. It follows that any unidentified coin which had been minted between 1654 and 1800 would likely have been predicted (mostly incorrectly) to have fallen into the subpopulation of 1708. In short, coins visually identified as having been minted in the 18th century were underrepresented in the database, leading to inconsistencies in the predictions of unidentified coins minted under sovereigns who reigned in that period.

From these results it has been concluded that given a much larger database of coins from a single mint, the process of identifying the year of minting of a coin could be successfully achieved using trace elemental composition.

The results of this research have identified the possibility of using trace elemental composition as a platform to date archaeological artefacts. Many of the predicted years given by the LDA algorithm are inconsistent with the visual identification of the coin, in that the year or decade predicted will be inconsistent with the sovereign depicted on the coin or the year that the ship the coin was on departed. With a larger database, most of the confounding factors which lead to these inconsistencies could be eliminated, and the process could be used to confidently date artefacts.

7.4 Determination of method of manufacture of silver coins

7.4.1 The structure and morphology of copper-rich phases in silver coins

Two distinct types of copper-rich inclusions have been identified in a selection of sample coins using BSE imaging on polished sections of the coins. These represent the relatively small, elongated structures within silver-rich grains, and the larger areas of discontinuous precipitation of copper on silver grain boundaries.

A lack of observed dendritic segregation in the coins is consistent with a relatively pure alloy. Binary alloys exhibit dendritic segregation as one of the metals will solidify at a higher temperature than the other. This will lead to dendrites which are rich in that metal at their core, and rich in the metal which solidifies at a lower temperature at their outer regions. However, when the alloy consists of a high content of one metal, as is the case for the silver coins in this study, and is cooled slowly, dendrites may not form at all, rather equi-axed hexagonal grains will develop. Equi-axed hexagonal grains have been observed in the coins analysed in this study. This type of microstructure can also be achieved by annealing the metal during manufacture (Scott, 1991), however further evidence based on the microstructure of the coins in this study do not support annealing as a significant part of the manufacturing process. Interpretation of the microstructure of the silver/copper alloys confirm that the metal was cooled slowly from liquid state. This information is consistent with accounts of minting technology at the time. Annealing may have taken place after the initial cold working of the metal, which may also account for the equi-axed hexagonal structure observed. However, extensive annealing of silver/copper alloys is known to cause internal oxidisation, when oxygen can diffuse into the alloy and readily form cuprite in copper-rich phases of the alloy, creating a metal which is more prone to corrosion and thus unsuitable for use as coinage (Schweizer and Meyers, 1978; Smith, 1971).

Discontinuous precipitation occurs in silver/copper alloys over time and is not associated with their manufacture. Precipitation occurs over time at a predictable enough rate that it has been posited that the level of discontinuous precipitation of copper-rich phases at silver grain boundaries could be used to verify the antiquity of a silver/copper alloy (Schweizer and Meyers, 1978). However this method has been shown to be too inaccurate to be of use in the verification and authenticity of ancient silver (Wanhill, 2012). Discontinuous precipitation of copper has also been associated with increased corrosion-induced and microstructurally-induced embrittlement of ancient and historical silver (Smith, 1965), which has also been shown to be inconsistent based on case studies of several embrittled, ancient silver artefacts (Wanhill, 2012).

In terms of the present study, the observed discontinuous precipitation of copper at silver grain boundaries adds little information to the provenance, date or method of manufacture of the coins, however in combination with the observation of dendritic remnants, it does assist in characterising a typical microstructure of historical silver, as opposed to modern. This information can be used to identify silver alloys, in terms of what the alloy is, what the object is, and how the object was made, by using the imaging capabilities of SEM.

7.4.2 Electron backscatter diffraction pattern and method of manufacture

The progress and innovation of minting technology during the 16th to 19th centuries would indicate that the majority of the coins used in this study would have been minted by being hammered or using roller mills and a screw press. Mexican coins were of the crude 'cob' type until the late 17th century, when the screw press was introduced to the Mexican mint. Hammer-struck coins were also produced at the Potosí mint until 1767, when the screw press was introduced to Bolivia. As such, the coins investigated in this study using EBSD would have almost certainly been produced by hammer striking, rather than screw press. The microstructure of a hammer-struck coin would reflect the following coinage process: Ingots of silver/copper alloy were cast and then hammered to close to the desired thickness, annealed, and hammered again to precisely the desired thickness. From here, strips were cut into squares, and squares were cut into octagons, before being hammered into a circular shape. Alternatively, the metal may have been cast into rectangular rods, which were then cut into pieces of the desired weight, before being hammered until round. Coin blanks were then placed between a die mounted in an anvil and another die, to be struck with the inverse impressions of the dies.

The results of EBSD analysis are indicative of this type of minting, with twinning within grains indicative of the annealing, and significant deformation indicative of the many stages of hammering and striking involved in the manufacturing process. However, coins 372-J and 025 show indications of having been annealed after being hammered into a round coin blank. Evidence for further annealing based on EBSD results can be seen in the larger grain sizes in these two coins, as well as in BSE images of the coins, specifically intergranular corrosion and a lack of elongated copper-rich phases. The circumstances surrounding the decision to further anneal a coin, considering that it is known to make a metal more susceptible to corrosion (Schweizer and Meyers, 1978; Smith, 1971), are unclear. Based on historical accounts of minting practices, which do not mention a further annealing stage, it would appear that this was an uncommon practice.

Chapter conclusion - Complementary analytical techniques

In the most basic terms, questions regarding the identification, dating, movement, use and degradation of archaeological artefacts are important in order to further understand the human past. This study has shown that the use of complementary analytical techniques is important in order to gain a holistic understanding of an archaeological artefact.

The number of coins in the Western Australian Museum’s collection and their varying states of preservation has enabled this study to apply both destructive and non-destructive analytical techniques in order to understand both the history of the coins themselves, and also the applicability of different analytical techniques that can be used to answer the research questions posed in this thesis.

The applicability of non-destructive surface analytical techniques was assessed using a combination of LA-ICP-MS and solution ICP-MS, as well as imaging of the surface of coins using electron microscopy. Compositional analysis has been used to determine the mint and year or decade of origin of unidentified coins. This information was complemented with microstructural information gained through electron microscopy imaging techniques. The structure and morphology of the coins has revealed information about the manufacturing and corrosion processes that compositional information alone could not have indicated.

To conclude, this thesis has demonstrated the unique possibilities that come about from the opportunity to study a large collection of similar artefacts, in particular the ability to create and statistically analyse large databases based on analysis of artefacts. Further, this thesis has demonstrated the applicability of various analytical techniques to provide complementary results, in order to provide a more complete understanding of archaeological artefacts.

Chapter 8 - Conclusion

Chapter introduction

This study is concerned with identifying the mint of origin of coins based on their trace elemental composition, identifying the year or decade of minting of coins based on their trace elemental composition, and the determination of the manufacturing history of coins based on their elemental distribution and microstructure.

This chapter summarises the key findings of the research presented in this thesis. Further, the findings are put into the wider context of the implications of the techniques used and analytical results in terms of numismatics and archaeology. Finally, recommendations for future research are made, based on the results of the present study.

8.1 Summary of results

8.1.1 The manufacturing and use history of silver coins

This research has found that the coins in this study were initially smelted at a temperature over 900°C and allowed to cool slowly, rather than being quenched. A comparison of the microstructure of silver and copper-rich phases in the coins and a phase diagram for silver/copper alloys confirms this. Further, based on historical evidence and confirmed by microstructural evidence, ingots of silver were cold-worked into sheets, from which coin blanks were cut or punched. The design on the coin obverse and reverse was hammer-struck or pressed on to the coin. The microstructure of the coins reflects this, with the copper-rich phases within the silver-rich matrix being elongated into sheets parallel to the surface of the coin.

Corrosion from the depositional environment has been investigated in the sample coins in order to establish that surface analyses can be considered to be representative of the whole coin. Using electron microscopy it has been found that a corrosion layer of tens to 200µm thick can be observed at the surface of coins studied, characterised by increased porosity and fluctuating silver and copper content. Silver surface enrichment due to the preferential leaching of copper from a coin has been observed in coins of lower silver content (<95%), with little to no effect in coins with a silver content higher than 95%.

8.1.2 The mint of origin of silver coins and artefacts

Trace elemental analysis was used to determine the mint of origin of 26 previously unidentified coins. The trace elemental composition of the unidentified coins, determined using LA-ICP-MS, were compared to a database of compositions of identified coins using linear discriminant analysis. Trace elemental composition was also used to identify the source of silver used in a selection of artefacts intended for trade in the East Indies from the wreck of the *Batavia*. It was found that the silver used in these artefacts most closely represents a mix of silver from Germany and Spanish American silver, which reached the United Netherlands through indirect trade, as a trade embargo between Spain and the United Netherlands was in place at the time.

Further, concentrations of lead isotopes were used to assess the flow of Spanish American silver into Spain and Europe. Isotopic data from 218 coins in this study were combined with data from 91 coins from Desaulty *et al.,* (2011). The influx of Spanish American silver from the 16th century onward can be seen reflected in the changing lead isotope composition between Medieval European silver and American silver.

8.1.4 The year of manufacture of silver coins

Trace elemental composition was used in order to determine the year or decade of minting of unidentified sample coins. The trace elemental composition of the unidentified coins was compared to a database of the compositions of coins of known year of minting using linear discriminant analysis. Results of predicted year or decade of minting were in many cases inconsistent with other evidence identifiable on the coin in particular with the years of reign of the depicted sovereign. However, this study has shown that with a comprehensive enough database of artefacts of known year of manufacture it should be possible to determine the year of manufacture of an artefact based on its trace elemental composition.

8.2 Implications of this study in numismatics

This study has deepened our understanding of the influx of Spanish American silver into Europe and beyond. The results of this study have provided new information on how, when and where silver coinage was manufactured and when Spanish American silver flooded the European market.

This study has also concluded that silver surface enrichment has minimal effect on results of surface analyses of silver objects, when those objects are more than approximately 95% silver. The implications of this finding are that non-destructive surface analytical techniques can confidently be used on the surface of silver coins to gain representative results of the item's composition, while retaining the integrity of the artefact.

Further, analysis of assemblages and collections of coins has been shown to be integral to understanding individual coins. By creating a compositional database from the Western Australian Museum's extensive coin collection, the identification of individual coins year of minting, mint of origin and method of manufacture was made possible. This study can be used as an example of the importance of keeping collections, assemblages or hordes of coins together for future analysis and research.

8.3 Implications of this study in archaeology

This study has furthered our understanding of the ships represented and the circumstances surrounding their voyages. Coins were identified as originating in mints which had previously not been identified as part of the cargo of some of the ships. This information has added to our knowledge of the make-up of the cargo, where coins had been sourced from and how readily available silver was to the country of origin of the ships at different points in time.

Measurement of corrosion and surface changes on the coins has furthered our understanding of the effect of being submerged for hundreds of years on these coins. In terms of maritime archaeology, this information can be used to further best practice for conservation and preservation of submerged silver artefacts, as well as inform future analysis and research of silver artefacts.

8.4 Future research

It is recommended that a larger database of LA-ICP-MS trace elemental analyses be produced in order to have sufficient representative coins from different mints and decades, to enable more comprehensive analysis of provenance and date of manufacture. It is also recommended that the use of isotopic data as well as trace elemental data will better facilitate the tracing of metals from mine, to mint, through trade, reminting and counter stamping. This information would be invaluable in furthering our understanding of the flow of precious metals from the Americas, through Europe to the Far East during the 16th to 19th centuries.

Further investigation is recommended using destructive methods to enable imaging of the interior of coins, in order to further explore the microstructure of coins manufactured in various ways. This would enable a conclusive ‘typical’ microstructure of coins of different origins, providing a potential platform for coin identification based on microstructure.

It is also recommended that museum collections of coins, indeed significant collections and assemblage of any type of artefacts, be kept together for future research and analysis. As this thesis has demonstrated, due to the foresight of the Western Australian Museum to keep their large collection of silver coins together, many important conclusions have been drawn from the present study.

Finally, the techniques used in this study are certainly not limited to coins, silver, or metal artefacts. It is recommended that similar research be conducted on artefacts of other materials, as the possibilities of analysing archaeological artefacts ever increase our opportunities for understanding both the artefacts themselves and their contribution to our shared human past.

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Provenance determination of silver artefacts from the 1629 VOC wreck *Batavia* using LA-ICP-MS

Liesel Gentelli

Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, M010, 35 Stirling Highway, Crawley, WA 6009, Australia

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ABSTRACT

Silver artefacts from the shipwreck *Batavia*, known to have been made on commission by the Dutch East India Company in 1627–1628 for trade in the Dutch East Indies, were analysed using LA-ICP-MS for trace elemental composition. The results were compared to a database of trace elemental compositions of Spanish, Spanish American and other European silver coins of known provenance. At the time Spain, which controlled the vast majority of world silver, was at war with the United Netherlands, and was enforcing a trade embargo, severely limiting the supplies of precious metals accessible by the Dutch. Based on their trace elemental composition, the *Batavia* silver artefacts were found to have been most similar to silver known to have originated in Germany and silver that reached the Dutch indirectly from Spain. These results shed light on the movement of silver as a commodity throughout the world during a unique time in history.

1. Introduction

1.1. World silver movement and Dutch silver sources, 1627–1628

During the 16th century, precious metals in Europe were almost exclusively sourced from the Americas (Attman, 1986). The Spanish crown held a monopoly on much of this American treasure which, upon arrival in Spanish ports, was quickly dispersed throughout Europe and beyond through trade, warfare and the payment of royal debts (Hamilton, 1965). Prior to European colonisation of the Americas, European silver originated from mines in Germany, from Saxon-Erzgebirge and the Kuttenberger mines in Bohemia (Soetbeer, 1880). Silver was also acquired through trade from the Arabian silver mine of Penjir in the mountain range of Hindu Kush in present day Afghanistan, and from Shash, a silver mine in present day Tashkent, Uzbekistan (Attman, 1981). Output from these mines was quickly dwarfed by the unprecedented output from American silver mines. To put this into perspective, in the six centuries between 250 BCE and 350 CE, 40,000–50,000 t of silver were produced in the Mediterranean world. The silver mines of the Americas produced the same amount of silver in only 200 years (Stein and Stein, 2000).

Spanish silver during the 17th to 19th centuries was a trusted currency, considered to be of generally good weight and fineness by the rest of Europe and other parts of the world. Spanish *reals* were trusted trade coins in their original form either as denominations of one, two, four and most commonly eight *reals*, or as the counter-stamped or reminted currency of other countries. Despite concerted efforts by the Spanish to retain as much Spanish American gold and silver as possible in Spain, much of the Spanish American treasure was lost to the rest of Europe. The reasons for this loss of currency are due to a combination of paying off royal debt, funding warfare and trade. The drain of precious metals from Spain is apparent in the following example: on 23rd May 1590, the Spanish Cortes complained that by the middle of the year, despite the amount of treasure being brought to Spain from Spanish America, there was no money except *vellon* (copper currency of small denominations) to be found anywhere in Spain, and little *vellon* at that (Hamilton, 1965, p. 62). The drain of precious metals was to continue unabated. In 1617 the Spanish Cortes noted that, upon arriving in Spain, American silver "… immediately goes to foreign kingdoms, leaving this one in extreme poverty." (Actas de las Cortes de Castilla XXXVII). The Netherlands in particular were known to use foreign coins, especially Spanish *reals*, as local currency. In 1626, the Netherlands Parliament published a coin tariff catalogue, detailing a large range of foreign coins and how much they were worth in Netherlands *guilders*, to circulate in the Netherlands. As will be discussed, Spanish-Dutch relations were tense during the 17th century, but the Spanish seemed to have little control over American silver imports and exports, and further, were aware and concerned over their silver reaching other European nations. In the same report quote above from 1617, the Spanish Cortes asserted that Castile "…serves as a bridge over which the products of our mines pass to foreign hands at time even to our worst enemies" (Actas de las Cortes de Castilla XXXVII).

In the years prior to the *Batavia*'s maiden voyage of 1628, the majority of silver in global circulation originated in the Americas, distributed

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E-mail address: liesel.gentelli@research.uwa.edu.au.

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through Europe via Spain. However, at the same time, Spain and the United Netherlands were engaged in the Eighty Years War for Dutch independence. Despite the Spanish monopoly on silver, and the trade embargoes put in place with the Dutch, Spanish silver rapidly drained out of Spain to the rest of Europe (Parker, 1979; Attman, 1983). As such, it is of particular interest to determine the provenance of Dutch silver artefacts during this time, to investigate world silver movement at a time when Spain held a monopoly over American silver.

Despite being at war with Spain, the United Netherlands still found themselves with a significant influx of Spanish precious metals via the trade centres of Europe, including Hamburg, France and England, or via Barcelona and Genoa (Attman, 1983:33–35). In fact, it has been estimated that between 1566 and 1654, the Dutch Military Treasury received 218 million ducats worth of silver either directly or indirectly from Spain (Parker, 1979:188), and Amsterdam became a centre of trade in Spanish silver (Israel, 1977). For many years, the Spanish crown spent more waging war in the Netherlands than it received from the Americas. In an unsuccessful attempt to make up the difference, taxes were raised to the point that a third of a Spanish peasant's yearly income was consumed in tax (Parker, 1979). Despite the immense cost of the war, the Spanish crown maintained strict trade embargoes with the United Netherlands in order to wage a defensive rather than offensive war to minimise effort and cost. At the same time, halting trade with the United Netherlands was intended to wear down the Dutch into agreeing to peace terms that were advantageous to Spain (Israel, 1982). So strict were the trade embargoes enforced by the Spanish that foreign ships, despite not being Dutch, if they had been built in the United Netherlands were not permitted to trade with Spain (Israel, 1982). In turn, the Dutch also enforced a blockade of their rivers and ports, preventing trade of Spanish goods or with Spanish vessels (Israel, 1982).

It was during this time that the *Batavia* sailed on her maiden voyage, with the specially made speculative trade items suggested by the *Batavia*'s captain, Francisco Pelsaert and commissioned by the *Verenigde Oostindische Compagnie* (United Dutch East India Company) (VOC). These items provide a unique opportunity to further understand the movement of a commodity that was controlled almost exclusively by one country, and to investigate how the Spanish utilised their silver monopoly in ways other than trade in the form of besieging the United Netherlands through a trade embargo at a time of war.

1.2. The *Batavia*

The *Batavia* was a VOC ship on her maiden voyage from Texel in the Netherlands, to *Batavia* (Jakarta), Indonesia. She left Texel on 27th October 1628 with a cargo consisting mostly of silver specie, and notably the sandstone blocks required to build a portico at the entrance of the city of *Batavia*. With 322 aboard, rounded the Cape of Good Hope on schedule but ran aground on Morning Reef off the coast of what is now Western Australia. Several ships bound for the Dutch East Indies found themselves within sight of and occasionally wrecked on Australia's west coast, due to a combination of the use of the Brouwer route to the Dutch East Indies, utilising the strong Roaring Forties trade winds between South Africa and Australia, and imprecise methods of calculating longitude. From 1616, all VOC ships travelling to *Batavia* used the Brouwer route, which called for ships to turn northeast after sighting Amsterdam or Saint Paul islands in the Indian Ocean. However, at the time there was no precise way of calculating a ship's longitude, and without sighting one of the aforementioned islands, a ship could very easily travel east into Australia's west coast. The *Batavia* is one of four Dutch ships known to have been wrecked off the Western Australian coast, with another three presumed to have been wrecked there during the 17th, 18th and 19th centuries. The *Batavia* story is particularly grim. A mutiny and massacre ensued among the survivors of the *Batavia* wreck on Beacon Island, which is well documented in the literature and popular culture of the 17th Century and also in recent decades following the discovery of the wreck site (Dash, 2002; Drake-Brockman, 2006; Edwards, 2012; Fitzsimons, 2011; Green, 1989; Pelsaert, 1647).

The *Batavia* was rediscovered in 1963, with artefacts and a large portion of the hull recovered from 1971 to 1975 (Green, 1975; Green, 1989). The artefacts were stabilised, cleaned and conserved, with many now on display in the Western Australian Maritime Museum and the Geraldton Maritime Museum. The silver was cleaned of concretions and conserved using the alkaline dithionite method (MacLeod and North, 1979).

Interpretation of the silver artefacts (see Table 1 below) by the WA Maritime Museum after their recovery from the wreck site speculated that they were similar in style. Only one, the plate, had a legible maker's mark, and so based on their similar styles it was inferred that all the artefacts were made by the same manufacturer in 1628, with the possible exception of the candelabrum (Green, 1989:195).

The silver trade items on board the *Batavia*, commissioned specifically by the VOC Gentlemen Seventeen, represent a unique opportunity to understand Dutch silver sources during the Eighty Years' War trade embargoes with Spain.

1.3. The *Batavia*'s speculative trade silverware

The artefacts used in this study were several items of silverware, which formed part of the cargo on board the *Batavia* intended for trade in the Dutch East Indies. The *Batavia* silverware was made for speculative trade at the suggestion of the captain, Francisco Pelsaert.

From Europe, precious metals rapidly moved east to the Dutch East Indies and Asia in trade. The drain of precious metals to the East was a well-known problem facing European economies, given the large imbalance between European demand for Eastern goods, especially pepper, spices, fabrics and dyes, and the almost exclusive demand from the East for precious metals over European goods (Attman, 1981). As Pelsaert saw it, meeting the Eastern demand for precious metals in the form of already manufactured items would provide a compromise to try to correct the demand imbalance by sparking an interest in European manufactured goods, and would attract a higher price for a manufactured item than the equivalent amount of silver in ingots or coins.

In 1627, Pelsaert presented the governing body of the VOC, the *Heeren XVII* (Gentlemen Seventeen), with his *Remonstratie* (Report), suggesting new avenues of trade to explore in the Dutch East Indies. In the *Remonstratie*, Pelsaert suggests manufacturing precious metals into objects already in use in the Dutch East Indies rather than trading

Table 1
Silver artefacts from the *Batavia* analysed for this study.

Sample number	Museum registration number	Artefact description
S404	BAT3032	Part of an engraved bedpost
S405	BAT3563	An incomplete chalice, engraved with scroll and motif
S406	BAT3565	Unidentified engraved fragments, possibly from the foot rim of chalice. The underside displays zigzag contemporary assay tooling marks.
S407	BAT3568	Cherub section and fragments
S408	BAT3573	A copper coated ring. It appears to have a flat base as if part of a tubular object.
S409	BAT3606	An unidentified, worn object, possibly part of a sword hilt.
S410	BAT3626	A flat, engraved section of a plate.
S411	BAT3643	Candelabrum
S412	BAT3651	Bed post fragments engraved with scrolls and other designs.
S413	BAT3744	Unidentified object (3 fragments), possibly from a sword hilt.
S414	BAT3835	A screw top in two sections.

them in coin or ingot form (Pelsaert, 1925 (1627)). As Pelsaert details from the point of view of Dutch merchants in the Dutch East Indies "Many of the great men express surprise that we do not have the gold and silver (coined and uncoined), which we import in large quantities, manufactured by us into articles which are here in common use. Provided the workmanship is good, half the silver might be paid for manufacture, which would give ample payment for Dutch work; or in any case manufactured goods would yield quite as much profit as reals or Holland dollars, and could meet the taste of the nobles everywhere without loss to us." (Pelsaert, 1925 (1627):27). The Gentlemen Seventeen immediately commissioned several silver items to be manufactured for speculative trade in the Dutch East Indies, to be shipped with Francisco Pelsaert on the *Batavia*.

1.4. Trace elements and provenance determination

From an archaeological perspective, provenance determination based on trace elemental composition is an important tool for investigating artefact movement and trade networks over time.

Trace elemental analysis and provenance determination of archaeological silver was first attempted in the 1970s and 80s 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). The provenance of ores of precious metals is explored by Guerra et al. (1999), in an attempt to explore the possibilities of using ICP-MS in this field of study. In the study, it is demonstrated that a coin can be matched to its mint of origin based on its trace elemental composition, and it is posited that this is due to mints using metal from local ores (Guerra et al., 1999).

Problems identified with provenance determination of archaeological metals using trace elemental analysis have been identified by Ernst Pernicka (2014). Firstly, ores are inhomogeneous, and so it can be problematic to attempt to match a metal to its provenance ore based on their trace elemental compositions. 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 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 a different locations (Desaulty et al., 2011), which would have been the case through trade when silver coins were exported and reminted or resmelted.

In the case of the silver artefacts 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 of 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, combining to create a new combination of trace elements unique to the mint in question (Gentelli, 2012).

2. Experimental

2.1. Samples and sample preparation

Samples for analysis were taken from a number of different silver artefacts recovered from the *Batavia* wreck site, detailed in Table 1 below. Small (<0.5 cm^2) pieces of the artefacts were clipped off, mounted in epoxy resin, ground to a flat surface with P800 Norton sandpaper, and cleaned in an ultrasonic bath for 15 min. Samples were then subjected to laser ablation inductively coupled plasma mass spectrometric analysis with results compared to a database of the elemental composition of contemporary silver coins of known provenance.

Silver coins recovered from both the *Batavia* and other contemporary wrecks are a close comparable database for the artefacts in question. The majority of silver exported from the Americas, via Spain, into Europe, was in coin form rather than ingot (Garner, 2006), and so it is expected that the silver artefacts in this study were imported into the United Netherlands as coins. However, the artefacts, while they were manufactured from coins, are necessarily re-manufactured under different conditions than the silver coins, and so necessarily display some consistent compositional differences, detailed below.

The silver artefacts from the *Batavia* were also analysed for bulk elemental composition using scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) and are reported in Table 2, along with the mean bulk elemental composition of the database of silver coins used in this study. The main difference between the composition of the silver artefacts and the silver coins is the silver to copper ratio. Where the silver coins are on average 2.7% higher in silver, the silver artefacts are 1.6% higher in copper and 0.8% higher in lead. This difference in bulk elemental composition will necessarily affect the trace elemental composition investigated in this study, and there is no way of knowing which trace elements were introduced with the silver metal and which with the copper. (See Tables 3 and 4.)

2.2. LA-ICP-MS parameters

Laser Ablation Inductively Coupled Plasma Mass Spectrometric analysis (LA-ICP-MS) was completed using a New Wave Research Co. Ltd. (Cambridgeshire, England) UPI 213 nm Nd:YAG laser system coupled with an Agilent Technologies (Tokyo, Japan) Agilent 7500CS inductively coupled mass spectrometer. The ICP-MS is tuned prior to the commencement of each day's analysis and after every ten samples using a National Institute of Standards and Technology (NIST) 610 glass standard for optimal system sensitivity and to eliminate mass bias effects, and to allow normalisation of the data for instrumental drift, which could be corrected for after processing the data for the entire analytical run. NIST glass standards are homogenous with a level of precision and accuracy of at least 2%. Approximately 10 s of instrumental gas blank were collected prior to each analytical run to allow for background

Table 2
Bulk elemental composition of *Batavia* artefacts and the mean bulk elemental composition of the database of silver coins used in this study.

(%)	Ag	Cu	Pb	Au
S404	92.2	6.3	0.8	0.2
S405	92.2	5.8	1.8	0.2
S406	89.9	9.4	0.6	0.0
S407	97.0	1.7	0.4	0.8
S408	91.8	6.8	0.7	0.2
S409	92.2	6.7	0.9	0.1
S410	92.2	6.9	0.9	0.0
S411	91.1	8.2	0.5	0.1
S412	92.4	5.6	1.0	0.8
S413	91.9	6.3	1.7	0.1
S414	91.0	7.8	1.0	0.1
Silver artefacts ($\bar{x}$)	92.2	6.5	0.9	0.2
Silver coins ($\bar{x}$)	94.9	4.9	0.1	0.2

Table 3
Isotopes determined using LA-ICP-MS.

Be^{9}	Na^{23}	Mg^{24}	Al^{27}	P^{31}	K^{39}	Ca^{44}	Ti^{48}	V^{51}	Cr^{52}
Mn^{55}	Fe^{57}	Co^{59}	Ni^{60}	Zn^{64}	Cu^{65}	As^{75}	Se^{82}	Rb^{85}	Sr^{88}
Y^{89}	Zr^{90}	Nb^{93}	Mo^{98}	Rh^{103}	Pd^{108}	Cd^{111}	In^{115}	Sn^{120}	Sb^{123}
Te^{126}	Ba^{138}	Pt^{195}	Au^{197}	Hg^{202}	Pb^{208}	Bi^{209}	U^{238}		

correction. The isotopes that were measured during each analysis are detailed in Table 3.

It is of utmost importance to do as little damage to the sample silver as possible during laser ablation. However, if the ablated area is too small the concentration of the trace elements may be below the detection limit of the mass spectrometer. To satisfy both of these conditions it is necessary to set parameters to optimise the size of the crater created by the laser, the intensity of the laser, the length of ablation time and the pattern of ablation.

These parameters were set by analysing each sample in triplicate, using 1 mm × 50 μm × 50 μm areas of ablation, with the laser operating at 60% power, at 6 Hz for 30 s. National Institute of Standards and Technology (NIST) glass standards were used to allow the counts per second data to be quantified and reproducible. Over the course of the day, a NIST 610 glass standard was periodically analysed. NIST standards were chosen for reproducibility as they are Certified Reference Materials and are used internationally for calibration in LA-ICP-MS analysis.

For the purposes of this research, analysing the components of the central metal core of the samples would have been ideal, but in many cases, due to corrosion, this core was simply too deep. However, analysis of the silver coin data supplied by the LA-ICP-MS indicates that the compounds in the corrosion layer do not affect separation into known subpopulations of the samples. Previous research has shown that silver coins of known provenance can be reliably identified into subpopulations of their mint of origin, despite their surface composition having been affected by corrosion (Gentelli, 2012).

2.3. Statistical analyses

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.

The trace elemental profiles of the silver artefacts were then compared to a database of profiles of American and European silver coins from ships wrecked off Western Australia (Gentelli, 2012). The database includes samples of known provenance from the mints detailed in Table 4. The samples in the database have been subjected to the same LA-ICP-MS analysis as the silver artefacts in this study. It has been demonstrated that the trace elemental composition of silver items is indicative of their mint of origin, and that different mints produce items of different trace elemental compositions (Gentelli, 2012).

Table 4
Mint of origin of silver coins of known provenance.

Country	Mint	Number of samples	
Spanish America	Guatemala	8	206
Peru 74	Lima	24	
New Spain 132	Mexico	124	
	Potosi	48	
	Santa Fe	2	
Spain	Cadiz	4	104
	Madrid	50	
	Segovia	4	
	Seville	46	
Spanish Netherlands	Brabant	6	6
United Netherlands	Gelderland	8	31
	Holland	2	
	Utrecht	7	
	West Friesland	7	
	Zeeland	7	
Germany	Lubeck	5	20
	Nuremberg	7	
	Sachsen	8	

XLSTAT discriminant analysis was used to group the *Batavia* artefacts that are of unknown provenance, among coins of known country and mint. Discriminant analysis requires the user to assign the data into subpopulations prior to analysis. During analysis, a controlled number of samples is retained, and then blindly assigned to a subpopulation. The accuracy with which these validation samples are assigned is reported, and can be considered to be representative of the accuracy with which the unknown artefacts will be assigned to a subpopulation.

3. Results

The artefact data were compared to coins of known provenance country using discriminant analysis. In Fig. 1 it can be seen that 81.25% of the variation between samples is described by the two components (F1 and F2); these components are made up of a combination of all of the analytes. In order to be able to plot each sample in two dimensions, based on their entire trace elemental composition, each of the two components is represented on an axis in the plot. The samples are plotted with centroids representing the location of the mean of the relevant subpopulation, as well as confidence ellipses for each subpopulation at a confidence of 0.95. Fig. 2 details a factor analysis of the same data, showing which analytes most discriminate between populations. The direction of the vector of the relevant analyte correlates with how an individual sample will be plotted in discriminant analysis, based on its relative composition of that analyte. In this way, samples of similar composition will necessarily plot in clusters, and subpopulations will become visually distinct groups of points.

In the plot, some overlap between populations can be seen, which is to be expected as the composition of samples in the database is necessarily very similar. Based on the factor analysis detailed in Fig. 2, it would appear that the analytes most indicative of Spanish and Spanish American silver is tellurium and gold, silver minted in the Spanish Netherlands is indicated by cobalt, zinc and arsenic, silver minted in the United Netherlands is higher in indium and antimony, while platinum is indicative of German silver.

The *Batavia* artefacts all plot in the lower right quadrant of Fig. 1, outside any of the established subpopulation confidence ellipses. Based on factor analysis, they would appear to have a higher palladium, nickel, bismuth and sodium content than the silver coins. Since the artefacts are not coins, it is to be expected that they will not fit precisely into a subpopulation of coins, because while the artefacts are manufactured from silver from the same source, they are not manufactured under the same guidelines and conditions. Of most interest in this plot is the distinction between the *Batavia* artefacts and the coins known to be from Spain and Spanish America.

There is significant overlap between Spain and Spanish America, which is to be expected, as Spanish silver was sourced almost exclusively from the Americas. It is also interesting to note that samples from the United Netherlands have some overlap with silver from Spanish sources, and more overlap with German silver. It would appear that United Netherlands silver had German and Spanish origins. The unknown *Batavia* samples have been predicted to be from Germany, the United Netherlands and the Spanish Netherlands. These predictions are further detailed in Fig. 3. Note that all samples carried a reported 0% likelihood of originating from Spain or Spanish America.

4. Discussion

It is known that all the items in this study were manufactured in the United Netherlands during 1627–1628, after Francisco Pelsaert's submission of the *Remonstratie* to the Gentlemen Seventeen and before the voyage of the *Batavia*. At the same time, Spain had introduced strict

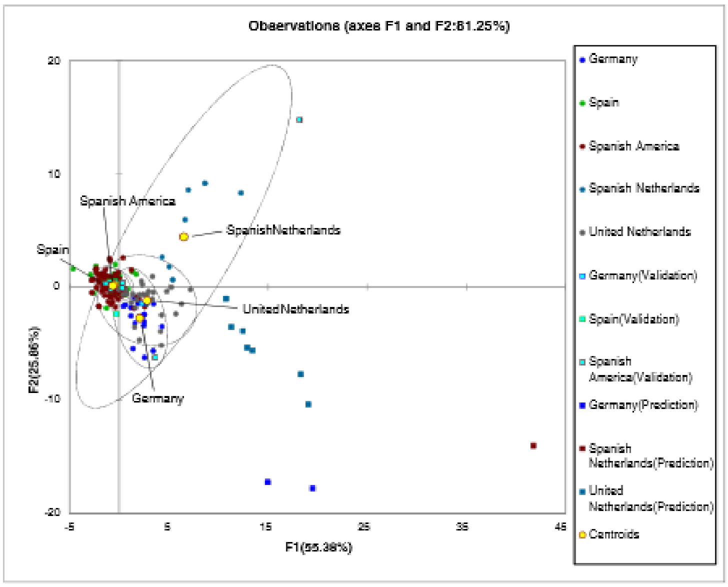

Fig. 1. Distribution of samples of known provenance country, and predictions of provenance of unknown *Batavia* artefacts.

trade embargoes with the United Netherlands, in what has been interpreted as a siege on the Dutch economy, to weaken them militarily. This was due to the Spanish military being over extended when on the offensive, and after costly and ineffective sieges on Dutch fortresses, the Spanish reverted their military to a defensive position, waging their major attack on the Dutch by severely limiting trade and issuing in an

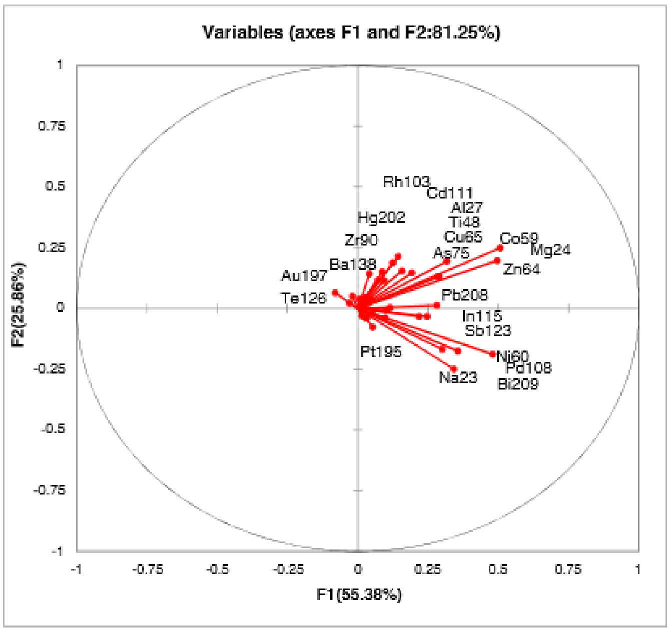

Fig. 2. Factor analysis detailing the analytes which most discriminate between populations.

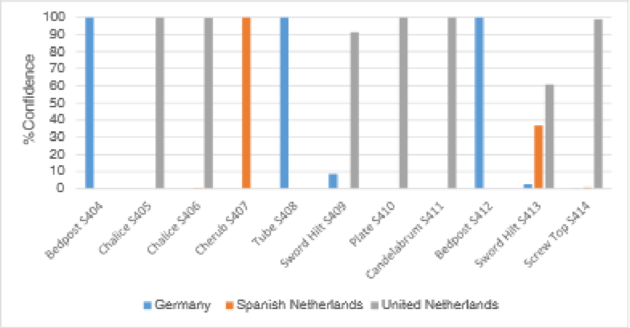

Fig. 3. Predicted country of origin of *Batavia* artefacts.

economic depression; essentially attempting to besiege the United Netherlands from Spain.

A truce between Spain and the United Netherlands had been in place between 1609 and 1621, as both parties had suffered heavy financial losses in the years prior. However, due to Dutch mercantile skill during the truce, silver continued to drain steadily to the United Netherlands from Spain, and in 1621 the war and the trade embargo, resumed (Israel, 1990). It follows that in 1628, when the *Batavia* commenced her voyage east, Spanish silver was certainly not reaching the United Netherlands directly.

The results of analysis clearly demonstrate that none of the samples in question is of Spanish or Spanish American provenance. This is not to say that some of the silver itself did not originate in Spanish America, but rather that it has been mixed and remixed sufficiently to have taken on the trace elemental signatures representative of German or Dutch silver. It is worth remembering here that the trace elemental signature of worked silver is not necessarily equivalent to the trace elemental signature of a silver ore, although it will certainly retain those trace elements, albeit in different ratios with the addition of silver from different ores.

Prior to, and during the Spanish utilisation 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.

The key finding of this study is the demonstration that the source of the silver used in the trade items on board the *Batavia* is not Spain or Spanish America. These results are significant as they provide evidence for the movement of silver from Spain, which held a monopoly on most of the silver in global circulation at the time. These results would indicate that Dutch silversmiths were working silver from a combination of sources. Based on the results, Dutch silver would appear to have been sourced from both Spanish silver (from Spain, Spanish America and the Spanish Netherlands, likely through trade with other European countries) and German silver, two nations that were producing silver from its source. Spanish and Spanish American silver is very similar in trace elemental composition, as the source mines were essentially identical and controlled by the Spanish Crown. These results support the theory that despite trade embargoes, the Dutch were still receiving some American silver through avenues other than direct trade with Spain, while apparently supplementing this with silver from other sources, such as German silver.

5. Conclusion

The samples used in this study represent a unique assemblage of silver artefacts, having been made in 1627 and 1628 in the United Netherlands specifically to investigate potential avenues of trade in the Dutch East Indies. This very narrow origin, both spatially and temporally of the silver in question, as well as the knowledge that the artefacts had yet to be used for their intended purpose, provides a rare opportunity to investigate Dutch silver sources in 1627 and 1628. Of particular interest at this time was the Spanish monopoly on world silver after colonisation of the Americas, and the trade embargo in place between Spain and the United Netherlands in the midst of the Eighty Years' War. After several failed sieges on Dutch fortresses, the Spanish moved their military to a defensive position, and instead besieged the entire United Netherlands by ceasing trade with them, and in theory severely limiting their access to precious metals over which Spain had considerable control. However, precious metals drained rapidly out of Spain to the rest of Europe, and so the Dutch still had access to a limited supply of Spanish silver via other European trading centres.

LA-ICP-MS trace elemental analysis of the samples was undertaken in order to compare their composition to contemporary silver coins of known provenance. The trace elemental composition of the silver samples has revealed that the source silver is not Spanish, but rather would appear to be a combination of Spanish silver mixed with silver from other sources, specifically German silver acquired by the Dutch through trade with other European countries.

The significance of these findings is that the trace elemental composition of the *Batavia* artefacts has been shown to be indicative of Dutch silver sources at the time, confirming that the Spanish trade embargo with the United Netherlands diminished, but did not halt, the Dutch acquisition of Spanish silver. Future research into Dutch silver sources may involve further analysis of artefacts, and the supplementation of the database of silver of known provenance with more samples. The methodology described in this study has applications to many materials other than silver or metals, and could be applied to any item of cultural heritage significance if there is an available database of samples of the same material of known provenance.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jasrep.2016.08.044.

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