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Portuguese silver from the 15th to the 17th century, the *11 dinheiros* silver coins

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Dedicated to my family

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"Tudo que existe existe talvez porque outra coisa existe. Nada é, tudo coexiste: talvez assim seja certo".

Fernando Pessoa, Livro do Desassossego, 1888-1935

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Resumo

Os teores de prata elevados na superfície de moedas de elevado título de prata têm sido considerados, em alguns casos, como resultantes de ligas de prata muito puras e fidedignos da composição original do seu núcleo. Até agora, tem-se desvalorizado a influência do enriquecimento superficial de prata nos resultados analíticos da superfície em moedas de prata com um título superior ao teor de prata indexado ao valor máximo da solubilidade sólida do cobre em prata (91,2 % em peso). Esta investigação, direcionada para a caracterização microestrutural e composicional das moedas de prata portuguesas de *11 dinheiros*, demonstrou a existência de importantes enriquecimentos superficiais de prata nas moedas de elevado título de prata. Nestas ligas de prata, o processo de fabrico das moedas origina uma camada subsuperficial com uma microestrutura modificada resultante de corrosão seca intergranular provocada pelas operações de recozimento e relacionada principalmente com a lixiviação preferencial da fase rica em cobre numa profundidade subsuperficial. Esta camada subsuperficial origina uma sobreestimação do teor de prata analisado por PIXE ou EDXRF, 4 a 7 % maior do que aquele do núcleo das moedas, com um gradiente de composição elementar e uma profundidade desconhecida que pode estender-se até cerca de 70 µm. Este estudo mostra através da combinação de diferentes métodos de análise, EDXRF, PIXE, SEM-EDS e LA-ICP-MS, que pode perder-se informação metalúrgica relevante resultante do processo de cunhagem com base apenas numa análise superficial das ligas de elevado título de prata.

Embora existam gradientes composicionais de elementos menores/traço entre a superfície e o núcleo das moedas, a correlação dos seus teores à superfície permite discriminar diferentes origens da prata processada durante os séculos XV a XVII em Portugal, e nas casas da moeda de Lisboa e do Porto em diferentes períodos históricos. Os rácios de Au/Bi relacionados com a composição inicial da prata processada e os rácios de Pb/Bi relacionados com os processos metalúrgicos da parta são discriminadores importantes das ligas de elevado título de prata. O Hg é também um elemento importante para a discriminação das diferentes origens da prata.

A cunhagem da moeda portuguesa processou diferentes origens de prata durante os séculos XV a XVII. A prata europeia com teores de Au e Hg elevados, e de Pb e Bi baixos, forneceu as cronologias mais antigas de Dom Afonso V e Dom João II no século XV, sendo substituída no dealbar do século XVI por um novo metal precioso que entra na capital portuguesa, com baixo teor de Au e Bi, derivado provavelmente do processamento de minério de cobre argentífero. No 2º e 3º quartel do século XVI, o teor dos elementos menores/traço de Lisboa e do Porto evolui para a homogeneização composicional observada no período dom Sebastião I, devido provavelmente a grandes operações de reciclagem da moeda anterior realizadas em cada reinado. As cronologias Filipinas revelam a presença da nova prata americana de Potosí, introduzida em Portugal por Dom Filipe I (Felipe II da Espanha), distinguida da prata europeia em uso até 1578 no território português, pelo teor de Au < 100 ppm e de Bi muito baixo. A prata de Potosí é identificada pela primeira vez através de um método analítico superficial, como o PIXE, ao contrário da anterior análise global multielementar por NAA.

PALAVRAS-CHAVE

Ligas de prata, enriquecimento superficial, prata de Potosí, prata Europeia, discriminantes das ligas de prata, moedas de prata

Abstract

High silver surface contents of high fineness silver coins have been considered in some cases as deriving from very pure silver alloys, being reliable for original bulk composition. Until now, the extent in which surface silver enrichment influences surface analytical results in coins alloys with finenesses greater than the silver content indexed to the maximum value of copper solid solubility in silver (91.2 wt.%) have been disregarded. This investigation, focused on microstructural and compositional characterization of Portuguese *11 dinheiros* silver coins, has revealed important surface silver enrichments in high silver fineness coins. In these silver alloys, coin manufacturing process induces a subsurface microstructurally modified layer resulting from intergranular dry and wet corrosion in annealing operations, primarily related to preferential leaching of Cu-rich phase in subsurface depth. This subsurface layer originates a silver overestimation by PIXE and EDXRF analysis, 4 to 7 % higher than the bulk of the coins, with unknown elemental compositional gradient and depth that can extend up to to about 70 µm. This study shows, through the combination of different analysis methods, EDXRF, PIXE, SEM-EDS and LA-ICP-MS, that important metallurgical information resulting from the minting process may be missed, when relying only on the judgment of high silver alloys surface analysis.

Albeit the existing minor/trace elements compositional gradients between coins surface and bulk, surface contents correlations discriminate distinct silver sources processed during the 15th to 17th centuries in Portugal, from different historical periods and mints, Lisbon and Porto. Gold/bismuth ratios related to the processed silver initial composition and lead/bismuth ratios related to the silver metallurgical processes, are important discriminators of these high silver alloys. Mercury appears also to be an important element for the discrimination of silver alloys sources.

Portuguese minting depended and relied on different silver sources during the 15th to 17th centuries. European silver with high Au and Hg, and low Pb and Bi contents, supplied the oldest chronologies of *Dom Afonso V* and *Dom João II* in the 15th century, being replaced at the dawn of the 16th century by a new precious metal entering the Portuguese capital, with low Au and high Bi contents, probably derived from argentiferous copper ore sources processing. In the 2nd and 3rd quarters of the 16th century, minor/trace elements contents of Lisbon and Porto mints evolve towards the compositional homogenization observed in *Dom Sebastião I* period, probably due to major recycling operations of the earlier currency realized in each kingdom. Philippine chronologies reveal the presence of the new discovered Potosí American silver, introduced in Portugal by *Dom Filipe I* (*Felipe II* of Spain), distinguishable from the European silver in use until 1578 in the Portuguese territory, by Au contents < 100 ppm and very low Bi contents. Potosí silver is identified for the first time through a superficial analytical method, such as PIXE, rather than by NAA multielement global analysis.

PALAVRAS-CHAVE

Silver alloys, surface enrichment, Potosí silver, European silver, silver alloys discriminators, silver coins.

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Symbols and notations

BdP	Banco de Portugal
BSE	Backscattered Electrons (in SEM observations)
CENIMAT	Centro de Investigação de Materiais
C2TN	Centro de Ciências e Tecnologias Nucleares
DCM	Departamento de Ciências dos Materiais
DECN	Departamento de Engenharia e Ciências Nucleares
DF	Departamento de Física
EDS	Energy-dispersive X-Ray spectrometry
EDXRF	Energy Dispersive X-Ray Fluorescence
FCT	Faculdade de Ciências e Tecnologia
INCM	Imprensa Nacional Casa da Moeda
IST	Instituto Superior Técnico
IUPAC	International Union of Pure and Applied Chemistry
I3N	Instituto de Nanoestruturas, Nanomodelação e Nanofabricação
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LDA	Linear Discriminant Analysis
LJF	Laboratório José de Figueiredo
MNAA	Museu Nacional de Arte Antiga
NAA	Neutron Activation Analysis
PAA	Proton Activation Analysis
PCA	Principal Component Analysis
PIXE	Particle Induced X-Ray Emission
SEM-EDS	Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry
TFNAA	Thermalized fast neutron activation analysis
UEvora	Universidade de Évora
UL	Universidade de Lisboa
UNL	Universidade Nova de Lisboa
XRD	X-Ray Diffraction

Preamble

Coins are cultural heritage objects of great value because they contain plenty information relevant for the understanding of a given epoch or historical period, unravelling different aspects of our history, economics, technological progress, art, and numismatics.

The Portuguese medieval bullion coins were already the object of several analytical composition studies (e.g., Araújo, M.F. et al., 1984; Guerra, M.F. et al., 1989; Pessanha, S. et al., 2015) which have permitted to identify different periods of minting characterized by diverse contents of silver. However, in case of Portuguese silver coins, in addition to their intrinsic characteristics, such as alloy and weight, the various attributes of their history, as engravings, effigies, iconography, inscriptions, lettering, and other marks and symbols, have been the mainly subject of numerous studies (e.g., Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992). These studies have enabled the chronological cataloging of coins, as well as the identification of an endless variety of dies used for each coin (e.g., Gomes, A., 2003).

In the absence of systematic investigations on the chemical composition of the Portuguese silver coins that circulate in the fifteenth and sixteenth centuries, and the existence of a few from the subsequent one hundred years (e.g., Magro, F.C. and Guerra, M.F., 1998) it was imperative to complement the former numismatic studies with analytical investigations that could attest the knowledge acquired based on historical sources and on coins direct observations, providing a better understanding of the technology and metallurgical processes associated with mint production, as well as concerning the evolution and the differentiation of the monetary production from each mint over time.

The investigations carried out under the framework of this thesis focused on a large program of nondestructive elemental compositional analysis of the ancient Portuguese silver coins from the 15th to 17th centuries, mainly from the sixteenth century, aiming to contribute to the understanding of the Portuguese economic and monetary history through the characterization of the silver alloys used on minting.

The purpose of this thesis is plural: (i) an analytical investigation dedicated to the compositional characterization of monetary alloys based in about three hundred coins belonging to three centuries and from two Portuguese king dynasties, minted between 1438 and 1640, (ii) the understanding of elemental content variations along the coins depth due to silver surface enrichment, a phenomena neglected until now for high silver content alloys, (iii) a better knowledge of the monetary production and the unravelling of several numismatic aspects inscribed in precise historical questions and numismatic problematics, (iv) the recognition of the entrance of New World silver in the Portuguese monetary production and the identification of the chronological period for this introduction, accomplished for the first time through the application of Proton Induced X-Ray Emission (PIXE) analysis, and (v) the establishment of chronologically valid silver alloy compositions references, which could be used not only in the context of numismatic studies, but that could be correlated with alloys from silverware objects contemporaneous of those coins.

These objectives are perfectly clear but had involved a complex study to obtain relevant and meaningful results. It was necessary to integrate different fields of knowledge related to the analysis methods used for the elemental compositional characterization of ancient silver alloys, to the silver alloys metallurgy, to the monetary production, to the utilization and circulation of coins and silver ingots during the studied time period, as well as to the ancient silver sources, past silver circulation flows and their relationship with the historic chronological context and economic events. All these subjects are presented in a briefly manner in Chapter 1 – Introduction.

The Portuguese silver coin collections belonging to the Numismatic Museum from Imprensa Nacional Casa da Moeda, S.A. (INCM) and to the Money Museum from Banco de Portugal (BdP), holders of two of the most important referenced Portuguese numismatic collections, keep a great number of representative coins from the different types that circulated in the Portuguese territory, and putted challenges from the beginning due to an obligatory elemental composition analysis whose sampling must not involve physical removal of material from the coins. These requirements have forced the use of the surface analytical methods available, PIXE and Energy Dispersive X-Ray Fluorescence spectrometry (EDXRF). Also, the limitation of access to a significative number of coins from each type or variety and the difficulty of their transportation from the museums to the analytical laboratories, involving assurances obligations, has constrained the initial intended investigation, but nevertheless the study has achieved an acceptable representativeness of the major part of the studied chronologies.

Albeit the primary research focused on a large program of nondestructive analysis of a significant statistical number of coins investigating numismatic questions as the differentiation of the output of the two mints in operation during this period, Lisbon and Porto, or the discrimination of the various silver alloy chronological productions based on some minor elements likely to serve as silver tracers, it turned to be fundamental in the initial development of the study to investigate the coins with a microstructural approach linked to the compositional contents of the coins, in order to understand the results obtained with the two different surface analytical methods used.

The standard surface analytical methods used so far, whatever are their characteristics, do not reflect the elemental composition variations between the surface and the interior of the silver alloys, which affects their global compositional estimations when looking for the fineness of the coins. Also, the unpredictability of occurrence and development of surface silver enrichment obliges a better interpretation of the analytical results.

As the metallurgical history impacts the current state of the coins, the present investigation aimed thereafter to understand in what way the coins microstructure and the analytical limitations of the used methods could affect the determination of the silver fineness on the surface of these high silver alloys. This microstructural examination could only be carried out through a destructive examination of a small number of coins permitting to relate the obtained surface elemental composition with the morphology and distribution of existing phases in the near surface silver microstructure, to detect the coin core composition revealing its fineness and the major and minor elemental compositional gradients along the thickness, and to investigate and gather information related to the coin manufacturing process.

The combination of other compositional and microstructural analytical techniques for the examination of silver coins proves thereafter fundamental to understand the metallurgy of these alloys and the coin production process.

The investigated coins that provided the Corpus of analysis and the used analytical methods and procedures are presented in Chapter 2- Materials and methods.

The chemical composition investigation of the silver coins produced during the studied period is justified by the great historical and economic events that changed the world history, namely the Discoveries of the New Worlds that originated the establishment of new economic and trade relations between different geographies, wherein Portugal played an important role. From an economic viewpoint, the new discovered American silver ores generated great silver inflows in the European and world economies, however, the diffusion of this new metal and its presence in the European minted currency have still many aspects to be unveiled.

The need to acquire a better knowledge of the American and European silver ore sources, and the changeover of the latter from argentiferous lead ores to argentiferous copper ores verified by the end of the 15th century, forced to have in Chapter 1 a glimpse of the historical issues linked to the new silver sources findings, in the first case, and to the understanding of the involved metallogenies and of the distinct ore beneficiation processes. It was also necessary to briefly gather the former available analytical investigations used to characterize silver from both provenances, regardless of the analytical approaches, from the 16th century onward.

The investigation under this thesis had focused thereafter particularly on the sixteenth century, and interest has been given to the coins minted by King Dom Sebastião I and by the subsequent Philippine dynasty, trying to figure out if it would be possible to assign the arrival of this metal to Portugal.

Other issues were also object of attention from the beginning, as for instance the currency reform initiated by Dom João II and continued by Dom Manuel I. The distinction of silver sources through the coins compositions minted in Lisbon and Porto was central in the study, to possibly reveal the Portuguese silver trade relations in a Nation-wide or European context. It was then necessary to investigate a large number of coins detecting the various minor and trace elements that allowed to distinguish possible regional or local peculiarities, in view of the existent numismatic and monetary minting knowledge through the ages.

Though in a very few coins from Lisbon and Porto it was also important to answer to numismatic questions regarding the silver fineness of the coins verifying if their monetary production strictly followed the monarch's monetary laws or involved any undocumented fineness variation or debasement, as the determination of the alloy contents permits to understand the monetary policies of the monarchs and their relations with political and economic events. On the other hand, in the case of coins that do not support the mint monetary letter, L or P, which identify the mint where they were produced, and in the absence of any related historical documentation, it would be possible to assign these coins to their respective mint or to discriminate their production based in some distinctive compositional correlations.

The results attained with the study of all the above subjects are presented in Chapter 3 – Results and discussion, as well as the correlations obtained between de different chronological compositional data.

This investigation had detected also a non-authentic coin, considered a modern counterfeited coin. Similarly, some coins produced during the chronological evaluated periods but with silver contents well below the legal fineness have been detected. Always related to the Porto mint, these can be considered as contemporaneous counterfeited coins or a result of fraud from this monetary workshop and constitute nevertheless important historical evidences.

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— C2TN – Centro de Ciências e Tecnologias Nucleares, Departamento de Ciências e Engenharia Nucleares, Campus Tecnológico e Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10 ao km 139.7, 2695-066 Bobadela LRS, Portugal; e

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A general conclusion of the study and suggestions for future work is presented at the end of the thesis, being expected that this investigation entails new elements for historical and scientific reflections to the numismatist, historian and materials scientist, and renders new insights to the various underlying subjects.

Chapter 1

INTRODUCTION

1.1 | Portuguese silver minting at the beginning of modern times

The processes by which the European mints transformed silver raw materials, namely silver ingots, in the minted coins circulated as later as the sixteenth century, are ancient and originate from that used on the beginning of the medieval period.

The sixteenth European century witnessed some innovations designed to improve the productivity of monetary production workshops. There existed attempts at the beginning of this century in Italy (Craig, J., 1953) and in Germany (Challis, C.E., 1978) to replace some of the manual monetary processes, and in 1550 with origin in Germany starts the mechanization of the mints in various European countries, such as France (Challis, C.E., 1978). The improvements and benefits achieved with the mechanical processes due to progresses and developments related to metallurgical and mining tasks, detailed described by Georgius Agricola in his work De Re Metallica first published in 1546, and the introduction of these new techniques in the mints, will gradually replace the coinage by hammer (Murray, G., 2003).

In Portugal also, there were such attempts of mechanization. The first of these developments was the introduction of a screw press in 1561 by João Gonçalves, known for "ingenious", in the mint of Lisbon (Aragão, A.C.T., 1875). However, this innovation will show up impractical and without success, as had occurred in other European countries, and the primitive monetary process by a single blow of a hammer on a metal disc between two dies will remain unchanged until the last quarter of the seventeenth century, when Prince Regent *Dom Pedro* introduces the mechanical coinage. Only after 1677, the new introduced steering wheel press will allow the production of coins with a better quality of stamping (Gomes, C.M., 2009).

Detailed descriptions of the contemporary practice of monetary manufacturing processes and coin minting in Portugal are unknown prior to the fifteenth century, but its procedures can be taken from disperse coeval references (Ferro, M.J.P., 1974) or from the practice of the next two centuries (Gambetta, A.F., 1978).

In the sixteenth century, coin manufacturing processes have remained firmly in the medieval tradition and continued to be controlled in practice by goldsmiths, as happened during the fifteenth century (Gambetta, A.F., 1978). The minting process of Portuguese silver coins was like the procedure followed in England in the second half of the sixteenth century (Allen, M., 2012), in fifteenth and sixteenth century in France (Bompaire, M. and Dumas, F., 2000; Arles, A. and Téreygeol, F., 2011), in medieval or modern Spain (Torres, J., 2003; Fantom, G. *et al.*, 2006) or in medieval Venice (Stahl, A. M., 2000).

We do not know to what extent the Portuguese Mint Houses were able to approach the metallurgical and minting expertise in the rest of Europe, but Portugal certainly had not ignored the knowledge of the new processes and practices that arose beyond its borders, and the recommendations transcribed in the middle of 16th century on the metallurgical treatises of Vannoccio Beringuccio and of Georgius Agricola, concerning, for example, the mint practice,

> "… a very great and constant diligence is required by one who wishes to operate a mint well, or to have it operated, because it has many parts which it is necessary for anyone who enters this work to understand very well…" (Vannoccio Biringuccio, De La Pirotechnia, pp. 358),

and

> "For, truly, since silver is a valuable thing and every bit is worth much, a man should not enter into refining it with closed eyes" (Vannoccio Biringuccio, De La Pirotechnia, pp. 159)

or the care to have with the assay tests,

> "…a test of this kind shows whether coins are good or are debased; and readily detects silver, if the coiners have mixed more than is lawful with the gold; or copper, if the coiners have alloyed with the gold or silver more of it than is allowable." (Georgius Agricola, De Re Metallica, pp. 219).

Movements of skilled minting technicians have proceeded in European Mints, sometimes to ensure the opening of new monetary workshops (Craig, J., 1953), which motivate and originate a permanent exchange of knowledge and experiences, updating the different techniques and improving the minting processes in many countries. Portugal followed the other European countries, with some minting technicians traveling to several foreign workshops to acquire new knowledge (Gambetta, A.F., 1978), where they incorporated the up-to-date understanding of the various operations and procedures of the minting practice and probably the important issues of testing the silver to evaluate its fineness and the care needed to add copper to obtain the desired silver law.

The long production process of a sixteenth-century monetary workshop implied movement of metals in various stages of production and in various specific spaces within the mint houses, (Spufford, P., 2005), unlike the well-known European contemporary representations in illustrations (Figure 1.1) or stained glass that show the labour practice of the mints linked to a production process located and condensed inside a single space. That would not be an exception in Portugal, as revealed by the Porto mint archaeological excavations which have allowed to determine and propose administrative and productive spaces for this mint (Dordio, P., 1999; Lopes, I.A., 2000).

In Portugal, the first contemporaneous detailed description of the practice related to the minting process of coins of the officers of the Lisbon mint dates from the reign of *Dom Manuel I*. King *Dom Manuel I* establishes on March, the twenty-third, 1498, the first Regiment to the Lisbon mint, defining the functional and administrative organization of the work, in order to meet the growing needs of currency necessary for the rising commerce open with the new discoveries and to ensure the necessary minting volumes, setting out at the same time the competences, duties and professional advantages of all the participants in the manufacturing structure.

The silver, on behalf of the King or from individuals that bring this metal to be minted, was received by the treasurer of the mint, in any condition and from any provenance, and weighed. If it did not come marked, the average fineness of the lot was estimated by the touchstone test in its various parts, and the weight corresponding to the transformation of the metal in coins according to the practiced monetary law was determined. The touchstone test was necessary to determine how much metal to form the silver alloy, *i.e.*, copper or silver, should be added on a later stage to correct the composition and obtain coins in accordance with the current monetary law.

The silver was then retained at entry of the mint until a sufficient amount allowed its melting. Although with a practice unclear in the King *Dom Manuel I* regiment, the ingots were melted in a reverbero furnace with the addition of copper to obtain an appropriate mix, being this metal added in the required amount to fulfill the monetary law fineness. The well-known amount of copper to be added by the founders was imposed by the purity of the silver bullions at entry. The melted silver alloy was then poured in ingots or bars whose moulds remained on a water pit to easily retrieve all the projections, splashing's and excesses that occurred during this operation, and to obtain a fast cooling of the bars.

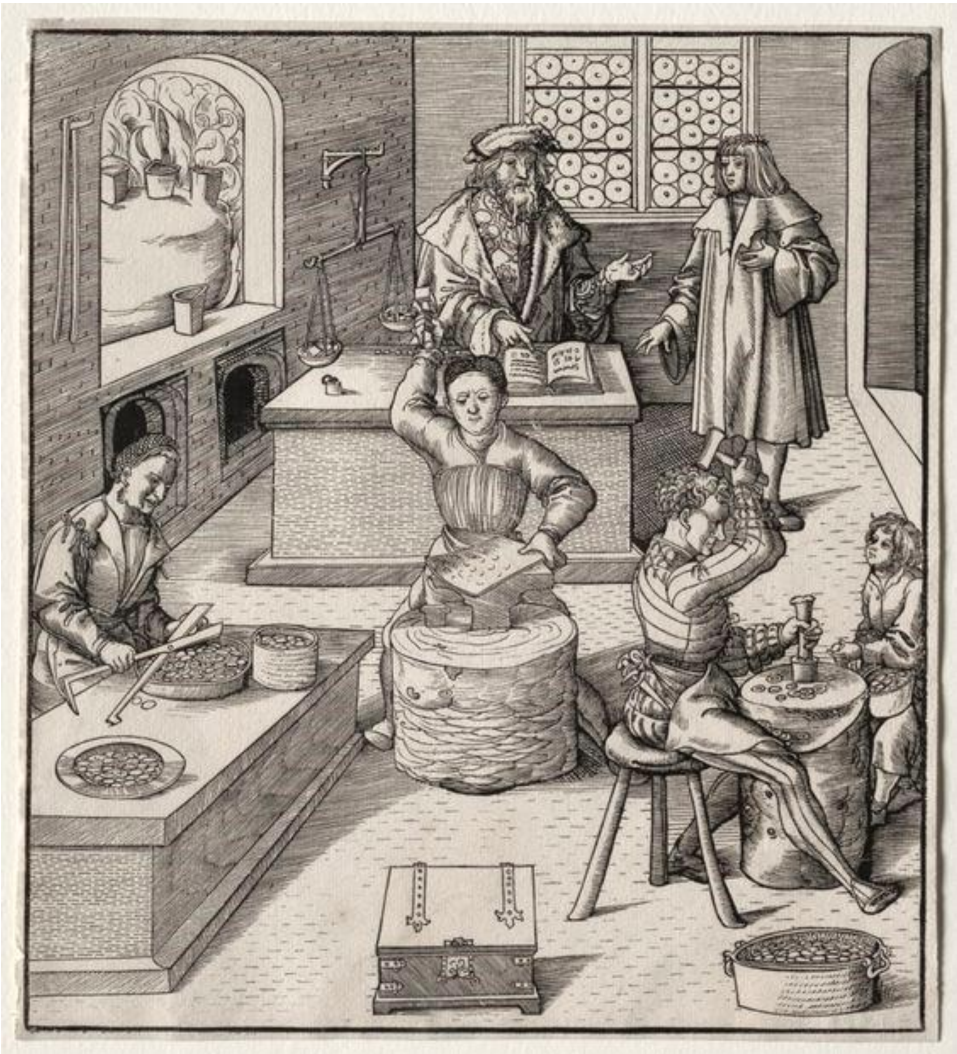

Figure 1.1 – Young Emperor Maximilian I visit the Hall mint in Tirol, ca. 1510. Wood engraving from Hans Burgkmair, Museum of the National Bank of Belgium.

The resulted bars where then submitted by the assayers to the touchstone test, which determine the bars fineness, marking them accordingly, ensuring that the metal that proceed in the production process had to agree with the monetary law.

The tested ingots were then successively heated and quenched to make them more malleable and flexible, allowing them to be worked by hammering. With the hammer, the silver metal was beat and spread in plates until the calculated thickness was obtained, at the expense of manual physical strength. After beaten the bars flat and thin, a task that involved various annealing operations, and checking the thickness and regularity of the plates, the metal was cut in discs with scissors, and rounded with the aid of gauges. The hammerers had the metallurgical expertise to soften metals after mechanical work, *i.e.*, to do their annealing to make them less brittle during hammering.

In a subsequent operation it was necessary to clean and polish the discs, blackened during the previous tasks, through a bleaching operation. This bleaching operation consisted of placing the disks in water and let them boil with salt and potassium tartrate to enhance its purity of appearance. The used ingredients were "salt, vinegar, dry wine lees, olive oil and coarse waste from ground cereals". The first three ingredients were used for the bleaching solution and the last two probably to clean and/or polish the surface without scratching the silver, as the coin surface have probably a matte finishing after the treatment. This operation removed all traces of copper oxides and confers the silver surface with a pure appearance and an adequate brightness.

The disk well washed in water, could later be coined by using two dies that impress their drawings. The disk was placed and fixed on a lower die, and the die-hammerer held an upper die in place with one hand and with the other struck the coin striking over the top of this die. The coins were not able to run immediately after minting as they could be darkened and were delivered once more back to bleaching. After 1517 the coins were bleached only once, immediately after the striking operation, and not before (Gambetta, A.F., 1978).

The finished minted coins were then verified again by the assayer to check for their fineness according to the monetary law. If the coins did not have the respective fineness or were bad stamped were cut and send to be remelted.

1.1.1 Portuguese mints

Following the foundation of the Kingdom of Portugal and the constitution of the Portuguese monarchy, the monetary production workshops have organized around the King's court, in political and economic centres, and followed the political authority territorial movement, moving with the King from one place to another, from city to city, as the coin minting was the King's privilege (Vaz, J.F., 1960). A few other workshops that worked in a regional context have also constituted, having a great importance during periods of political and military crisis due to the necessity of quickly minting large amounts of currency.

Until the 13^{th} century, the currency was minted in the North of Portugal in Guimarães or Braga, then in Coimbra and finally in Lisbon (Aragão, A.C.T., 1875; Vaz, J.F., 1960).

The first currency minting in Lisbon occurred in the civil war context between King Dom Sancho II (1223-1248) and his brother *Dom Afonso*, later King *Dom Afonso III* (1248-1279). From the mid-13th century the authority and administration institutions have been concentrated in Lisbon, who came to play the role of first city of the Kingdom and of administrative and market centre. It is in this context that this city will have a permanent mint during *Dom Afonso III* kingdom, being the only city that minted currency from the third quarter of the 13th century all through the next hundred years (Ferro, M.J.P., 1974).

In the second half of the 14th century, in the context of the war with Castile with King *Dom Fernando I* (1367-1383), coin minting's have occurred in several locations and for the first time the coins begin to display explicit coinage marks that allowed the identification of these different locations (Vaz, J.F., 1960). *Dom Fernando I* had minted coin in Lisbon, Porto and Miranda do Douro, and even in parts of the Castile Kingdom, as Samora, Coruña, Tui, Quiroga and Valencia de Alcántara. These latter coins minting's were intended to pay the troops and were made in locations related to the movements of the armies.

After the death of *Dom Fernando I*, in addition to the monetary production of Lisbon and Porto, *Dom João I* (1385-1433) has ordered the minting in Évora for payment of the armies concentrated at the border, involved in a new conflict with Castile, which monetary production workshop came into operation in 1385, and have lasted a few years, closing before the end of the 14th century (Ferro, M.J.P., 1974).

From 1385, the beginning of the second Portuguese dynasty, until 1580, the minting of currency will be made mainly in Lisbon and Porto. However, *Dom Afonso V* in the context of his pretensions to the Castile crown has also minted between 1475 and 1479 some Real Grosso silver coins for Castile and Leon, bearing a bull head signing the minting mark of Toro.

The Porto mint will mint currency from its beginning at the end of the 14th century for about two hundred years in a building near the Douro River in the centre of this city and would not be working at the time of the regiment of King *Dom Manuel I* dedicated to the Lisbon Mint in 1498 (Gambetta, A.F., 1978).

From 1580, with the union of the Portuguese and Spanish Crowns, the Porto mint house will decrease its monetary production not existing notices of production at a date later than 1590, and King *Dom Filipe II* (1598-1621) will declare the extinction of the Porto mint in 1607, after a long period of inactivity.

Lisbon will continue its monetary production until the end of the Philippine dynasty (1640) and will be the only active currency minting centre till 1642.

1.2 | European sources of silver in the 15th - 17th centuries

The circulation of silver in Europe in the 15th-17th centuries and the amount of American silver that was used on this continent in this period, are historical issues still open, particularly regarding to Portugal.

From the Middle Ages to the beginning of the second quarter of the 16th century, until the 1530's, most of the silver supply of all European countries originate from Germany and other parts of the former Roman Empire (Neff, J.U., 1941). Frankfurt, which ensured the silver movement to the Mint Houses in Northern and Western Europe through Flanders, and Milan, constituted the most important points of the silver trade in Europe in the early years of the 1470's (Spufford, P., 1988; Munro, J.H., 2006). Also, the African gold brought from the West coast of this continent in the second half of the 15th century by merchants and traders, came to Europe via Lisbon and spread through Castile or by boat via Genoa or Bruges, (Figure 1.2) allowing Flanders to maintain a direct access to the Portuguese gold from Africa (Spufford, P., 1988). The historical information demonstrates that especially the cities of Lisbon and Porto were frequent passage centres of boats linking northern Europe, the Mediterranean and North Africa (Ferro, M.J.P., 1974).

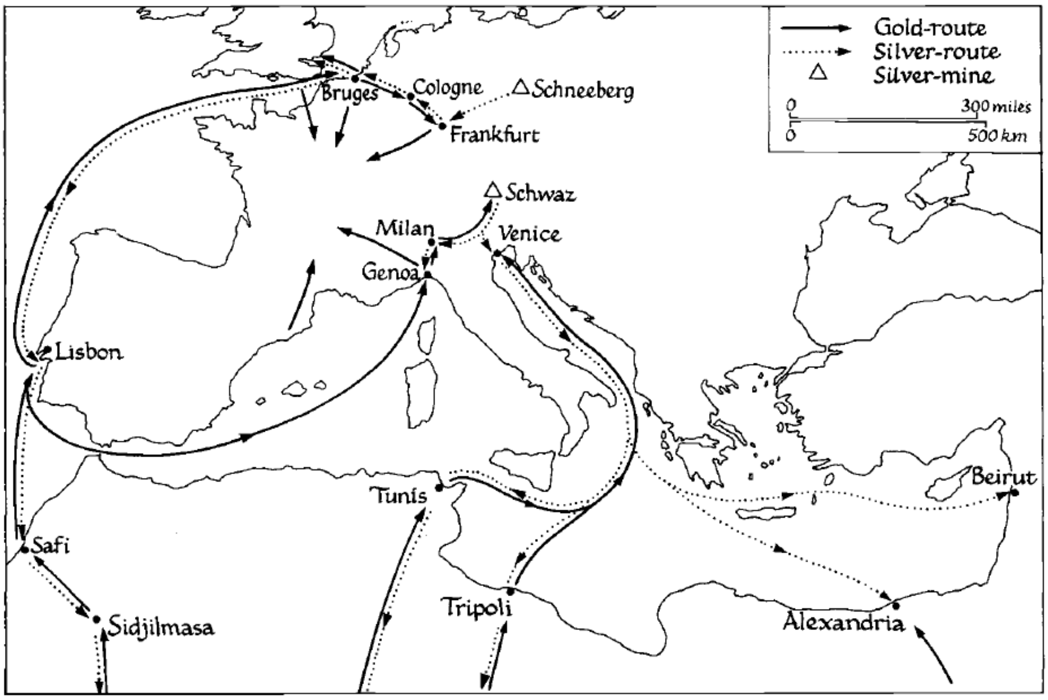

Figure 1.2 – Movements of gold and silver from 1465 until about 1500. From Spufford, P., 1988.

During the first half of the 15th century, efforts to discover and explore new silver ores in England, Wales and Ireland have proved fruitless, and various argentiferous lead ore mines came out to be unproductive for exploration of this metal in the late twenties of this century, being abandoned. Only in the next century, in the reign of Elizabeth I (1558-1603), some modest silver reserves would be found which enabled a successful exploration. However, despite obtaining precious metals from mineral deposits in suitable amounts for minting, it is not clear the direct contribution of these resources in the English monetary production operations. The largest silver stock in England remained in the form of circulating currency, and because of the economic necessities and the undervaluation of the currency, there occurred the reminting of the coins (Neff, J.U., 1987).

The difficulties being felt in Europe in the early 15th century, caused by the scarcity of silver and of coin, were quickly alleviated with the discovery of new sources of silver ores between 1460 and 1540, mainly in Central Europe, in the Alps in Erzgebirge, in Saxony, and in Tyrol, and even in Sweden and on Alsace (Neff, J.U., 1987; Spufford, P., 1988). Also, the technological innovations achieved with the invention of the *Saigerprozess* (liquation process) that from the mid-15th century would allow the silver recovery from argentiferous copper ore by adding lead during the copper reduction process, the modification of the furnaces for higher smelting capacities, and the introduction of drainage galleries and of pumps that would allow water drainage in stages to the surface from much deeper mines, will lead to a major expansion of the silver-rich copper deposits mining of Southern Germany and Central Europe (Neff, J.U., 1941 and 1987; Spufford, P., 1988; Munro, J.H., 2003 and 2006). Together with these practical advances, appeared specialized treatises, *De la Pirotechnia* of Vanoccio Biringuccio and *De Re Metallica* of Georg Bauer (Agricola) which would promote and diffuse these innovations in the field of mining and metallurgy.

Old mines who were formerly the richest mines in Europe are reopened, such as Kutná Hora in Bohemia, Freiberg in Saxony and Goslar in the Hartz, and the mines of Schwaz and Schneeberg will produce the greatest amount of silver after 1460 (Neff, J.U., 1987; Spufford, P., 1988; Munro, J.H., 2006). The great mining expansion of argentiferous copper ores initiated circa 1460 and without large amount of produced silver until 1510, will reach a peak in the Decade of 1540 (Neff, J.U., 1941 and 1987; Spufford, P., 1988; Munro, J.H., 2003 and 2006). In the early 16th century, new sources of silver are discovered and exploited being the most important the mines of Annaberg in Saxony and Joachimsthal (1516) in Bohemia, and Antwerp becomes an important financial and economic centre receiving the silver streams of southern Germany and Hungary through the establishment of new continental trade routes or revitalization of the existing ones (Spufford, P., 1988; Munro, J.H., 2003 and 2006).

The growth of annual production of silver mined from the mines of Saxony, Bohemia, Slovakia, Thuringia, Hungary and Tyrol, will increase five times until about 1540, and most of the mines will reach a greater prosperity between 1515 and 1540. This wealth will then decrease until the arrival of silver from the Americas, being exceeded by this new source of precious metal from the early 1560's (Neff, J.U., 1941; Spufford, P., 1988; Munro, J.H., 2003 and 2006).

The most productive mines of this cycle will be found in Erzgebirge in the Alps, in Annaberg, Marienberg and Schneeberg in Saxony and in Joachimsthal, Kutná Hora and Kasperska Hora in Bohemia, in Thuringia in Eisleben and Hettsedt, in Alsace in Leber-Tal, in the Austrian Tyrol in Schwaz, in Hungary in Neusohl, Nagybanya and Körmocbanya, and in the Hartz mountains in Mansfeld and Rammelsberg, among many others (Neff, J.U., 1941 and 1987; Munro, J.H., 2003).

Just before the mid-16th century, the large amount of silver obtained in the territories of the New World will have Spain as the major destiny in Europe, and from here the silver will move from West to East with a constant and regular flow, balanced in the opposite direction by exotic products. This silver influx from South America will substantially change the economy of European countries in the 16th century (Neff, J.U., 1987), representing in total possibly the equivalent of half of all the existing silver amount in Europe (Challis, C.E., 1978). As the 16th century progresses, more and more silver ingots are available for purposes of minting, especially from the international market, and the silver replaces gold as the dominant metal (Neff, J.U., 1941).

In England after 1540, during the reign of Elizabeth I, almost all imported ingots will come of the new Spanish Silver, which by the end of the century will be a dominant supply of silver to the Mint House (Craig, J., 1953). The surviving historical documentation, the accounting books of the British Mint House of the late 16th century, identify a clear influence and predominance of Spain ingots in the supply of the Mint House, giving also the information that, in addition to the silver ingots, quantities of Spanish, French and Portuguese currency entered this monetary workshop, being the Spanish coins the most significant (Challis, C.E., 1978). For example, the English silver coin produced in 1555 was made at the expense of Spanish *Reais* provided through Antwerp, and the base metal in circulation has been refined between December 1560 and October 1561, in order to debase the coin without losses to the Crown (Challis, C.E., 1978; Craig, J., 1953). In the next century, the Madrid or Cottington Treaty signed by England and Spain in 1630, resulted in a peace agreement and restored the trade relations between both countries, giving rise to the silver from South America required to support the Spanish armies and the Government of the Spanish Netherlands to pass by England, where two thirds of its amount were sent to the Royal Mint in London (Craig, J., 1953; Marsilio, C., 2015). London has become one of the most active market for the Spanish silver, in strong competition with Genoa, and the Portuguese and Genoese bankers profit by sending silver to English ports from the Atlantic Spanish ports of Corunna, San Sebastián and Bilbao (Marsilio, C., 2015).

Some mines, like Freiberg and Goslar, will continue to prosper after the second half of the sixteenth century, but the fall that will happen in the production of silver of all the mining centres of Central Europe after the middle of the first quarter of the 17th century, will reach the lower values, about one third of the production recorded in the 20's to 30's years of the previous century (Neff, J.U., 1941 and 1987).

1.2.1 The silver processed in Portugal

Portugal was poor in precious metals like silver, coming this metal from Central and Northern Europe until the mid-15th century, although there is no documentary evidence that certifies this assumption (Ferro, M.J.P., 1974). The silver obtained in bar, in the form of currency or transformed into precious objects, would be recast in Portuguese monetary workshops. On the other hand, it was common the circulation of foreign silver coin in Portugal, mainly from France, also existing some movement of this metal from England to Portugal (Ferro, M.J.P., 1974).

There are no known studies on the silver supply origins that reach Portugal during the 15th and 16th century. During the 15th century, trade with Flanders interested to the entire country and copper was a current commodity in the Luso-Flemish trade. In the early 1440's there are reports of copper being brought from Flanders for minting in Lisbon Mint House, and with copper would probably come also silver. It seems that by the 1480's the German copper inflows increased due to State initiative. In 1484, an undisclosed group of merchants (possibly Flemish) was granted a 3-year monopoly on cork export in exchange for 1,500 to 2,000 hundredweight of copper (88.1 – 117.5 t); the cork was to be shipped to the markets of Brittany and France (Arquivo Municipal de Lisboa, Arquivo Histórico, Chancelaria Régia, Livro 2.º de D. João II, f. 30r. – v.; Arquivo Municipal de Lisboa – Arquivo Histórico, Chancelaria Régia, Livro 2.º de D. João II, f. 32r).

By the 1490's and 1500's, there is evidence that Portugal was acquiring silver through the royal factory in Flanders: 67 marks (15.7 kg) in 1495-1498, from Nuremberg, and an additional 1,515 marks (354.4 kg) in 1498-1505. In this last period, the Portuguese factory bought 639.7 hundredweight of copper (30 ton) (Arquivo Nacional da Torre do Tombo, Chancelaria de D. Manuel I, liv. 31, f. 31v.; Arquivo Nacional da Torre do Tombo, Chancelaria de D. Manuel I, liv. 36, f. 17r.). Apparently, the country was also receiving German silver through Mediterranean trade. In late 1484, king Dom João II concluded a 5-year agreement on leather export by which he expected to receive 3,000 marks of silver (688.5 kg), thus solving the shortage of this precious metal in the country. The leather was to be exported to Eastern Mediterranean markets (Arquivo Municipal de Lisboa – Arquivo Histórico, Chancelaria Régia, Livro 2.º de D. João II, f. 50r.).

The existing documentation at Lisbon Mint House, namely the book *Apontamentos para a História da Moeda em Portugal* (Annotations for the currency history in Portugal), with cover and introduction signed by José de Saldanha Oliveira e Sousa and dated from 28 February 1878, has transcriptions of the oldest book of the Mint House accounts, relating to silver and gold movements made in 1517, 1521, 1523 and 1524. A thorough historical study of the various individual records of the incoming silver quantities and the names of who had brought the silver to trade for currency, may eventually clarify what were the origins of silver in the first quarter of the 16th century.

According to Munro, J.H. (without date), the Portuguese used during the sixteenth century principally South German silver. In Antwerp, a major European Centre for trading and financing, the Portuguese sought since 1501 financial and commercial support from bankers and traders of southern Germany, as well as copper and silver metal for trade with Asia (Godinho, V. M., 1981-1983; Munro, J.H., 2003). The argentiferous copper of Neusohl, in Hungary, and from great part of Tyrol, was controlled by the Fugger-Thurzo, important copper suppliers to Spain and Portugal, having the exportations of Hungarian copper to Antwerp strongly increased since the beginning of the 16th century until the 1530's, counter-cyclically with the exports of this metal to Venice (Godinho, V. M., 1981-1983; Munro, J.H., 2003). The same copper mines would surely supply the silver since the German merchants were sometimes reticent in selling copper separately from silver, as attested by a letter dated of 7 May 1517 from Lourenço Lopes, merchant in Antwerp, submitted to the King Dom Manuel I, with the various proposals to convince the Portuguese King to acquire the two metals together (Arquivo Nacional da Torre do Tombo, Corpo Cronológico, parte 1, maço 22, n.º 25).

In the first decade of the sixteenth century there is a notice (Pereira, J.C., 1983) of silver arriving through the Vila do Conde customs in Northern Portugal, mentioned in two books concerning the tax payment on imported goods, for the period between February of 1504 and January of 1506 (Arquivo Nacional da Torre do Tombo, Contos do Reino e Casa, Núcleo Antigo, livros 511 e

512). From 299.6 marks of imported silver (about 68.8 kg), 227.75 marks came from unidentified harbours in Flanders, 63.75 marks came from Rouen and 7 marks from La Rochelle, and 265.5 marks of the total amount of silver were sent to the Porto Mint House for minting at this location. The references to Flanders in the royal documentation of these years relate normally to Antwerp, to where the Portuguese trading post, that was previously in Bruges, was displaced in 1499. The silver sent to the Mint House would mint about 6 200 *Tostões* or 31 000 *Vinténs* (João Pedro Vieira, personal communication). During the first quarter of 16th century, the Lisbon Mint House received large inputs of silver mainly brought by Portuguese and especially foreign merchants. Between 1516 and 1525, these merchants were responsible for delivering more than 160,000 marks of silver (36,7 tonnes) to the Lisbon Mint (Godinho, V. M., 1969; Godinho, V. M., 1981-1983).

In the second quarter of the same century, in a letter dated from 20 May 1537 addressed to the Treasurer of the Porto Mint House, Diogo Leite, King Dom João III reproduces the information provided earlier by the first, concerning the arrival of much gold to the North of Portugal bought on the Islands by the merchants from the region of *Entre Douro e Minho* to the Castilians returning from Peru, and carried to the Mint House to be minted in coin (Peres, D., 1957). The mentioned Islands were the Azores, where the return route scale from New Spain to Europe, longer than the outward journey, was made, bringing the silver from Peru and New Spain and which would have a peak in the New Indies itinerary in the mid-16th century.

It is in the decade of 1530 's, that are found the first records of gold and silver production in Peru (actual Bolivia) and Mexico. In parallel with the influx of the new American gold would probably also arrive the silver, being significant amounts of both metals recorded from the first locale.

The presence of American silver in Portuguese national territory should have also occurred in the last quarter of the 16th century. When *Felipe II* of Spain becomes King of Portugal, 8500 marks of silver entered in Lisbon possibly from Seville in November 1582 to mint coin to circulate in the Kingdom (Mauro, F., 1997). However, at the end of this century, the Spanish Silver was not enough for the monetary needs due to quick business developments which withdraws the country currency to India and abroad, a situation that originated complaints of the King in 1588 (Mauro, F., 1997).

During the 17th century, it is unknown the source of the silver that enters in the Lisbon Mint House in the form of coin or bullion. Portugal benefits from the large amount of American metal that enters Europe through Seville, his monetary stock increases and the maximum of gold and silver arrivals happens around 1627 (Marsilio, C., 2015). At the beginning of this century, in view of the positive commercial balance with Spain, Lisbon could obtain a large quantity of silver required to the monetary market, a situation, however, that would change later from 1630 to 1640, becoming the Lisbon Mint a minor buyer of American silver ingots (Marsilio, C., 2015).

Later, after the Portuguese Restoration (1640), most of the monetary production in Portugal will depend on a massive coin reminting operation of the Spanish currency that still circulate in the Portuguese territory (Marsilio, C., 2015).

1.3 | Silver ores of the New World

1.3.1 Mexico and Potosí silver discovery

The search for precious metals in the American territories during the sixteenth century was an earlier imperative of the Spanish Crown, which led the Viceroyalty of Peru to structure itself around the silver ore during the first three decades after the Spanish conquest (circa 1530) and to constitute itself as the main centre of silver production in the Americas until the seventeenth century.

After Charles V authorization for an expedition to the southern territories, Francisco Pizarro arrives in the Andean region and in the great Inca Empire following the reports of the existence of a rich gold indigenous Kingdom to the South (Deveza, F., 2006), and later in 1533 large amounts of silver and gold reach Seville (Heydt-Coca, M., 2005). In 1538, the first mining region of Porco began to be exploited following the ancient extractions of the Incas and in the following year the city of La Plata de La Nueva Toledo, also known as Chuquisaca, now Sucre (Bolívia), was founded near the future town of Potosí due to the numerous waste rock dumps that were carried out in the nearby mountain chains (Fernández, J.M., 2000).

The mining of some important silver ore formations initiated in the 1530's, will culminate with the discovery in 1543 of the Porco mines, the most important mines before the discovery of the silver mountain of Cerro Rico in Potosí, on 21 April 1545, constituted of rich veins of this metal. Until 1562, new silver ore veins are discovered that will strengthen Potosí as the main economic centre of the Spanish Indies.

The first silver ore veins of Potosí, known from the Spaniards when in 1545 started the first exploration of Villarroel, brought indigenous people from nearby places to the Cerro Rico (Potosí), as from Porco and La Plata de La Nueva Toledo, promoting their settlement. It will be in the future city of Potosí, forthcoming essential production silver centre, that the silver ore extracted from this hill will be later benefited by grinding mills, using the hydraulic energy provided by the ponds built close to the city at height locations at Kari-kari hill, and will be then converted in bars or coins after being refining (Fernández, J.M., 2000), being later "*quintada*". Enacted since 1504, the privilege of mining forced the payment to the Spanish Crown of a fifth ("*quinto*") of the obtained silver, only changed later in 1548, in the case of Mexico, to the "*diezmo*" (tenth) (Garner, R.L., 1988; Heydt-Coca, M., 2005).

The Cerro Rico with at least 35 very rich silver mineral veins that ramify to the surface from the interior in six major groups, had the richer silver mineral located in the upper layers of the hill, closest to the surface, that were quickly depleted, and the said less rich mineral in the interior, in harder to access locations. In 1562, it was discovered Veta Rica and later more silver mines became known, as Centeno, Mendieta, Rey Socavón, Estaño, La Puríssima, Pampa, Oruro, Forzados, Caracoles, Polo, Amoladera, Cieneguillas, Oñate, San Juan de la Pedrera (Fernández, J.M., 2000).

Other mining fields opened during the 16th century, as Cuzco (1571), Lima (1574) and Huancavelica (1577), receiving Potosí the silver from other sources and not only from the Cerro

Rico. Since 1607 silver came from Oruro, and until 1650 other districts as Pasco (1567), Porco, Berenguela, Lipes, Sica Sica (1600), San Antonio del Nuevo Mundo and San Antonio de Padua (1652) also contributed to the declared "Potosí" silver (Garner, R.L., 1988; Fernández, J.M., 2000).

Mexico has also seen since the mid-16th century and during the 17th century the opening of major mining fields. The conquest of the territories of Nueva España, initiated with the expedition of Cortés from Cuba until Tecnochtitlan, had incorporated the Mesoamerican area in the Spanish Empire in the 1520's. The coloniser impulse associated to the search for mineral formations, was directed to rich, organised and densely populated regions with the aim of replacing the local elites, taking their place. Meanwhile, the first silver ore veins in Zacatecas were discovered in 8 September 1546 (later called Veta Pobre) and others will follow until 1548 in these Nueva Galicia territories, Veta de La Albarrada, Veta Grande, Veta de San Barnabé and Veta de Pánuco, converting this location in the second major exploitation of silver in the Americas. The connection between the Zacatecas mines and Mexico City was accomplished in 1555, and other mining centres were discovered and established in areas further away from the capital, as for example, Real del Monte and Pachuca (1551), Guadalajara (1553), Sombrerete (1555), Durango (1555), Guanajuato (1557), Trestrillo (1562), and San Luis Potosí (1591) (Muňoz, J.J.L., 2010).

The American silver will begin to reach Europe and the Mediterranean economy, through Seville, considered the European gateway to the American precious metals, and Castile feels, especially from 1550 onward, the effects of the silver shipments sent to the *Casa de la Contratación* of Seville, initiated in the 1530's (Hamilton, E., 2000; Munro, J.H., 2003).

1.3.2 Ore exploitation and technological processes

Before the arrival of the Spaniards to Peru, the Indians already knew the existence of silver in the Cerro Rico, performed rock breaking works, developed metallurgy works, as for example, in Porco, 35 km southwest of Potosí (Fernández, J.M., 2000; Van Buren, M. and Cohen, C.R., 2010), and silver production depended on a sequence of optimal extraction operations with respect to fuel efficiency.

The first step of smelting in pre-Columbian South American society was made in the *huayra*, an inverted cone furnace with about a meter tall, with an open top and with small openings on the sides, built of stone and clay, suitable to reduce the silver ores rich in lead. Although extremely fuel efficient and thereafter suitable to the scarcity of wood from the high-altitude Andean environment (about 4000 m above sea level), this native furnace had a low metal yield. The *huayra* depended on the strong and permanent wind flows for its operation, being placed in particularly windy locations that take advantage of the large number of small openings that it possessed. Its load consisted of 2/3 of silver ore, *i.e.*, galena (lead sulphide), mixed with charcoal, and 1/3 of lead slags recycled from previous production processes, rich in lead oxide (Van Buren, M. and Cohen, C.R., 2010; Rehren, T., 2011). It carried out an imperfect fusion due to operate at relatively low temperatures, obtaining an incomplete separation between metal and slag. This process caused significant silver losses that were minimized through the slag fragmentation and metal globules collection, the later subsequently resmelted in small crucibles. This process allowed to get silver from high silver content ores, exploited during the first years after the discovery of Potosí, and it is estimated there were about 6000 *huayras* in 1570 (Fernández, J.M., 2000). The product obtained from the ore fusion was then placed in a clay container and heated in a furnace for carrying out the silver refining separating the silver from the lead (Garavaglia, J.C., 2000).

This native silver extraction technology would be adapted during the colonial period to the European technology of the *reverbero* furnaces brought by the Spaniards, and both will coexist later with the amalgamation patio process of large scale, that required large amounts of ore, mercury, energy and labour supervision. The *reverbero* furnaces introduced by the Spaniards, as opposed to be used especially for cupellating the product obtained by ore reduction, as was the European practice mentioned by Georgius Agricola (1556), will also be used to directly carry out the argentiferous galena reduction, alongside with the native *huayras* (Van Buren, M. and Cohen, C.R., 2010). Alonzo Barba, priest and miner of Potosí, refers in 1640 the use of these *reverbero* furnaces for ore roasting and reduction, as well as for silver refining.

In Potosí, from the Hill discovery until the arrival in 1569 of the sixth Viceroy Francisco de Toledo, the mines exploitation conditions were very dependent on the natives and also on their labour, who controlled the mining technical processes, the ore extraction and the consequent transformation into silver (Garavaglia, J.C., 2000). Silver production will decrease over time because of the decreasing in the silver content of the extracted mineral, and the process used up till then by indigenous people, adapted to the fusion of high quality minerals, very rich in silver, will not achieve the desired silver yields (Fernández, J.M., 2000; Garavaglia, J.C., 2000). The need to increase the mineral production will lead to the specialisation of the mining works, tunnels drilling, and of the silver extraction process.

From 1554, the Sevillian Bartolomé de Medina introduces in Pachuca mine in "Nueva Espaňa", Mexico, the amalgamation procedure, also known as the patio beneficiation, that used mercury to process the metals without the need of fusing them (Muñoz, J.J.L., 2010). The great advantage of this process, which was also tried at Guadalcanal in Spain in 1558, resulted from the capacity to use the mercury from the Almadén mines, not far from Seville, and to rely easily on the Slovenian mines of Idria. An important silver production rate was achieved through a fluid and abundant mercury export to the Indies, later improved and guaranteed by the mercury mines of Huancavelica, discovered in 1563 in High Peru (Muñoz, J.J.L., 2010). From the 1570's, Spain will have sufficient mercury sources to apply the new beneficiation process of silver ores through amalgamation also in Potosí.

This new process adapted to the beneficiation of low and medium silver content ores, which necessitated the construction of large grinding mills for ore fragmentation and milling, had allowed the reprocessing and the silver recovery from the waste rocks and slags from previous years, who accumulated nearby the first mines, and the mass production of silver with the subsequent sending to the Iberian Peninsula (Fernández, J.M., 2000; Garavaglia, J.C., 2000; Muňoz, J.J.L., 2010). After amalgamation introduction, the Spaniards had a greater control over the silver production and a productive growth with levels much higher than those in the previous decades will be noticed, whose maximum is reached in 1592 (Deveza, F., 2006). The energy for the grinding mills come from the hydraulic power from the water of the altitude Lakes which arrived through aqueducts to a set of wheels with metal hammers, that strike the mineral on a stone base. In the late 16th century there would be more than 140 of these machines working in Potosí (Fernández, J.M., 2000). As thinner the mineral was, the highest the surface exposed to the mercury action. The amalgamation process was structured in several courtyards, with small depth tanks where the ground ore was mixed with water, mercury, various salts and iron and copper sulphates, forming a mass that would be tossed and trodden during 3 to 4 weeks (Garavaglia, J.C., 2000). Then the silver and mercury amalgamated mass was separated from all impurities by washing in a stream of moving water, where the heaviest particles, the silver and mercury amalgam, set on the bottom. This amalgam was compressed in bags so that the non-amalgamated mercury could be filtered through the tissue and was subsequently heated to release the mercury by vaporization, being the silver product subsequently melted and casted into bars.

The ancient silver reduction technology will not be fully replaced by the mercury amalgamation and will coexist in use in *huayras* and in European *reverbero* furnaces, especially in places that did not have enough water to drive the milling and grinding machines (Van Buren, M. and Cohen, C.R., 2010). In Porco, where were located the first mines exploited by the Spaniards, and in Cerro Rico, silver will continue to be extracted and processed by Indian technology (Van Buren, M. and Cohen, C.R., 2010).

In Nueva España, the beneficiation of silver ores depended on the chemical nature of the ore, being the argentiferous galena processed only by the older reduction processes regardless of the silver content and the amalgamation process was applied to the sulphides silver ores (Quintero, S.J.G., 2015). The existing data concerning the levels of silver production show that about one third of the metal was obtained by the older reduction processes, coexisting both techniques between the 16th and 19th century (Quintero, S.J.G., 2015). Although Peru possessed the richer silver mining centre, Mexico has benefited the long-term advantages of owning a higher silver content ore and lower exploitation costs.

1.4 | American silver and the world economy

European economic history seeks to demonstrate that the influx of American silver was primarily the responsible for the inflation of the Price Revolution, principally for the period circa 1540 to 1600, due to the discovery of the abundant silver mines in America, which leads to the diminution of the value of silver in relation to sealable goods as corn (Munro, J.H. (without date)). The extention in which this metal flowed into Spain and also into other parts of Europe is thereafter a major issue, essencial for understanding this question.

From the 16th to the 18th century, silver constitutes an important good that will link the world trade, having China as the dominant end market. At the beginning of the sixteenth century, the European economy's liquidity was provided mainly by the German silver, and the production of this metal would decrease quickly from 1535, representing at the end of the century during the peak of the Potosí silver, only one tenth of the silver entering Spain (Heydt-Coca, M., 2005).

The discovery of the new American silver mines will originate an organized and systematic large-scale exploitation of the mineral formations and production of this metal which will become the engine of the Spanish economy growth and will assume an essential role in the international trade development. European countries will establish for the first time regular and lasting connections among the four continents dominating the overseas market, and silver will provide the exchange medium for the importation of goods to Europe and for the trade with Asia, representing approximately 50 % of the value of the exports of India (Chaunu, P., 1979). In this sense, silver trade and its influence in the world economy expansion during the sixteenth century until about the 1640's, a period which marks the birth of globalization, is regarded as a turning point in the Western history, when Europe took a big step in its development with social and technological advances without precedents (Heydt-Coca, M., 2005; Flynn, D. and Giráldez, A., 2006).

One of the active causes of the global trade was the existing imbalance in the silver market. During the 1540-1640 period, the American silver will flow through Europe to the final market of China (Flynn, D. and Giráldez, A., 2006) in counter current with the gold, which will move at the same time in the opposite direction, simply because the silver price in China was twice the price in Europe. Only a negligible fraction of the silver shipped through Europe for the global market will be produced in Europe during this period (Flynn, D. and Giráldez, A., 2006). In the early sixteenth century, the relationship between the values of gold and silver in the enormous Chinese economy that held at least one-quarter of the world's population was 1:6, contrasting with the existing relationship of 1:12 in Europe, of 1:10 in Persia and of 1:8 in India. The Japan, during the 16th and 17th centuries, after the discovery of rich silver mines in the west of the country, was also a major producer of world silver, whose biggest market was China, having produced possibly about half of American silver obtained during the same period.

The influx of this metal, motivated by the best price offered by the Chinese market, will terminate by the end of the abovementioned period, when the price of this metal decrease and reach the world value, ending a century of enormous profits arising in the global silver market, ending the cycle of Potosí silver and Japan silver (Flynn, D. and Giráldez, A., 2006).

American silver production presents two prosperity cycles, the silver from Peru and the silver from Mexico. Peru silver cycle is based on Potosí mining, encompasses the sixteenth and seventeenth centuries and during this period corresponds to the production of 75 % of the total American silver produced and about 60 % of the world silver production. These numbers illustrate the important role that the exploitation of Andean silver had concerning the incomes to the Spanish Kingdom.

The production of silver from Potosí will grow continuously since the ore discovery up to about half a century later, presenting a huge production growth around 1575. The high growth rate, which will reach its peak at the beginning of the following century, circa 1610, is mainly attributed to the accessibility of the ore, and to the introduction of innovative techniques for silver exploration (Garner, R.L., 1988). From 1620 onwards, began a slow crisis of the Andean silver production due to the decline of the mining operations caused by the decrease in the quality of the ore, and by the depletion of the readily accessible deposits, being this production breakdown quite apparent after 1640 (Heydt-Coca, M., 2005).

Also, the growth rate of the Mexican silver with an ever-growing trend in the 16th and 17th centuries, will have between 1559 until 1627 a figure about ten times higher than verified in Potosí during the same period, with a small breakdown afterwards. This productivity decrease seen in Mexico, such as the one with the greatest impact in Potosí, was also linked to the quantity and quality of the ore and its extraction difficulty (Garner, R.L., 1988). Potosí silver leadership will be only disputed in the late seventeenth century by the huge silver production increase from the Viceroyalty of New Spain (Mexico), which will be greatly felt during the 18th century (Flynn, D. and Giráldez, A., 2006).

The 16th-17th centuries silver and gold production data recorded by the Andean and Mexican *Cajas Reales*, used by Garner, R.L., 2006, to calculate the historical production evolution of both metals in colonial Spain, show that recorded Peru's silver production started on the decade initiated in 1531 in much more expressive quantities than those coming from Mexico. During the second half of the 16th and on the early 17th centuries a substantial silver amount will be exported to Europe (Chaunu, P., 1979; Garner, R.L., 2006), easily transported in the form of minted coins, ingots or bars (Garner, R.L., 1988) with different markings, as for example, P of Potosí and O (or the full name) of Oruro, as found in ingots produced in the first quarter of the 17th century recovered from the Atocha shipwreck (Gordus, A.A. and Craig, A.K., 1995). Reginaldo de Lizárraga, Dominican clergyman and Spanish chronicler, in its description of the lands of Peru made around 1570 acknowledged already the diffusion and the impact of this new source of silver in the European economy: "With the wealth that has come out of Potosí, Italy, France, Flanders and Germany are rich, and even the Turkish has in his treasure, bars of Potosí, and fears to the monarch of this Hill in which kingdom runs that money..." (Reginaldo de Lizárraga, Descripción del Perú, Tucumán, Rio de la Plata y Chile, 1605, pp. 223).

From around the 1530's until the 1570's, it is the Japanese silver discovered throughout this century that will meet China requests in this metal. China will be later an important recipient of the Peruvian and Mexican silver received through various circulation routes, in which the most important extends across the Pacific, from Acapulco to the Philippine Islands conquered by the Spaniards between 1560 and 1570 (Atwell, W., 1982).

A second silver route from the New World had as destination Seville, where this metal was transported illegally to Portugal along with other ingots from Peru obtained through Buenos Aires, and then distributed to Goa, in India, passing the Cape of Good Hope. The Portuguese had transported many silver tons between Goa and Macau since the late sixteenth and seventeenth centuries (Atwell, W., 1982).

1.5 | The geochemistry of European and New World silver ores

In natural ore sources, silver occurs together with an ample variety of other elements present in the ores that during the ancient processes of metallurgical extraction, smelting and refining were not completely removed, and remained as impurities in the form of minor or trace elements in the produced silver bullion. The resulting silver was thereafter not chemically pure, presenting very low contents of such elements found in the silver ores, normally not high than one percent. Hence, a general geochemistry perspective of some of the processed silver ores is fundamental.

In terms of structure, the silver ore deposits can be quite complex in their chemical profile and present distinct characteristics regarding geological origins and morphologies, and silver can be extracted from many different ores. In the absence of compositional studies made on silver ore samples belonging to each location and correlated with each chronological period, allowing the identification of its metallogeny, *i.e.*, mineral deposits formation, the challenge in studying silver coins is to understand the implications of ore geochemistry in their compositions, as well as the impact of the different processing technologies used over the times.

For clearness, it is important to notice that on the previous sections all the mine's names encompass generally a mining region and not a precise mine or vein, and thereafter the ore from each location could have different mineral contributions from veins with different chemical fingerprints.

1.5.1 Europe

In Europe, unlike the American continent where the interest of ore exploitation resided in the precious metal recovery as a major economic component, the silver was a secondary product resulting from a mining exploitation directed to the base metal extraction, from argentiferous galena or argentiferous copper ore.

The silver present in the argentiferous galena ore was found in Central Europe in mineral deposits with high geological ages from 252 Ma to 359 Ma consisting of minute silver sulphide crystals evenly spaced in the lead sulphide (Quintero, S.J.G., 2015). The silver extraction from this kind of ore was exploited in the Middle Ages in the Harz region around Goslar where the mines of Rammelsberg, Freiberg and Annaberg were located, in some mines of the Erzgebirge in Germany, in Kutná-Hora mine in the Czech Republic, in Schneeberg in Tyrol, and in the mines of England, Devon and Cornwall, among many others.

Polymetallic ore veins were found in Freiberg with a wide variety of sulphides, sulfosalts and native silver, having present Ag, Pb, Zn, Cu, Sn, Sb, In, Ge, U, Cd, Au, Bi, As and Tl (Cassard, D. *et al.*, 2008; De Vos, W. *et al.*, 2017). Rammelsberg started as a Pb-Zn mine and later produced mainly copper, lead and zinc (De Vos, W. *et al.*, 2017), the ore of Kutná Horá mine in Bohemia region had polymetallic veins of Pb-Zn-Cu with Ag, Cu, Sn, In, Ge and U (Cassard, D. *et al.*, 2008), and the Schneeberg mine has worked from the 15th century to produce silver and bismuth, and its ore veins had Ag, Bi, Co, Ni and U (https://www.mindat.org/loc-777.html).

The Devon and Cornwall British deposits of galena without importance for the exploitation of silver constituted lead sources to be used in the cupellation processes carried out in Europe and later in America (Quintero, S.J.G., 2015). From 1536, lead was sent directly from Seville to the New World, carried as ballast by the Indian fleets to Zacatecas, were the deposits were rich in silver and poor in lead, providing the required quantities of lead to smelting the ore (Blanchard, I., 1981), and this movement of English lead will continue intermittently until the 1640's of the next century (Blanchard, I., 1989).

From the 15th century, the exhaustion of the argentiferous galena mines and the need for deeper explorations for attaining the ore will encourage the development and the introduction of extraction processes enhancements and subsequent ore beneficiation improvements (Agricola, G., 1556). The advances then verified on copper reduction processes and in the used technology will allow to recover the secondary silver present in silver-rich copper ores in complex copper minerals (Agricola, G., 1556), such as tetrahedrite (copper and antimony sulfosalt minerals (Quintero, S.J.G., 2015)) from Erzgebirge, where was located the Joachimstahl mine, and from the mines of Schwaz in Tyrol, and of Neusohl in Hungary. Eisleben and Hettsedt in Thuringia, and Mansfeld in the Hartz mountains constituted also other examples of silver bearing copper mines, refererred by Agricola, that were active during the sixteenth century.

In the Harz mountains mainly copper, lead, zinc and silver were produced (De Vos, W. *et al.*, 2017). The Joachimstahl polymetallic copper ore veins rich in silver-bearing sulphoarsenides, sulphides and native silver were characterised by high contents of Ag and U, with minor amounts of Bi, Co, Ni, Zn, Pb, Sb, Hg, In and As (De Vos, W. *et al.*, 2017; https://www.mindat.org/loc-777.html), and the copper and silver ore bearing region near Schwaz had minor contents of Sb, As, Hg, Fe, Zn and Bi (Breitenlechner, E. *et al.*, 2012).

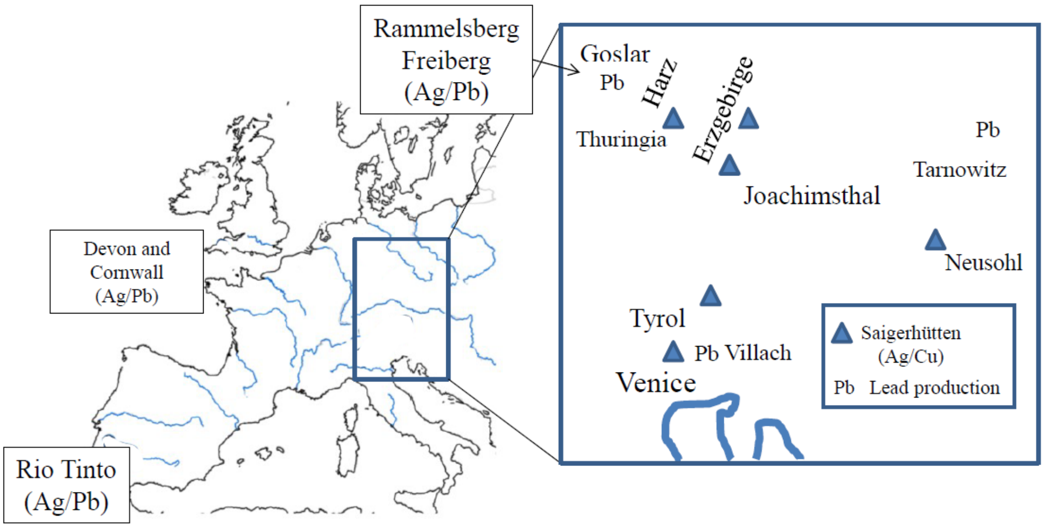

Figure 1.3 – Main mining regions of European silver extraction in the mid-16th century. From Quintero, S.J.G., 2015.

The silver-rich galenas or the argentiferous copper ores were only processed in Europe by smelting, and amalgamation was not implemented as a viable beneficiation process, contrasting with what happened in the New World, where the silver chloride and the silver sulphides were processed by amalgamation processes adapted to their variable chemical nature.

1.5.2 Mexico and the Andes

In the New World, the produced silver came basically from two chemical groups of silver compounds: i) silver sulphide compounds, simple and complex, which may have superficial layers of silver chlorides or other halides in conjunction with elemental silver and ii) argentiferous galena, *i.e.*, lead sulphide containing silver compounds (Quintero, S.J.G., 2015).

In the case of silver sulphides, the original chemical composition of the silver ore is altered in the oxidation layers, closest to the surface, because of weathering, being converted over the geological time in silver chloride and elemental silver. The ore chemical nature would then change as the ore in-depth extraction was performed, necessarily without an important decrease of the silver content, unless the original deposit has a significant negative silver gradient (Quintero, S.J.G., 2015).

The chemical profile of the silver deposits was visually known by colonial miners that name the surface deposits consisting of silver sulphides as *colorados*, containing native silver and silver chloride produced by weathering and coloured by iron oxides and some silver sulphide, and as *tacana*, the native silver. These important superficial silver ore deposits could be benefited by the primitive reduction techniques and also by using the amalgamation technique implemented from 1550, already used in Europe for the gold. At greater depths below the water table, the silver ore consisted in black silver sulphide, *negrillos*, with native silver and complex silver sulfosalts as pyrargyrite, containing antimony (Quintero, S.J.G., 2015).

These silver sulphides, difficult to process, have leaded to assume the existence of a lower silver content in the ore, and their processing has been improved with the help of Germany technicians and with the importation of lead from England (Quintero, S.J.G., 2015).

The Mexican silver ore deposits offered both options, being accompanied by the lead, gold, zinc, antimony and arsenic, and the Andean deposits were formed mainly by the first group of compounds (Finndley, A.A., 2010; Quintero, S.J.G., 2015).

According to the contents of the *Carta y Provincias Metalogenéticas de la República Mexicana* of 1980 elaborated by Guillermo Salas, reported in Quintero, S.J.G., 2015, there exists in Mexico two most important locations of silver ore deposits (Figure 1.4): The *Sierra Madre Oriental* and the *Provincia del Eje Neovolcanico Mexicano*, known as the Mexican volcanic belt. The first comprises the miner districts of Zacatecas, Guanajuato and San Luis Potosí, and their main deposits are rich in argentiferous lead, Pb-Zn, and Pb deposits, and contain lead, copper, zinc and silver, from galena or silver sulphides. The second metallogenic province encompasses the districts of Pachuca, Real del Monte, and Taxco, and produces silver, from galena and silver sulphides deposits, and lead (Quintero, S.J.G., 2015).

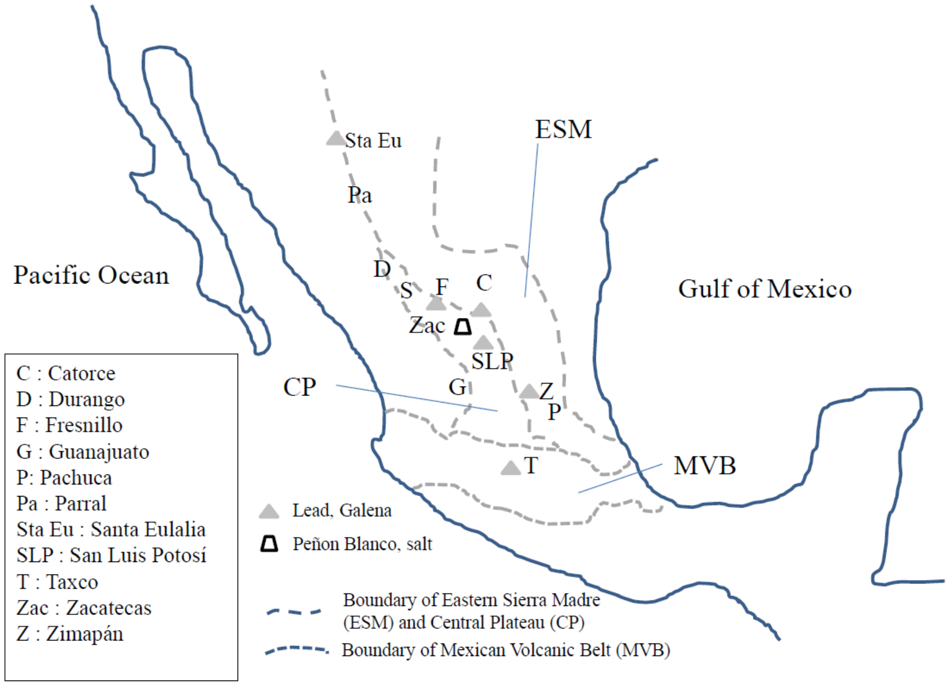

Figure 1.4 – Main historical deposits of silver, lead and salts of New Spain. From Quintero, S.J.G., 2015.

There are no detailed studies to assess the composition of the ore deposits of the old Andean colonial mines, and comparative analyses between minefields are also exceptionally rare (Vaughn, K.J. and Tripcevich, N., 2013).

The Eastern Cordillera from the Bolivian Andes is a volcanic complex with 500 million years of geological history and one of the largest mineral provinces of the world rich in precious metals deposits, resulting from multiple metallogenic events that include various metals such as tin, tungsten, silver, zinc, lead, gold, antimony and bismuth. Three types of deposits are present in this Cordillera (Ericksen, G.E., et al., 1991), (a) polymetallic base metals veins (the term "base metal" refers to low-value metal elements present in high volume such as lead, zinc and copper), rich in silver and locally rich in gold, (b) veins and stockwork, *i.e.*, veinlets and small veins network, of tin, polymetallic, rich in silver, and poor in gold, and (c) stockwork with low gold content or disseminated deposits with or without silver and base metals. Many veins present mineral zoning, with base metals in central areas, with gold and tungsten being abundant in some deposits, and with high levels of silver, arsenic and antimony in outer areas. In the vertical zoning occurring in some locations, the base metals are abundant in depth and silver is richer near the surface.

In this Bolivian Cordillera, polymetallic deposits are characterized essentially by tin, silver and antimony sulfosalts (Table 1.1) (Alarcon, B.H. and Fornari, M., 1994), there existing important variations in the ratio of tin-silver-gold in the deposits (Redwood, S.D., 2011). Overall, the Au content in the silver-rich veins are smaller than 1 g/t Au, but some veins may contain 100 or more g/t Au (Ericksen, G.E. *et al.*, 1991).

Table 1.1 – Abundance of minerals in polymetallic deposits of various locations of the Eastern Cordillera of the Andes in Bolivia. Mineral abundance increases from small to large circles. Taken from Alarcon, B.H. and Fornari, M., 1994

Metal	Composición Química	Potosí	La Joya	Chorolque	Tasna
Pirita	FeS_2	●	●	●	●
Marcasita	FeS_2	•	•	•	•
Arsenopirita	$AsFeS$	●	•	•	•
Calcopirita	$CuFeS_2$	•	•	•	•
Galena	PbS	•	•	•	•
Esfalerita	ZnS	●	•	•	●
Wurtzita	ZnS	•			
Estannina	Cu_2FeSnS_4	•	•	•	•
Tetraedrita	$(Cu,Ag,Fe,Zn)_{12}(Sb,As)_4S_{13}$	●	•		•
Bismutinita	Bi_2S_3				•
Estibina	Sb_2S_3	•	•		
Bismuto Nat.	Bi				●
Hessita	Ag_2Te			•	
Tetradimita	Bi_2Te_2S			•	
Electrum	(Au,Ag)		•	•	•
Franckeita	$FePb_6SbSn$	•		•	•
Cosalita	$CuPb_7Bi_8S_{20}$			•	•
Aikinita	$CuPbBiS_3$				•
Cosalita	$CuPb_7Bi_8S_{20}$				•
Gustavita	$Ag_3Pb_3Bi_{11}S_{23}$				•
Pirargirita	Ag_3SbS_3	•			
Miagirita	Ag_3SbS_2	•			
Polibasita	$(Ag,Cu)_{16}Sb_2S_{11}$	•			
Andorita	$AgPbSb_3S_6$	•			
Bournonita	$CuPbSbS_3$	•			
Jamesonita	$FePb_4Sb_6S_{14}$	●			●
Zinckenita	$Pb_6Sb_{14}S_{27}$	●	•		
Boulangerita	$Pb_5Sb_4S_{11}$	●	●		
Wolframita	$(Fe,Mn)WO_4$		•		●
Cassiterita	SnO_2	•		●	•
Turmalina	$NaFe_3AL_6B_3Si_6O_{27}(F,OH)_4$	●	•	●	●
Cuarzo	SiO_2	●	●	●	●
Alunita	$(K,Na)Al_3(SO_4)_2(OH)_6$	●	●	•	•
Sericita	$KAlSi_3O_3(OH)_4$	●	●	•	•
Caolinita	$Al_2Si_2O_5(OH)_4$	●	●	●	
Jarosita	$KFe_3(SO_4)(OH)_6$	•	●	●	•
Siderita	$FeCO_3$	•	•	•	•
Baritina	$BaSO_4$	●	●	•	•

Except for the region corresponding to the auriferous District of La Joya, at Northwest of Oruro, where the gold is present with an average concentration of 2 g/t, gold minerals are relatively scarce in the various deposits (Ericksen, G.E. *et al.*, 1991). Kori Kollo near Oruro, is an example of a gold-rich deposit in this region (Redwood, S.D., 2011). There exists many tin and silver mineral deposits, such as Cerro Rico which produced 60,000 t of silver from ores on average with approximately 0.5 kg/t Ag (Ericksen, G.E. *et al.*, 1991), San José and Oruro, and some of these deposits also contain gold, as Ubina, Tasna and Chorolque (Redwood, S.D., 2011). The silver mineral deposits are usually accompanied by lead and zinc, and sometimes by bismuth, existing in some mineral deposits a gold-bismuth-copper association (Redwood, S.D., 2011), as for example, in Ubina, Chorolque e Tasna, in the South of the Bolivian tin belt, southwest of Potosí, where, in the latter case, the gold is associated with bismuthinite, arsenopyrite and pyrite (Alarcon, B.H. and Fornari, M., 1994). For example, in the region of Carguaicollo, near Potosí, mined during the colonial period, silver occurs mainly with Zn mineral deposits although it is also present in the Sn-Pb mineral deposits (Turneaure, F.S. and Gibson, R., 1945).

Arce-Burgoa, O.R. and Goldfarb, R.J., 2009 depending on the chemical elements present in the mineral deposits, identify in the Eastern Cordillera (Figure 1.5) a stannous belt, an Au-Sb belt, and a Zn-Pb belt.

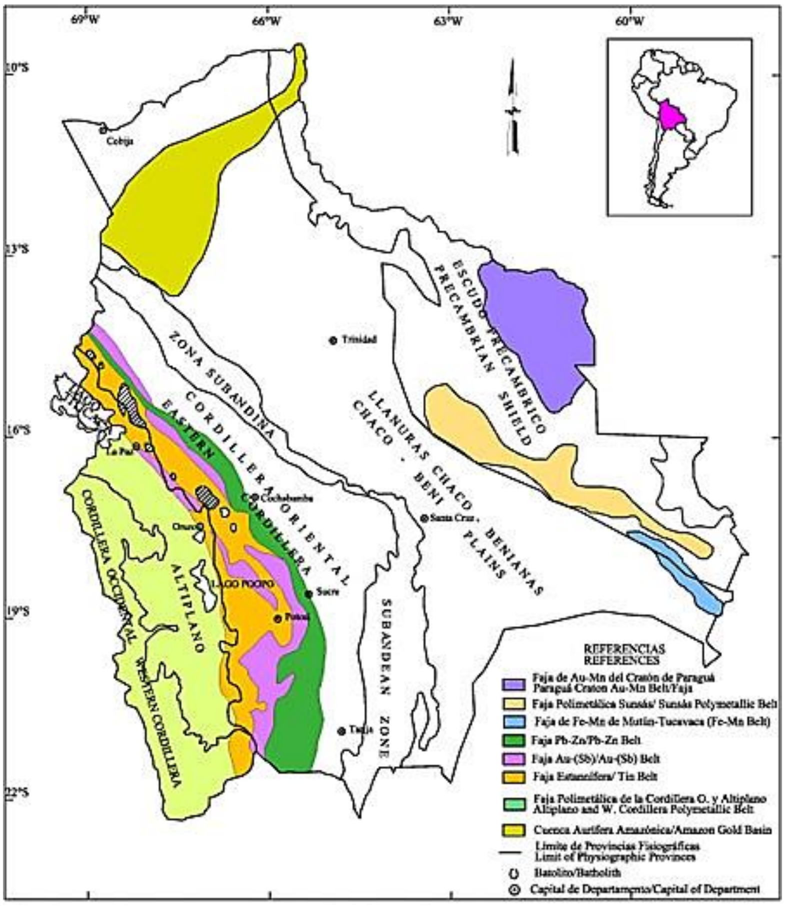

Figure 1.5 – Metallogenic belts and physiographic provinces from Bolivia. Taken from Arce-Burgoa, O.R. and Goldfarb, R.J., 2009.

1.6 | Coin composition and microstructure characterization

Knowledge of coins elemental chemical composition has the potential to allow a better understanding of the metallurgical technology and processes associated with minting, along different timelines and within different geographical spaces, and to attest and complement the acquired information based on the numismatic attributes resulting from coins direct observation, as iconography, inscriptions, letterings and other marks, and on historical events and coeval documentation, such as the decreed legal fineness, *i.e.*, the silver content of the metallic alloy.

The chemical composition as allowed generally to identify various chronological silver alloys and diverse minting workshops outputs from silver coins pertaining to the most diverse geographies, as well as to characterize the used metal sources in some cases.

In addition to the chemical composition, a specific phenomenon of the silver alloys must be considered when interpreting surface composition analysis results: the silver surface enrichment. This phenomenon is caused by variations in composition between the interior and the surafce of the objects, due to preferential oxidation and leaching processes, leading to higher silver contents and lower copper contents on the surface, which due to its unpredictable nature can only be evaluated based on phase constitution and elemental distribution within the microstructure of the alloys.

1.6.1 Chemical composition assessment of Portuguese ancient silver alloys

1.6.1.i) Definition of silver coin

The definition of silver coin in the context of this thesis is that used by Gomes, A., 2003, which corresponds to a coin made of a silver alloy with more than 500 thousandths of silver content, and therefore does not include bullion coins with a silver content lower than 50 %. This definition taken today by numismatists, has ancient roots in the understanding given by medieval Mints and merchants to the silver content present in the metal, that is clearly noticeable for example in an excerpt of the *Tractatus nove monete* probably written by William de Turnemire master of the London mint, circa 1280:

> *"You must know then, to explain what is to follow, that any bullion or coin half or more of which is pure silver, is called 'silver.' But below half it is by no means to be considered silver. Some silver, recognized as such, is bought as ' pure,' some as alloyed."* (Red Book of the Exchequer, translated by Johnson, C., 1956, pp. 68).

1.6.1.ii) Silver fineness

The fineness corresponds to the silver content in the metal forming the coin. The Portuguese silver coin alloys used in the 15th – 17th centuries, apart from the silver, have added copper as a major element, introduced in controlled amounts to achieve the intended fineness within the range of very rich silver alloys. The Portuguese silver coinages were then issued with a *11 dinheiros* silver alloy, corresponding to a fineness of eleven parts of silver in twelve of metal, *i.e.*, 916.6 thousandths.

There was never for silver as much care in the Portuguese mints as existed for gold, a high valuable metal, regarding the determination of silver fineness in operations previous of coin striking (Gambetta, A.F., 1978). The silver was tested only by the touchstone, in contrast to the gold that was assessed by cupellation, an assay considered by Beringuccio as the only indicated method to evaluate the fineness:

> "Certainly, no mint master, jeweler, or goldbeater can practice his art well without cupellation….", (Vannoccio Biringuccio, De La Pirotechnia, 1540, pp. 160).

In the touchstone test a piece of silver was rubbed in a very fine grained compact surface of a black stone, a black Jasper stone, leaving a streak that differed in colour which depends on its fineness, *i.e.*, the silver content in the alloy. After passing an acid solution, by comparing the colour of this streak with those left by silver touch-needles of well-known fineness's, with silver contents above and below the tested piece, it was possible to estimate the purity of the later.

According to Craig, J., 1953, in this procedure, an expert could estimate differences of silver not more closely than 10 parts per 1000, and as the needles or the composition master pieces from each mint could introduce a variation at least in the same magnitude, it should be expected that the coins fineness's of different mints had a larger range of variation, without considering any malpractice.

Gambetta, A.F., 1978, transcribes a technical statement given in 1509 by João da Maia, Fernão Lourenço, Diogo Rodrigues and Pedro or Pêro Gonçalves, experts of the Lisbon mint, regarding the gold touchstone test:

> "*when the weather was clouded and not clear, and they were not with the perfect view, in every golden mark could pass 6 grains (one and a half carat) of the alloy without feeling it in the touch; and being good weather and passing them by the touch the way they used to, it appeared to them that in the touch could not go alloy that was not as well-known and so perfectly as by assay*".

The same would happened with the silver metal.

The obtained silver alloy was thereafter quite arbitrary because it depended only on the information of the touchstone test, a test that was much faster than a cupellation silver assay, but also much more unreliable, as was also believed by Georgius Agricola. Hence, the silver fineness assessment by the touchstone test fixed a comparative and not an absolute silver content.

Besides the high silver content and the alloyed copper, the investigated coins for this thesis are also constituted by several minor and trace elements, which derive primarily from the silver bullions used for casting the coins, and in a lesser extent from the copper.

When rating the legal monetary fineness in relation to the fineness of the silver coins produced by the mints, it should be considered that elements such as gold, lead, or bismuth, among others present on the initial silver bullion, remained in the casted silver alloy in residual quantities

(Metcalf, D.M. and Northover, J.P., 1972; Butcher, K. and Ponting, M., 2005; Gitler, H. *et al.*, 2008 and 2009). Thereafter, the analytical measured silver content does not directly indicate the coinage fineness of the alloy that was mixed in the melting furnace and the precision with which the founders adjust the silver melting's with copper, nor the exactitude with which the assayers tested the silver ingots.

The silver bullion content, that is, the perceived silver content assayed at the mint is more realistically calculated as the sum of the silver, plus all the minor elements present in the silver alloy except copper (Metcalf, D.M. and Northover, J.P., 1972; Butcher, K. and Ponting, M., 2005; Gitler, H. *et al.*, 2008 and 2009), which the moneyers were unware and weighed as silver.

1.6.1.iii) Minor and trace elements

The analysed silver alloys compositions could be characterized in terms of their alloy compositions and their geochemical metallurgical signature imparted by minor and trace elements contents geochemically associated with the silver ores, retained in small amounts after smelting and cupellation/refining processes of the silver. In this thesis, the elemental compositional is used to answer numismatic questions of the minting process, to distinguish silver alloys from different mints and to identify dissimilar silver sources, through establishment of relationships between the minor elements measured in this investigation: gold, mercury, lead, bismuth, nickel and zinc. Hence, discriminating elements should have small variabilities forming robust compositional groups that could be assigned to a single silver origin.

Other elements would probably be present, but these are the ones that could be detected by the used analytical techniques, and some of them are considered as the most useful to characterize different alloys, as for instance gold and bismuth together with lead.

All the mentioned elements could also have been introduced through the added copper in the alloys, but for coins with a high silver content, the measured values would be strongly related to the silver bullion and unlikely to enter from copper additions, which contributions would be negligible.

Lead is present in argentiferous lead ores and in argentiferous copper ores but is also related to the employed metallurgical technology and refining processes. It would have been added in the processing of argentiferous copper ores later during the liquation process for producing argentiferous lead which was then subjected to cupellation for silver extraction. Also, ancient silver refining and recycling processes would have added lead to the processed silver metal, and most of the lead measured is thereafter associated with the silver bullion. It is present in silver bullions after cupellation ranging from a few hundred ppm, typically 0.1 % (Pernicka, E., 2013), to 1-2 weight percent.

Gold and bismuth are present as impurities in silver alloys, ranging normally from a few hundred ppm to several tenths of weight percentage, being important silver ores discriminators for fingerprinting ancient silver alloys, as both have been regarded as associated solely to the silver sources (Mckerrell, H. and Stevenson, R.B.K., 1972; Metcalf, D.M. and Northover, J.P., 1986; Gitler, H. *et al.*, 2009; Pernicka, E., 2013).

Gold trace amount is associated with the silver ore sources and not affected by the silver metallurgical processes being retained in the silver bullion in a quantity similar to that of the original ore and has allowed to successfully differentiate silver sources from diverse silver artefacts based on concentration variability (Pernicka, E., 1981; Gitler, H. *et al.*, 2009; Butcher, K. and Ponting, M., 2014; Wood, J.R. *et al.*, 2017). However, gold can vary within a single deposit, diverging for example in silver argentiferous lead ores from two or more orders of magnitude, something which reduces the potential for differentiation of silver sources (Pernicka, E., 2013), being 0.1 wt.% Au the maximum empirical value obtained on objects made with silver bullions originating from galena ore sources (Pernicka, E., 1981).

The bismuth/silver ratio can allow some differentiation between various silver origins, (Pernicka, E., 2013), as the bismuth content is reduced by a factor of 5 during the silver cupellation process of argentiferous lead ores (Pernicka, E. and Bachmann, H.G., 1983). Also, according to L' Héritier, M. *et al.*, 2015, the bismuth/lead ratio can be used as a silver ore discriminator, however, in the case of finished objects, the bismuth content in silver does not depend of its initial concentration in the processed metal, but on the final progress of cupellation, the step in which the oxidation and the consequent removal of this element occurs. On finished objects, where the geological signature may have also been erased due to mixtures and metal re-melting's, this bismuth/lead ratio will allow to judge on the initial composition of the cupellation processed silver ingots and may serve to discriminate different metallurgical production sites.

1.6.2 Microstructures of silver-rich alloys

The Portuguese coins under investigation were manufactured from silver-copper alloys, whose casting microstructures were subjected to mechanical work in association with annealing heat treatments. Hence, it is important to recognise the microstructures and the phase distribution and morphologies associated with the silver-copper alloys with compositions near those under study, as these can elucidate about the manufacturing process and help to clarify the data obtained by elemental analytical techniques.

The expectable silver-copper alloy equilibrium microstructure is determined through the binary phase diagram for the Ag-Cu system (Figure 1.6). This diagram, though prepared for equilibrium conditions achieved through very slow cooling, allows to predict which are the existing phases for any given composition of a silver-copper alloy at a given temperature, and should be therefore sensibly interpreted for historical objects.

The melting temperatures of the two pure metals are 961.78 °C for silver, and 1084.62 °C for copper, and the Ag-Cu system consists of a simple eutectic equilibrium with a composition of 71.9 % Ag and 28.1 % Cu (in weight) at a temperature of 779.1 °C (Subramanian, P.R. and Perepezko, J.H., 1993).

From the identifiable zones of this diagram, that of interest within the scope of this thesis is the one assigned to silver-copper alloys made up mostly of silver, *i.e.*, silver-copper alloys containing more than 91.2 % Ag in weight, the silver content indexed to the maximum of copper solid solubility in silver.

During solidification, very rich silver alloys with copper contents lower than 8.8 % (in weight), form initially large dendrites of silver-rich solid solution, *i.e.*, the primary solid phase of silver, which coexist in equilibrium below the transformation temperature with the copper-rich phase in very small eutectic regions.

However, in ancient silver alloys, for a wide range of cooling speeds and due to decreased solubility of copper in silver until about 0.1 % in weight until room temperature (Schweizer, F. and Meyers, P., 1978), a silver solid solution supersaturated in copper is formed which will originate a very thin copper precipitate with the morphology of bands or drops within the silver phase (Northover, S.M. and Northover, J.P., 2014) (see (a) in Figure 1.6).

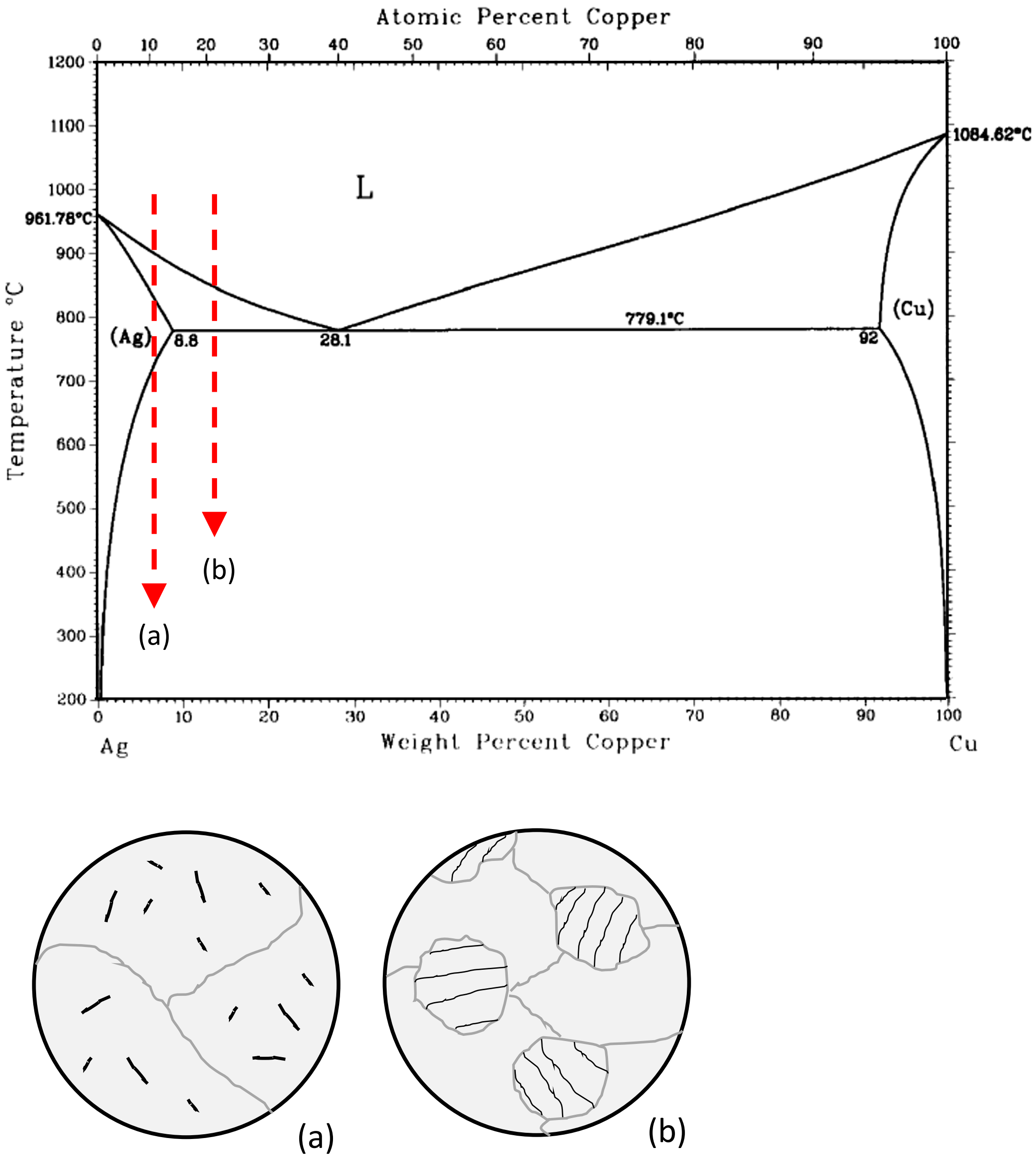

Figure 1.6 – Phase diagram of Ag-Cu system and microstructures of (a) very high silver content alloy and (b) hypereutectic silver-copper alloy. Adapted from Subramanian, P.R. and Perepezko, J.H., 1993.

This metastable equilibrium condition is produced by imediate quenching of hot silver alloys objects, a process that reduces the precipitation of copper and leads to a homogenous structure at room temperature, with a high supersaturation of copper in Ag-rich phase. For rich silver alloys with low copper supersaturations, the microstructure will decompose if heated to higher temperatures below the transformation temperature, or over long periods of time at room temperature, and will cause the slow nucleation and precipitation of the copper-rich phase within the silver grains (Schweizer, F. and Meyers, P., 1978).

For silver contents below 91.2 % Ag but greater than the eutectic composition of about 71.9 % Ag, the cooling of the melted silver-copper alloy originates a two-phase microstructure, constituted by silver-rich phase primary grains which solidify first at temperatures above the eutectic temperature, surrounded by a eutectic structure. This eutectic structure is originated by solidification of the remaining liquid below the eutectic temperature and consists of small lamellae of copper-rich and of silver-rich phases disposed alternately (see (b) in Figure 1.6).

Due to its electrochemical potential, it is the copper-rich phase that is more susceptible to oxidation during the different steps of the monetary production process or to corrosion during coins circulation and will be preferably oxidized and leached from the subsurface regions to the surface of the coins through solid state ionic diffusion via the grain boundaries, resulting possibly in silver subsurface enriched layers.

For this reason, ancient silver alloys would have been casted with relative fast cooling rates, aiming to prevent intense firescale, which removal would require much time and grinding effort. Firescale consists of copper oxides layers which forms very quickly on the surface and subsurface of the metal in the presence of oxygen and heat, with dark reddish-brown to black colours, that would need metal removal to get rid of it, being thereafter very time consuming (Sage, P., 2010).

Also, the subsequent intermediate annealing steps of the hammered silver metal bars after thickness reduction would have been made always in reducing atmospheres to prevent the oxidation of copper, with fast cooling’s probably effectuated by quick metal immersion in acid diluted solutions to achieve a bright silver surface by removal of the formed oxides.

These steps would lead to silver enrichment and hence, the silver content can be overestimated when using surface analytical methods, not representing the original fineness of the coins.

1.6.3 Silver surface enrichment

Depending on the previously production and environmental conditions to which silver alloy coins were subjected during its existence, copper is depleted from their surface and originates higher silver compositional content of surface layers with variable thicknesses, which are not representative of the original silver alloy (Carter, G., 1964; Metcalf, D.M., 1983; Šmit, Ž. and Kos, P., 1984; Klockenkämper, R. et al., 1999; Linke, R. and Schreiner, M., 2000; Linke, R. et al., 2003; Beck, L. et al., 2004; Sarah, G., 2008; Butcher, K. and Ponting, M., 2009; Rodrigues, M. et al., 2011; Mass, J.L. and Matsen, C.R., 2012; Corsi, J. et al., 2015).

This copper depletion mainly due to the technological monetary production process (Cope, L.H., 1972; Šmit, Ž. and Kos, P., 1984; Tate, J., 1986; La Niece, S., 1993; Zwicky-Sobczyk, C.N. and Stern, W.B., 1997; Klockenkämper, R. et al., 1999; Bompaire, M. and Dumas, F., 2000; Linke, R. and Schreiner, M., 2000; Beck, L. et al., 2004; Butcher, K. and Ponting, M., 2005; Gitler, H. and Ponting, M., 2007; Butcher, K. and Ponting, M., 2009 and 2014; Arles, A. and Téreygeol, F., 2011), to previously conservation treatments (Tate, J., 1986; Sándor, Z. et al., 2002; Flament, C. and Marchetti, P., 2004; Beck, L. et al., 2008; Butcher, K. and Ponting, M., 2009) or to the former corrosion/archaeological history (Condamin, J. and Picon, M., 1964; Cope, L.H., 1972; Šmit, Ž. and Kos, P., 1984; Tate, J., 1986; Brissaud, I. et al., 1990; Zwicky-Sobczyk, C.N. and Stern, W.B., 1997; Klockenkämper, R. et al., 1999; Linke, R. and Schreiner, M., 2000; Sándor, Z. et al., 2002; Linke, R. et al., 2003; Butcher, K. and Ponting, M., 2009 and 2014) have a larger effect on copper-rich coins and pose challenges to the characterization of the original fineness of these coins with non-destructive analytical techniques such as PIXE and EDXRF.

The surface analytical data of the coins can be influenced thereafter by a number of aspects related to the material, that is, the nature of the alloy, *i.e.*, the content of silver and copper, the morphology and distribution of existent phases, the segregation of certain elements in silver during casting, the deliberated heat and/or chemical treatments carried out during the coin production, such as successive annealing's after hammering work, and the final blanching of the coins, or during the time that has elapsed since their production until the integration on numismatic collections, and the presence of corrosion layers that modify the initial surface chemical composition.

Until now, most of the studies which relate the surface composition to the microstructure (Linke, R. and Schreiner, M., 2000; Linke, R. et al., 2003; Beck, L. et al., 2004; Linke, R. et al., 2004 and 2004[a]; Butcher, K. and Ponting, M., 2005; Civici, N. et al., 2007; Rodrigues, M. et al., 2011[a]; Ager, F.J. et al., 2013; Calliari, I. et al., 2013; Butcher, K. and Ponting, M., 2014) have focused particularly on Ag-Cu alloys mostly with silver finenesses under that indexed to the maximum value of copper solid solubility in silver, i.e., 91.2 wt.%. In these alloys, significant silver and coper differences between the coin core and surface are expected, as there was a well-known intentional alteration of the coin surface silver content during the monetary production process (Cope, L.H., 1972; Zwicky-Sobczyk, C.N. and Stern, W.B., 1997; Butcher, K. and Ponting, M., 2005, 2009 and 2014) to create an Ag-rich surface layer, while giving the metallic silver brightness to which a high perceived coin value was associated. In these lower fineness coins, silver enrichment assessment is complicated once previous research has considered the cut section of coins found in archaeological contexts where, depending on the alloy composition, very variable thicknesses of silver enriched layers were detected, that could extend from 50 to 250 μm in depth, associated in most cases with corrosion processes resulting from the burial conditions to which the coins were subjected (Tate, J., 1986; Constantinescu, B., et al., 1999; Linke, R. and Schreiner, M., 2000; Linke, R. et al., 2003; Blet-Lemarquand, M. et al., 2005; Constantinescu, B. et al., 2005; Sarah, G., et al., 2008; Butcher, K. and Ponting, M., 2005; Gitler, H. and Ponting, M., 2007; Ager, F.J. et al., 2013; Calliari, I. et al., 2013; Moreno-Suárez, A.J. et al., 2015). In some cases, compositional silver differences between the core and the surface of the coins attain values up to 100 % (Linke, R. and Schreiner, M., 2000; Linke, R. et al., 2003) as a result of the metallurgical history of the coins. The existence on these coins of this altered surface layer, irrespective of the far depth useful penetration reachable by surface analytical techniques, that in most of the cases is insufficient to reach the unchanged core, will always give elemental silver composition values different from the core metal due to its contribution to the analysis (Tate, J., 1986; Constantinescu, B. et al., 2003 and 2005; Linke, R. et al., 2003; Beck, L. et al., 2004; Kantarelou, V. et al., 2011; Ager, F.J. et al., 2013).

The Ag K and L X-ray lines and their emission depth differences can be used to determine variations in surface composition of silver alloys. According to Linke et al., 2003, the determined Ag Kα/Lα ratios on the coins may be compared with those obtained on a standard of similar composition to estimate the error that occurs while determining the fineness of coins by EDXRF analysis, allowing estimating the deposition of corrosion products or silver enrichment on a silver surface. Linke et al., 2004, determined up to 20 % K/L ratios variations for differences between the core and the surface composition reaching almost 100 %. Kantarelou et al., 2011 determined that the K/L ratio may change approximately 10 % for a homogeneous silver alloy in the range of 80-100 % Ag and was not able to make a clear assessment of the existence of silver surface enrichment in coins with high silver EDXRF results, 87.6 – 99.4 %, due to the high error associated with these ratios. This Ag Kα/Lα intensity ratio method has been used, however, to classify coins with high silver compositions (above 90 %) as not possessing detectable silver enrichment, assuming therefore the values of the analysis to be consistent of the original fineness of the coins (Hoyo-Meléndez, J.M. et al., 2015).

The levels of the main trace and minor elements such as gold, lead and tin present also compositional gradients from the core to the outside of the coins, linked to the diffusion of these elements in the silver matrix (Carter, G., 1964, Condamin, J. and Picon, M., 1965; Šmit, Ž. and Kos, P., 1984). Considering the existence of a corrosion free surface without silver alloy alteration products, all the elements more oxidable than silver, such as lead and tin, present decreasing concentration gradients from the interior to the surface, where their contents are the lowest, as happens for the copper. Gold will have a compositional gradient increasing to the surface of the coins caused by its diffusion to near-surface areas free of stresses, being present as an enrichment just under the surface in almost all the coins, (Condamin, J. and Picon, M., 1965).

After digging, the archaeological hordes of coins usually much corroded due to long time burial are in most cases subject to conservation treatments with the purpose of preservation and to allow numismatic characterization. Also, the numismatic collections in museums can be treated in order to present the metallic shine of silver and to remove layers of tarnishing. For high silver alloys, previous chemical conservation treatments corresponding in practice to a blanching process have been considered as having an irrelevant influence in the alteration of the silver surface composition of coins, when compared with results obtained on coins not subjected to chemical treatments (Kantarelou, V. *et al.*, 2011). Carter, G., 1964, found lead as being generally the only element along with copper that could be influenced by a nitric acid cleaning of silver coins surface. In addition, modern sterling silver coins treated with ammonia or tartaric acid did not show significant changes in the copper content after a blanching treatment (Zwicky-Sobczyk, C.N. and Stern, W.B., 1997). In contrast, the consequences of blanching are especially important for copper-rich silver alloys (Beck, L. *et al.*, 2008).

1.7 | The analytical question of European and *New World* silver provenance

The differentiation of silver alloys chemical composition used in European and American minted coins, namely from Spain, France, England, Potosí, Lima and Mexico, has been investigated by several authors (Gordus, A. *et al.*, 1972; Gordus, A. and Gordus, J., 1988; Stallard, B.W., 1988; Guerra, M.F., 1990; Le Roy Ladurie, E. *et al.*, 1990; Barrandon, J.-N. *et al.*, 1992; Guerra, M.F., 2004 and 2011; Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012; Desaulty, A.-M. and Albarède, F., 2013) with the purpose of dating the arrival of American silver on the European continent and of characterizing silver from different sources. In this context, ingots saved from shipwrecks of Spanish ships responsible for global circulation of silver during the 16th-17th centuries (Armstrong, D.R., 1993; Gordus, A.A. and Craig, A.K., 1995) and coins collected on the West coast of Australia from two Dutch ships sunken during the 17th and 18th centuries (Gentelli, L., 2012), have also been investigated. The available data of ingots chemical composition analysis are, however, of little use and could not be related with other published data.

1.7.1 Minor and trace elements analysis approach

The presence in European minted coins of *New World* silver inflows and the identification of their geographical origin, Mexico and Peru (Lima and Potosí), have been studied by elemental chemical composition analysis methods based on the determination of the minor and trace elements which characterise the different sources of silver (Gordus, A. *et al.*, 1972; Gordus, A. and Gordus, J., 1988; Stallard, B.W., 1988; Guerra, M.F., 1990; Le Roy Ladurie, E. *et al.*, 1990; Barrandon, J.-N. *et al.*, 1992; Guerra, M.F., 2004 and 2011).

Neutron Activation Analysis (NAA) results obtained on sets of coins minted in various geographical origins had allowed to detect major, minor and trace chemical elements, present in very small amounts (ppm), characteristic of the silver alloy "signature" or "fingerprint" of the various sources of silver (Gordus, A. *et al.*, 1972; Gordus, A. and Gordus, J., 1988; Stallard, B.W., 1988; Guerra, M.F., 1990; Le Roy Ladurie, E. *et al.*, 1990; Barrandon, J.-N. *et al.*, 1992; Guerra, M.F., 2004 and 2011). This non-destructive method obtains a multielement global analysis that reflects the average composition of the coins, including the surface silver enriched layer, which, in some cases, may overestimate the determined coin silver fineness. The samples are bombarded with a neutron source that induces radioactivity in a small fraction of atoms, whose nuclei capture free neutrons entering excited states. It is possible to identify the chemical elements present in the sample through the produced activated products (radioisotopes), and through the specific γ radiation produced during their decay, being the intensity proportional to the amount of element. A variant of this technique is the thermalized fast neutron activation analysis (TFNAA) (Guerra, M.F., 1990; Le Roy Ladurie, E. *et al.*, 1990; Barrandon, J.-N. *et al.*, 1992; Guerra, M.F., 2004 and 2011), which uses a cyclotron moderated neutron beam to perform a non-destructive, multi-elemental chemical analysis of the coins.

Trace elements determination has been carried out also by Proton Activation Analysis (PAA) (Guerra, M.F., 2004). As the designation of this technique implies, the analysis consists of irradiating coins with a proton beam produced by a cyclotron, being the method also based in the production of nuclear reactions and in the production of radioisotopes which are measured by γ spectrometry after irradiation. It is also a non-destructive analysis technique that gets, however, multi-elemental semi-global results.

The main limitations of these methods are the need of access to a nuclear reactor, or to a cyclotron, the presence of radioactivity in the sample for long periods of time, and the low sensivity of some relevant elements for the study of silver alloys, such as bismuth and lead, which can be present in coins with a global content up to 1-2 %, and whose activated products do not present enough radioactivity to be quantified. Also, in the case of analysis carried out on micro-samples taken from the coins (Gordus, A. *et al.*, 1972; Gordus, A. and Gordus, J., 1988), the data may be less representative of the original alloy, as would be much more influenced by the surface silver enrichment originated by copper depletion in the subsurface region.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has been used in recent years to characterize the silver alloy composition of some coins belonging to the 17th – 19th centuries minted with South American silver (Guerra, M.F., 2004), based on trace elements contents, and has allowed to discriminate the chemical compositions of marine corroded coins sets minted in different geographies from Europe and America, dated namely from the 17th century (Gentelli, L., 2012).

1.7.1.i) Gold impurities in silver

In 1972, Gordus, A. et al., published some NAA results obtained in micro samples taken from European and South American silver coins with the purpose to discriminate the different geographical origins of silver, and to determine and chronologically date the Potosí silver introduction in the coins minting's from countries such as Spain and France. His approach was based on the existing ratio between the gold content and the silver content in the coins, unchanged by the process of silver beneficiation and/or refining, as a differentiation provenance criterion of the various origins. A gold in silver content <0.010 % identifies the Andean silver from Potosí distinguishing it from the Mexican silver or the silver circulating in Europe. However, the presence of a similar gold impurity content in Mexican and European silver, >0.015 %, had not allowed to differentiate these two silver sources on European minted coins, based only on this trace element.

Later, Gordus, A. and Gordus, J., 1988, reported an impurity mean value of gold in silver of 17 ppm, obtained also by NAA in 38 Andean silver coins belonging almost globally to the *Felipe II*, *Felipe III* and *Felipe IV* of Spain chronologies, which clearly differentiates these coins from the European, Mexican and Islamic coins minted prior to the discovery of Potosí. All but three of these coins, two Bohemia thalers of 1548 and a Hungarian coin of 1544 that show very low levels of gold impurity possibly resulting from a low gold silver source located in the Bohemia region in Central Europe (Joaquimsthal), featured gold in silver contents higher than 0.02 %. Figures 1.7 and 1.8 present the summary of results.

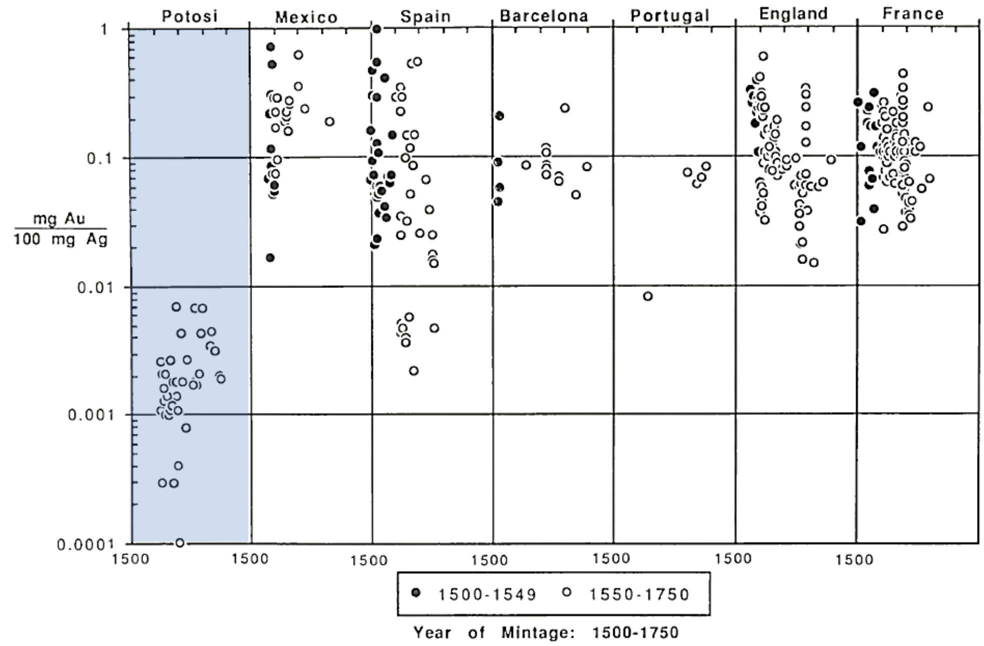

Figure 1.7 – Gold in silver impurity content in Potosí, Mexican and European silver coins. Adapted from Gordus, A. and Gordus, J., 1988.

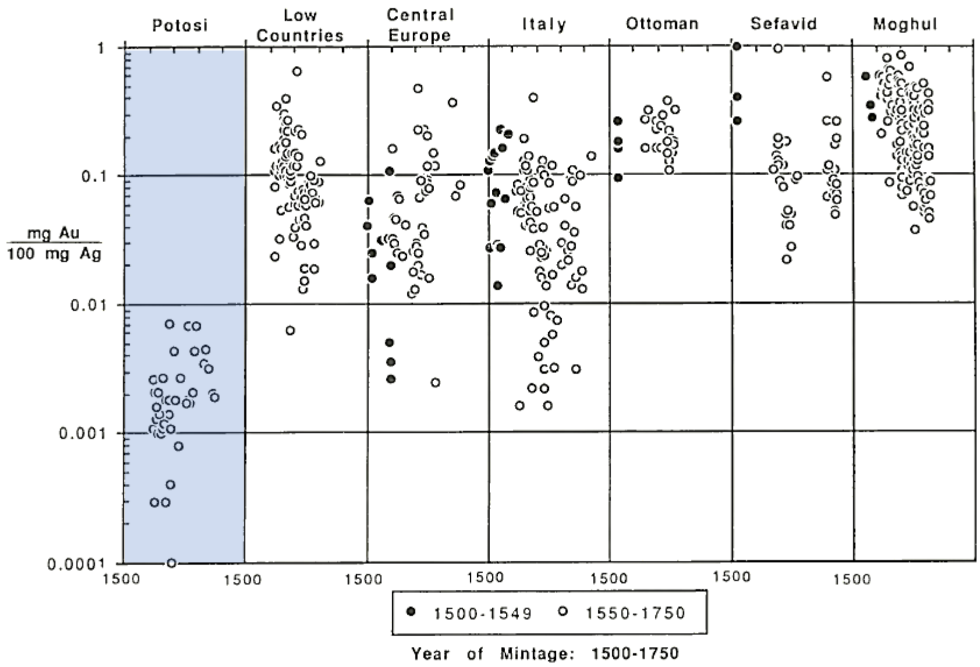

Figure 1.8 – Gold in silver impurity content in Potosí, European and Islamic silver coins. Adapted from Gordus, A. and Gordus, J., 1988.

Through the elemental composition analysis of the coins minted after the discovery of the Potosí mines during the affluence period of the Andean silver to Europe between 1556 and 1665, that occurred in majority during the reign of *Felipe II* of Spain (1556-1598) but also in the following kingdoms, it was possible to verify that the Potosí's silver is present in just a small amount in the European minting's. Only a small fraction of the coins minted in Spain, Portugal, Flanders, Italy, and Germany was produced with purely Andean silver, persisting the historical issue of the absence of Potosí's silver in the English minting's.

The fact that the coins minted after 1550 in European countries like France do not show evidence of Potosí silver, led Gordus, A. *et al.*, 1972, to consider that Andean silver will have entered in restricted quantities in the minting workshops of these country's or under the form of currency. Also, the Ottoman (Turkey), Sefavid (Iran, Afghanistan) and Moghul (India) coins, from places historically considered as American silver trading locations do not revealed the presence of pure Andean silver.

The elemental composition analysis of the coins minted in Lima, the older Andean mint funded in 1565 with the first coin minted 1568 (Chamot, E.D., 1988), are scarcer in the literature. Stallard, B.W., 1988, published a graph (Figure 1.9) where lists and compares the gold in silver contents obtained by Gordus, A. and Gordus, J., 1988 by NAA on coins minted during the second half of the 16th century in Potosí, Lima, and Mexico, and minted during the reign of *Felipe IV* of Spain in Colombia in the mid-17th century.

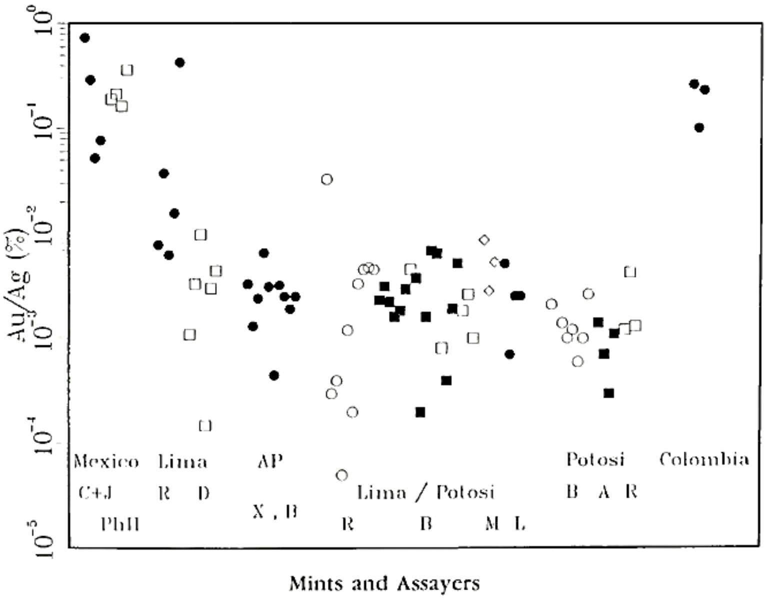

Figure 1.9 – Comparison of the gold in silver contents of coins minted in Mexico, Lima, Potosí, and Colombia. The different symbols labelled in the bottom of the chart area, are related to different assayer's letter marks. Adapted from Stallard, B.W., 1988.

With reference to Figure 1.9, the first coins from Lima and marked with the assayer Alonso Rincón R letter, have Au/Ag contents above the maximum value of 100 ppm established by Gordus, A. and Gordus, J., 1988, being about 10 times higher than the average content of the coins minted with Potosí silver, being thereafter not minted with silver from this later provenance. It should be noticed that Potosí silver has a gold content 10 to 100 times less than the Colombian and Mexican silver (Stallard, B.W., 1988).

In resume, the analysis based on the gold content in silver did not allowed to distinguish the European silver from the Mexican silver where gold contents are of the same order of magnitude, nor to identify coins produced in Europe with mixtures of European and South American silver or to deepen the knowledge of the American silver introduction and dissemination in Central Europe. However, the results revealed the existence of European coins made certainly with an Andean pure composition, mainly from Italy and from Spain, which occurred during the reign of *Felipe II* of Spain (1556-1598).

1.7.1.ii) Gold and indium contents

To discriminate the silver alloys of various geographical origins, Guerra, M.F., 1990, Le Roy Ladurie, E. *et al.*, 1990 and Barrandon, J.-N. *et al.*, 1992, analysed the minted coins made, in the great majority, in various timelines of the 16th to 18th and belonging to differentiated monetary workshops, as Potosí, Lima, Mexico, Spain, France, and Flanders. The geological knowledge pertaining to Andean silver ore allowed them to identify the indium and germanium as discriminant elements that characterize this ore. Unable to determine the germanium through global activation methods due to the difficulty of determining this element by a non-destructive analysis when present in ppm contents, they investigated the content of the indium in coins of various geographical origins during several minting periods, correlating it with the gold content.

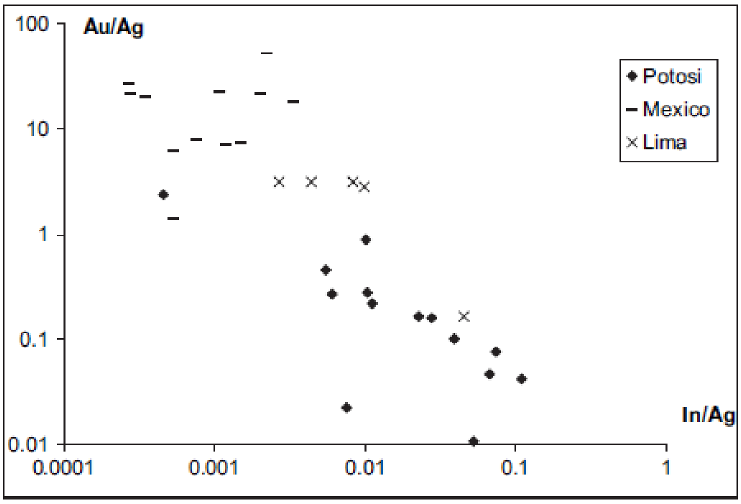

Figure 1.10 – Ratio of indium and gold (in ppm) in relation to silver content (in percentage) measured by TFNAA, for the coins minted in Potosí (16th, 17th and 18th centuries), Mexico (16th century) and Lima (17th and 18th centuries). Only one of the coins minted in Lima in the 17th century is produced with pure Andean silver. From Guerra, M.F., 2004.

The development of an NAA method with moderated fast neutrons in a graphite system allowed to determine this element "… present in the coins of Potosí in contents in the order of 10 ppm in relation to silver, being completely absent from the composition of Mexican and Spanish coins minted in the late 15th century and early 16th century" (Guerra, M.F., 1990, pp. 358) , and present in very low contents in the order of 0.1 ppm in the French coins from the 2nd and 3rd quarter of the 16th century. The indium was then considered as a typical Andean trace element, which together with the gold allows to discriminate Andean silver from Mexican Silver (Figure 1.10), and to identify the Potosí silver arrival in Europe through Spain (Figure 1.11).

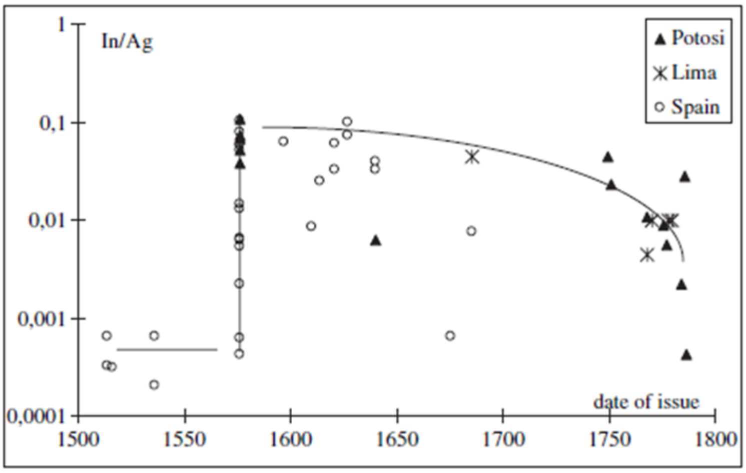

Figure 1.11 – Ratio of In content (in ppm) in relation to Ag content (in percentage) measured by TFNAA, for the silver coins minted in Potosí, Lima and Spain according to the mint date. From Guerra, M.F., 2004.

Despite the impossibility of accurately dating the arrival of Potosí silver to Spain due to the absence of a minting inscription date in the Spanish coins, the previous authors related the In/Ag ratio evolution with the American mines production during the various minting periods in Spain and Potosí, to point out a date for this occurrence during the reign of *Felipe II* of Spain, between 1565 and 1570 (Figure 1.11).

However, these authors (Guerra, M.F., 1990; Le Roy Ladurie, E. et al., 1990; Barrandon, J.-N. et al., 1992) could not distinguish the European silver from the Mexican silver based on the correlation analysis of the indium and gold contents, once they consider that there is no specific trace element for discrimination and introduce also the existence of "mixtures" of Potosí silver with European silver.

In case of the coins minted in Spain, the former research had identified three distinct silver alloys (Figure 1.12 (Left)), respectively differentiated by:

- a high gold content and a low indium content, in coins minted by *Felipe II* of Spain and also from chronologies prior to this reign, produced with silver just from the "European continent";

- a low gold content and a high indium content, with a composition representative of Potosí's silver, identified in coins minting's of *Felipe II* and *Felipe III* of Spain; and

- a high level of gold and indium, existing in coins minting's of *Felipe II* and *Felipe IV* of Spain, attributed to "mixtures" of Potosí's silver with European silver.

These analyses identified the existence of several coins minted only with Potosí silver during the reign of *Felipe II* of Spain (1556-1598), as Gordus, A. et al., 1972, determined before only through the gold content present in silver, but from these coins only one, minted in 1597 at the end of the former monarch reign, could be accurately dated.

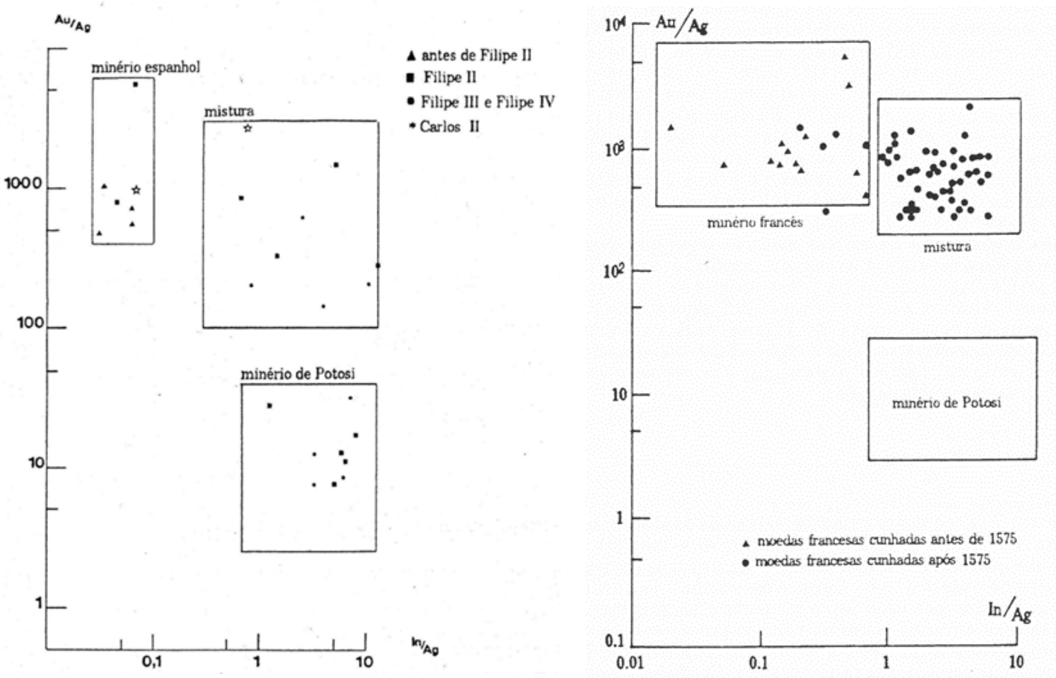

Figure 1.12 – Graphical representation of Au/Ag and In/Ag for the coins minted in (Left) Spain, and (Right) France. From Guerra, M.F., 1990.

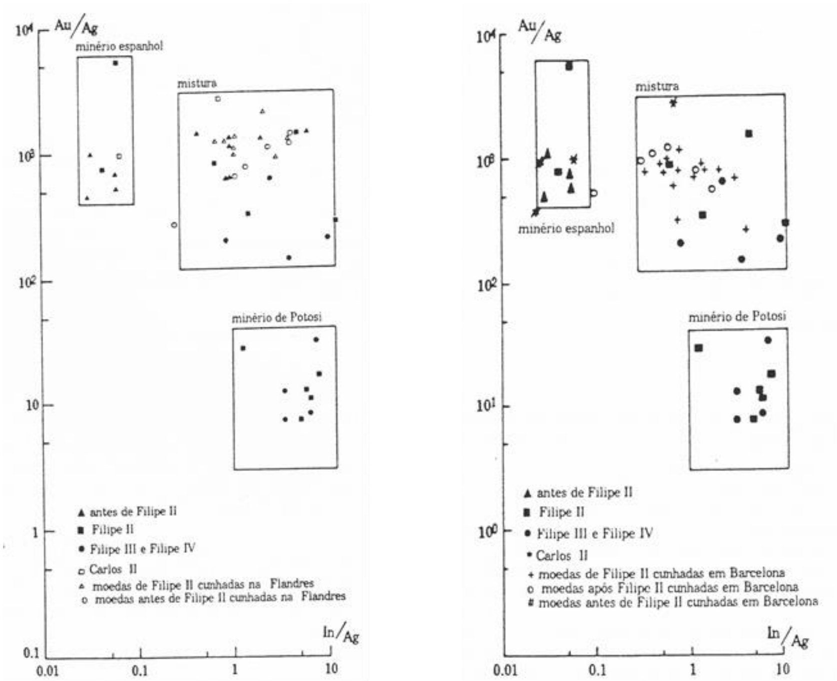

Figure 1.13 – Graphical representation of Au/Ag and In/Ag for the coins minted in (Left) Spain and Flanders, and (Right) Spain and Catalonia. From Guerra, M.F., 1990.

For France, where the minting date is inscripted on the coins since 1549 and the coins have the monetary letter that identifies the location where they were minted, the authors distinguish two groups of coins based on the analysis results (Figure 1.12 (Right)): one minted before 1575 with "European silver" with high gold content and low indium content, and another one minted after

1575, with alloys that also exhibit higher indium contents, referred to be made of a mixture of European and Andean silver. Coins minted exclusively with Potosí's silver were not found in France.

The analysis results of the coins minted in Flanders (Guerra, M.F., 1990) show that during the 16th century the coins produced at the various mints of this territory have a composition resulting from the "mixture" of Potosí's silver with European silver, with no coins produced exclusively with pure Potosí silver (Figure 1.13 (Left)). However, in dates earlier to the reign of *Felipe II*, prior to the arrival of Andean silver in Europe, there exists already high percentages of indium in coins minted in Flanders, said to be originating from an existent association between this element and the copper. As mentioned above in Chapter 1.5, silver mining regions from the North of Europe, as Freiberg, Bohemia and Joachimstahl, for instance, have indium in their ores metallogeny (Casard, D. *et al.*, 2008; De Vos, W. *et al.*, 2017). This, together with the fact that the coins minted in Flanders clustered in the same location of the referred chart, regardless of their minting dates prior or after the arrival of American silver to Europe, open questions about a clear or strong Potosí and European silver mistures identification based only in the mentioned elements correlations.

Contrary to Spain, Catalonia have not minted coins with a purely Andean silver composition (Figure 1.13 (Right)), and as occurred in France and in Flanders, the coins are referred to have been minted with a mixture of this silver with European silver (Guerra, M.F., 1990; Barrandon, J.-N. *et al.*, 1992).

In resume, these investigations consider the indium and the gold as silver discriminating elements and like the previous studies, have not achieved a differentiation between the Mexican and the European silver. This approach also considers the existence of European silver and Potosí silver mixtures resulting from a massive input of the Potosí silver in Europe, particularly in Spain and France, and does not consider the contribution of Mexican metal in European minting's.

1.7.1.iii) Gold correlations with antimony and tin

Guerra, M.F., 2004, reports that the gold and antimony contents differentiate the silver composition of the coins minted in Potosí, with low gold and high antimony contents, and in Mexico, with high gold and low antimony contents (Figure 1.14). In the case of Potosí, the analysis is based on coins minted from the 16th century to the 18th century, and for Mexico, all coins except for two, refers to 16th century minting's.

The Portuguese coins minted in Brazil at the end of the 17th century (1695-1698) form a group of distinct composition between Potosí's silver and Mexican silver, together with two coins minted in Portugal during the reign of Afonso VI (1656-1683). Three other coins from this monarch also minted in Portugal are in the group of Potosí's silver compositions (Guerra, M.F., 2004), showing that in the second half of the 17th century after the decline felted from 1640 in Andean silver production, this silver was still present in the Portuguese coins. Acording to Marsilio, C., 2015, after the *Restauração* of 1640 the main part of the monetary production depended on a massive operation of melting and re-minting de Spanish silver money that was still legally in circulation on the Portuguese monetary circuit. Have these coins resulted from this action?

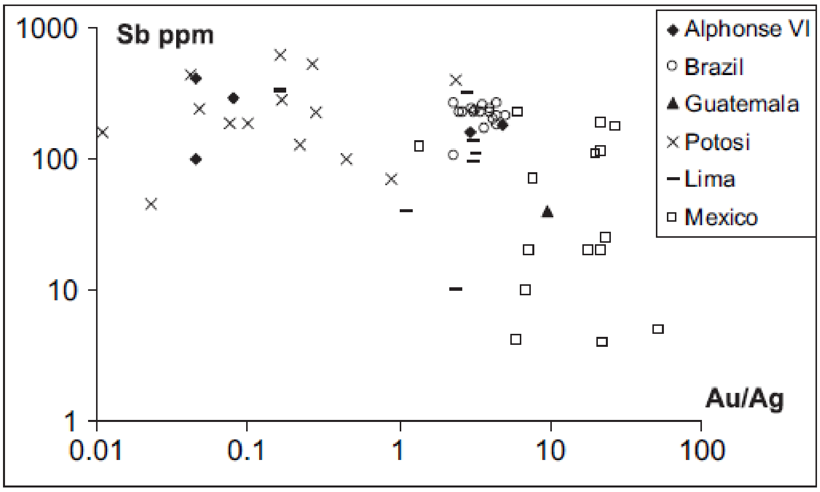

Figure 1.14 – Ratio of Au (ppm)/Ag (%) in relation with Sb content (ppm). Taken Guerra, M.F., 2004.

Guerra, M.F., publishes also in 2011 another graph (Figure 1.15, with wrongly exchanged axis titles) correlating the composition of coins from Potosí, Lima, Mexico and Spain based in the existing relationship between the Au/Ag and Sb contents. This data could suggest that the Spanish minted coins would have contributions from both origins of American silver, existing coins with purely Andean silver and with purely Mexican silver and reinforces the concept of "silver mixtures" introduced before (Guerra, M.F., 1990; Le Roy Ladurie, E. *et al.*, 1990; Barrandon, J.-N. *et al.*, 1992).

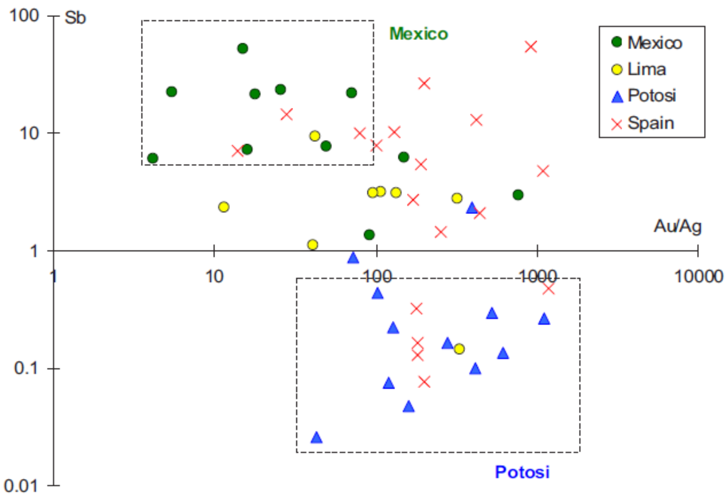

Figure 1.15 – Sb content (ppm) in relation to the ratio of Au (ppm)/Ag (%) for the coins minted in Potosí, Lima, Mexico and Spain. The axis titles are wrongly exchanged. From Guerra, M.F., 2011.

Also, for tin content (Figure 1.16) it was found a similar correlation with Au/Ag between Potosí and Mexican coins (Guerra, M.F., 2004).

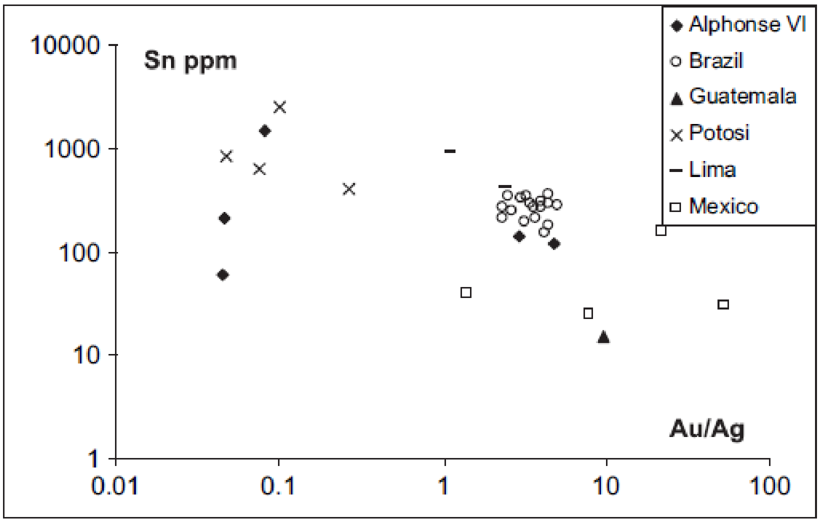

Figure 1.16 – Ratio of Au (ppm) /Ag (%) in relation to Sn (ppm) content obtained by PAA. From Guerra, M.F., 2004.

These graphs show that antimony and tin are characteristic elements of the "signatures" of the Andean and Mexican silver and possibly allow to differentiate in some extent these silver sources on the coins minted in Spain.

1.7.1.iv) Bismuth content

Bismuth content obtained by LA-ICP-MS analysis (Guerra, M.F., 2004) of a reduced number of silver coins minted in Lima (n=2) and Mexico (n=3) in the 18th-19th centuries, and in Portugal (n=5) during *Dom Afonso VI* reign (1656-1683) present extremely low ppm contents, between 0.0002-0.0045, 0.14-0.34 and 0.01-0.19 respectively. The American silver data, albeit indicative, are not representative of the chronological period under review on this thesis (15th-17th centuries), once the analysed silver metal is not originated from contemporary extraction sites of the investigated period and may represent different mineral deposits and/or different zonings or metallogeny events. As mentioned in the previous point, Portuguese silver data could had been influenced in this period by the occurrences verified in the monetary circuit.

1.7.1.v) Global elemental composition analysis

Gentelli, L., 2012, correlated the elemental chemical compositions of 306 coins recovered from four shipwrecks off the western coast of Australia, minted in nine different locations of Spain, and in Mexico, Lima, Potosí, Guatemala and Santa Fe de Bogotá, of various chronologies from 1621 (*Felipe IV* of Spain) and extending to 1813 (Joseph Napoleon).

In order to clearly identify the minting geographical location of any coin recovered from the shipwrecks, the elemental composition was investigated by LA-ICP-MS, though in corrosion modified layers, and the different minting locations were identified based on the trace elements contents correlation. The data were further processed by statistical techniques, such as Principal

Component Analysis (PCA), and Linear Discriminant Analysis (LDA), to clarify the elements correlations.

LA-ICP-MS average data for the various minting's allow differentiating the Mexican silver from Potosí's silver. However, it is not perceived from the investigated chronologies, after 1621, the extension with which the European silver was present in peninsular Spanish minted coins, but it seems that Madrid and Seville had used silver alloys that approximate better the Potosí's contents. Figure 1.17 shows that:

- Mexican silver presents smaller As, In, Sn and Sb contents, when compared with Potosí's silver;

- in these two silver sources, the Au content seems to be greater in Mexican silver and the Bi content is also slightly larger;

- Potosí minting's present important values of Bi in the analysed chronologies;

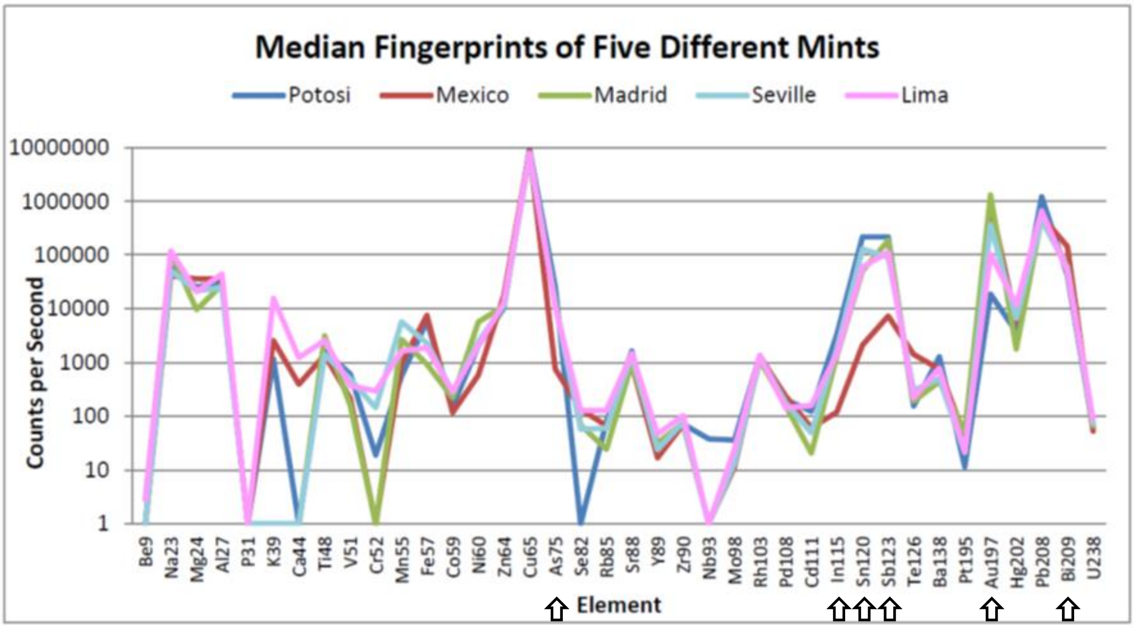

Figure 1.17 – LA-ICP-MS average results obtained on coins from Potosí, Mexico, Madrid, Sevilla and Lima. From Gentelli, L., 2012.

- the coins minted in Lima, have an Au content higher than the values obtained for Potosí, but the other previously referred elements reach similar contents levels as in Potosí's composition; and

- Madrid and Seville coins, present compositional analysis similar to Potosí's silver with the exception of Au content.

Also, PCA statistical analysis of the coins minted in colonial Spain, particularly from Potosí and Mexico, had differentiated these two sources based on the chemical elements Sb and As, more present in Potosí's silver, and Pd, Pt and Au, more present in Mexico's silver, in agreement with the previous studies from other authors. Based on results dispersion, Gentelli, L., 2012, mentions the existence of important compositional variations in the silver originating from each of the locations of Potosí and Mexico, which derived probably from silver metal obtained from different silver ores mined from different locations over different timelines.

The total number of coins minted in Spain, Mexico and Potosi could also be differentiated by LDA statistical analysis based on their global elemental composition. Also, the various geographical origins of American colonial Spain, as Guatemala, Lima, Potosí could be differentiated, showing that the silver from each of these sources has an elemental composition constituting a specific "signature". However, this statistical analysis was not able to differentiate the coins produced in the different Spanish Mints, as Cadiz, Madrid, Segovia, Sevilla, which possibly used the same silver alloy coming from the same silver source.

Also, the silver minted in each peninsular Spanish chronological period present a clear temporal differentiation, possibly related with differences linked to the metallurgical procedures and to the evolution of the monetary production processes and technology verified along the times, beyond the used silver sources.

For this thesis, the interest of Gentilli, L., 2012, investigation lies particularly in the 125 coins minted at the time of *Felipe IV* (1621-1665), from the ship Vergulde Draeck sailing for the Dutch East India Company and sanked in 1656. The coinages, except for two coins, were executed in their clear majority in Potosí and Mexico, being the remaining from the Mints of Seville, Madrid and Segovia.

1.7.2 Notes on minor and trace elements approach

The NAA approach to determine silver origin based on minority and trace elements analysis, has been directed to the elemental composition determination of the coins, particularly the fineness, and to the correlation of some chemical elements contents which have allowed coin grouping and differentiation of geographic locations of monetary production. However, these analyses are not suitable *per si* to investigate the elemental composition, since they do not determine two important discriminating elements, lead and bismuth, important to distinguish different origins of silver (Pernicka, E., 2013).

Mineral deposits formation is determined by the geology of a region, being the deposits diverse in each different location. The investigations carried out to date are based on the research of groups of coins that are chronologically distributed along extensive time periods, whose metal inevitably reflects different mineralogical events resulting from existing geological variations, in time and on the territories, in each of the considered different geographic locations.

Until now, there is no individualized composition investigation of (i) the several contemporary colonial mining sites in Potosí and New Spain that differently contributed to silver ore exploration and beneficiation, of (ii) local monetary production and local metal circulation, or of (iii) the metal flows to Europe. Hence, the correlations found between the different chemical elements contents and proposed by the abovementioned investigations, attained on the coin minting's of each of the various origins, are necessarily influenced by a greater dispersion of the data that could mask possible specificities of each geological formation and each epoch. They should not be considered as representing *per si* the "original signature" of the contemporaneous metal compositions, mined and extracted in the various locations at the same time of coin production. For example, many different local sources of silver were identified in Potosí in the same ore deposit, and Potosí's Mint had processed silver besides Potosí also from Porco and Oruro regions, occasionally from Cerro de Pasco, and from other mines as Sicasica (1600), Tatasi (1612) and Padua (1652) from Potosí district, that registered their production in Potosí (Garner, R.L., 1988). Also, in Mexico, there was a contribution from several mining camps to the global amount of metal that was transformed in silver coins or silver ingots (Garner, R.L., 1988).

On the other hand, some of the former investigations are centred on the discovery of Potosí's silver and do not consider other relevant historical events, such as the beginning of American silver sending's to Europe, from Mexico and Peru, initiated in the 1530's, and the discovery, arrival and circulation of Mexican silver in the European context before Potosí's silver. For this reason, the results of elemental compositional analysis of European coins from the first half of the 16th century should not be understood as unequivocally representing results of monetary silver productions from European origins, devoid of any contribution of Mexican silver.

From the previous studies, Potosí's silver analyses are readily distinguished from other geographical origins being characterized above all by the extremely low levels of gold, which remained unchanged by the smelting and cupellation processes, differing from the Mexican coins by its high contents of indium, antimony, tin and arsenic. So far, the coins minted with silver merely from this source seems to represent a very small fraction of the coins minted in the European context, having been found in Spain, Italy, Portugal, Flanders and Germany. In the case of Germany, the existence of low-Au coins minted in dates prior to the Potosí ore discovery advises further investigation.

1.7.3 Isotopic analysis approach

From a geological point of view, the existing relationships of coins trace elements abundances have been considered as having a small correspondence with specific geological contexts or with the minerals from which they originated. In this sense, the lead isotopes are understood as a far superior characterization tool of metal artefacts, namely the metal constituting the coins, having a chemical "fingerprint" that could allow the identification of ore provenance and in some cases, to rebuild the old economic circuits. This approach is supported on the fact that the lead isotopes ratios varies from mineral deposit to mineral deposit, being these isotopic variations closely linked with the geological history of the places and of ores, and that this "signature" is not affected over time or by environmental actions, being not modified by metallurgical processes (Polard, A.M. and Heron, C., 1996; Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012; Pernicka, E., 2013). However, subsists the question of the uniqueness of an isotopic signature of a specific ore. Since a metal could be obtained from an ore consisting of an aggregation of different metalliferous minerals or of mixtures of different mineral types from the intended metal, there may be differences between the data obtained today on an ancient metal and the present-day mineralogical constitution of its ore (Polard, A.M. and Heron, C., 1996).

The isotopic variation determination of elements such as lead, and more recently, silver or copper, linked to the geochemical distribution and ore genesis, and the use of isotope ratios of these elements, have constituted a tool capable of providing information about the isotopic signature of specific coins minting's and to correlate different silver provenances (Ponting, M. *et al.*, 2003; Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012; Desaulty, A.-M. and Albarède, F., 2013; Butcher, K. and Ponting, M., 2014), identifying trends and discriminating differences between processes and production centres, *i.e.*, between minting's and geographies.

The information on the silver ore's lead isotopes compositions, especially the galenas from several mines and geographies, has been collected (Stos-Gale, Z.A. *et al.*, 1996; Santos Zalduegui, J.F. *et al.*, 2004; Scaife, B., 2011) and used in provenance studies of silver coins (Stos-Gale, Z.A., 2001; Guénette-Beck, B. and Serneels, V., 2010) and silver archaeological artefacts (Véron, A. and Le Roux, G., 2004; Guénette-Beck, B. and Serneels, V., 2010), having been constructed lead isotopes databases specifically designed for archaeological purposes (Stos-Gale, Z.A. and Gale, N.H., 2009).

Although of undeniable quality, these databases do not always identify the mineral nature, for example, if is a copper, silver, lead or polymetallic mineral, and the mineral deposits complexity is still poorly studied (Guénette-Beck, B. and Serneels, V., 2010). The available data are not, however, unique data, since many mines and mining regions may have very close isotopic lead signatures, sometimes identical, and the trace elements analysis will allow to distinguish between various objects (Guénette-Beck, B. and Serneels, V., 2010).

The archaeometric provenance studies usually determine and correlate the ratios of the radiogenic Pb isotopes obtained in the objects, ^{206}Pb, ^{207}Pb e ^{208}Pb, respectively caused by radioactive decay of ^{238}U, ^{235}U and ^{232}Th, and of the stable ^{204}Pb isotope, without progenitor, with the ratios of minerals from a specific geographical location. Due to the difficulty in measuring the ^{204}Pb resulting from its little abundance, the prevailing graphics are based on ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb (*e.g.*, Ponting, M. *et al.*, 2003; Polard, A.M. and Heron, C., 1996; Véron, A. and Le Roux, G., 2004; Stos-Gale, Z.A. and Gale, N.H., 2009; Butcher, K. and Ponting, M., 2014) being the results more difficult to relate with the ore geological history and origin (Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012). The isotopic compositions ratios of various archaeological artefacts have been compared between the individual objects, or with data relating to historical and ancient mines, in cases where these are known (*e.g.*, Stos-Gale, Z.A. *et al.*, 1996; Stos-Gale, Z.A., 2001; Stos-Gale, Z.A. and Gale, N.H., 2009; Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012), and this comparison may be successful in many cases.

Recently, other discrimination possibilities of the "signatures" from various silver sources have been presented (Desaulty, A.-M. *et al.*, 2011; Desaulty, A.-M. and Albarède, F., 2013) through the isotopic copper composition, δ^{65}Cu, based on the deviation found between ^{65}Cu e ^{63}Cu stable isotopes measured on coins and on a standard, as well as through the silver isotopic composition, ε^{109} Ag, based on the deviation found between the natural isotopes ratio of ^{109}Ag e ^{107}Ag, measured also on coins and on a standard.

In a geochemical information perspective, a different approach of the techniques commonly used in the "fingerprint" determination based on comparison of lead isotopic ratios obtained on ore samples or artefacts, considers the ratios measurements used in archaeometry, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb and ^{204}Pb/^{206}Pb, as not being the ideal method to make a geological or geochemical assignment about the metal provenance (Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012; Desaulty, A.-M. and Albarède, F., 2013), once with these ratios magmatic and mineral modern provinces tend to form correlations with very narrow alignments that overlap with a very limited resolution (*e.g.*, Blichert-Toft, J. *et al.*, 2005). In this approach, the lead isotopes ratios are related to several independent parameters, such as the model age T of the tectonic province where the minerals were formed and can distinguish geologic provinces based on their $^{238}U/^{204}Pb$ (μ) and $^{232}Th/^{238}U$ (Κ) ratios, which are two characteristic parameters of metal sources, the μ and Κ ratios. The μ ratio is a measure of how U and Pb have separated over time in each geological province and Κ reflects the province dynamic history where the minerals are found. These ratios distinguish between geological formations with respective high and low values and can discriminate segments within the geological provinces. The tectonic lead model age T is a geochemical measure of the tectonic formation age of the provinces where the minerals have originated derived from lead isotopic ratios, and has been useful to distinguish and identify the geological origins of the various ores, as for example, the oldest Hercynian basement with the silver mines from central Europe (> 250 Ma), the Potosí and Mexico regions of colonial Spain (20-130 Ma) or the southern Spain region with very recent ages (20 Ma).

These three parameters allow to determine a "fingerprint" of each geographical area of production of silver coins, as is for example the case of Potosí's and Mexican silver, are relevant for the understanding of a specific ore evolution, and can be used in provenance studies or in other archaeometric investigations, even in the absence of the isotopic data of the referenced ores (Albarède, F. *et al.*, 2012).

1.7.4 Lead, silver and copper isotopic compositions, geological model ages, $^{238}U/^{204}Pb$ (μ) and $^{232}Th/^{238}U$ (Κ) ratios

1.7.4.i) Europe versus America

In a geological provenance perspective based on $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ ratios (Figure 1.18), Desaulty, A.-M. *et al.,* 2011 determined the Pb, Cu and Ag isotopic compositions from coins minted in Antiquity (Greek, Hellenistic, Roman and Middle East), Spain, and medieval Europe, which were correlated with the same data from Mexican and Andean coins from the 16th-18th centuries.

The $^{206}Pb/^{204}Pb$ ratios from the seven European medieval coins from Bohemia, Hungary and France, as well as from the eight medieval Spanish coins minted prior to the Catholic monarchs, are lower than 18.5, indicating a provenance from ores of the Hercynian basement of Eastern Europe (~ 300 Ma). The eight pre-colonial Spanish coins from the Catholic Kings chronology (1479-1504), excepting one coin with the Hercynian signature, have generally higher values, > 18.6, approaching the values found on the Betic geological province, in Spain, with younger tectonic ages (~ 20 Ma). The ratios of the coins minted in colonial Spanish America, generally higher than 18.6, discriminate the eight Mexican coins from the ten Potosí coins, showing that they were minted with silver belonging to younger geological formations (< 130 Ma) overlaying therefore the ratios from the Aegean (n = 24 coins) and from the pre-colonial Spanish coins of the Betic Cordillera.

These $^{206}Pb/^{204}Pb$ ratios are similar in the case of the younger geological provinces, and do not allow to differentiate, for example, the Catholic Kings Spanish coins from the coins minted in the new American world.

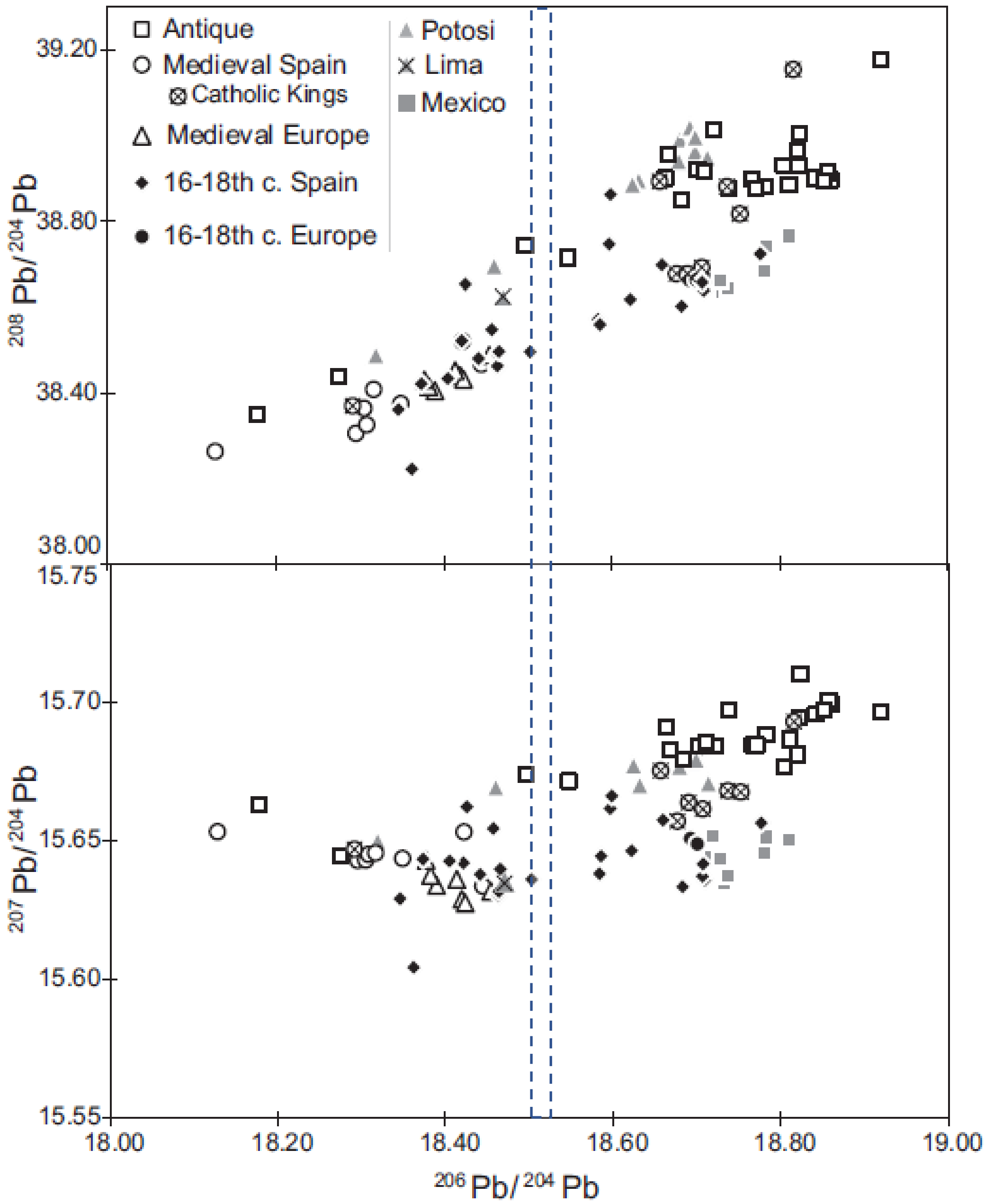

Figure 1.18 – Lead isotopic ratios of coins from Antiquity, medieval Spain and Europe, Spanish and European 16th-17 th centuries, Potosí, Lima, and Mexico. Adapted from Desaulty, A.-M. et al., 2011.

The twenty-three Spanish coins minted between the 16th and 18th centuries have $^{206}Pb/^{204}Pb$ ratios distributed over the two groups of data, <18.5 and >18.6, corresponding for the first case of coins with an isotopic composition typical of European Silver (this group comprise one coin of Charles V (1516-1555) minted in Flanders, possibly before the arrival of the American silver to the European continent). The second group of data, located on the figure closer to the Mexican coins, refers to coins minted possibly with American silver or constituted by mixtures of American and European silver.

The only two European coins of France and England, from the second half of the 16th century, have younger model ages <70 Ma and have the same isotopic signature as the Mexican coins.

$^{208}Pb/^{204}Pb$ ratios are higher on the coins minted in Antiquity, Potosí and Mexico, when compared with those of medieval Europe, and allow to discriminate also the Potosí coins, with higher values, from the Mexican coins.

The copper and silver isotopes relationship (Figure 1.19) allows to infer some of the previous relationships, grouping and discriminating the Potosí coins based on δ^{65} Cu and the Mexican and European coins prior to the 16th century based on ε^{109} Ag, and locates a great number of post 16th century European coins near the Mexican coins.

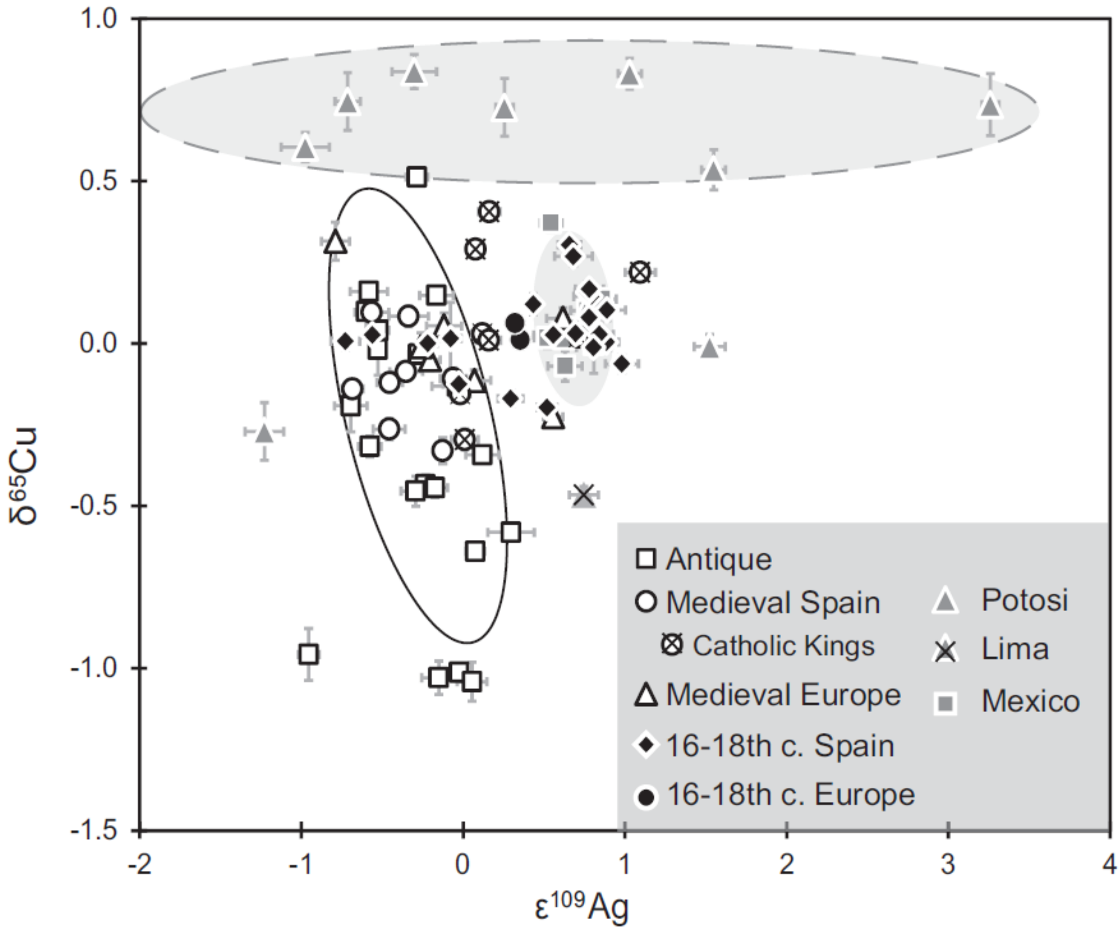

Figure 1.19 – δ^{65} Cu, in parts per 1.000 versus ε^{109} Ag, in parts per 10.000. From Desaulty, A.-M., et al., 2011.

However, this analysis does not explain *per si* the question of silver provenance, introducing the copper provenance issue also associated with the copper trade circuits, and do not obtain a clear distinction of all the coins groups, presenting a greater results variability. The addition of copper to the alloy to attain the intended silver fineness, performed in each Mint during the monetary production, could not represent also the Mint geographic location. For example, American silver bullion exported and refined in another geography will have inevitably the signature of the copper locally added on the monetary process (Desaulty, A.-M. *et al.,* 2011).

1.7.4.ii) Potosí and Mexico

Albarède, F. *et al.*, 2012 use the Pb isotopic data from existing data bases concerning the Central Andes mineral deposits and relate them with those obtained on the minted coins of Potosí and Mexico (Figure 1.20) by Desaulty, A.-M. *et al.*, (2011). Of the investigated ten coins of Potosí, only one may have been coined in the late 16th century (*Felipe III*, 1598-1621), and the remaining are from the 17^{th} (n=4) and 18^{th} (n=5) centuries. As for Mexican coins, two belong to the *Felipe II* chronology of (16^{th} century), and the others to the 17^{th} (n=1) and 18^{th} (n=5) centuries. Figure 1.20 shows that the coins isotopic ratios reflect those of the ore exploration considered regions, have a good correlation within these two geographies, and presents a lower Pb isotopic data scattering, which, according to Albarède, F. *et al.*, 2012, results from the metallurgical processing.

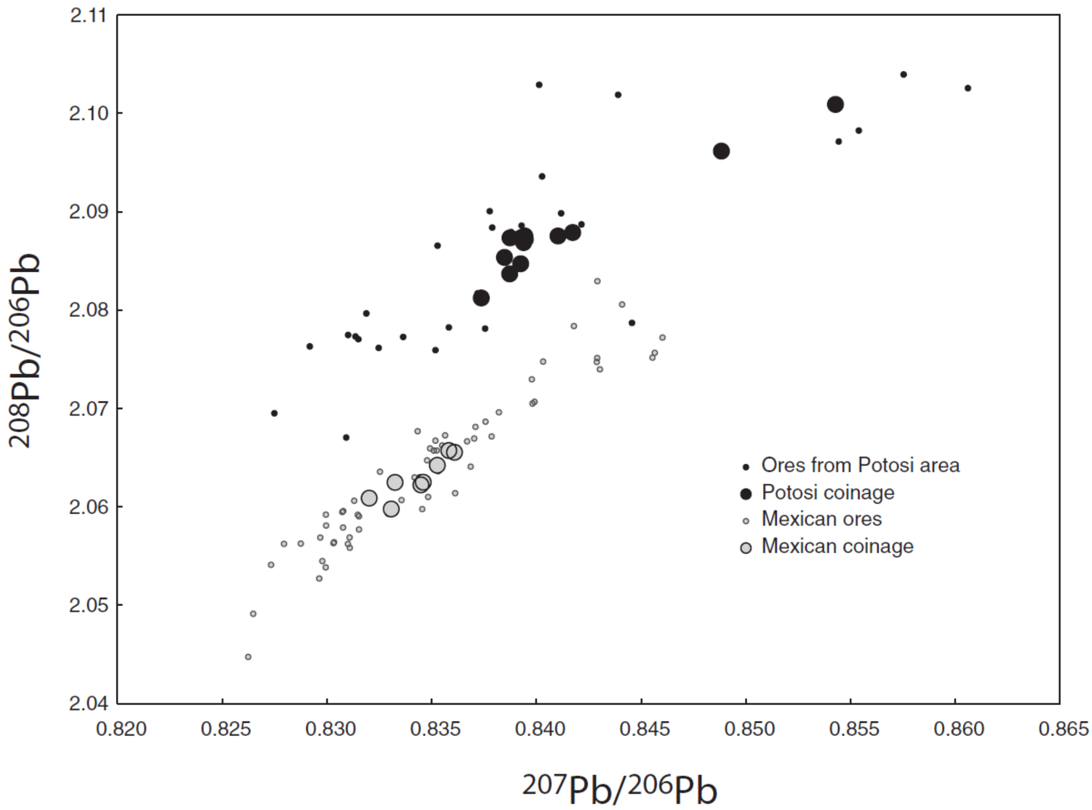

Figure 1.20 – Comparison between the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios from the coins investigated by Desaulty, A.-M. et al., 2011, minted in Potosí and Mexico and the ores from both geographies. From Albarède, F. et al., 2012.

Despite the good overall data consistency, this author refers the existence of a poor indexation for most of the Mexican ores sites regarding the determined Pb isotopic compositions, and that so far, the Pb isotopic compositions of the historic Potosí silver ores have not been measured (Albarède, F. et al., 2012). However, it is unknown if the coins resulted from one specific ore exploitation or from mixtures of numerous ores from several exploitations. The reduced isotopic ratios scattering of the coins assigned to metallurgical processing of Potosí's and Mexico's ore sources would be difficult to assess for both origins, especially without relating the isotopic data from the exploited ancient silver mines with those from the contemporary coins.

Desaulty, A.-M. *et al.*, 2011, refers that the lead isotopic composition of the coins minted in Potosí is consistent with the existing values in the literature for the deposits of Cerro Rico, Oruro, and Purku, being the ones from Cerro Pasco, a location next to Lima, clearly different.

The Mexican coins in Figure 1.20 group closely, showing that the Mexican mined sites constitute a low μ and low K lead isotopic province, younger when compared to Potosí (Figures 1.21 and 1.22). The Pb model age of Potosí's coins is older than the Pb model age of Mexican coins, being visible, in the first case, however, a contribution from an older basement (Figure 1.22).

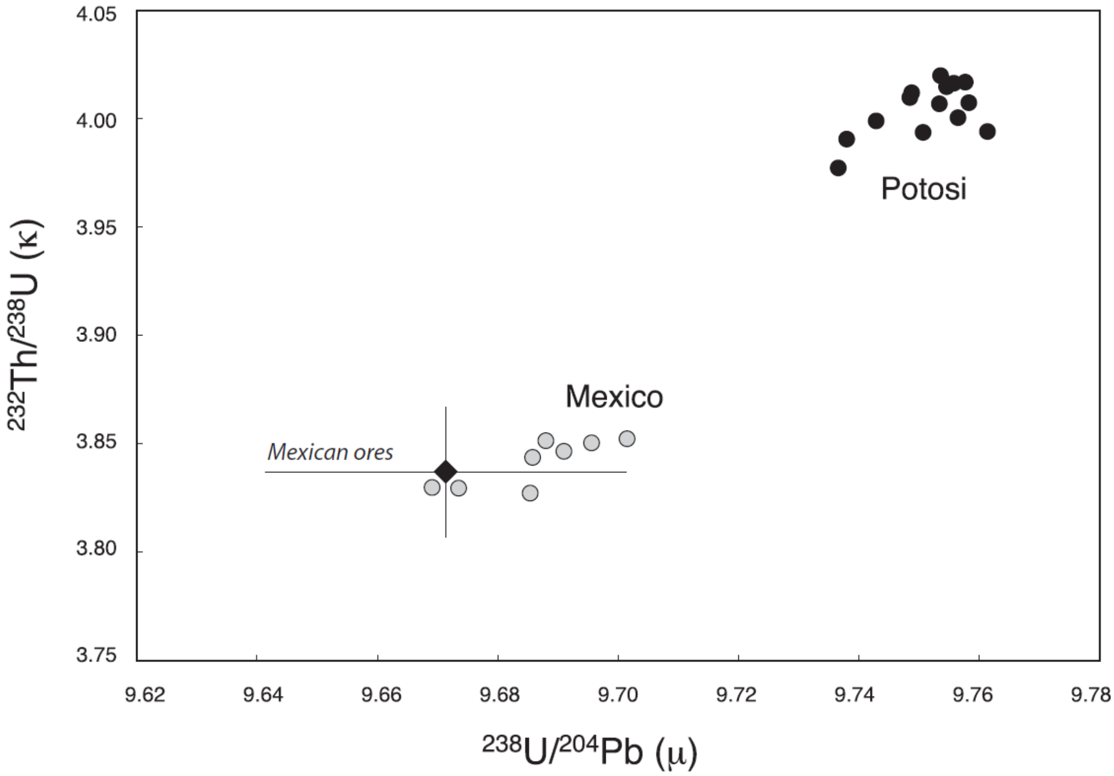

Figure 1.21 – $^{238}U/^{204}Pb$ (μ) versus $^{232}Th/^{238}U$ (K) ratios for Potosí and Mexico minted coins from 16th-18th centuries, calculated using Desaulty, A.-M. et al., 2011, data. The diamond symbol represents μ and K average values calculated for Mexican mines, and the lines represent 95 % dispersion of the data. There are no lead isotopic data for Potosí's silver mines. From Albarède, F. et al., 2012.

This latter approach obtains a good silver provenance assignment of the coins minting's from both geographic origins, with a good discrimination.

In resume, Mexican coins have low lead model ages (<50 ma) and low $^{232}Th/^{238}U$ (K) ratios, and Potosí's coins present higher $^{232}Th/^{238}U$ (K) ratios and higher lead model ages (>100 Ma).

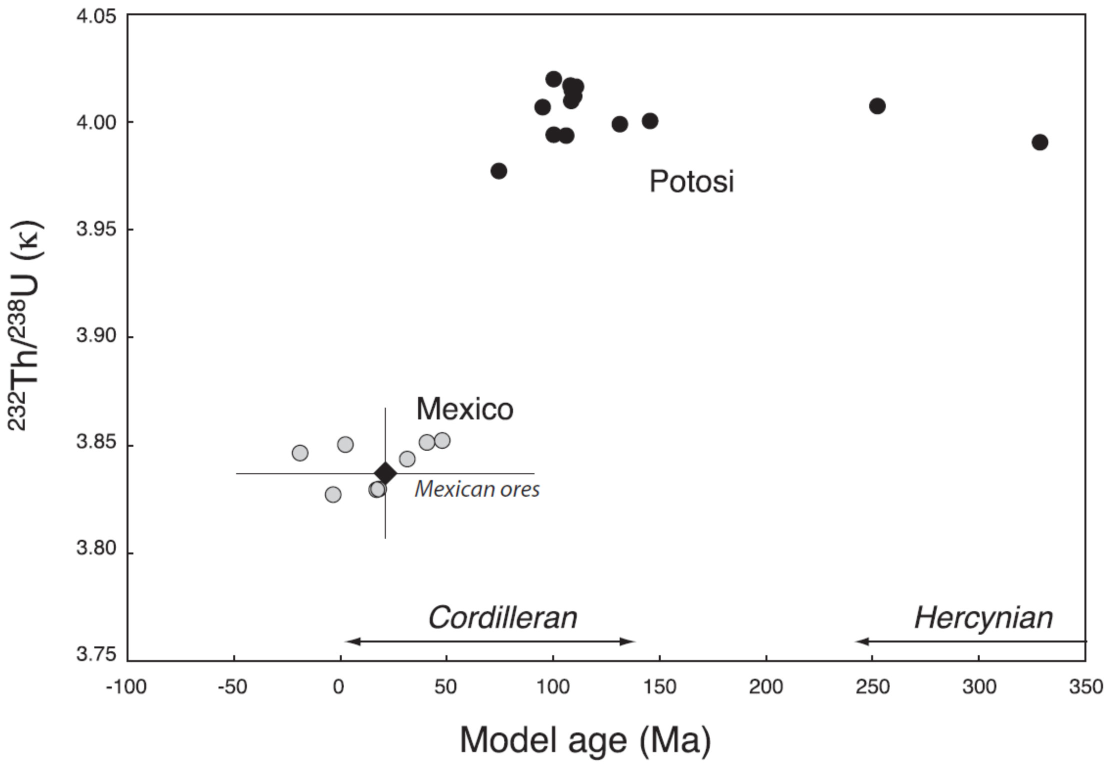

Figure 1.22 – Pb model ages versus $^{232}Th/^{238}U$ (K) for Potosí and Mexico minted coins from 16th-18th centuries, calculated using Desaulty, A.-M. et al., 2011, data. The diamond symbol represents Pb model ages and K average values calculated for Mexican mines, and the lines represent 95 % dispersion of data. There are no lead isotopic data for Potosí's silver mines. From Albarède, F. et al., 2012.

1.7.4.iii) England

Desaulty, A.-M. and Albarède, F., 2013, analysed fifteen coins minted in England from various chronologies of the 13th to 17th centuries and compared the data with those previously obtained by Desaulty, A.-M. *et al.*, 2011, for other geographies. Through the correlation of Pb, Ag and Cu isotopic ratios of the English coins produced between 1248-1649, they found a preponderance of Mexican silver in dates later than 1553 (9 on 11 coins), and a very small contribution of Potosí's silver, only one coin minted in the timeline of 1641-1643 just at the end of the apogee period of the silver production from this provenance.

From Figure 1.23, it is noticed that the Pb isotopic ratio which best discriminates Potosí, Mexico and medieval Europe is $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$. The data of the four coins from Edward I-Edward VI, three minted in timelines previous to the 14th century and one from 1551, group closer to the medieval European coins data, as expected at least for the previous ones.

In the group of coins of Mary I – Charles I, all coins but two, are positioned near the Mexican lead showing the prevalence of this source of silver in England during the 17th century. The coexistence of Mexican silver with Potosí's and European silver is attested by a coin minted in the Charles I chronology, between 1641-1643, with lead isotopic ratios closer to Potosí's silver composition, and another of the same chronology minted between 1625-1649 with European silver lead isotopic ratios.

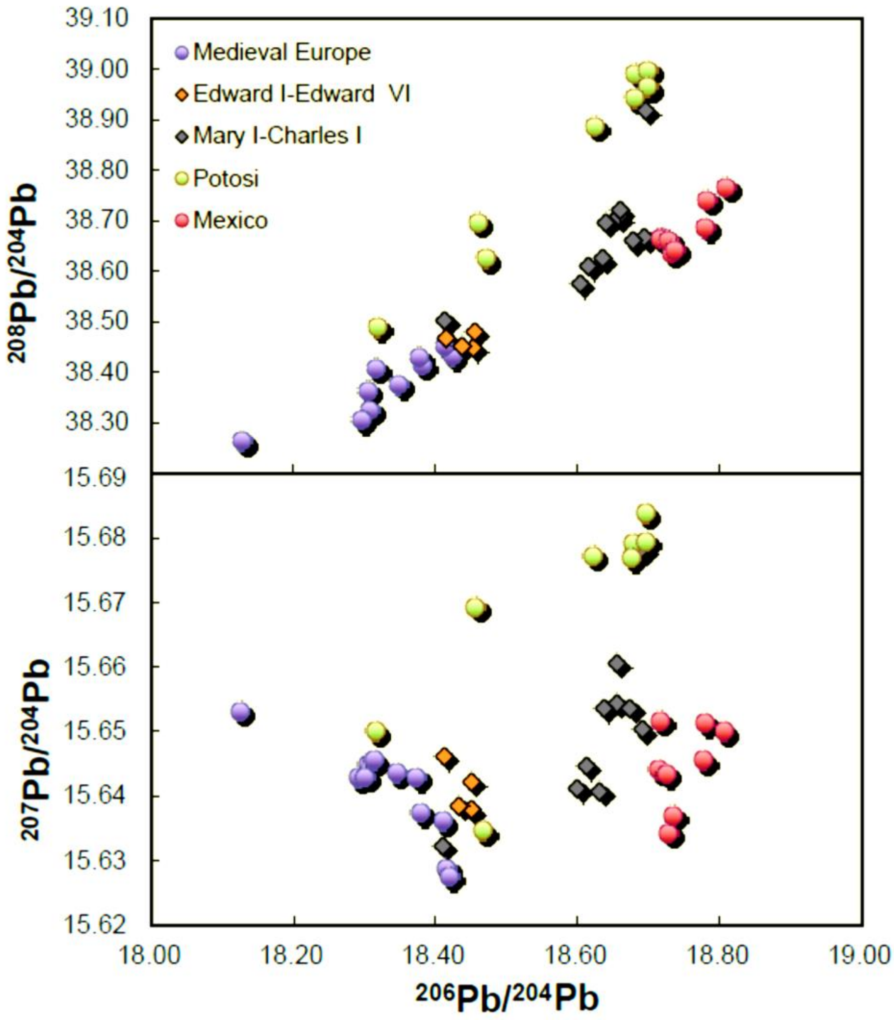

Figure 1.23 – $^{206}Pb/^{204}Pb$ ratio related to $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios for English coins minted between the 13th-17th. Adapted from Desaulty, A.-M. and Albarède, F., 2013.

The $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ ratio correlation supports the previous analysis but locates the ratios of the two Potosí coins from an older basement closer to the ratios from the medieval European coins.

The Cu and Ag isotopic compositions analysis are far more ambiguous (Figure 1.24), discriminating, however, English silver coinages from Potosí's silver, and placing the coins from the Mary I – Charles I chronologies at an intermediate location between European and Mexican silver. This isotopic composition correlation places also the coins minted prior to these chronologies (Edward I – Edward VI), in the group of data from the European medieval coins.

An analysis based on the correlation between silver and copper isotopic compositions will always be conditioned by the question of provenance of the copper present in the alloy.

$^{232}Th/^{238}U$ (Қ) ratio versus the Pb model age (Figure 1.25) confirms that the four coins from the Edward I – Edward VI group are located next to the medieval European coins, with $^{232}Th/^{238}U$ (Қ) ratios intermediate between the Mexican and Potosí's coins and have high lead model ages > 220 Ma, indicating a provenance from the mines of the Hercynian basement in central Europe (Desaulty, A.-M. and Albarède, F., 2013).

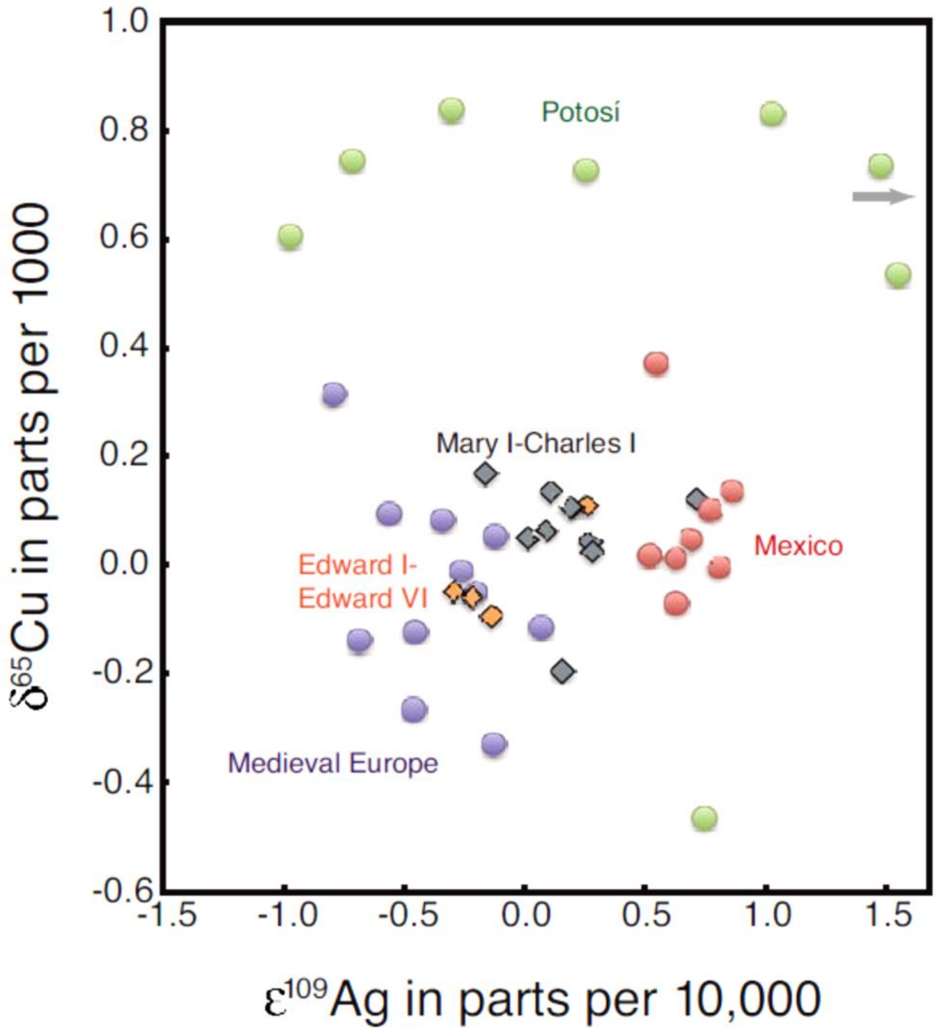

Figure 1.24 – Silver and copper isotopic compositions of the coins from Figure 7.23. Adapted from Desaulty, A.-M. and Albarède, F., 2013.

Also, all English coins of the various chronologies of Mary I to Charles I (1553-1649) are located closest to the Mexican coins, have low $^{232}Th/^{238}U$ (Қ) ratios, except for a coin of Charles I of 1641-1643 situated near the Potosí's silver, and low model ages values, except for a 1625-1649 coin located near the European silver.

The least-squares deconvolution of the lead isotopic ratios, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ (Figure 1.25) on the three origin components of medieval Europe, Potosí and Mexico, made in twelve English coins, points to an important contribution of the Mexican Silver (nine coins dated from mid-16th century to mid-17th century). Only two coins, one of 1551 (Edward VI) and another of Charles I (1625-1649), show a small contribution of Mexican silver standing closest to their European silver origin, being the Potosí's silver contribution reduced to a coin.

In the latter case, the identification of this coin (ChId) in Figure 1.25 inset does not correspond to that of the coin (ChIa) close to the Cordillera region I of Potosí, which, in the absence of a misidentification of the coins does not reflect a clear correspondence between the data.

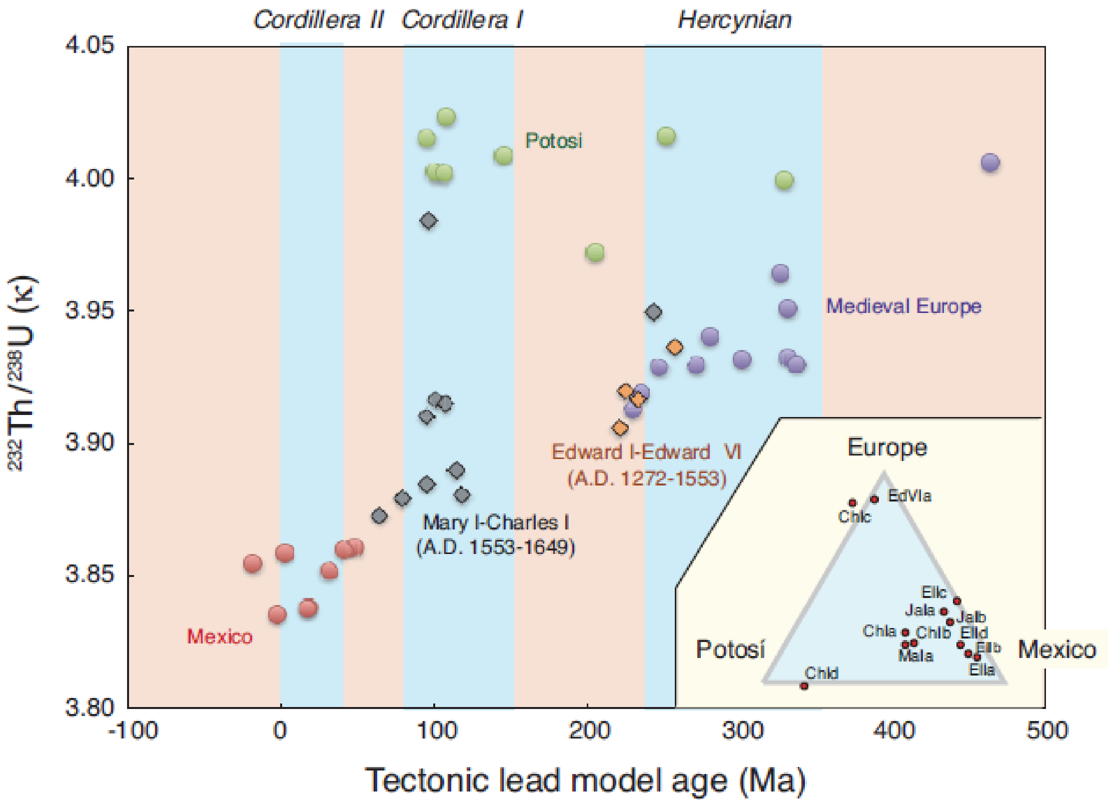

Figure 1.25 – ^{232}Th/^{238}U (K) ratios versus lead tectonic model ages in millions of years for the coins minted in England between 1248-1650, using Desaulty, A.-M. et al.,2011, data of medieval Europe, Potosí and Mexico. The age ranges of the main tectonic formations characteristic of the major ore fields are at the top of the diagram - Hercynian, South American Cordillera I and Mexican Cordillera II. The inset shows a least-squares deconvolution of the lead isotopic ratios, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, in the three components of origin, medieval Europe, Potosí and Mexico, where the tags match the examined coin references (see Desaulty, A.-M. and Albarède, F., 2013). From Desaulty, A.-M. and Albarède, F., 2013.

This investigation indicates that Potosí's and European silver contributions were quite low in England, from 1553, being dominant the Mexican silver.

1.7.4.iv) Spain

Desaulty, A.-M. *et al.*, 2011 analysed sixteen medieval Spanish coins from the period between 1109 and 1504 (Figure 1.26), of which eight belong to the chronology of the Catholic Kings - Ferdinand II of Aragon and Isabella of Castile (1479-1516). These last coins, when compared with the others medieval coins, show non-Hercynian Pb model ages <100 Ma, which are attributed to the Cartagena-Almeria volcanic belt silver mines, that are geological formations belonging to the Betic belt (~ 20 Ma) and distinguished from the old European mines formations (~ 300 Ma). The remaining coins have Hercynian Pb model ages of central Europe (Albarède, F. *et al.*, 2012).

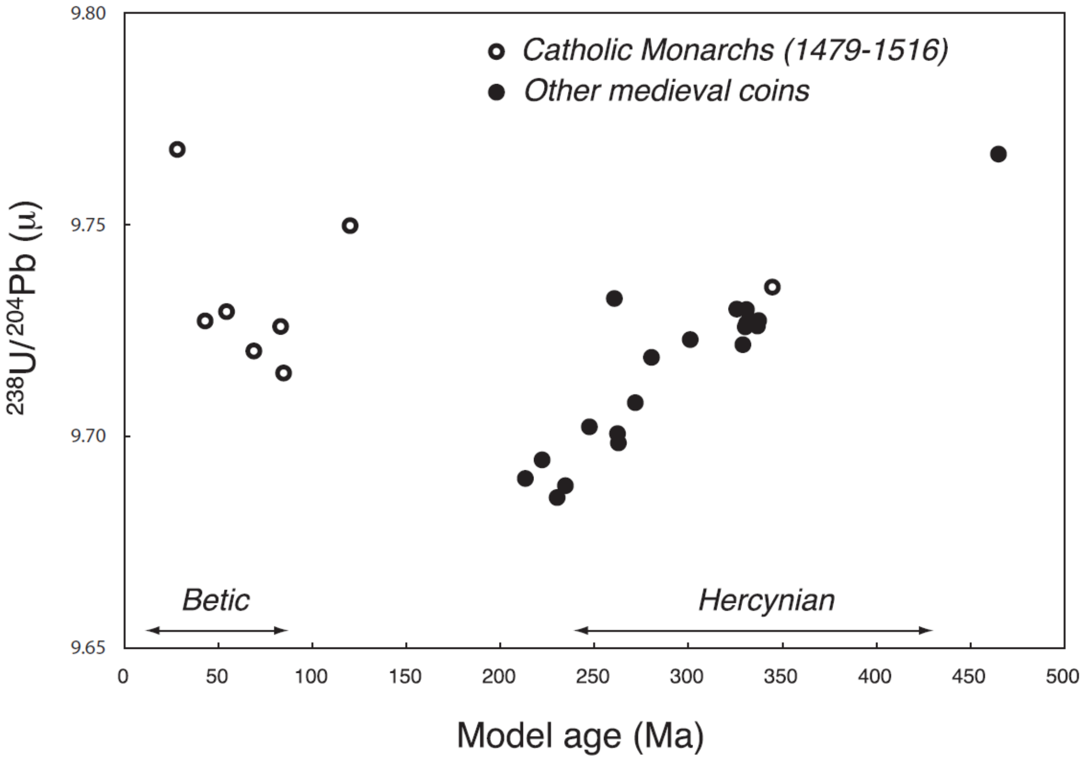

Figure 1.26 – $^{238}U/^{204}Pb$ (μ) ratio versus Pb model ages for medieval Spanish coins from Desaulty, A.-M. et al., 2011, data. With one exception the coins of the Catholic Kings have Pb model ages younger than the geological formations of the remaining coins. From Albarède, F. et al., 2012.

1.7.5 Notes on isotopic analysis approach

The provenance analysis through lead isotopic ratios in silver coins is possible since the produced silver metal contain minor lead contents, which resulted in a first period of time from argentiferous lead ores and latter from argentiferous copper ores, and also involved the introduction of lead in the smelting and refining (cupellation) processes for silver recovery. However, Pb isotopic ratios are in some cases closely related with each other, and do not provide a sufficiently clear discrimination for provenance assignment, but their utility can be strengthened using lead model ages.

From the existing data, it is possible to discriminate silver sources between three compositional groups related to the coins minted in Potosí and Mexico, and in Europe with silver extracted before America's silver ores discovery. The coins investigated in the last group involved coins minted in England before the 1553 (n = 4), in medieval Spain prior to 1504 (n = 8) except for the coins of the Catholic Kings, and in central Europe – Bohemia (14th century, n=1), Hungary (first half of the 16th century, n = 3), France (15th century and 1551, n = 2) and Duchy of Brabant (13th century, n = 1). These data are confirmed by the relationships obtained between the $^{232}Th/^{238}U$ (K) ratio versus the Pb model ages, which differentiate the same three groups.

Based on the relationship between the $^{232}Th/^{238}U$ (K) ratio versus Pb model ages, the coins data belonging to the English coinages after 1553 locate near the group of coins minted in Mexico.

The analysed coins minted in Spain belong to *Felipe III* (1598-1621) (n = 5) and to later (n = 16) chronologies, except for a coin of *Felipe II* (1556-1598) and another minted in the first half of the 16th century in Antwerp. The data which belongs unequivocally to the 16th century refers to the Spanish coin of *Felipe II*, but the coins from the following chronology of *Felipe III* have more probability to have been minted in the 17th century. Thereafter, this small number of 16th century coins is not statistically representative, and do not allow to make a clear evaluation of the period of the American silver arrival in the Iberian Peninsula, just after it discovery.

However, the data show that the Spanish European minted coins from the chronologies after the 16th century split and overlap over the European coins group, with dates earlier than the first half of the 16tth century, and especially over the coins minted in Mexico. The silver provenance references of the Spanish European minted silver (Desaulty, A.-M. et al., 2011) are based on a direct correlation of the lead model ages of the coins with the lead model ages from the several Spanish geographies of the Mints where the coins where produced, assuming that the lead present in the coins was originated at these sites, and do not consider the circulation of silver ingots of various origins within the Spanish territory.

Also, the correlations based on lead isotopic ratios and model ages indicate the existence of a greater contribution of Mexican silver in European mints after the 16th century, but do not allow to apprehend the extent of the presence of Potosí's silver in coinages minted in Spain or in other countries with an Atlantic dimension, as France, during the 16th and 17th centuries. For example, the only analysed French coin from the mid-16th century has only Hercynian lead (Desaulty, A.-M. et al., 2011), being not representative of the presence and/or movement of Mexican or Potosí's silver in France.

Spanish coins of the Catholic Kings constitute a group distinguishable from the coins minted with silver from central European mines, from which they differ based on the $^{238}U/^{204}Pb$ (μ) ratio versus lead model ages, being minted with silver from a peninsular origin.

In a general manner, lead isotopic analyses could reveal good results from the point of view of indexing the silver metal to the ore source geological location, despite the need of a clear indexation of the isotopic data to the exploited mines and to the specific local mineral deposit metallogeny, within each time period (Guénette-Beck, B. and Serneels, V., 2010). However, with reference to the silver that entered in the European economy, hardly an evaluation can be made based only in a few coins analysis from the different geographical sources. It is necessary to investigate a greater number of coins from each country and each chronology, to know whether the metal of the different American silver origins equivalently arrived at the various countries, if reminting of coins would be mandatory in European countries or if European coins minting's were made with new available ingots a large number of times.

The study of an important group of objects to better understand and detect the metal sources of supply (Guénette-Beck, B. and Serneels, V., 2010), is then essential to obtain a knowledge of the contemporary silver circuits that supported the European economy during the 16th and 17th century, as well as the used monetary silver sources.

The lead isotopic analysis of the referred previous studies (Desaulty, A.-M. *et al.*, 2011; Albarède, F. *et al.*, 2012; Desaulty, A.-M. and Albarède, F., 2013) based the provenance of this element within the geological origin of the silver ore. However, the lead used for exploitation and recovery of silver may not reflect the silver origin, since it could come from another region far away from the ore processing site, being the isotopic signature of a specific mining location lost simply by the mixture of metals from various origins (Pernicka, E., 2013; Butcher, K. and Ponting, M., 2014). For example, the lead from Bleiberg in the South of Austria and from Tarnowitz in the North of Poland has been exported to Nuremberg, Aachen and Cologne where it was used in the liquation processes of these European argentiferous copper mines (Lynch, M., 2002), and England was already an important supplier of lead to the European silver and copper processing centres in the 1540’s (Quintero, S.J.G., 2015). Concerning the new Spanish American silver sources from the 16th century, also great amounts of English lead was exported from Seville to New Spain carried as ballast by the Indies fleets and was used in the Zacatecas silver processing (Blanchard, I., 1981; Lynch, M., 2002). This English lead export movement to New Spain will continue until to the 1640’s, despite the introduced amalgamation process (Blanchard, I., 1989). It is evident that this lead introductions could have influenced the lead isotopic data above referenced.

However, the mixed lead isotope signature could be important to characterize, together with trace elements analysis data, the outputs of different minting workshops for the study of coin production through time.

1.7.6 Minor and trace elements analysis versus isotopic analysis

In most cases, the coins silver alloys compositions studies carried out to date based on minor and trace elements determination cannot be directly correlated with each other and have focused on compositional grouping linked to some available historical information. This approach, while not constituting a real provenance determination of the silver sources, has contributed to the identification of possible silver origins increasing numismatic and economic history knowledge.

There's always some ambiguity when pretending to link the composition of a silver coin to the ore formations, due to the possibility of using silver bullions from different origins and in different production amounts, that could also have been recycled over time, turning this task problematic. Thus, to answer questions from numismatic, archaeological, economic history, monetary production, metal origin and authenticity fields, silver coins should, as far as possible, be characterized by several analytical techniques in terms of the alloy composition, metallurgical microstructure and isotopic and geochemical signature (Pernicka, E., 2013). Metallurgical microstructure investigation, variations of impurities and alloying elements correlated with the alloy major components, and isotopic analyses have the potential to indicate how the silver coins could be related to each other, and could allow to identify different chronologies and minting’s, as well as different sources of the used metal.

This kind of alloy chemical composition characterization approach to the geochemical and geological signatures, has been used in the study of Roman (Butcher, K. and Ponting, M., 2014) and Celts (Bendall, C., 2013) silver coins and has the potential to clarify the relationships between groups of coins, better responding to the numismatic questions related to different chronologies and coinage production centres, as well as to the possible sources and/or metal supplying circuits.

The silver coins provenance assignment obtained with the above-mentioned methodologies could be considered strong when there is an unambiguous attribution based on a joint analysis of the lead isotopes and trace elements. An assignment just based on lead isotopes analysis or only in the trace elements analysis will be less secure and will be open to review as more data are obtained concerning monetary production and known mining sites (Butcher, K. and Ponting, M., 2014).

Chapter 2

MATERIALS AND METHODS

2.1 | Studied objects

2.1.1 *Portuguese silver coins from the 15th to 17th centuries*

Later than other European countries, such as England, France or Spain, the Portuguese silver coins do not bear a minting date until mid-seventeenth century, being the monetary types design modified in the extent period of each reign, for instance, with the introduction of the crowned monogram and the surrounded lettering with each monarch's name. The minting date will appear with *Dom João IV* in 1641, on the coins of *Meio Tostão* and *Tostão*, and only in coins historically assigned to Lisbon shortly produced after the restoration of Portuguese independence, preceding of about four decades the beginning of mechanical coinage. From this, it results that the coins elementary and chemical composition analysis and the subsequent correlation of data could be only referred to the various chronological regency periods of the Portuguese Kings.

Hence, the silver coins emissions of the second and third dynasties of Portuguese Kings, mostly the ones minted in the 16th century in the Lisbon and Porto mints, stored in two large numismatic collections, respectively from INCM (200 coins analysed) and BdP (91 coins analysed), were studied in a chronological framework (Tables 2.1 and 2.2) with precise historical and numismatic issues. Coin's selection had considered the surface (preservation) condition of the coins made by visual inspection.

The two hundred INCM coins are identified in the book authored by C.M. Almeida do Amaral, Catálogo descritivo das moedas Portuguesas – Museu Numismático Português, Lisboa, Imprensa Nacional Casa da Moeda, 1977, whose description can be accessed through the referrenced inventory number (which appears in Appendix 4). The ninety-one BdP coins are presented in Appendix I.

In the analytical results tables included in Appendix 4, all coins are identified by their inventory number, and presented in a chronological order as in the above tables, with the names, coronation and death dates of each King, starting each chronology by the less valued coin type. Also, whenever possible the mint identification is given, as obtained from the engraved monetary letter, L or P, on the surface of the coin. The coins from the Philippine dynasty are historically said to have been produced in Lisbon mint and are as such considered in Chapter 3 – Results and discussion.

For the understanding of a precise issue, it has been considered coin representativeness of each Portuguese king chronology to obtain statistical data enabling to infer reliable historical interpretations of the analytical data.

In the context of correlation of the second dynasty silver coins with the American silver sources, a few colonial Spanish coins, minted in the Andes, pertaining to the Money Museum (BdP) were investigated (Table 2.3). It is known that Potosi mint was operating by 1574 after the dies and the machinery brought from La Plata mint, funded before in 1565 and coining from the beginning of 1573, were installed (Cunietti-Ferrando, A.J., 1988).

Table 2.1 – Chronology, denomination and number of analysed coins from the Joanine King's dynasty, selected from INCM and BdP numismatic collections

Chronology	Coin denomination	Mint		
		Lisbon	Porto	Unidentified
Dom Afonso V (1438-1481)	*Leal*	1		
	Chinfrão	1	2	
	Real Grosso	3	2	
	Real Grosso for Castile and Leon			2
n = 11				
Dom João II (1481-1495)	*Vintém*	6	8	
n = 14				
Dom Manuel I (1495-1521)	*Meio Vintém*			13
	Vintém	10	18	
	Meio Tostão	6		
	Tostão	4	3	5
n =59				
Dom João III (1521-1557)	*Cinquinho*	1		1
	Meio Vintém			3
	Vintém	16	7	11
	Real Português		7	6
	Meio Tostão			6
	Real Português Dobrado			3
	Tostão	11	7	7
n = 86				
Dom Sebastião I (1557-1578)	*Meio Vintém*			1
	Vintém			18
	Meio Tostão			10
	Tostão		6	15
n =50				
Total =220		66	64	90

Table 2.2 – Chronology, denomination and number of analysed coins from the Philipine King's dynasty, selected from INCM and BdP numismatic collections

Chronology	Coin denomination	Mint
		Lisbon
Dom Filipe I (1580-1598)	*Vintém*	5
	XXXX Reais	3
	Meio Tostão	1
	LXXX Reais	7
	Tostão	8
n = 24		
Dom Filipe II (1598-1621)	*XX Reais*	7
	Meio Tostão	13
	Tostão	16
N =36		
Dom Filipe III (1621-1640)	*Meio Tostão*	4
	Tostão	7
n =11		
Total=71		71

Table 2.3 – Chronology, denomination, minting date and location of colonial Spanish analysed coins, selected from BdP numismatic collection

Chronology	Coin denomination	Date	Mint
Felipe II	*8 Reales*	1576-1586?	Potosi
Felipe III	*8 Reales*	1613-1617	Potosí
Total=2			

A small number of coins from Lisbon and Porto mints in some cases with great wear of the engravings and with small intrinsic value or numismatic interest, were provided by some collectors for invasive analysis (labeled as C1 to C4 in Table 2.4).

Table 2.4 – Chronology and mint of the four coins used in invasive analysis

Reference	Chronology	Mint
C1	*Dom João II*	Lisbon
C2	*Dom João II*	Porto
C3	*Dom Manuel I*	Lisbon
C4	*Dom Manuel I*	Porto

2.1.2 *Portuguese silverware objects from the 16th century*

A few silverware objets of the second dynasty of Portuguese Kings, minted in the 16th century pertaining to MNAA and to private collectors or dealers were respectively analysed and studied in a compositional comparison chronological framework. The following objects were analysed:

- Salver with low foot, gilded silver with Porto hallmark, historically attributed to circa 1490-1500, represented in the book authored by Nuno Vassalo e Silva, 15th and 16th century Portuguese Cerimonial Silver, Scribe, Lisboa, 2012, pages 34-35, hereinafter denoted as the "Dragon salver" because of its ornamental figuration (see Figure 3.69);
- Salver with tall foot, gilded silver without marks, wherein the dish is dated drom 1548 and the foot is a latter 19th century addition, represented in the above-mentioned book, pages 216-217, hereinafter denoted as the "1548 salver" (see Figure 3.72);
- Salver, gilded silver without marks, dated from 1553, from the collection of King *Dom Fernando II*, represented in the above-mentioned book, pages 92-93, hereinafter denoted as the "1553 salver" (see Figure 3.72);
- Jug, silver and gilded silver, without marks, attributed to the end of 16th century, Portuguese (?) work, represented in the book authored by Nuno Vassalo e Silva and Pedro Bourbon de Aguiar Branco, Prataria, do século XVI ao século XIX em Portugal, author edition, V.O.C. Antiguidades, Lda, Porto, 2009, pages 16-19, hereinafter denoted as the "Jug" (see Figure 3.75, left);

- Salver, silver and gilded silver, without marks, dated from last quarter of 16th or beginning of 17th century, from the MNAA collection, inventory number 1021 Our, supporting a central Felipe III gilded medallion, hereinafter denoted as the “MNAA 1021 salver” (see Figure 3.75, right).

The analytical results obtained in ungilded surfaces of the above silverware objects are included in Appendix 6.

The analytical compositional results from an oratory-reliquary (MNAA 99 Our), a missal lectern (MNAA 100 Our) and a pax (MNAA 98 Our) making part of the important *Vidigueira* treasure belonging to MNAA collection were gently provided by Luís Cerqueira Alves (personal communication based on the Instituto Tecnológico e Nuclear Report from 2012) and correlated with the results of the present investigation. Until now all these objects have been assumed to be an Indo-Portuguese work from the end of the 16th century. The identification and description of these objects can be accessed through their inventory numbers from www.matriznet.dgpc.pt.

2.2 | Analytical methodology and methods

The Portuguese silver coins investigation was initially conceived, on the one hand, to permit an analytical interpretation of results based on the majority elements contents of silver and copper, that would allow to verify during the studied period if the coins fineness would be within the decreed value imposed by the various monarchs. On the other hand, it was intended to discriminate the various productions of the various mints, based on levels of minority elements, to identify silver origins within at least a geographical regional context resulting from the various silver supplies and distinct metallurgical practices.

The impediment to clean the coin's surface before analysis, avoiding possible effects of surface contaminations and/or silver enrichment, had also constrained the elemental composition analysis to the use of nondestructive and noninvasive analytical techniques available, as Particle Induced X-Ray Emission (PIXE) and Energy-Dispersive X-Ray Fluorescence (EDXRF).

On an initial phase, the above-mentioned objectives seemed to be achievable by the two-available elemental composition analysis methods, as the coins were produced from very pure silver alloys. Surface elemental analysis has been regarded as reliable for original bulk composition and not influenced by silver surface enrichment phenomena in high fineness coins, and measured surface silver contents higher than 94 % have been considered relevant for coins bulk composition (Bugoi, R., et al., 1999). Also, in silver-copper alloys expected to have more than 91.2 % Ag the silver surface composition has been regarded as following the composition of the Ag-rich primary phase, wherein no significant surface and bulk silver compositional differences are assumed (Beck, L., et al., 2004).

These surface analysis techniques have been extensively applied in numismatics in ancient silver coins characterization (Uzonyi, I., *et al.*, 2000; Sándor, Z., *et al.*, 2002; Linke, R., *et al.*, 2003, 2004 and 2004a; Denker, A., *et al.*, 2004; Constantinescu, B., *et. al.*, 2003 and 2005; Santra, S., *et al.*, 2005; Pistofidis, N., *et al.*, 2006; Šmit, Ž. and Šemrov, A., 2006; Civici, N., *et al.*, 2007; Hajivaliei, M., *et al.*, 2008; Pitarch, A. and Queralt, I., 2010; Kantarelou, V., *et al.*, 2011; Pitarch, A., *et al.*, 2011; Rodrigues, M., *et al.*, 2011; Ager, F.J., *et al.*, 2013; Corsi, J., *et al.*, 2015; Hoyo-Meléndez, J.M., *et al.*, 2015) and allow an expedite quantitative multi-elemental nondestructive analysis, albeit obtaining information from a limited surface depth in a silver matrix.

However, the resulted data have shown that besides the analysis composition, it was indispensable to understand and to characterize the relevant aspects related to the coins microstructure, to obtain reliable analysis results.

The results from the surface analytical techniques, EDXRF and PIXE, were then complemented by μ-PIXE analyses along the thickness sections of some coins to determine the core original fineness and the compositional gradients of major and minor chemical elements, and by Scanning Electron Microscopy with Energy Dispersive X-ray Spectrometry (SEM/EDS) and X-Ray Diffraction (XRD) analyses in order to understand microstructure features and gather information related to the coin manufacturing process or to evaluate any corrosion development.

This complementary analytical methodology has been the traditional approach to investigate microstructure and composition of silver coins, due to differences of composition between the surface and the bulk (Linke, R., *et al.*, 2000, 2003, e 2004a; Rodrigues, M., *et al.*, 2011a; Calliari, I., *et al.*, 2013; Buccolieri, A., *et al.*, 2014; Butcher, K. and Pointing, M., 2005 e 2014). However, to clarify the previous EDXRF, PIXE and SEM/EDS analysis, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analysis was conducted to obtain elemental content profiles in the near-surface thickness to elucidate the overestimation of silver content by surface analytical techniques. LA-ICP-MS has been applied to characterize the silver alloys in objects (Devos, W., *et al.*, 1999; Moor, C., *et al.*, 2000) and coins (Hollstein, W., 2000; Sarah, G., *et al.*, 2007 and 2008), and the silvering processes of roman coins (Vlachou-Mogire, C., *et al.*, 2007) and has a wide potential of application in the ancient metals examination due to no need of sample preparation, low detection limits, a spatial resolution associated to a micro-sampling with very small size of ablated material, and the possibility to carry out depth compositional profiling, which provides the information about the distribution of elements in the structure, and a compositional fingerprinting.

Finally, the analytical compositional results were subject to statistical treatment and interrelated with the historical context to bring new elements of reflection to the silver sources question, to formulate working hypotheses and to offer clues to future research on the possible origins of silver. All the resultant data will contribute forcibly to the economic and social history linked to the Portuguese monetary production and to the silver metal supply and circulation, construed in a European and worldwide context.

2.2.1 Coins sample and preparation

The selected coins showed generally a good state of preservation with more, or less dark patina of unknown thickness on the surface, and present different degrees of engraving wearing.

The INCM coins were cleaned with acetone and placed in an ultrasonic bath for 3 minutes to remove any contamination particles adhered to the surface, BdP coins were analyzed as they were, once most of them present a bright silver surface.

PIXE analysis were made on two points on the obverse of each coin, in a surface that presented the lowest degree of alteration or patina, and EDXRF analyses on the obverse and reverse in a great number of coins.

Some of the coins acquired for invasive analysis were cut to a half-diameter and examined along the thickness to characterize the microstructure and to determinate any elemental composition variation.

2.2.2 Energy-Dispersive X-Ray Fluorescence (EDXRF)

A Kevex 771 EDXRF spectrometer with a primary beam of photons from a 200 W Rh X-ray tube was used in the secondary target excitation mode (Ag and Gd secondary targets) for EDXRF analysis. The radiation produced by the secondary target and filter induces the emission of the characteristics X-ray lines of the coins constituents. The source-detector system has a 45° incidence angle and a 45° output angle. The EDXRF beam cross-section permitted only a global analysis on each face. The characteristic X-rays from the sample spot area close to 2.5 cm in diameter, are acquired by a Si (Li) detector cooled by liquid nitrogen after being collimated to 90° in a 5 mm in diameter collimator.

The coins were irradiated with a beam of monochromatic X-rays using two different excitation conditions: (a) to detect Cu, Zn, Ni, Au, Hg, Pb, Bi it was used a silver secondary target with a voltage of 35 kV, a current intensity of 0.5 mA during 300 s, and (b) to detect silver it was used a gadolinium secondary target with 57 kV, 1.0 mA and 300 s. The spectra were processed using a Gaussian deconvolution, and the elemental composition was determined using the EXACT computer program based upon a fundamental parameter method.

The certified reference material 133X AGQ2 (batch C) from MBH analytical® (England), a quaternary silver alloy with a composition close to the expected coins composition, was analysed using the same experimental conditions to calculate experimental calibration parameters for the elements of interest of the silver-based alloys. This reference material was also used to calculate the quantification limits of Cu, Au and Pb for the EDXRF analyses of the high silver content alloys (*Table 2.5*). The quantification limit for mercury, bismuth, nickel and zinc were estimated using the elements with similar absorption and enhancement effects in the silver-based matrix, Au, Pb and Cu, respectively.

Table 2.5 – Quantification limits in ppm for EDXRF analysis calculated as 10xbackground$^{1/2}$/sensitivity (IUPAC, 1978) using the certified reference material133X AGQ2 (batch C) from MBH analytical®. The values for Ni, Zn, Hg and Bi are estimated.

Cu	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
300	300	300	220	220	170	170

The accuracy of the EDXRF results of silver alloys was estimated through the quantification of the certified reference material on each coin’s batch, and the relative error was calculated as ((certified content – obtained content)/certified content) x 100) (*Table 2.6*). The relative error was found to be lower than 5 % for major and minor elements, evidencing a good overall accuracy for the method.

Table 2.6 – Accuracy of quantitative EDXRF analysis using the certified reference material 133X AGQ2 (batch C) from MBH analytical®

Element	Ag	Cu	Au	Pb
Certified value (wt.%)	92.745	5.808±0.072	0.978±0.003	0.469±0.007
EDXRF obtained value (wt.%)	92.94±0.16	5.67±0.13	0.98±0.01	0.46±0.02
EDXRF relative error (%)	0.21	2.45	0.35	2.69

2.2.3 Particle Induced X-Ray Emission (PIXE)

The coins were irradiated in vacuum with a 2 MeV proton beam produced by the 2.5 MV Van de Graaff accelerator from CTN, using a 1.5 mm diameter beam collimator and a beam current intensity of 15 nA for a total accumulated charge of 10 µC. A 145 eV resolution Si(Li) detector placed at 70° relative to the proton beam direction was used together with a 350 µm Mylar filter for strongly reducing the Ag L lines intensity enhancing the Ag K lines contribution to the spectra. Spectra analysis and elemental quantification was performed through the GUPIXWIN computer program. Process validation was accomplished through the analysis of the MBH analytical® certified reference material.

The composition analysis along the thickness of the coins was realized with a nuclear microprobe from Oxford Microbeams. The 2 MeV proton beam was focused on the section of the coin with a spatial resolution of 3 x 4 μm^2. Successive 70 x 800 μm^2 scanning's were carried out along the section of the coin in vacuum conditions, using an X-ray detector SDD with a resolution of 145 eV and positioned at 45° relative to the incident beam, and a 50 µm Mylar filter to suppress the low energies signals. Spectra analysis and elemental quantification was performed as above mentioned. The compositional analysis of the silver objects was made outside the vaccuum chamber with an external 2 MeV proton beam, that was focused on the object surface with a spatial resolution of 75 x 75 μm^2. In this case, a 250 µm Mylar filter was used in the detector.

The good accuracy of PIXE quantification method was ascertained by analyzing the certified reference material 133X AGQ2 (batch C) from MBH analytical® on each coin's batch and calculating the relative error as ((certified content – obtained content)/certified content) x 100) (*Table 2.7*). Excepting for Au, the relative error is better than 5 % for major and minor elements, evidencing a good overall accuracy for the used method.

Table 2.7 – Accuracy of quantitative PIXE analysis using the certified reference material 133X AGQ2 (batch C) from MBH analytical®

Element	Ag	Cu	Au	Pb
Certified value (wt.%)	92.745	5.808±0.072	0.978±0.003	0.469±0.007
PIXE obtained value (wt.%)	92.88±0.26	5.63±0.23	1.04±0.03	0.46±0.03
PIXE error (%)	0.14	3.16	6.05	1.99

2.2.4 Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM/EDS)

The microstructural characterization was conducted with SEM-EDS in backscattering electron imaging mode using a scanning electron microscope with a conventional tungsten filament (Zeiss DSM 962). This equipment has an energy dispersive spectrometer Oxford Instruments INCAx-sight. The analyses were performed at a working distance of 25 mm, with an accelerating voltage of 20 kV, a filament current of approximately 3 A and an emission current of 70 µA. Other analyses were realized with a Hitachi S3700N SEM-EDS using a high vacuum, with an accelerating voltage of 30 kV and an optimum working distance of 10 mm. The EDS compositional data were obtained using a Bruker AXS microanalysis system with a XFlash Detector 5010.

2.2.5 Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

LA-ICP-MS analyses were performed using an Agilent 8800 ICP-MS Trip Quad coupled to a CETAC LSX-213 G^{2+} laser ablation system. The equipment was calibrated and tuned prior to the analysis with the certified reference material NIST 612. Elemental fractionation was monitored using the $^{238}U/^{232}Th$ and the oxide formation was evaluated using the $^{248}ThO/^{232}Th$ ratio. ICP-MS was performed in TRA mode (Time Resolved Analysis) and with the scan type MS/MS mode (no gas in the collision/reaction cell). The monitored isotopes were: ^{63}Cu; ^{107}Ag with dwell times of 10 ms, and ^{197}Au, ^{201}Hg, ^{208}Pb, ^{209}Bi with dwell times of 20 ms. The ICP plasma has operated at 1550W of RF Power, 1.4 V of RF matching, sample depth of 4.0 mm and dilution gas (Ar) at 0.7 L/min. The laser conditions used for the analysis were 50 µm laser beam diameter, 5 % energy, 60 µm/s of scan rate (for lines with about 1300 µm), frequency of shot 5 Hz, and He flow 1 L/min.

2.2.6 X-Ray Diffraction (XRD)

XRD microstructural identification of the Ag and Cu phases on the diametral section of the coins was made using an X-ray diffractometer system XPERT-PRO. XRD patterns were recorded directly on samples using a non-monochromatized Cu Kα radiation (λ = 1.54178 Å), operating with a 45 kV accelerating voltage and a 40 mA current. The scanning was made over the angular range $20° \leq 2\theta \leq 140°$, with a step size of 0.03° and a sampling time of 50 s.

2.2.7 Results correlations and statistical analysis

Two compositional analyses were made in the same coin, which allows to estimate the variability between the two analized points and therefore the accuracy of the estimated composition. Even with two analyses, assuming that the variability of one coin is the same as in other coins of the same type, it is possible to have a good estimation of their composition based on multiple analysis from a group of similar coins (Reedy, T.J. and Reedy, C.L., 1988).

In studies made on large samples of coin chemical compositional data, the complexity of the chemical composition interpretation deriving from the interference of each chemical element in the global results, and the difficulty of determining correlations between the several chemical elements, constitute a reason for performing a data analysis by a multivariate statistical method.

The used Principal Component Analysis (PCA) is a multivariate statistical analysis method that allows to transform a set of variables (chemical elements contents), possibly correlated with each other, in another set of a small number of new variables, not correlated, independent, and orthogonal, denominated as principal components, which results from all the linear combinations of the initial variables.

Through the reduction of the initial number of variables (multidimensional) effectuated with the least possible loss of information contained in it and keeping the set variability unchanged, it is possible to reveal relationships that were not provided in advance between the original variables, turning their study understandable. This variables reduction is only possible if the initial variables are not independent and have correlation coefficients different than zero.

The new variables (principal components) are calculated by decreasing order of contribution to the explanation of the total variance of the original data. The first principal component explains most of the total variation observed in the original data, followed by the second principal component, and so on, until a last principal component of lesser importance. The first principal components are usually sufficient to reveal a significant result that allows the understanding of the data.

PCA analysis was made using IBM SPSS software (v. 15) and the Au, Hg, Pb and Bi compositional contents presented in Appendix 4, unless otherwise indicated in Part 3 – Results and discussion, and include in its presentation the variance percentage explained by each of the principal components, the total variance explained, and a table with the contribution of each initial variable for each component (factor loadings).

It is thus possible to identify the original variables that contribute more to the multidimensional data variance and have a higher influence in the formation of a particular principal component, or on the contrary very little, and to discriminate groups of coins, for example, through data presentation in two-dimensional scatter charts.

To avoid skewed results in the statistical/correlation analysis produced in Chapter 3 – Results and discussion, in cases where a specific chemical element was under the detection limit, a value lower than the minimum content found within all coins from all chronologies and for that specific element was considered.

Chapter 3

RESULTS AND DISCUSSION

3.1 | Surface composition of Portuguese 11 dinheiros alloys: the issue of surface silver enrichment in ancient high silver alloys

The mean elemental compositional data obtained by PIXE and EDXRF in *11 dinheiros* coins comprising the Appendix 4 tables, identify the metal as being a Ag-Cu alloy with an unexpected high fineness, with low contents of minor and trace elements, as gold (Au), mercury (Hg), lead (Pb), bismuth (Bi), zinc (Zn) and niquel (Ni), all of them primarily associated to the ores from which the silver was extracted or to the process of silver extraction.

The occurrence of iron (Fe), almost always present on the spectra of the silver coins, is attributed to outdoor pollution manifested with varying degrees of surface contamination that causes Fe enrichment in the surface of the coins due to encrusted dust (Uzonyi, I. et al., 2000; Flament, C. and Marchetti, P., 2004). Fe is virtually insoluble in solid Ag, immiscible with Ag in the liquid phase and was not found as inclusions on the Ag matrix microstructure, and for these reasons its surface content was not considered for the overall composition of the coins.

Other elements as bromine, calcium, titanium and manganese were not considered for surface composition analysis. Bromine, like chlorine, is involved in the silver corrosion process being associated with the superficial tarnishing, and the other refered elements could be related to different kinds of surface contamination after minting.

The analysis data are comparable in all the investigated coins showing a trend to higher Ag contents than the nominal value imposed by the known sixteenth century monetary laws for these coins. The Portuguese silver coinages were issued then with a 11 dinheiros Ag alloy, corresponding to a fineness of eleven parts of Ag in twelve of metal, i.e., 916.6 thousandths, but these results present positive deviations from the standards, 4 % up to 7 % higher, something which wouldn't be feasible for the Portuguese monetary production from this century.

Selenium has also been detected on both surfaces of some coins from the Money Museum from BdP, involving different chronologies and presenting a lustrous appearance characterized by a very well outlined engraving and a very clean and bright surface with a small iridescence, as show in the example presented on the following figure.

Figure 3.1 – *80 Reais* coin minted by *Dom Filipe I* (BdP 9004189300).

All these coins, identified by the sequencial numeral 65, 71, 73, 74 83, 84, and 91 on Appendix 1, present however the tipical composition based on the minor elements for the chronologies from where they belong, and hence should not be considered as counterfeits. Selenium is a common element used in abrasive products, and it appears that these coins should have been subjected to an abrasive mechanical action involving a polishing grinding wheel intended to "enhance" their surface appearance.

3.1.1 PIXE versus EDXRF

Taking as an example, the average elemental composition obtained for 40 of the coins minted by *Dom Sebastião I* (1557-1578) that do not bear the monetary workshop identification (see Table 3.1), the major as well as the minor elements have a similar content and standard deviation magnitude irrespective of the used analysis method, therefore the high standard deviation values should express the composition heterogeneity present in the set of analyzed coins.

Table 3.1 – Mean values and standard deviation of Ag, Cu, Au, Pb, Hg and Bi expressed as weight percent obtained with PIXE and EDXRF on the *11 dinheiros* coins minted by *Dom Sebastião I* (1557-1578)

		Ag	Cu	Au	Pb	Hg	Bi
11*dinheiros*		91.67	-	-	-	-	-
Coins	PIXE	96.37±1.60	2.79±1.34	0.13±0.07	0.42±0.25	0.19±0.90	0.09±0.04
	EDXRF	95.82±1.51	3.30±1.32	0.12±0.05	0.54±0.33	0.13±0.60	0.10±0.04

Figure 3.2 shows a similar trend for the silver and copper contents measured by PIXE and EDXRF on each of these 11 dinheiros coins, with a slightly surface silver enrichment due to copper depletion, linked to the lower depth of information obtained by PIXE from the nearest surface layer, evidencing the heterogeneity present on the sample of analyzed coins.

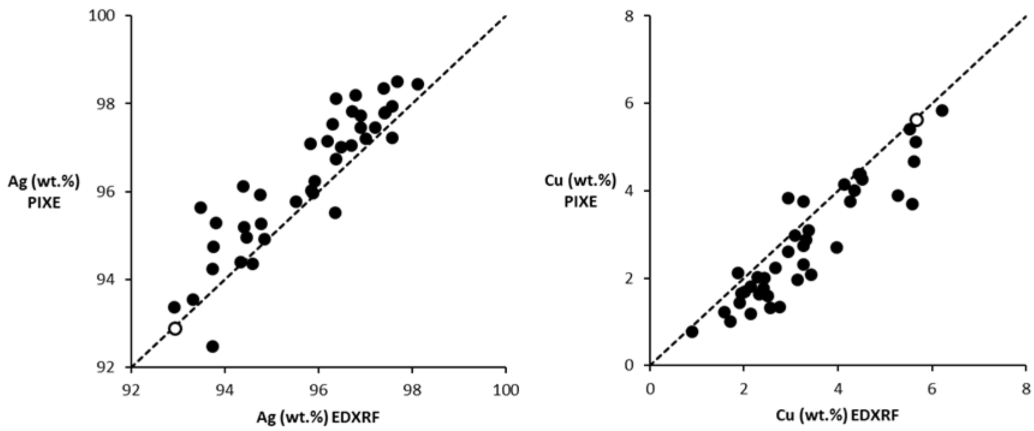

Figure 3.2 – PIXE and EDXRF Ag and Cu compositional values obtained for *Dom Sebastião I 11 dinheiros* coins. A dotted line of equal content was drawn for purposes of clearness and the open circle represents the mean data obtained from the certified reference material.

Also, the individual surface analyses on different areas of the same coins have indicated no significant variation in composition revealing a material homogeneity within each coin.

The Ag Kα/Lα ratios determined using the intensities of EDXRF Ag Kα and Ag Lα X-ray lines on the obverse and reverse of a representative group of 41 coins minted during the sixteenth century period by *Dom Manuel I*, *Dom João III* and *Dom Sebastião I,* were compared with the the same ratios obtained on MBH analytical ® reference Ag alloy in Table 3.2.

Table 3.2 – Ratio between Ag Kα and Ag Lα intensities measured on the MBH analytical ® reference silver alloy and on obverse and reverse of the coins

Sample	Number of measurements	Ag Kα/Ag Lα
MBH 133X AGQ2	9	80.63±4.81
Obverse of silver coins	41	78.57±7.06
Reverse of silver coins	41	79.16±7.41

The mean Ag Kα/Ag Lα intensity ratio obtained on the obverse and reverse of the coins are very close to the acquired on the reference alloy. Knowing that for a 92 % Ag composition alloy the information depth for Ag Lα intensity does not exceed a thickness of about 2 µm and that 90 % of the Ag Kα intensity (higher energy emission) comes from a layer of 40 µm thickness (Kantarelou, V. *et al.*, 2011), the comparison between the EDXRF quantification using Ag Kα and Ag Lα lines on this group of coins (Figure 3.3) reveals a slightly lower silver content on the surface of the coins due to the presence of a tarnishing layer, not supporting the direct existence of a subsurface silver enrichment and still not explaining the up to 98 % Ag measured content.

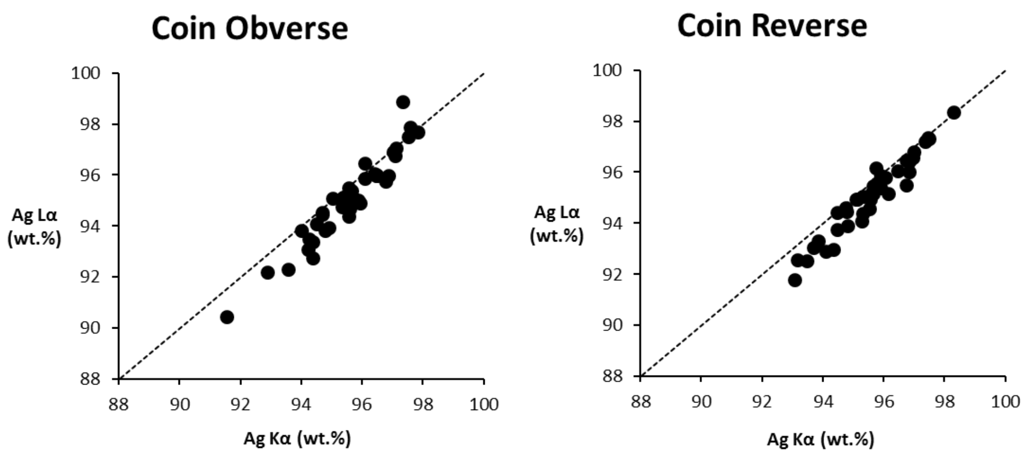

Figure 3.3 – Comparison of EDXRF Ag quantification using Kα and Lα lines for the obverse and reverse of the coins minted during the sixteenth century by *Dom Manuel I*, *Dom João III* and *Dom Sebastião I*. A dotted line of equal content was drawn for purposes of clearness.

It is known that tarnishing submicronic layers with a more or less dark coloration could influence the quantitative compositional surface analysis of Ag alloys. Mass, J.L. and Matsen, C.R., 2012, have reported for an incipient tarnished sterling silver coupon, XRF silver compositional deviations 0.1 wt.% lower than the content of the silver alloy after polishing, and a lower silver content in the range of 0.5-0.9 wt.% for a fully tarnished surface in some objects. Kallithrakas-Kontos, N. *et al.*, 2000, investigated the elemental compositional differences on tetradrachms silver coins by EDXRF, before and after a cleaning patina procedure, stating that this layer should have a small influence on the contents of several elements, as Ag, Au, Pb and Bi. However, these former investigations do not correlate the obtained data with the subsurface microstructure of the coins, or to the degree of selective corrosion consequences on the surface.

The variation found in the coins Ag Kα/Ag Lα ratio could be related to the amount of a submicrometer tarnishing layer on the surface of each of the coins, or to the influence of the surface roughness in the measurements of Ag Lα intensity, as the rough or flat regions would gave large count rates variations, contrary to the stronger Ag K intensity (Zwicky-Sobczyk, C.N. and Stern, W.B., 1997). Also, in agreement with the results, the MHB analytical® reference silver alloy Ag Kα/Ag Lα ratio is nearly the same as the one reported by Kantarelou, V. *et al.*, 2011, for the CNR- 141 reference standard (81.1±1.1) with a very close silver content (92.5 % Ag, 7.5 % Cu).

3.1.2 PIXE versus LA-ICP-MS

To provide an estimation of the silver bulk content of the coins and to investigate if the surface composition has been modified by the minting operations, the composition was determined with a nuclear microprobe on the cross-sections along the thickness of a few coins. Table 3.3 indicate the composition obtained by μ-PIXE on approximately 70 μm thick successive layers taken along the diametral cross-sections of four coins (C1 to C4) minted in *Lisboa* (C1 and C3) and in *Porto* (C2 and C4).

These analyses show that the surface copper depletion results in an overestimation of the superficial measured silver, with a value 2.5 to 5 % higher. This copper depletion represents 45-50 % less copper on surface than on the bulk of the coins and originates in most cases from the first 70 μm thickness subsurface layers.

The coins minted during *Dom João II* reign present higher gold and lower bismuth contents than the coins minted by *Dom Manuel I*, pointing to different provenances of the minting silver bullions in these different reigns. The mean coin bulk analysis (Table 3.4) indicate for three of the coins a silver content slightly higher, and for the other one slightly lower, than that for the maximum copper solubility on silver (91.2 wt.%), *i.e.*, the silver content below which it is possible a silver-copper eutectic formation on equilibrium cooling conditions.

Albeit the obtained silver bulk content in three of the coins is under the fineness fixed by the monetary law (91.7 %), but nevertheless very close, this value does not directly reveal the coinage fineness of the alloy that was mixed in the melting furnace and the precision with which the founders adjust the silver melting's with copper, nor the exactitude with which the assayers tested the silver ingots. On the beginning of the sixteenth century, the silver assays were made at *Lisboa* Mint House virtually by the touchstone, and not by the cupellation test, a test much more fallible and influenced by the weather and ambient conditions, depending of the available amount of light as attested in 1509 by the *Lisboa* Mint House technicians (Gambetta, A.F., 1978).

Table 3.3 – Composition obtained by µ-PIXE on diametral cross-sections taken on four coins minted in Lisboa and Porto, by *Dom João II* (C1, C2) and *Dom Manuel I* (C3, C4)

	%		**ppm**					
Position	**Ag**	**Cu**	**Zn**	**Ni**	**Au**	**Hg**	**Pb**	**Bi**
C1 - *Dom João II* (1481-1495) – *Lisboa* Mint								
Obverse	94.65	4.00	n.d.	n.d.	7524	n.d.	5834	n.d.
Obv. subsurface	93.75	4.97	n.d.	n.d.	6158	n.d.	6675	n.d.
Depth obverse	90.84	7.82	n.d.	n.d.	7067	n.d.	6305	n.d.
Bulk	90.11	8.62	n.d.	n.d.	7179	n.d.	5528	n.d.
	89.63	8.96	n.d.	n.d.	7500	n.d.	6561	n.d.
	89.75	8.86	n.d.	n.d.	7290	n.d.	6604	n.d.
	90.29	8.46	n.d.	n.d.	6238	n.d.	6254	n.d.
Depth reverse	91.56	7.12	n.d.	n.d.	6984	n.d.	6213	n.d.
Rev. subsurface	92.68	5.81	n.d.	n.d.	8158	n.d.	6849	n.d.
Reverse	94.26	4.25	n.d.	n.d.	8030	n.d.	6067	n.d.
C2 - *Dom João II* (1481-1495) – *Porto* Mint								
Obverse	93.95	4.04	n.d.	n.d.	9824	n.d.	9975	n.d.
Obv. subsurface	94.08	3.99	463	n.d.	8657	n.d.	10181	n.d.
Bulk	93.12	4.57	393	n.d.	10741	n.d.	11936	n.d.
	93.16	4.55	342	n.d.	10717	n.d.	11871	n.d.
	93.28	4.51	496	n.d.	10061	n.d.	11538	n.d.
	92.64	4.96	497	n.d.	10733	n.d.	12717	n.d.
	92.69	5.08	422	n.d.	9485	n.d.	11907	n.d.
	92.75	4.98	370	n.d.	10858	n.d.	10807	n.d.
Rev.subsurface	93.99	4.04	390	n.d.	8871	n.d.	11236	n.d.
Reverse	95.98	2.44	284	n.d.	7961	n.d.	7608	n.d.
C3 - *Dom Manuel I* (1495-1521) – *Lisboa* Mint								
Obverse	95.64	4.02	52	37	165	49	1267	1856
Obv. subsurface	92.53	6.93	n.d.	n.d.	n.d.	n.d.	1400	4000
Bulk	91.07	8.32	n.d.	n.d.	n.d.	n.d.	1900	4200
	91.21	8.19	n.d.	n.d.	n.d.	n.d.	2200	3900
	91.77	7.46	n.d.	n.d.	n.d.	n.d.	2600	5100
Rev. subsurface	91.77	7.46	n.d.	n.d.	n.d.	n.d.	2600	5100
Reverse	93.91	5.39	n.d.	34	108	113	1839	3319
C4 - *Dom Manuel I* (1495-1521) – *Porto* Mint								
Obverse	93.61	4.26	446	n.d.	3938	n.d.	15682	1065
Obv. subsurface	94.63	3.68	408	n.d.	2659	n.d.	13023	775
Bulk	92.52	5.43	442	n.d.	2589	n.d.	16336	1145
	91.92	6.00	526	n.d.	3063	n.d.	15909	1253
	90.82	6.92	565	n.d.	3142	n.d.	17815	1101
	91.16	6.69	683	n.d.	3370	n.d.	16644	766
	90.40	6.77	625	n.d.	3163	n.d.	17658	1214
Rev. subsurface	91.06	6.62	599	n.d.	3449	n.d.	18038	1089
Reverse	93.40	4.44	437	n.d.	3870	n.d.	16153	1061

n.d. – not detected

After adding copper to adjust the monetary silver fineness all the minor elements present on the entry silver bullion remained in the melted silver metal with the same residual quantities. The silver assayed at Lisbon mint house, *i.e.*, the bullion content (see Table 3.4), corresponds closely to the values of the pretended silver fineness of *11 dinheiros*. The higher bullion fineness encountered on the *Porto* minted coins must be an evidence of poor minting control related to the fact that this monetary workshop worked with long inactive periods and without a continued production, which adversely affects the alloy preparation as well the assaying expertise.

Table 3.4 – PIXE obverse, reverse and mean bulk compositions from four coins minted in Lisboa and Porto by *Dom João II* (C1, C2) and *Dom Manuel I* (C3, C4)

		%		ppm						Bullion
Coin		**Ag**	**Cu**	**Zn**	**Ni**	**Au**	**Hg**	**Pb**	**Bi**	**(%)**
C1	Obverse	94.65	4.00	n.d.	n.d.	7524	n.d.	5834	n.d.	
	Bulk	89.95	8.73	n.d.	n.d.	7052	n.d.	6237	n.d.	91.27
	Reverse	94.26	4.25	n.d.	n.d.	8030	n.d.	6067	n.d.	
C2	Obverse	93.95	4.04	n.d.	n.d.	9824	n.d.	9975	n.d.	
	Bulk	92.94	4.78	439	n.d.	10249	n.d.	12008	n.d.	95.18
	Reverse	95.98	2.44	284	n.d.	7961	n.d.	7608	n.d.	
C3	Obverse	95.64	4.02	52	37	165	49	1267	1856	
	Bulk	91.35	7.99	n.d.	n.d.	n.d.	n.d.	2233	4400	92.01
	Reverse	93.91	5.39	n.d.	34	108	113	1839	3319	
C4	Obverse	93.61	4.26	446	n.d.	3938	n.d.	15682	1065	
	Bulk	91.36	6.36	568	n.d.	3065	n.d.	16872	1096	93.46
	Reverse	93.40	4.44	437	n.d.	3870	n.d.	16153	1061	

n.d. – not detected

The investigation of concentration gradients between the surface and the bulk of four coins were realized by LA-ICP-MS elemental concentration depth profiles (Figures 3.4 and 3.5) with the determination of intensity ratios of Cu and four minor elements, Au, Hg, Pb and Bi, with reference to Ag. It should be noted that the first data on the LA-ICP-MS profiles are influenced by the tarnishing layer on top of the surface, and that the duration of the analysis was long enough to reach the core of the coins.

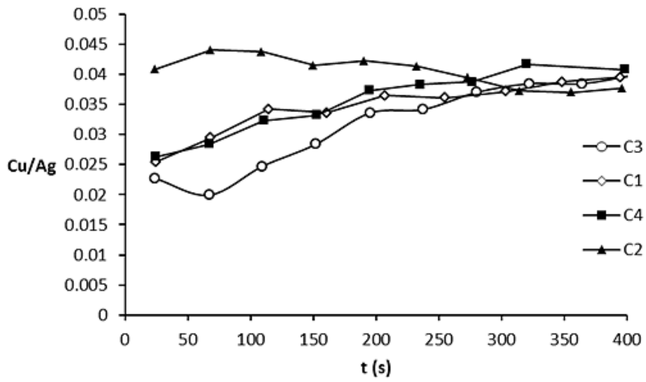

Figure 3.4 – Copper compositional depth profiles determined by LA-ICP-MS on obverse of coins C1, C3 and C4 and on reverse of coin C2.

A very significant finding was the confirmation of important copper depletions on the near surface region of the two coins minted in *Lisboa*, C1 (*Dom João II*, 1481-1495) and C3 (*Dom Manuel I*, 1495-1521), and one coin minted in *Porto*, C4 (*Dom Manuel I*, 1495-1521), resulting in important copper composition differences between the surface and the bulk of the coins of approximately 40 %. Albeit the subsurface copper profile was found to be different on these coins minted in successive reigns and on different chronological periods of currency emission, they show a consistency of the minting executed in both mint houses over time and indicate a distinctive feature of the subsurface region possibly introduced by the monetary production process.

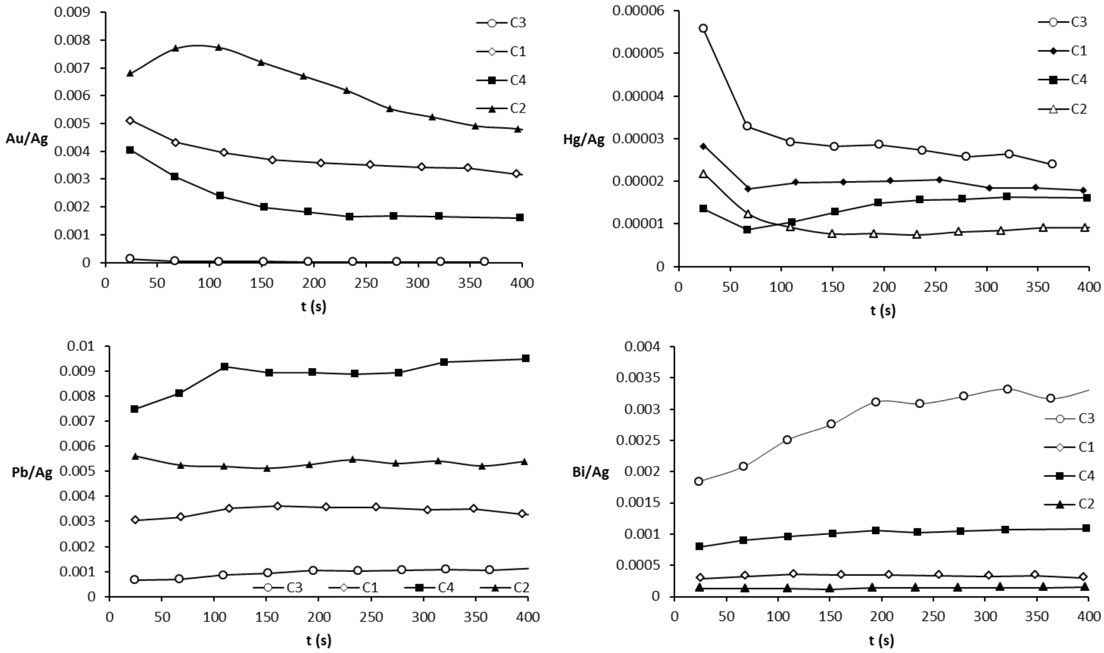

Figure 3.5 – Au, Hg, Pb and Bi compositional depth profiles determined by LA-ICP-MS on obverse of coins C1, C3 and C4, and on reverse of coin C2.

The other coin minted in *Porto*, C2 (*Dom João II*, 1481-1495), does not show significant surface copper depletion on the analyzed location, and has a silver content on the internal layers similar to that measured on the other coins. µ-PIXE results also suggest that the LA-ICP-MS copper compositional profile from C2 coin was realized in a non-representative region of this coin.

The minor elements Au, Hg, Pb and Bi (Figure 3.5) also show superficial contents distinct from the internal layers, which are in most cases not representative of the bulk composition of the coins. Ignoring the first measure in C2 coin, all coin's present compositional gold profiles decreasing from the surface, in correspondence with the µ-PIXE data obtained along the thickness of the same coins, being the coins minted by *Dom João II* (C1, C2) richer in this element than the coins minted by *Dom Manuel I* (C3, C4). Coins with low contents of Pb or Bi show relatively uniform compositional profiles of these elements along the thickness, but coins with larger contents have important lower compositions on surface, when compared to the bulk, revealing the propensity for these elements for being lost from the surface during the metallurgical history of the coins. Also, PIXE results confirm generally the compositional profiles for lead and bismuth obtained by LA-ICP-MS. The gold and lead variation trend agree with the data reported by Carter, G., 1964, and by Condamin, J. and Picon, M., 1964.

The mercury, present in these coins in very low contents under the limits of detection by PIXE, rapidly decreases in the initial outer layer (first two measures) but remains almost constant in the rest of the inner core.

3.1.3 SEM-EDS and XRD

Figure 3.6 show representative high magnification examples of back-scattered scanning electron micrographs obtained on diametral cross-sections taken from C2 and C3 *Vintém* coins. These images reveal a banded structure composed of a fine and darker Cu-rich solid solution phase, clearly identified by EDS and XRD analysis, in a brighter Ag-rich matrix, and an inhomogeneous subsurface region with a different copper to silver phase proportion when compared to the existent on the core of the coin. This near surface altered region almost without Cu-rich phase could vary in the same cross-section from approximately 25 to 60 µm deep. According to Table 3.3, it seems that this altered subsurface layer should be in most cases enclosed in a subsurface thickness under 70 µm.

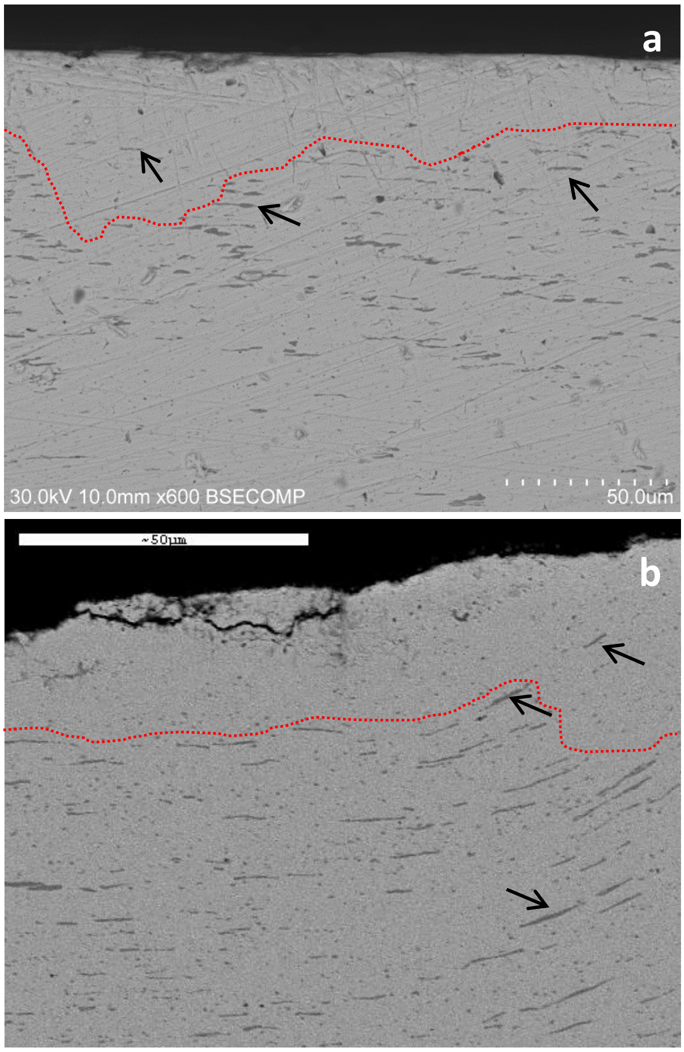

Figure 3.6 – SEM-BSE images in diametral section on Vintém coins minted (a) by *Dom João II* (C2) and (b) by *Dom Manuel I* (C3). The dotted red line identifies a subsurface area nearly devoid of the Cu-rich phase, which on the upper left of (a) extends from a depth of about 60 µm to as lower as 20 µm on the remaining image. This region extends also in (b) from about 25 µm on the left to about 40 µm on the right. Black arrows identify examples of the Cu-rich phase banded structure.

The XRD diffractogram of C2 coin (Figure 3.7) identified α-Cu and α-Ag solid solutions, presenting the silver peaks a slight angle shift attributable to the presence of copper in silver solid solution, affecting the phase lattice parameter.

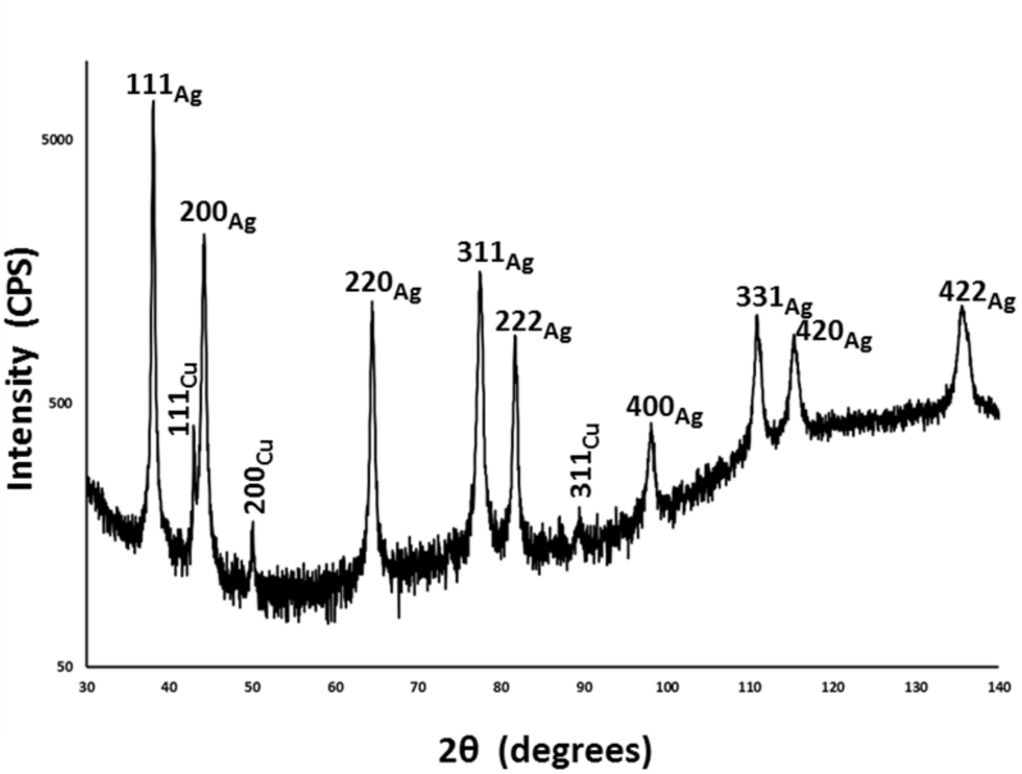

Figure 3.7 – XRD spectrum obtained in diametral cross section from C2 coin (Cu Kα radiation).

Also, all microstructures show no clear surface layer indicating that copper have been completely stripped out at the subsurface regions, no intergranular corrosion products, and any presence of voids replacing zones of the prior Cu-rich phase, aspects related to copper oxidation and leaching due to corrosion processes associated in most cases with burial environments, as presented in several investigations concerning coins with lower silver contents (Condamin, J. and Picon, M., 1964; Linke, R. and Schreiner, M., 2000; Linke, R. *et al.*, 2003, 2004 and 2004; Butcher, K. and Ponting, M., 2005; Moreno-Suárez, A.J. *et al.*, 2015) and that could extend to significant deeper thicknesses or to the entire coin.

SEM-EDS analysis in the darker phase regions of two coins (C1 and C2) belonging to the same chronological period of *Dom João II* gave an elemental composition very close to the eutectic composition, revealing that the metallurgical process led, in these cases, to the formation of small eutectic infillings due to the solidification process of the alloy. SEM-EDS analysis of the bright phase shows compositions of a copper supersaturated silver phase with copper contents lower than that related to the maximum copper content in silver solid solution. The silver and copper contents determined continuously by an EDS line scan from the bulk metal to the surface edges indicated a rather homogeneous elemental distribution in each phase without a compositional gradient.

3.1.4 Surface silver enrichment

The depth of information on Ag-Cu alloy coins depends on the matrix elemental composition and on the primary radiation and fluorescence radiation energy, with the greatest amount of Ag characteristic fluorescence radiation being emitted from the nearest surface layer. Linke, R. et al., 2003, have determined EDXRF relations between different compositions of Ag-Cu alloy matrixes and Ag Kα and Cu Kα radiation depth of information. From these relations, we could roughly obtain for a *11 dinheiros* Ag-Cu alloy depths of information for Ag Kα and Cu Kα radiation of about 20 µm and <4 µm for 63.2 % intensity, and between 60-70 µm and <10 µm for 95 % intensity, respectively. PIXE is known to have an information depth of 5-10 µm (Linke, R. et al., 2003; Šmit, Ž. And Šemrov, A., 2006).

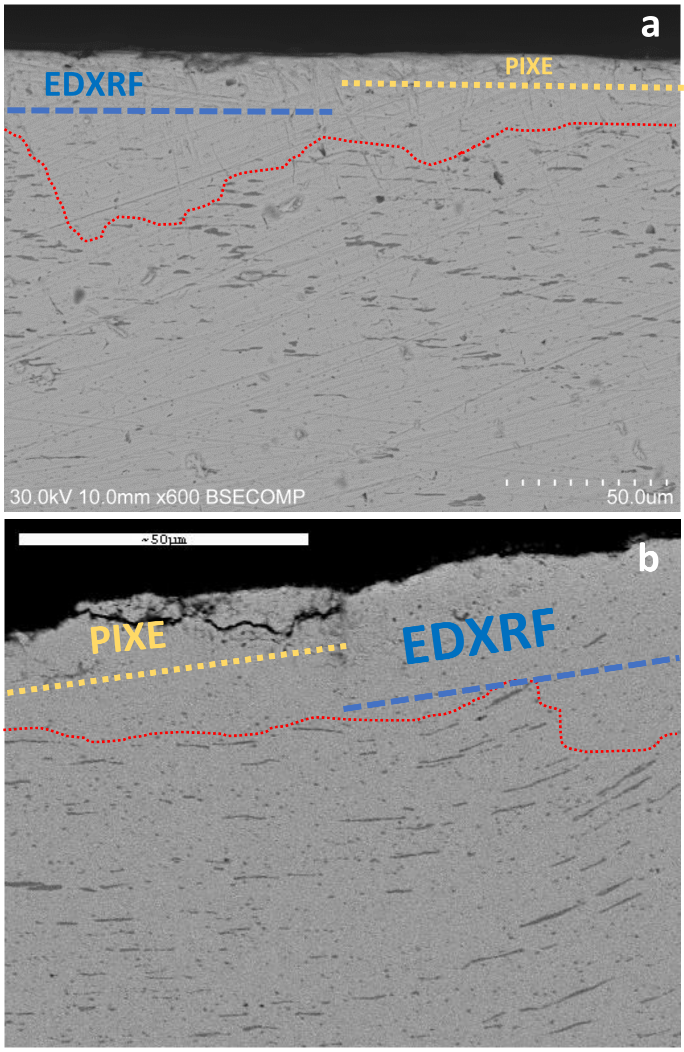

Figure 3.8 – SEM-BSE images in diametral section on Vintém coins minted (a) by *Dom João II* (C2) and (b) by *Dom Manuel I* (C3), showing EDXRF depth of information for 63.2 % intensity (≈20 µm) and maximum information depth for PIXE (≈10 µm).

Influenced by the effect of the metallurgical microstructure, EDXRF and PIXE obtain near identical copper contents as both methods are getting information coming mostly from a layer with the same microstructural morphology (Figure 3.8). Also, much of the silver detected by EDXRF analysis will come from this near surface region with a depth of some tens of micrometers with restricted proportions of Cu-rich phase in the microstructural arrangement adjacent to the surface, resulting on a higher silver EDXRF analysis content when compared to the core of the coin.

As expected, Ag-rich phases with similar compositions will give similar Ag-Kα and Ag-Lα intensities ratios, and the difference between Ag and Cu contents measured at the surface and bulk of the coins, results therefore in these coins from the contribution of the Cu-rich phase present in each of these regions. It derives apparently from the existent lower proportion of the Cu-rich phase in the near surface region and not from the depletion of copper in solid solution in the Ag-rich phase present in this region, as indicated by the homogeneous elemental distribution in the Ag-rich phase detected by SEM.

The conjunction of all the above results lead us to assume that the coin manufacturing process involved intergranular dry and wet corrosion in the annealing operations, primarily related to the preferential leaching of the Cu-rich phase in the subsurface layer depth. Also, to support this, there was not detected a silver gradient for the Ag-rich phase across this region and the inner core, which is in agreement with the Ag-Kα and Ag-Lα intensities ratios on coins and standards regardless of the higher Ag surface contents.

The monetary production process after ingot casting originate important silver compositional differences between surface and bulk in Cu-rich Ag alloys (Cope, L.H., 1972; Zwicky-Sobczyk, C.N. and Stern, W.B., 1997; Butcher, K. and Ponting, M., 2005; Arles, A. and Téreygeol, F., 2011), and also in the case of these Portuguese silver coins, a characteristic microstructure morphology results from the multiple hammering and annealing/quenching stages involved in the thickness reduction of the silver bar after casting, previously to obtaining the metal blank for minting, associated with the blanching on the end of the monetary process. All these operations contribute to the depletion of copper near the surface impacting the silver fineness obtained by superficial analytical methods. The fact that coins from different chronologies and different metallurgical histories have comparable microstructural features suggests that these resulted from similar manufacturing operations or treatments during the minting process.

It is also important to relate the thickness of this altered subsurface region with the monetary production process. According to experiments made with modern Ag alloys (Zwicky-Sobczyk, C.N. and Stern, W.B., 1997), the thickness of a replicated Cu depleted layer obtained by annealing and blanching before striking coins was reported to be in the range of 20 to 30 µm. Also, an archaeometric replication with four steps of thickness reduction and an annealing temperature of 700 °C originated a layer of about 15 µm thick in a eutectic Ag-Cu alloy (Arles, A. and Téreygeol, F., 2011). In addition, Butcher, K. and Ponting, M., 2005 found a 120 µm silver enriched layer on a Nero denarius with a core composition of 78.4 % Ag alloy, assuming that without an intentional prolonged oxidation with the removal of the copper oxidation by acids, this layer would be approximately 20 µm depth. However, when compared to these replicated results, it seems that the observed microstructural subsuperficial distribution of phases on these high silver alloy coins originates an unexpected higher thickness on this altered subsurface layer.

The lack of published data relative to possible surface silver enrichment in high silver content coins has hampered the understanding of this phenomenon for silver contents higher than 91.2

%, not allowing to know in what extent the surface elemental composition investigated by surface analytical methods will be influenced. Measured surface silver contents higher than 94 % have been considered relevant for coins bulk composition (Bugoi, R. *et al.*, 1999). Also, for Ag-Cu alloys expected to have more than 91.2 % Ag the silver surface composition has been regarded as following the composition of the Ag-rich primary phase, wherein no significant surface and bulk silver composition differences are assumed (Beck, L. *et al.*, 2004).

In Table 3.5, a collection of compositional data published in literature for these high silver alloys is present. For very pure roman silver coins, over 98 %, the obtained results have been considered reliable by Butcher, K. and Ponting, M., 2005, once the coins were produced without the employment of copper depletion and used the silver bullion composition that was regarded as pure silver at the time of coin production, which includes gold, bismuth, lead and small amounts of copper from the ores. According to the results presented on this table, there are no significant compositional surface/bulk differences (<1 %) in coins having low copper content under 3 %, *i.e.*, bulk analysis higher than 97 % Ag, and the determined surface concentration can be considered reliable for the original bulk composition in most cases.

However, silver compositional differences increase with the percentage of copper in the alloy and represent up to almost 7 % deviation for alloys with copper contents near the maximum value of solubility of this element in silver, well in correspondence with our results. Alloys with silver contents under 91.2 % show maximum compositional differences between the bulk and surface.

Table 3.5 – Calculated surface and bulk Ag content data of high Ag fineness coins from published literature.

Reference Analysis Method	Coin	Ag % Bulk	Ag % Surface	Surface/bulk difference (%)
Civici, N. *et al.*, 2007	7922	99.00	99.05	0.1
Surface XRF, Bulk PIXE	7890	89.95	95.65	6.3
	7882/7	88.75	96.50	8.7
Gitler, H. *et al.*, 2007 and 2008	JR18	98.1	98.1	0.0
Surface XRF, Bulk ICP-AES	JR4	98.1	98.6	0.5
	JR28	98.0	98.3	0.3
	IM26154	97.7	98.3	0.6
	JR26	96.0	96.7	0.7
	JR11	95.4	96.8	1.5
	JR17	94.8	98.9	4.3
	PC	93.8	96.0	2.4
	JR21	93.2	99.4	6.7
	JR2	92.3	96.3	4.3
	JR3	90.0	97.5	8.3
Ager, F.J. et al., 2013	N2	97.1	97.9	0.8
Surface XRF, Bulk micro-XRF	N8	97.2	97.5	0.3
	N9	96.2	98.3	2.2

Also, high purity Viking Age silver ingots with a silver content higher than sterling silver present significant compositional differences measuring 4 % less copper by XRF due to silver enrichment (Kruse, S.E. and Tate, J., 1992), and PIXE results obtained on an eighteenth century

Belgian fork (Weber, G. et al., 2000) with a very similar silver content (bulk - 91.8 %, surface > 94 %) to the *11 dinheiros* coins, has presented an altered depth layer of 20 µm, disclosing a great correspondence with our results. However, more investigation is needed to clarify the microstructural effects.

3.2 | Coins from the Joanine Kings dynasty

Please refer to the Table 2.1 for the identification of the number and type of analysed coins from each chronology, as well as to the mint workshop coin identification, and to Appendix 4 for the elemental compositional analysis of each coin.

3.2.1 *Evolution of silver alloys purity*

The elemental analysis revelead that the coins from the Joanine dynasty, representing the minted output of one hundred and forty years from 1438 to 1578, were made of silver alloys with global impurity contents generally under 2 %. They consist primarily of six minor/trace elements, nickel, zinc, gold, mercury, lead and bismuth, present of course in the coins along with silver and copper. A few coins of *Dom Afonso V* contain also arsenium as impurity.

Figure 3.9 shows the variability of the global impurity content of all the silver coin alloys from each chronology and permit to compare the evolution of silver purity over the years.

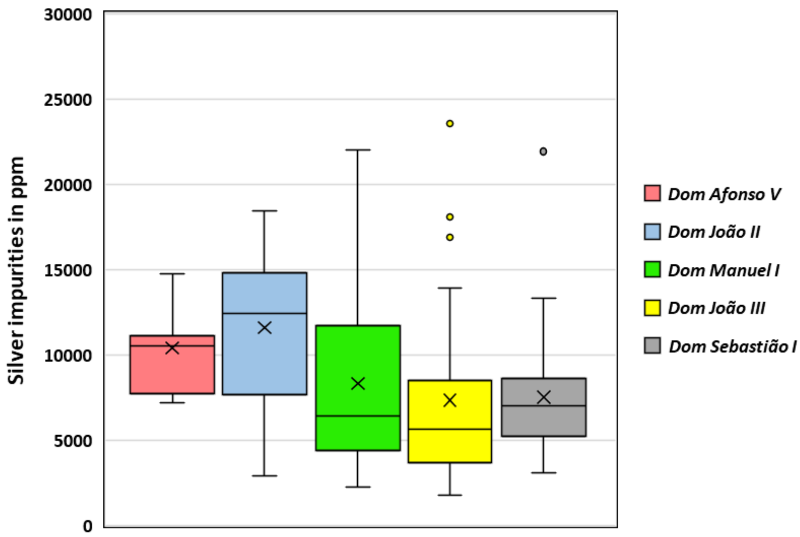

Figure 3.9 – Evolution of silver impurities content in ppm in the Joanine dynasty silver alloys. Important Hg outliers of *Dom Sebastião I* coins were removed for clearness of the results in terms of average and median values.

On the earliest chronologies from *Dom Afonso V* and *Dom João II* silver alloys with higher impurity contents were processed, having higher average values and median lines, situated in both cases above 1 % (10000 ppm) when compared with the following timelines.

This assumption is more apparent when based only on the data from the coins identified with the minting monetary letter (Figure 3.10). However, in the analised currency from *Dom Sebastião I* the Lisbon group was formed in a first moment by all the coins not bearing the monetary leter and considered thereafter to have an undetermined mint attribution, once these are considered by numismatists to have been minted in Lisbon, contrary to Porto minted coins which supports the P letter.

Albeit the small number of analysed coins from the two 15th century timelines, the results confirm that the chronologies pertaining to the 16th century from king *Dom Manuel I* onwards, exception made to the coins minted by this king in Porto, used silver metal with a purity on average better than the metal used on the previous century.

The increase in silver metal cleanliness would be certainly related to the novel processing of silver bullions extracted from European argentiferous copper ores sources, as from the latter second half of the fifteenth century, which contrast with the processing of earlier silver bullions produced from galena silver-rich ores. It should be noticed, however, that the value of global impurity content does not permit to assign individually each coin to a kind of silver source.

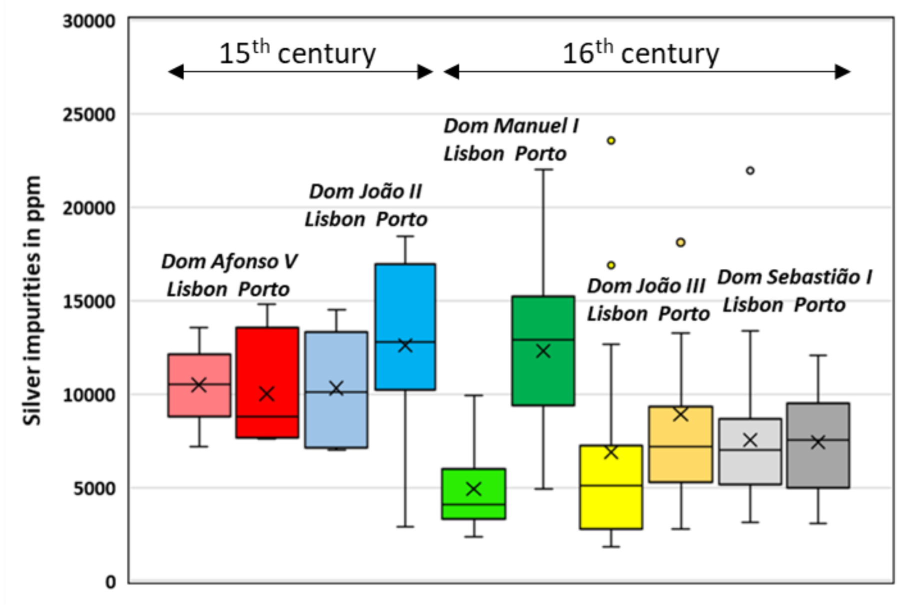

Figure 3.10 – Evolution of silver impurities content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint. Important Hg outlyers of coins from *Dom Sebastião I* were removed for clearness of the results in terms of average value.

Referring to Figure 3.10, the new silver source seems to arrive in Portugal only at the beginning of the sixteenth century, something that is well in accordance with the silver production growth and exploitation prosperity of argentiferous copper ores verified namely after 1510 (Neff, J.U., 1941 and 1987; Spufford, P., 1988; Munro, J.H., 2003 and 2006). Also, the increased silver refining quality from the 16th century coins point to the conclusion that coinages were made from better refined silver bullions, which would have benefited from the new practical tecnological advances in the silver production processes, and from the improvements in the assays methods compiled and described in the treatises of Vannoccio Biringuccio and Georgius Agricola.

Apparently, Porto mint continued to operate during *Dom Manuel I* reign with the metal used in the earlier chronologies, something to be further investigated.

The separate study of Au, Pb and Bi contents and their graphic representation during the analysed period permit to enhance the perceived evolution trends of the used silver metal (Figures 3.11 to 3.13). Au and Pb are the most concentrated elements forming together the main impurity content of the coins, and Bi can be exceptionally important for the differentiation of the silver alloys, albeit the normally low contents.

The coins from the two earlier chronologies are particularly characterized by a silver alloy having on average higher Au and lower Bi contents, as opposed to the following coinage periods with lower Au and higher Bi contents. Despite these seemingly marked tendency, the small number of coins from these earlier mintings from the 15th century encourages the additional analysis of more specimens to confirm these trend patterns.

According to these data, the currency reform of *Dom Manuel I* would seem to have not involved the recycling of the earlier currency in circulation in the major mint of Lisbon, where the minting of new coins was made at the expense of fresh metal supplies. In fact, the decline of more than ten times in Au average content in *Dom Manuel I* Lisbon coinage is therefore consistent with the shift of the silver source.

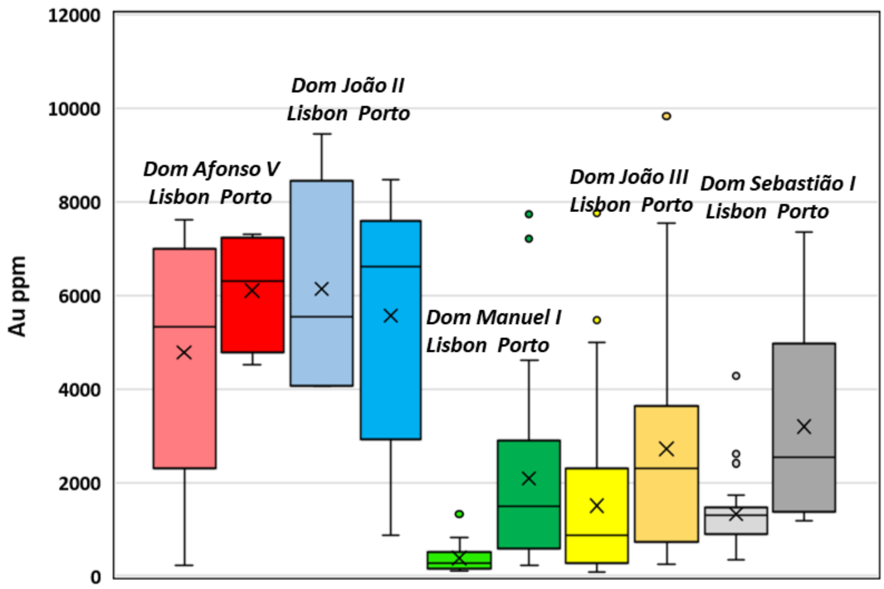

Figure 3.11 – Evolution of Au content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

Also, the shift from high gold/lower bismuth to low gold/high bismuth suggests a sudden change of silver bullion source. This is attested in Lisbon minted coins by the particularly reduced dispersion and the extremely low content of gold and minor lead composition suggesting a more carefully refining operation, and by the very high levels of bismuth which discriminate the produced silver alloy from the earlier coinage of *Dom João II*.

The Porto mint during *Dom Manuel I* reign is an exception. Porto mint seems to have had a gradual shift to this new silver source presenting higher gold and lower bismuth than Lisbon mint, suggesting the occurrence of a gradual dilution of the new source of silver with amounts of the older silver metal used on the previous century, which would gradually increase the gold content of the silver alloys in the Porto coinage.

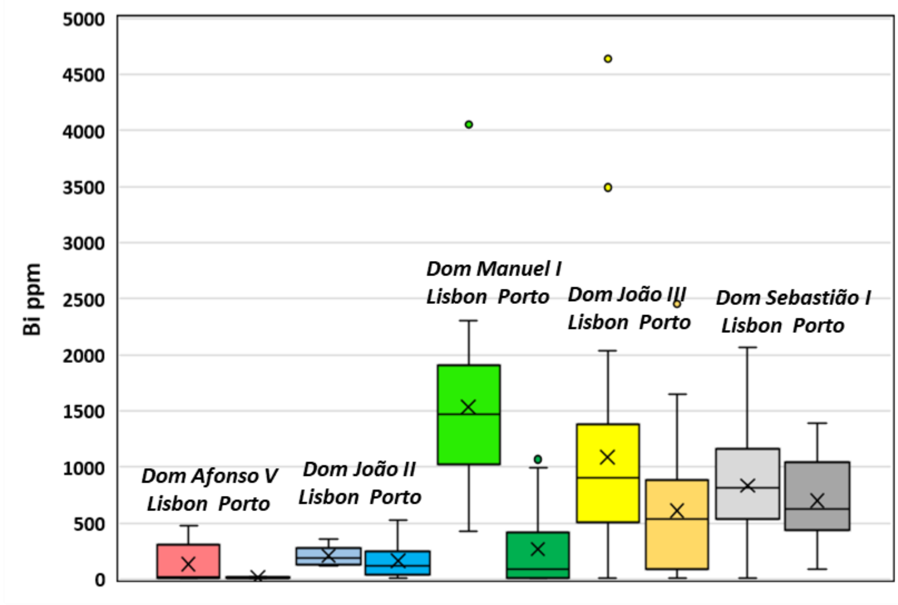

Figure 3.12 – Evolution of Bi content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

It would appear that during *Dom Manuel I* period, Porto mint still used silver from the earlier silver sources, based on the Pb content higher than that of *Dom João II* Porto mint, and on the global impurity and Bi contents, which follows the trends of the earlier chronologies.

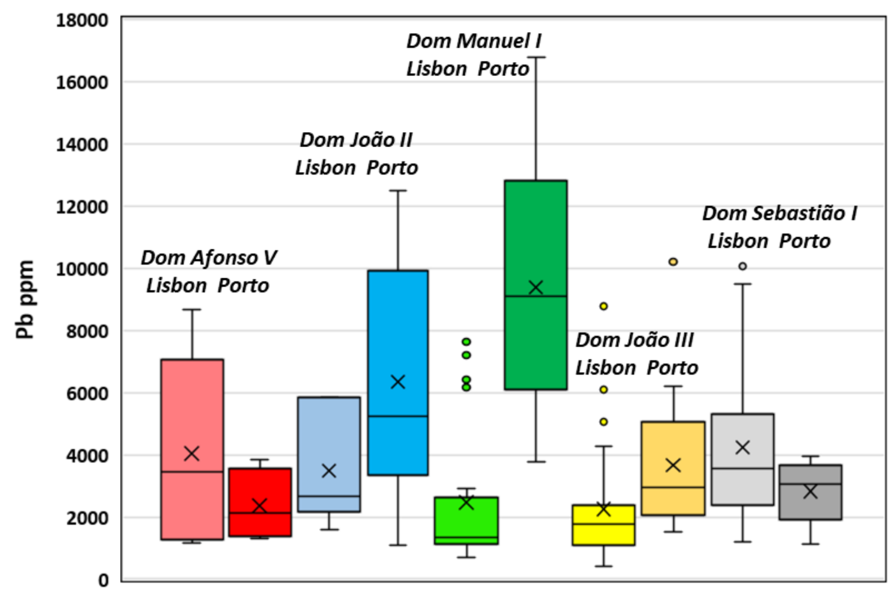

Figure 3.13 – Evolution of Pb content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

However, knowing that the gold concentration originates from the used source(s) of silver metal, the similarity of the Au content trend along approximately eighty years of the 16th century chronologies, namely from this mint, seems to contradict this. Nevertheless, when compared with Lisbon coins, the important Au dispersion of Porto coins group give the impression that we could be in the presence of significant silver recycling's involving the remelting of earlier coins together with the processing of silver, or mixtures of metal from the older and new silver sources, which in both cases could have altered the elemental signature of the Porto minted silver. If this was the case, why is this so marked only in the Porto minted coins from this chronology? The management of metal sources for the Porto monetary production process would have had specific and distinct features?

The Porto minted coins from *Dom Manuel I* chronology raise thereafter some questions to be further clarified. If the difference in chemical compositions resulted from i) the jointly processing of part of the earlier silver metal in the form of older currency and/or silver bullions, together with the novel exploited European silver metal that was possibly entering through Lisbon mint, or from ii) the supply and utilization on the North of the country of a silver metal source with a different chemical signature.

Over the sixteenth century, the graphical representation for each monetary workshop build up distinct Au and Bi contents tendencies for the processed silver alloys, which trends run toward an uniformization of the silver alloys of both centuries: Lisbon mint exhibits increasing Au and decreasing Bi contents trends over the three analysed chronologies, and Porto monetary workshop also presents an increasing Au tendency, on average with higher contents than Lisbon, and in contrast, an increasing Bi trend. Knowing that gold and bismuth are important silver discriminators and have been regarded as being solely associated with the silver sources (Gitler, H. et al., 2009; Pernicka, E., 2013), it could appear that both mints would receive and/or process during this period silver supplies with different chemical signatures.

Dom João III minted alloys seems to be influenced by important recycling's of the older currency, due to the lack of silver metal in the kingdom and to major weight debasements of the silver coins, which were responsible for the remelting of the circulating coins (Aragão, A.C.T., 1875-1880; Peres, D., 1957).

As suggested by the low Au content and small dispersion of the coins silver alloys, the production of the Lisbon monetary workshop during *Dom Sebastião I* reign, as occurred on the beginning of this period with *Dom Manuel I* timeline, would appear to have also relied more in the processing of fresh silver metal than on the recycling of earlier metal. However, that seems not to be the case, as evidenced in the further discussion.

3.2.2 *The coins minted by Dom Afonso V (1438-1481) and Dom João II (1481-1495)*

The investigated eleven coins of *Dom Afonso V* and fourteen coins of *Dom João II* from several types (see Table 2.1), pertaining to BdP collection, are shown in Appendix 1 by reference numbers 1 to 25.

Excepting the *Leal* (see number 1 in Appendix 1) which was mint according the earlier monetary law of *Dom Duarte I*, the other coin types from *Dom Afonso V* were introduced mostly during the second half of his reign: *Real Grosso* coins (see numbers 5 to 11 in Appendix 1) were produced from 1457 onwards, substituting on this date the earlier silver *Leal*, and the minting of the *Chinfrão* coin (see numbers 2 to 4 in Appendix 1) occurred after September 16, 1472 (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

The *Real Grosso* coins bearing in one face the Castile and Leon coat of arms (see numbers 7 and 8 from Appendix 1) were minted during the Portuguese pretension to the Castile crown succession. *Dom Afonso V* fighted for Castile crown rights of his niece *Dona Joana* going into war with the Catholic Kings and invading Castilian territory until he was defeated in the Battle of Toro in 1476. These rare coins involve an important historical and numismatic question with respect to the assignment of their minting place, being referred as having been produced in Toro between May 1475 and June 1476. The distinction of the silver used on these coins is thereafter of the utmost importance for validating this assumption.

In the monetary law from September 1472 criating the *Chinfrão*, *Dom Afonso V* mentions the scarcity of silver coins in the kingdom due to these being taken out in the merchantile trade, granting the free foreign silver admission in the country and instructing that the old currency from the past Kings, which still circulate, should be melted and refined together with some foreign silver coins and older silver medals to produce this new coin.

The *Vintém* coin type was introduced by *Dom João II* that, on December 25, 1489, encouraged the introduction of silver from out of the kingdom and renewed the circulation prohibition of *Leal*, *Real Grosso* and *Chinfrão* coins, demanding that these should be melted for minting this new coin.

According to Figure 3.14, the older *Leal* coin discriminates from all the other coins of *Dom Afonso V* chronology because of its highest Bi content, and a closer match can be found among seven out of the eight *Real Grosso* and *Chinfrão* coins, which form a unified group and were produced from a very low Bi content silver source. In most of these coins, Bi content is under PIXE detection limit (five in seven coins) and only one *Chinfrão* coin stands out for its extremely low Au and medium Bi contents. Could this coin be related with the recycling of old currency minted before 1438, or with the melting of other ancient silver metal artifacts, as requested by *Dom Afonso V* in 1472 for the minting of *Chinfrão* coins?

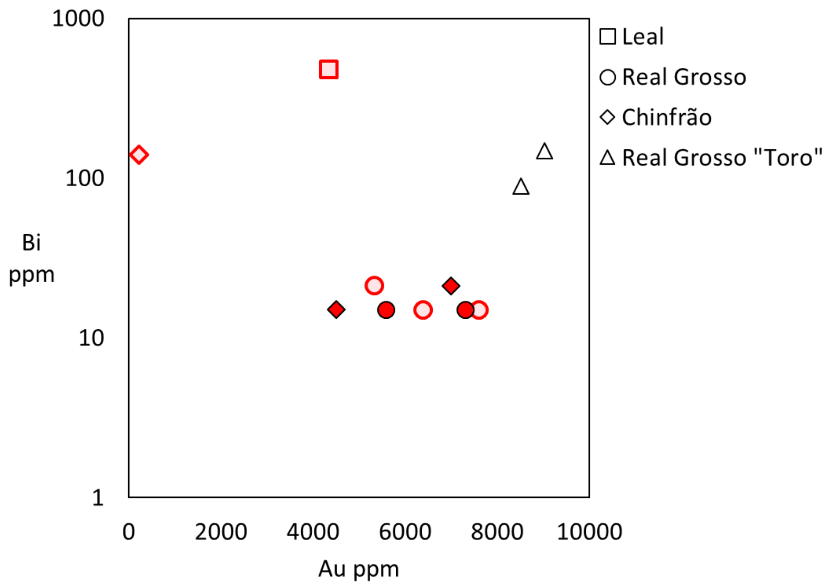

Figure 3.14 – Scatterplot of gold against bismuth in ppm of *Dom Afonso V* coins, identifying the type of coins and the Lisbon (pink) and Porto (red) workshops. Logarithmic scale on ordinates axis.

As for the *Real Grosso* coins minted for Castile and Leon (labelled hereinafter in the plots as *Real Grosso* "Toro"), they present medium Bi levels and the highest Au content, identifying them as being made with a silver metal distinct from all the above-mentioned coin types, only used during this reign for the minting of these coins.

It seems that Bi and Au constitute good chemical elements for the differentiation of the distinct silver metal sources from this chronology, failing however to separate the production of each of the monetary workshops, and albeit the small number of coins analysed, these elements also suggest the utilization of distinct silver sources during *Dom Afonso V* kingdom.

When correlating *Dom João II* and *Dom Afonso V* coins (Figure 3.15), a major aspect is that a part of *Dom João II Vintém* coins had a contribution of the silver source used to produce the *Real Grosso* for Castile and Leon in the previous timeline, having similar gold and bismuth contents, and another part of these coins had been produced possibly by recycling and remelting the former *Dom Afonso V Leal*, *Real Grosso* and *Chinfrão* coins as requested by *Dom João II* in 1489.

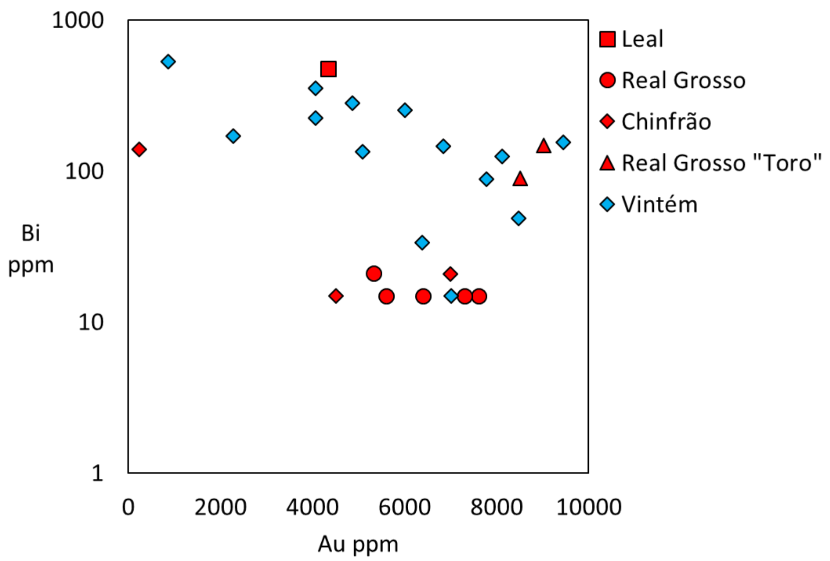

Figure 3.15 – Scatterplot of gold against bismuth in ppm of *Dom Afonso V* (red) and *Dom João II* (blue) coins, identifying the type of coins. Logarithmic scale on ordinates axis.

In addition, when indexing the gold/bismuth ratio against the lead/bismuth ratio, the first one more related to the initial composition of the extracted silver (Mckerrell, H. and Stevenson, R.B.K., 1972; Metcalf, D.M. and Northover, J.P., 1986; Gitler, H. et al., 2009; Pernicka, E., 2013) and the later to the silver metallurgical processes (L' Héritier, M. et al., 2015), it seems to result a chronological bias between both groups of coins, not considering *Dom Afonso V Leal* and the former *Chinfrão* outlier coin, presented as the two ▲ on the left of the plot (Figure 3.16). Also, this plot allows to highlight possible contributions from *Dom Afonso V* coin's remeltings's in *Dom João II Vintém* minting's, namely from Porto

A similar metallurgical production discrimination from both chronologies could also be seen in a scatterplot of Pb/Bi versus Hg content (Figure 3.17).

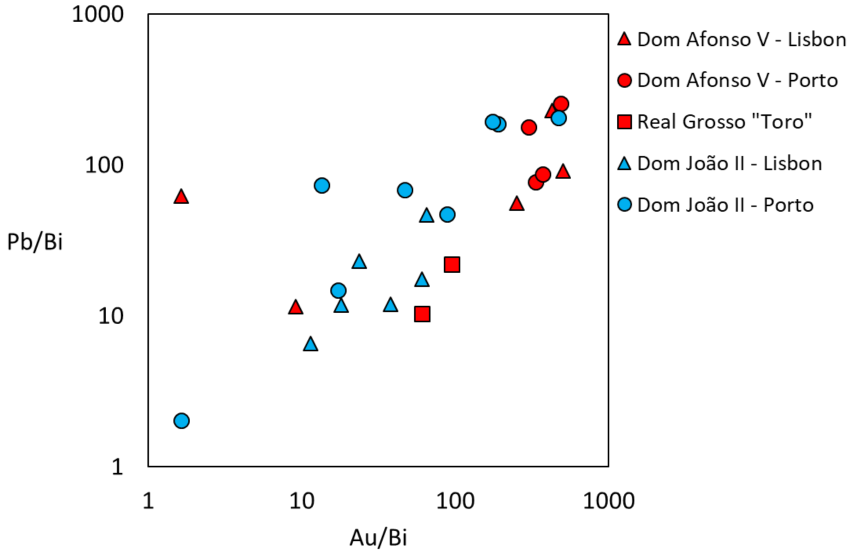

Figure 3.16 – Scatterplot of Au/Bi against Pb/Bi ratios of *Dom Afonso V* and *Dom João II* coins, identifying the Lisbon and Porto monetary workshops. Logarithmic scale on abscissas and ordinates axis.

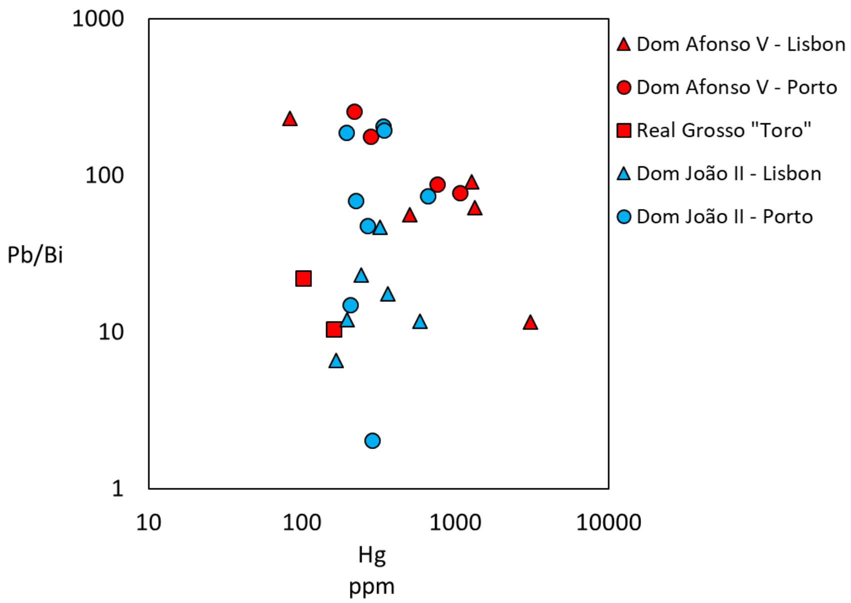

Figure 3.17 – Scatterplot of Hg content in ppm against Pb/Bi ratio of *Dom Afonso V* and *Dom João II* coins, identifying the Lisbon and Porto monetary workshops. Logarithmic scale on abscissas and ordinates axis.

From the later two plots, it appears that during *Dom João II* reign the Porto mint could have been more involved in the reutilization of the older silver currency, minting part of the new *Vintém* coin based on the remelting's of the ancient coins still in circulation. However, given the small number of the sampled coins originated from only one coin type of *Dom João II*, it would be wised to further investigate this assumption in the future.

3.2.3 *The coins minted by Dom Manuel I (1495-1521)*

A total of 59 coins from four types (see Table 2.1) representing in their major part emissions of the two monetary workshops of Lisbon and Porto were analized: *Meio Vintém* (see Figure 3.20 hereinafter), *Vintém* (e.g., 26-32 in Appendix 1), *Meio Tostão* and *Tostão* (e.g., 33-34 in Appendix 1).

The actual monetary legislation of this period is scarce (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992). The *Vintém* was minted in Lisbon and Porto by the law of the preceding reign, having the emissions of the last referred monetary whorkshop better quality of engravings. The *Meio Vintém* coin do not bear a monetary letter identifying the mint where they were produced, and thereafter have been attributed to the Lisbon mint. However, Gomes, A., 2003, had interrogated if the coins bearing a gotic letter Π on the king's name would pertain to the Porto mint.

Dom Manuel I was the first Portuguese king to mint the *Tostão*, still it is not recognized when this coinage had started, having occurred possible after 1504 (Trigueiros, A.M., 2016). As acknowledged from a document dated 26 Abril of 1509 (Aragão, A.C.T., 1875-1880), a great number of counterfeited *Tostão* coins had been disseminated near Guarda and their manufacturers had been captured, attesting that the *Tostão* coin was already widespread before this year. Regarding to the *Meio Tostão*, this coin was only minted in Lisbon in 1517.

It was found that Au/Bi and Pb/Bi ratios constituted good discriminators of *Dom Manuel I* coins. Beginning with the *Vintém* (Figure 3.18), the oldest coin type of this period, there can be little doubt about the existence of a serious compositional diference in the higher number of the coins sampled to warrant the conclusion that the material from the two different mints, Lisbon and Porto, have each a distint and dominant trace element signature.

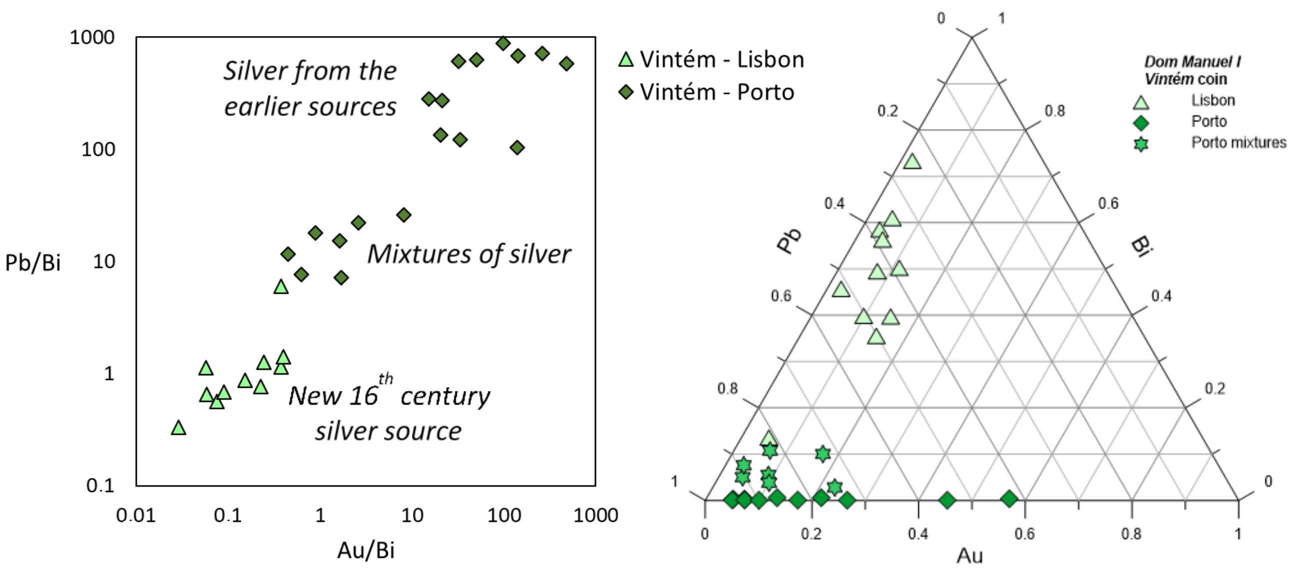

Figure 3.18 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Manuel I* Vintém coins, identifying Lisbon and Porto mints. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom Manuel I Vintém* coins, identifying Lisbon and Porto mints.

On the Au/Bi against Pb/Bi plot, all but one of the Lisbon minted coins locates in a correlation group characterized by a very low gold content, low lead and very high bismuth content. Porto coinage has higher gold contents than Lisbon and seems to be discriminated in two groups, one with very low bismuth and very high lead content and another with a bismuth content intermediary between this group and the Lisbon group of coins.

The Porto higher gold and lower bismuth content group (Figure 3.18, right) seems to relate to the alloy composition of the former 15th century silver sources used by *Dom Afonso V* and *Dom João II* (see Figures 3.11 and 3.12), representing the use of material obtained through the earlier established silver supply circuits, the use of older supply reserves, the remelting of silver coins from the previous chronologies, or even a combination thereof. However, Lisbon minted *Vintém's* were made with a new silver source material, clearly different from the silver alloys used up to now in the country, indicating that the Portuguese capital during this period was receiving silver supplies from a new European source, possibly involving new trade circuits of this metal. This compositional analysis agrees with that previously formulated with basis on the global silver impurity content. Further from Figure 3.18, it appears that a mixture of both silver sources was responsible for part of the Porto coinages, constituting a group of data closer to the Porto coins group.

Also, as occured during *Dom João II* chronology, it seems that Porto monetary production had relied more on older silver supplies, either in the form of bullions or of older circulating coins. As this mint had worked with long inactive periods and without a continued production, it is possible that its operation had depended more on the collection of *Dom Manuel I* predecessors' coins for further recycling?

When overlapping on the previous graphs the results of the *Meio Vintém* coins (Figure 3.19), a coin which do not exhibit the mint identification, we verify that their coinage was made unexpectedly both in Lisbon and in Porto mints.

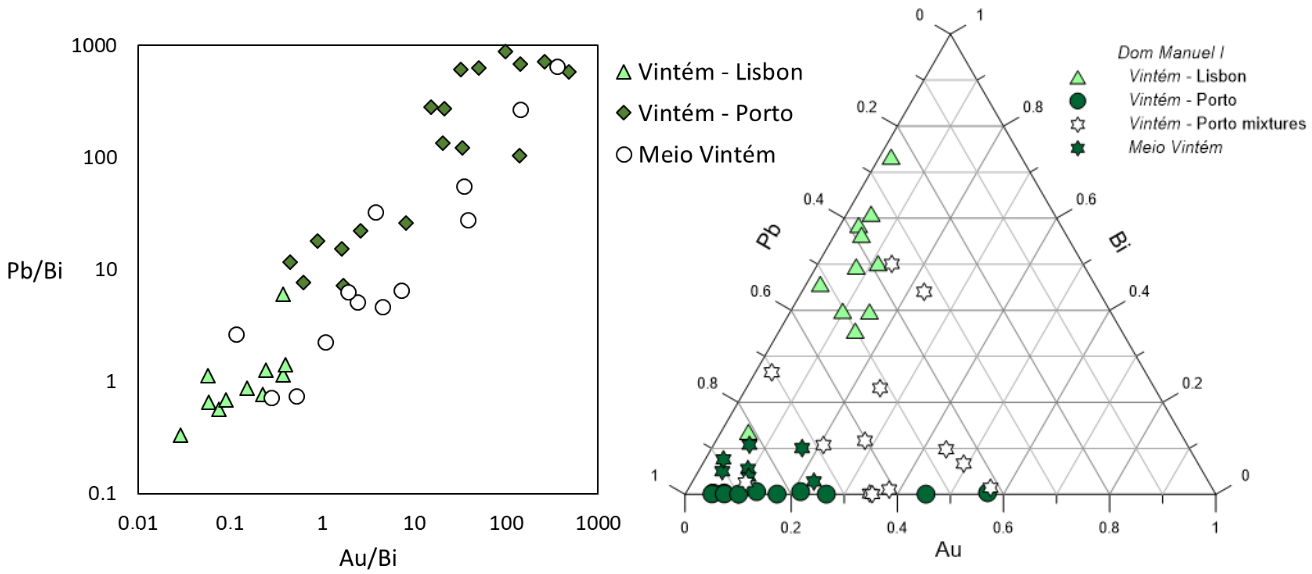

Figure 3.19 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Manuel I Vintém* (Lisbon and Porto mints) and *Meio Vintém* (without mint identification) coins. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm for the same coins.

According to the sampled coins, it could be inferred that nine out of thirteen *Meio Vintém* coins were produced in Porto, correlating within the former two discriminated groups, meaning that the minting of this coin was undertaken preponderantly on the Porto monetary workshop. Albeit this reveals a new important issue for numismatic knowledge, does it really imply that Porto mint was responsible for the major part of the coinage emissions of this less value coin?

Also, concerning the issue of the *Meio Vintém* engraved letterings, the presence of a gotic letter Π (Figure 3.20) was detected in the coins INCM 13187 and INCM 13191 whose composition correlates with the Porto silver mixture group and to the Porto group, respectively, agreeing with Gomes, A., 2003, previous presumption that this kind of engraving should have been used in the Porto mint.

Figure 3.20 – Above: *Meio Vintém* coins with a gotic letter Π assigned to *Dom Manuel I* name. The INCM 13183 have an intermediary N letter engraving between Π and a regular N letter. Below: *Meio Vintém* coins with the inverted N letter, "И", assigned to *Dom Manuel I* name. The coins are enlarged and not to scale (actual $\Phi \approx 16$ mm).

The coin INCM 13183, also from Porto mixture group, presents a N engraved letter somehow related to the former Π, being possibly an intermediary arrangement between this later and a regular N letter. All of the above identified coins also present the Porto typical "p", "r" and "E" script used by this mint. In eight of the investigated coins, which include all the coins minted in Lisbon, the king's name is written with an inverted N letter, that is, an "И", as shown for example in INCM 13182 and INCM 13186 assigned to Lisbon, and INCM13185 assigned to Porto. For example, the legend in INCM 13191 read, + EMAΠVEL . P . R . P . ET . A . D . G . compared with + I : EMAИVEL . R . P . ET : A . D : G . on the INCM 13182 coin.

With reference to the remaining coins, the engraved lettering supports a regular N letter in one of the coins, that could not be identified in the other coin due to its bad state of wear/conservation. Figure 3.21 denotes de *Meio Vintém* coins identified in Figure 3.20.

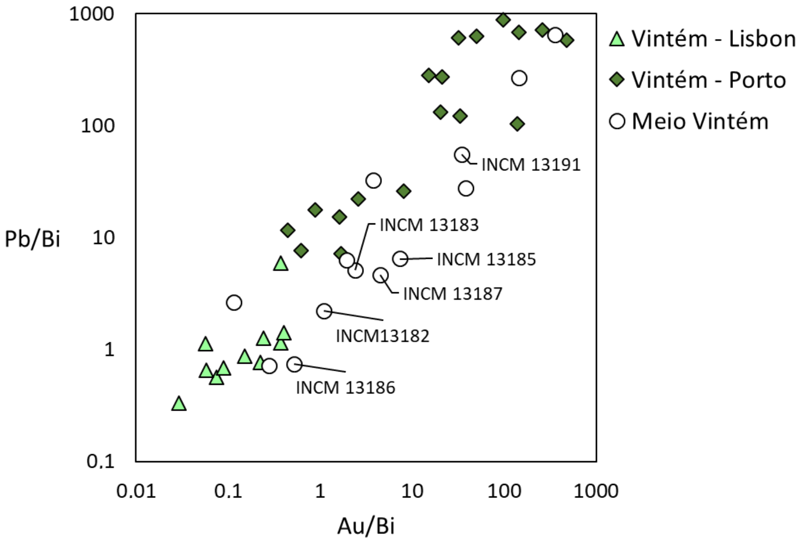

Figure 3.21 – Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Manuel I Vintém* and *Meio Vintém* coins, identifying Lisbon and Porto mints, denoting the *Meio Vintém* coins from Figures 3.20. Logarithmic scale on abscissas and ordinates axis.

The data from Lisbon minted *Tostão* and *Meio Tostão* introduce new information about the compositional character of the silver alloys used in this mint. The group of silver's sources mixtures, so far constituted by *Vintém* and *Meio Vintém* coins and for the most part related to Porto, enlarges to reveal a distinct component of the used Lisbon silver alloys (Figure 3.22), showing that this mint also relied on the utilization of earlier silver supplies just like the mint on the North of the country. Based on the evidence of the prevalence of mixed silver sources in the currency emissions of the newly introduced *Meio Tostão* and *Tostão* coin types at about the second half of *Dom Manuel I* reign, this minting practice seems to arise on a later date in the case of Lisbon, possibly indicating that these silver sources mixtures would have occurred toward the end of this monarchy period.

Would the Porto higher gold and lower bismuth minting group represent earlier coinages from this monetary workshop? Would the Porto silver's mixture group consist in later coinages from this mint?

It would be required a numismatic study of the coins different engraved lettering's and dies constituting each group, to assess whether these groups refer to different minting emissons in time, and to understand their association. It would also be required to acquire further data from Porto minted *Tostão* coins to confirm these suppositions.

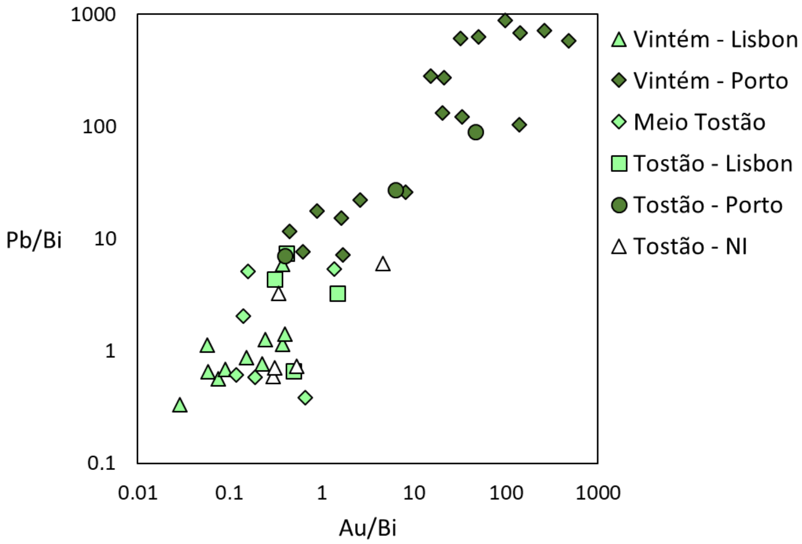

Figure 3.22 – Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Manuel I Vintém*, *Meio Tostão* and *Tostão* coins, identifying Lisbon and Porto mints. In some of the *Tostão* coins the mint house is not identified (NI). Logarithmic scale on abscissas and ordinates axis.

The results, according the existing historical numismatic knowledge, show that the *Meio Tostão* coins were minted in Lisbon and that the unidentified mint *Tostão* coins seems to have been produced in this monetary workshop as well. It is also perceived that *Meio Tostão* and *Tostão* coins were minted in Lisbon in campaigns other than those of the *Vintém* coins (Figure 3.23), integrating both coin types the two distinct Lisbon compositional groups. The same could not be inferred from the Porto minted *Tostão* coins, due to the small number of investigated coins.

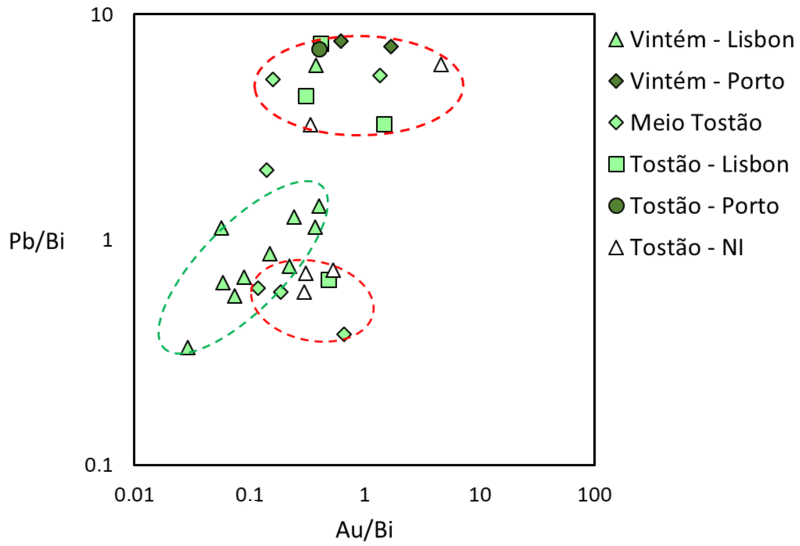

Figure 3.23 – Enlargement of the lower left quadrant of Figure 3.22. Scatterplot of Au/Bi ratio against Pb/Bi content denoting the Lisbon correlation groups of *Dom Manuel I Vintém* (green contour), *Meio Tostão* and *Tostão* (red contour) coins. Logarithmic scale on abscissas and ordinates axis.

The global correlation found for the four identified silver alloys groups is presented below, based on the results of the coins identified by the monetary letters, and on those unidentified which were previously attributed to each of the Lisbon and Porto mints, together with the correlation of all the mintings from the three chronologies already analysed (Figure 3.24, Left).

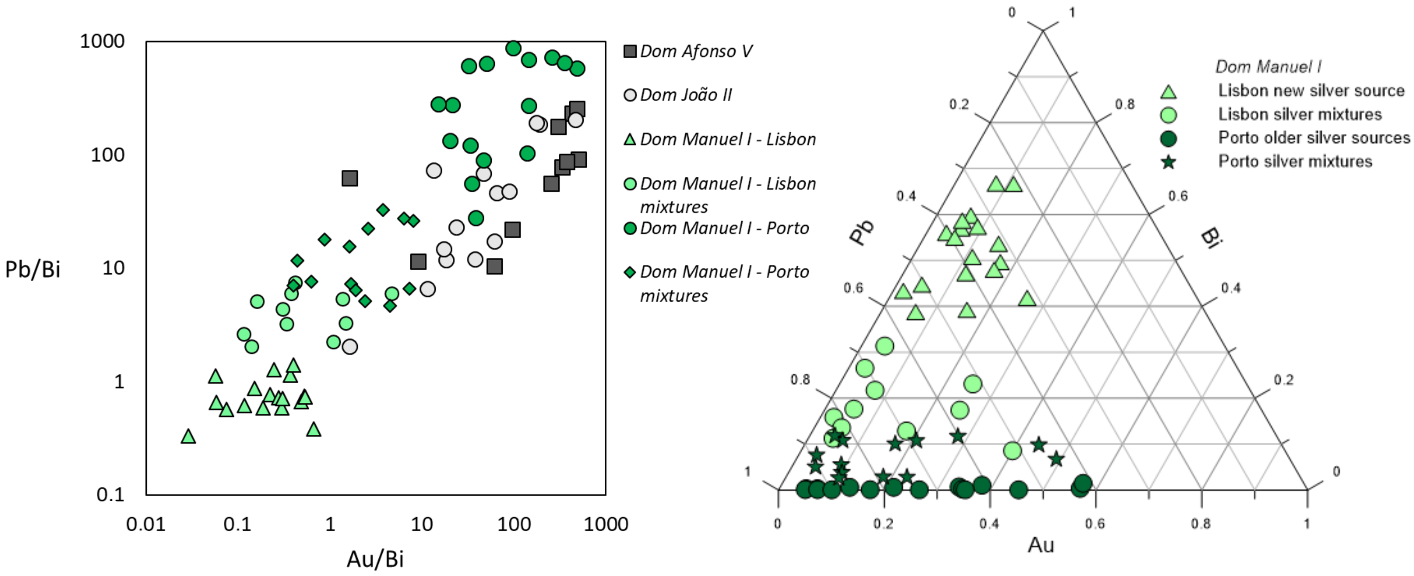

Figure 3.24 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom Afonso V*, *Dom João II* and *Dom Manuel I* chronologies. *Dom Manuel I* coins are discriminated by Lisbon and Porto mint workshop. Logarithmic scale on abscisssa and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of all *Dom Manuel I* coins, identifying Lisbon and Porto mints.

There can be little doubt about the overall trend of the *Dom Afonso V*, *Dom João II* and Porto *Dom Manuel I* mintings. The coins compositions of the first two timelines form distinct correlations on the right, with very narrow alignments that somehow overlap with the later Porto mintings from *Dom Manuel I*, confirming that the composition of the coins minted in Porto by *Dom Manuel I* are more related with the compositions of the earlier chronologies of *Dom Afonso V* and *Dom João II*.

Apparently, Porto mint had continued during *Dom Manuel I* reign to operate with metal pertaining to the sources used in the former century metal trade. It should be noticed that all, but three coins located in the *Dom Manuel I* Porto group have a Pb content from 0.8 to 1.6 wt.% (see Figure 3.25) and three of *Dom João II* coins also minted in Porto show the same order of magnitude of this element (0.9-1.2 wt.%). Is this a compositional characteristic of a specific silver source whose supplyings had initiated with *Dom João II*, or is it related with the practice of silver recycling through cupellation?

It is knowed that Porto still received silver metal from Flandres on the beginning of the 1500's and there is a notice of silver arriving before 1506 to the North of Portugal, to Vila do Conde, imported from this provenance and from some French Atlantic locations as Rouen and La Rochelle, whose major part entered the Porto mint (see Chapter 1 – 1.2). Would the importation of this silver metal follow the older established silver merchandising circuits? Could the composition of this silver source/circuit be related to that of the Porto coins group previously identified?

As can be seen, Lisbon coinage from *Dom Manuel I* stands out clearly from all the other coins mintings, representing a clear shift of the earlier silver trade circuits and/or sources.

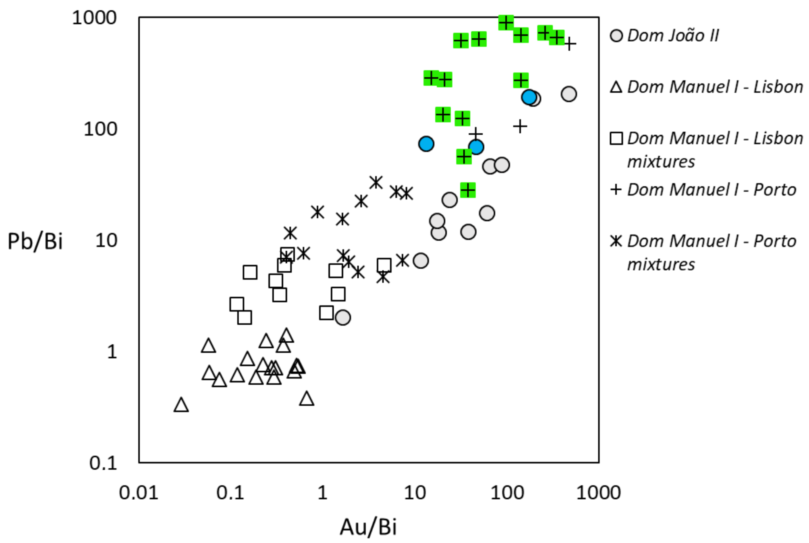

Figure 3.25 – Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom João II* and *Dom Manuel I* chronologies, identifiying the higher lead content Porto coins, respectively with blue and green colors. Logarithmic scale on abscissas and ordinates axis.

3.2.4 *The coins minted by Dom João III (1521-1557)*

A total of 86 coins from seven types (see Table 2.1) were analized: *Cinquinho* (e.g., 35-36 in Appendix 1), *Meio Vintém* (e.g., 37-38 in Appendix 1), *Vintém* (e.g., 39-43 in Appendix 1), *Real Português* (e.g., 44-47 in Appendix 1), *Meio Tostão* (e.g., 48-50 in Appendix 1*), Real Português Dobrado* (e.g., 51 in Appendix 1), and *Tostão* (e.g., 52-61 in Appendix 1). About half of the coins are not acknowledged to a specific mint, and the other half constitute emissions of Lisbon and Porto monetary workshops.

At the beginning of his reign, *Dom João III* had generally maintained the silver coin monetary system used by his father, based on the *Cinquinho*, *Meio Vintém*, *Vintém*, *Meio Tostão* and *Tostão*, without altering the alloy fineness, but only the coins weight, value and die-engraving. The first coins were minted with the name of IHOANES written with H, except for those of *Meio Vintém*, and this lettering was latter changed for IOANES (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880).

The coinage of the *Cinquinho* and *Meio Vintém* coins, in general without a monetary letter identifying the mint, has been attributable only to the Lisbon workshop (Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992). The inclusion of the «L» leter is only known from a restricted *Cinquinho* die variant (Gomes, A., 2003). The *Meio Vintém* minting was suspended by the monetary reform of 1555 (Gomes, A. and Trigueiros, A.M., 1992).

The *Vintém* coin present three different die-engravings, (i) the first coins minted in Lisbon and Porto between 1521 and 1525 have the crowned royal monogram «Y» flanked by annulets or by an annulet and the monetary letter (see 39-42 in Appendix 1), (ii) the second type which circulate from 1525 to 1555 after an engraving revision, has been minted with more ornamented dies with refined letterings style, where the «Y» or the royal arms are flanked by letters as R-L, L-R, P-O and R-P, from Lisbon and Porto (see 43 in Appendix 1, and INCM 13277 in Figure 3.26), and (iii) the last type minted after 1555 had supported a debasement of its silver weight, presenting the Roman numerals «XX» on the reverse (see INCM 9476 in Figure 3.26), distinguishing it from the previous two types (Gomes, A. and Trigueiros, A.M., 1992).

Figure 3.26 – *Dom João III Vintém* coins. Second type (INCM 13277) and third type (INCM 9476). The coins are enlarged and not to scale (actual Φ ≈ 20 mm).

By the law of November 26, 1538, a new coin type was introduced in the monetary system, the *Real Português* (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992). A great number of die variants of this coin have been numismatically attributed to Lisbon (L) and Porto (P) based namely on the quartered centred annulets (L), quatrefoils (L) or rosettes (P) engravings near the Greek cross on obverse. Only a very small number of the global coinage variants support the «P» letter from Porto (Gomes, A., 2003).

As acknowledged from the law dated March 18, 1540, *Dom João III* ordered the coinage of another new coin type, the *Real Português Dobrado*, that has been assigned only to Lisbon mint since it does not support a monetary letter (Gomes, A., 2003).

The minting of both the *Real Português* and the *Real Português Dobrado* was latter suspended by the monetary reform of 1555.

The *Meio Tostão* and *Tostão* were minted during this reign from 1521 till the law of November 26, 1538, introduced the new *Real Português* and suspended their production until 1555. In the first circulation period, the *Meio Tostão* was issued with a first engraving bearing the Greek cross on the reverse (first type, e.g., 48-49 in Appendix 1), that was changed by the law of June 10, 1555, to the Order of Aviz cross (second type, e.g., 50 in Appendix 1). The *Tostão* in a first period, from 1521 to 1525, followed the Manueline type with the cross of the Order of Christ on the reverse (first type, e.g., 54-55 in Appendix 1), and from this date until 1538 the arms, crowns and legends become more ornamented (second type, e.g., 58 in Appendix 1). As the *Meio Tostão*, the *Tostão* coins issued after 1555 have the cross of the Order of Aviz on the reverse instead of the cross of the Order of Christ (third type, e.g., 52-53 in Appendix 1) (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

In *Dom João III* chronology, mint's production could also be differentiated for Lisbon and Porto minted coins. The graph on the left of *Figure 3.27*, plot the data of first and second types of Tostão coins, minted in Lisbon until 1538, of *Real Português* coins, minted in Porto from 1538 until 1555, and of the first and second types of *Vintém* coins, minted in Porto from 1521 to 1555.

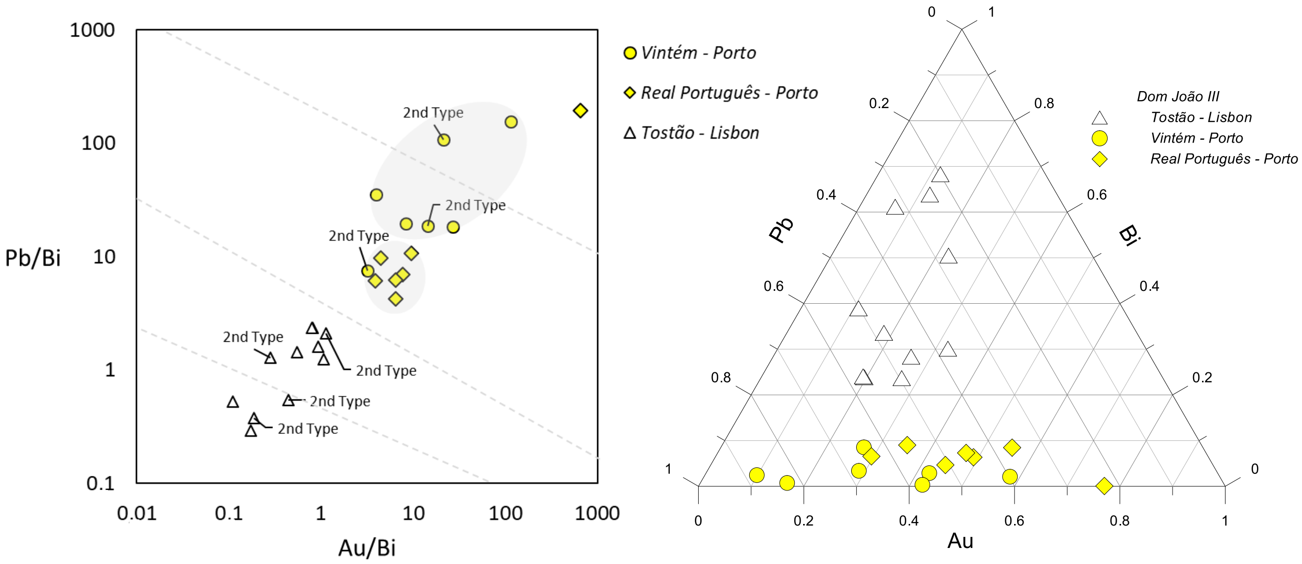

Figure 3.27 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III Vintém*, *Real Português* and *Tostão* coins, identifying Lisbon and Porto mints. *Tostão* and *Vintém* coins denoted with single markers for the first type, and markers with labels for second type. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm for the same coins.

The data show a Lisbon and Porto silver alloy correlation similar to that found for the Manueline period, with a major occurrence of the Porto minted coins in the formerly identified group assigned to northern silver alloy mixtures (refer to *Figure 3.18*). Albeit the small number of investigated coins, it also seems that *Vintém* and *Real Português* have been minted in Porto in different campaigns, and as shown, Lisbon *Tostão* coins revealed two different compositional groups (refer to *Figure 3.27, right),* apparently not indexed to the two different coin types.

Figure 3.28 shows the correlation between the various *Vintém* coin types, proposing also a differentiation between Porto and Lisbon monetary alloy compositions in the ternary diagram (doted line). Surprisingly, we find that, while the Porto mint seems to have produced this currency with silver alloy produced on its own, a condition verified practically during the *Dom João III* whole reign, from its beginning until 1555, this was not the case in Lisbon.

Lisbon had minted much of the second type of *Vintém* coin (1525-1555) using the metallic alloy composition processed in Porto (about 65 % of the analyzed coins), leading to assume that transferences of Porto produced silver bullions to be beaten and transformed into currency in Lisbon mint, the most important of the monetary workshops, had occurred.

Also, the unidentified *Vintém* first type coins, numismatically attributed to a Lisbon manufacturing, presents two large Lisbon and Porto composition groups, raising the following issues:

a) based in the above assumptions, could this unidentified coin have been minted in Lisbon being the minting carried out with processed Porto silver bullions, as probably occurred with the second type *Vintém* coin bearing the monetary L letter? Or,

b) during this reign the minting of unidentified coins occurred in Lisbon (about 55 % of the analysed coins) as well as in Porto?

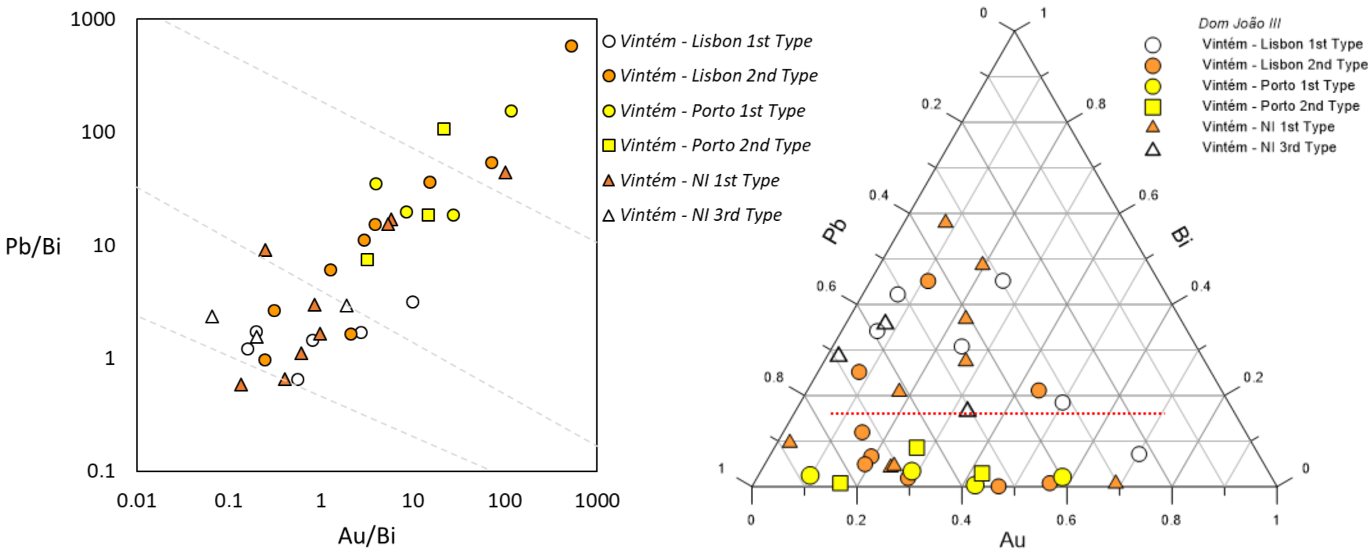

Figure 3.28 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III Vintém* coins, identifying Lisbon and Porto mints. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm for the same coins.

The third *Vintém* type produced on the latter period of this reign, only analysed from coins with no monetary workshop letter, relates to the silver alloy compositions processed in Lisbon.

As seen from Figure 3.29 and as already occurred in the former timeline of *Dom Manuel I*, all the three investigated *Meio Vintém* coins, a coin type which bears no monetary letter, are positioned in Porto compositional range, together with one of the *Cinquinho* coins (35 in Appendix 1).

The *Real Português* and *Real Português Dobrado* coins with unidentified monetary workshop seems to have been produced mainly in Lisbon, but possibly three of them have been strucked in Porto mint contrary to numismatic suppositions. Interestingly, the only *Real Português Dobrado* coin within Porto compositional range situates proximately to the several coins of *Real Português* produced by this mint, possibly indicating a jointly manufacturing of these coins after 1540.

A close examination of *Tostão* coins in Figure 3.30, show an inversely biased compositional relationship to that found for *Vintém* coins, being their composition also not correlated with their engraved type. The doted line in the ternary diagram propose a Porto and Lisbon monetary alloy composition distinction.

Porto minted *Tostão* coins, in addition to having been minted with the compositional silver alloys assigned to this workshop, were also strucked in this mint with Lisbon compositional silver alloys, something that happened at least at the beginning (1521-1525) and at the end (1555-

1557) of *Dom João III* reign (first and third type *Tostão* coins). Also, the third type *Tostão* unidentified coins were minted with silver alloy compositions of both mints.

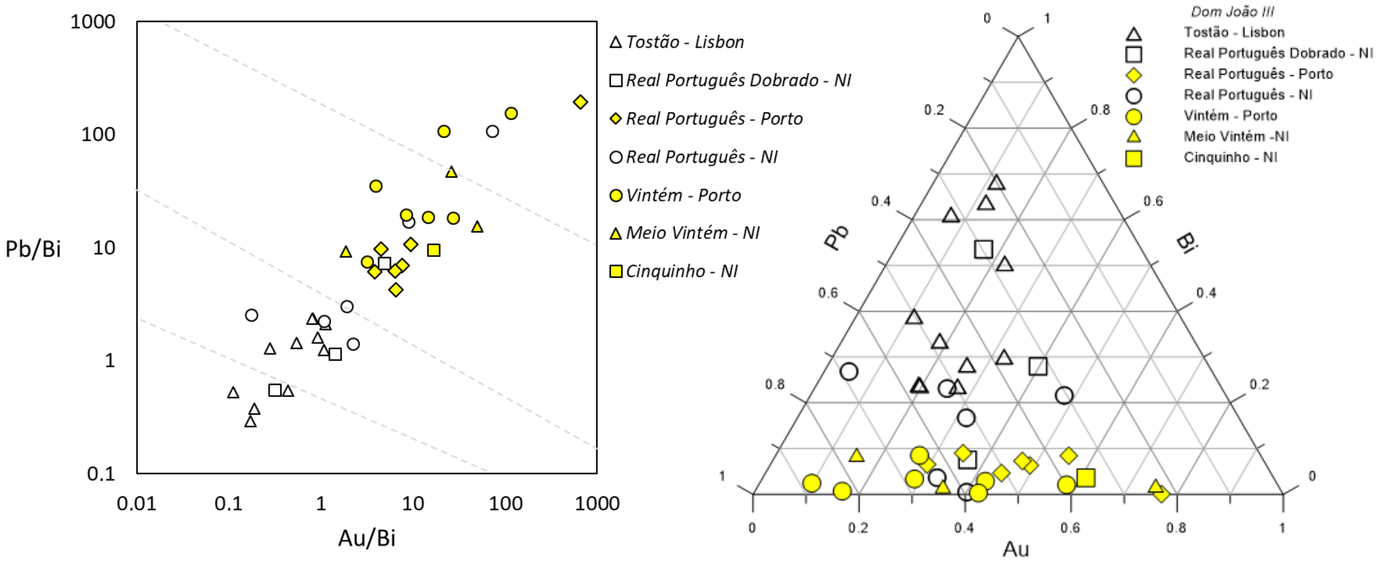

Figure 3.29 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III* coins based in Figure 3.27, left, plus *Cinquinho*, *Meio Vintém*, *Real Português* and *Real Português Dobrado* coins identifying Lisbon and Porto compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom João III* coins based in Figure 3.27, right, plus Cinquinho, Meio Vintém, Real Português and Real Português Dobrado coins, identifying Lisbon and Porto compositional groups.

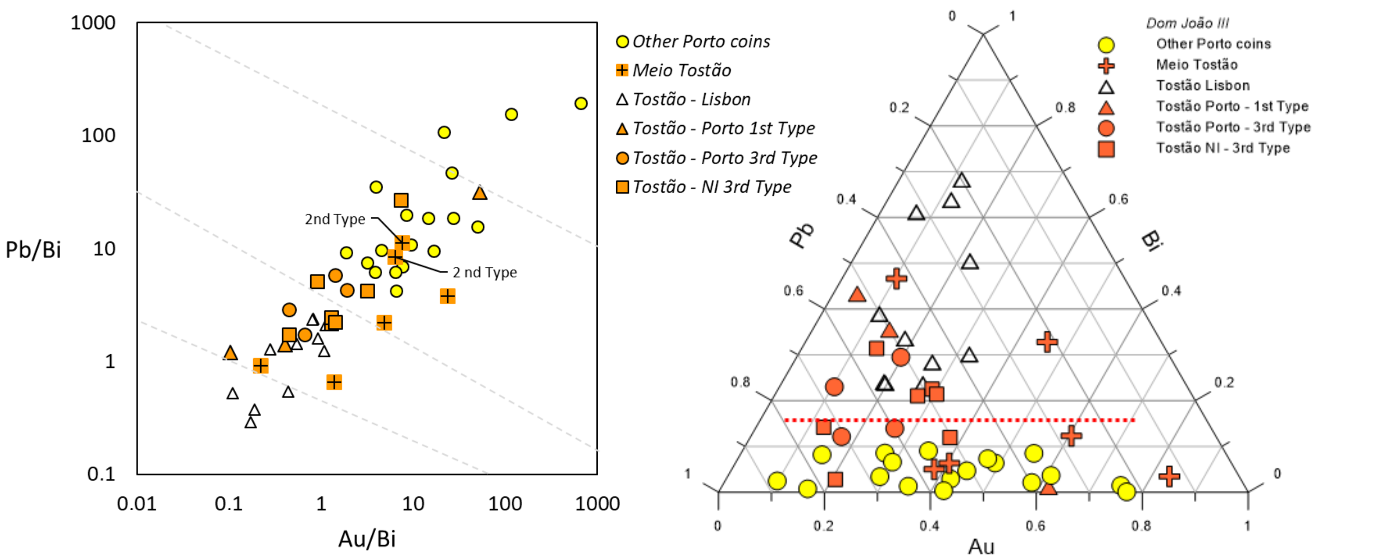

Figure 3.30 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III* coins based in Figure 3.27, left, with *Cinquinho* and *Meio Vintém* coins integrated in the Porto coins group, plus *Meio Tostão* and *Tostão* coins, identifying Lisbon and Porto compositional groups. *Meio Tostão* coins denoted with single markers for the first type, and markers with labels for second type. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom João III* coins based in Figure 3.27, right, with *Cinquinho* and *Meio Vintém* coins integrated in the Porto coins group, plus *Meio Tostão* and *Tostão* coins, identifying Lisbon and Porto compositional groups.

Four of the unidentified *Meio Tostão* coins were minted with silver metal of Porto composition, and the remaining with Lisbon composition.

In resume, it seems that the currencies of *Dom João III* chronology were mostly coined with the silver alloys compositions indexable to the previous chronology, constituting mainly the compositional groups of silver mixtures assigned to distinct Lisbon and Porto productions. As discussed above in 3.2.3, each mint workshop produced its own silver alloy based in the mixture of a certain amount of the 15th century "older" silver with the silver metal from the "new supplies" introduced earlier in the 16th century. However, each mint still has used pure silver metal from its own supllying source, albeit in very small amounts, for directly producing coins without the addition of recycled silver material. This fact is attested by the few coins minted in Porto and Lisbon with metal pertaining to the distinct silver sources supplied to these mints, seemingly the same of the former chronology (six coins out of forty-two coins minted with Lisbon alloys (14 %), and eight coins out of forty-four coins minted in Porto (18 %)). The minting of coins with this "unadulterated" silver metal was carried out over the entire reign in distinct coin types, as for example the *Tostão* in Lisbon, and the *Vintém* in Porto.

The reign of *Dom João III* is associated with a ruinous public finance structure of unmeasured public spending, whose financial difficulties led to monetary devaluation and creation of new currencies and was influenced by the scarcity of silver felt in the Portuguese territory and by influx variations of the precious metals (Peres, D., 1957). The silver scarcity periods could have leaded to transferences of silver bullions between both mints during the whole reign, with more incidence of metal coming from Porto to Lisbon, the major industrial labor intensive monetary facility. Moreover, the debasement of the silver coins determined on November 20, 1539, and years latter on June 10, 1555, accomplished through coin weight reduction and not through coin fineness adjustment, had attempted to extinguish the whole previous currency generating a coin influx to the mints due to the profit that would be obtained (Peres, D., 1957).

Based on the above-mentioned alloy considerations, when confronting global *Dom João III* compositional results (Figure 3.31) with those of the previous chronology, the reduced number of coins minted with "pure" or "unaltered" material in Porto and Lisbon, disclose a monetary production based on the recycling of the previous circulating currency, something already foreseen from the compositional trends presented in 3.2.1, with the utilization of a small amount of the "new" material supplied from out of the country.

Also, due to economical development and trading, there were time periods of a great need for *Tostão* coins, which manufacture could had exceeded Lisbon throughput and would had required the production of this coin in Porto mint. Probably the higher silver bullion capacity of Lisbon mint could have permited the supply of silver metal to Porto, without stopping the capital coin production. For example, on February 12, 1538, all the silver existent and even more to come to the mints was minted in *Tostão* coins until the departure on that year of the "India Armada" (Peres, D., 1957).

To ascertain if the coins with unidentified mint letter where produced only in Lisbon or both in Lisbon and Porto, a numismatic study of the used dies/engravings of the several coin types is needed. However, if we consider, as numismatically accepted, that the minting of the unidentified currency was carried out only in Lisbon, exception being made for the low-value currency of *Cinquinho* and *Meio Vintém* coins, it appears that the Port mint operation was dedicated largely to recycling of old currency into silver bullions, which were then sent to Lisbon for further coin production.

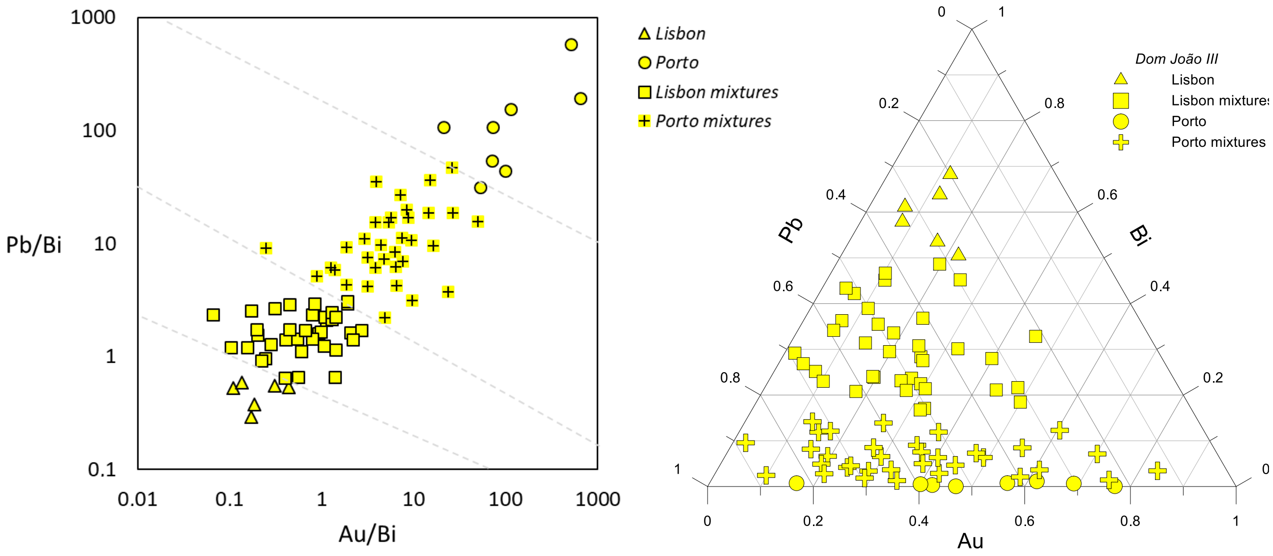

Figure 3.31 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III* coins, proposing Lisbon and Porto compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom João III*, proposing Lisbon and Porto compositional groups.

The Au/Bi versus PB/Bi ratios can not differentiate the coins minted by *Dom João III* from the coins produced during *Dom Manuel I* timeline (Figure 3.32).

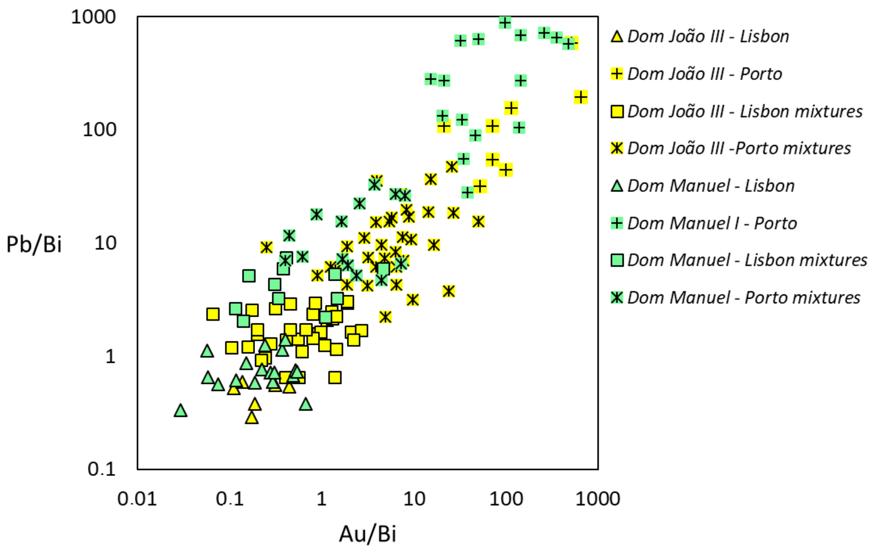

Figure 3.32 – Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom Manuel I* and *Dom João III* chronologies. The coins are discriminated by Lisbon and Porto proposed compositional groups. Logarithmic scale on abscissas and ordinates axis.

In summary, the data pertaining so far to all the examined chronologies, seems to indicate that Porto mint was a monetary facility much more dedicated to the recycling of earlier silver coins, than Lisbon was. However, as supported by the very small number of coins minted with pure metal in the capital, it seems that all through *Dom João III* reign Lisbon has also resorted more and more to this procedure.

Something to be clarified is the existence of four coins with an surprinsingly high mercury content (1.3 to 2.7 wt.%) probably related to process silver recuperations by amalgamation, occurring in Lisbon as well in Porto (Figure 3.33).

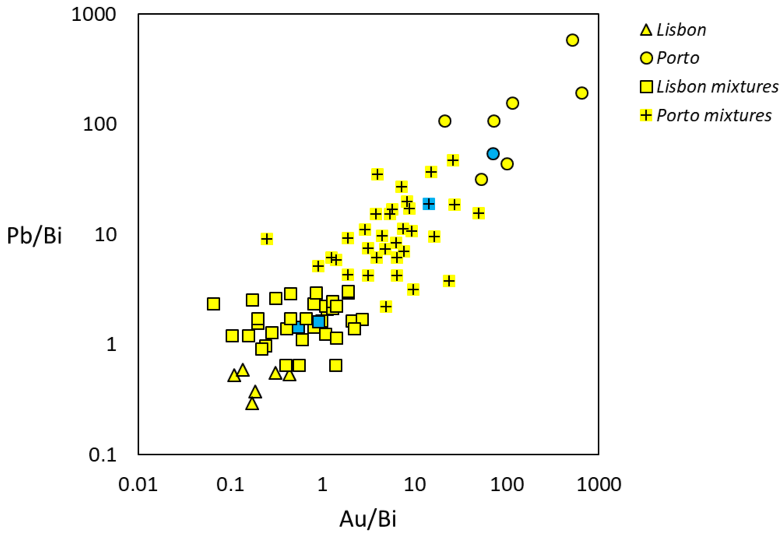

Figure 3.33 – Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom João III* coins, proposing Lisbon and Porto compositional groups, identifiying the high mercury content coins with blue color. Logarithmic scale on abscissas and ordinates axis.

3.2.5 *The coins minted by Dom Sebastião I (1557-1578)*

A total of 50 coins from four types (see Table 2.1) were analized: *Meio Vintém*, *Vintém*, *Meio Tostão*, and *Tostão* (e.g., 62-65 in Appendix 1). All the coins, excepting six *Tostão* coins minted in Porto, have no monetary letter being not assigned to a specific mint, but nevertheless have been attributable to Lisbon monetary workshop (Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

The *Meio Vintém* coin was minted according to the type and law of the previous reign. It is considered as having been coined only in Lisbon from 1560 onwards and suffered a devaluation by weight in 1573 (Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

The *Vintém* minted until July 27, 1558 in Lisbon and until November 3 in Porto followed the type and the monetary law of *Dom João III*. From 1558 the coin will have been minted with greater weight and according to a new type with the initial S in the obverse. After 1573 a currency devaluation reduced its weight (Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

The *Tostão* coins were minted until 1558 in Lisbon and Porto, according the earlier monetary law bearing the cross of Avis on the reverse, being identified by a monetary letter only in the

Porto emissions (e.g., 62-65 in Appendix 1). Afterwards, this former type was substituted by a new coin engraving bearing the cross of Christ (Figure 3.34) with a higher weight, which suffered in 1573 from the devaluation occurred in the silver coins. In the latter emissions of this reign, attributable to Lisbon, this coin type features a closed royal crown on the obverse (Aragão, A.C.T., 1875-1880; Gomes, A. and Trigueiros, A.M., 1992).

Figure 3.34 – *Dom Sebastião I* second type *Tostão* coin, minted in Porto, INCM 13410. The coin is not to scale (actual Φ ≈ 30 mm).

The Au/Bi versus Pb/Bi scatterplots dotted lines used in the discussion of *Dom João III* coin compositional results were kept for the discussion of *Dom Sebastião I* coins, in order to perceive the evolution of the silver alloy's data. The coins weight variations occurred in *Dom Sebastião I* reign should have contributed for continued recycling and remelting of the earlier produced silver coins, narrowing the global compositional distribution range presented hereinafter, as verified in the former timeline.

The plot of Porto and of unidentified minted *Tostão* coins (Figure 3.35) presents two distintct compositional groups, discriminating the coins produced in the northern mint.

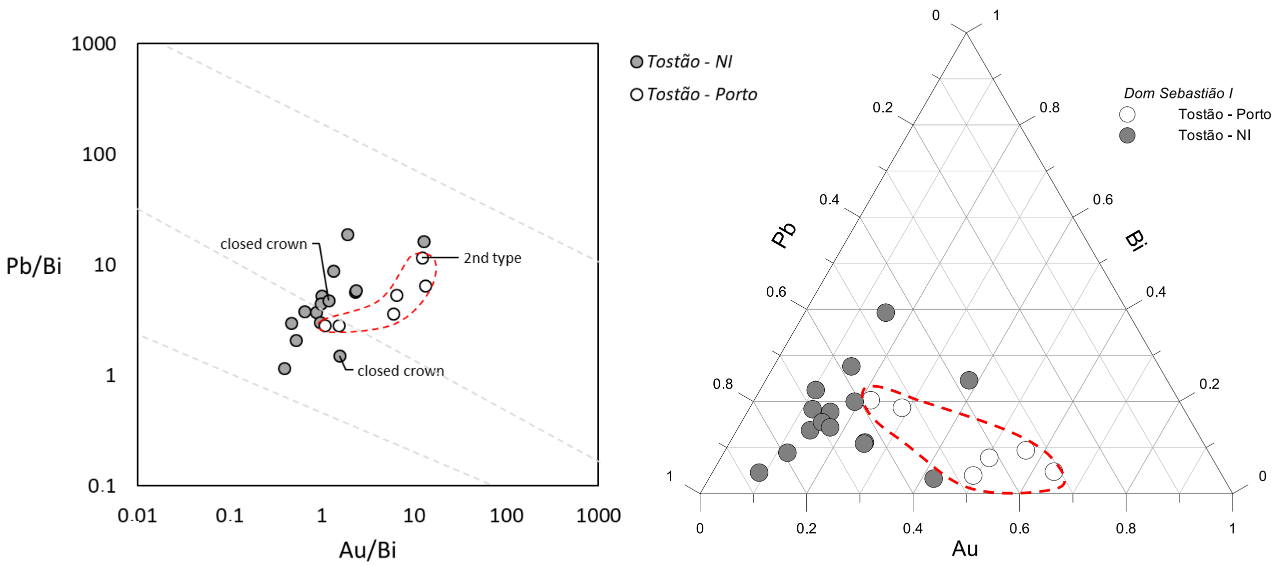

Figure 3.35 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Sebastião I Tostão* coins, identifying two distinct compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom Sebastião I Tostão* coins, identifying two distinct compositional groups.

As occurred with *Dom João III* coins, a few of the unidentified coins, numismatically attributed to Lisbon manufacturing, seems to have also a contribution from Porto silver alloys, raising once more the question of coin production without monetary letter in this mint. All the *Tostão* coins minted in Porto are from the first type except for INCM 13410 which belong to the second type together with all the unidentified coins, however, it does not exist a compositional differentiation based on the various coin types.

Also, each of the proposed compositional group comprises one coin from the last emissions with a closed crown engraving, a feature that does not constitute a distinctive characteristic as well.

The *Meio Vintém* coins analyzed, due to its weight, belongs to the first coinages made between 1560 and 1573 before the devaluation of the currency in weight, and the analyzed *Vintém* coins belong to the second type of this coin minted with the S initial. Most of the *Vintém* coins seem to belong to the period of coin devaluation after 1573, except for two that due to their higher weight are assigned to the period between 1558 and 1573. Also, two of *Vintém* coins have an engraved closed crown attributed to the last coins emissions made after 1573.

When correlating Porto minted *Tostão* coins with unidentified *Vintém* coins (Figure 3.36), the data of the latter divided between the above proposed compositional groups, leading to assume that some of these *Vintém* coins were in fact minted in Porto, or from silver bullions prepared in Porto and then supplied to be processed in Lisbon.

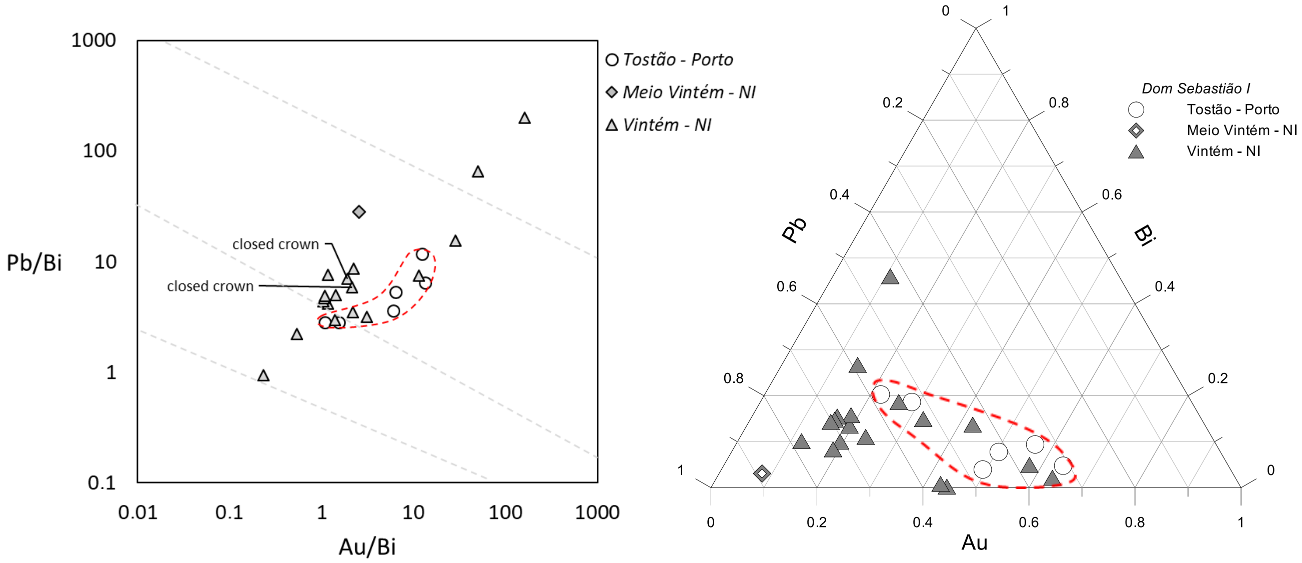

Figure 3.36 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Sebastião I Meio Vintém*, *Vintém*, and Porto minted *Tostão* coins, identifying two distinct compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom Sebastião I Meio Vintém*, *Vintém*, and Porto minted *Tostão coins*, identifying two distinct compositional groups.

The *Meio Tostão* follow the similar trend verified for the other coins above mentioned, with a Lisbon and a Porto compositional correlation (Figure 3.37).

Albeit the lower scattered compositional data presented by the silver alloys processed by *Dom Sebastião I*, the Au/Bi and Pb/Bi ratios appear to still allow to globally differentiate between Porto and Lisbon compositions (Figure 3.38).

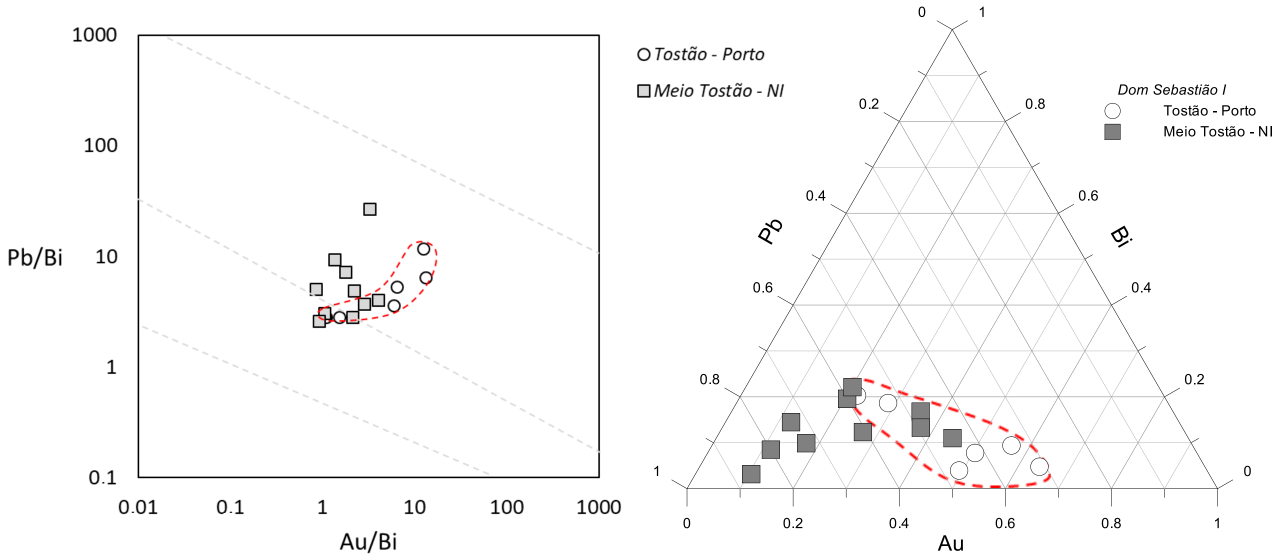

Figure 3.37 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Sebastião I* unidentified *Meio Tostão* coins, and Porto minted *Tostão* coins, identifying two distinct compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom Sebastião I* unidentified *Meio Tostão* coins, and Porto minted *Tostão* coins, identifying two distinct compositional groups.

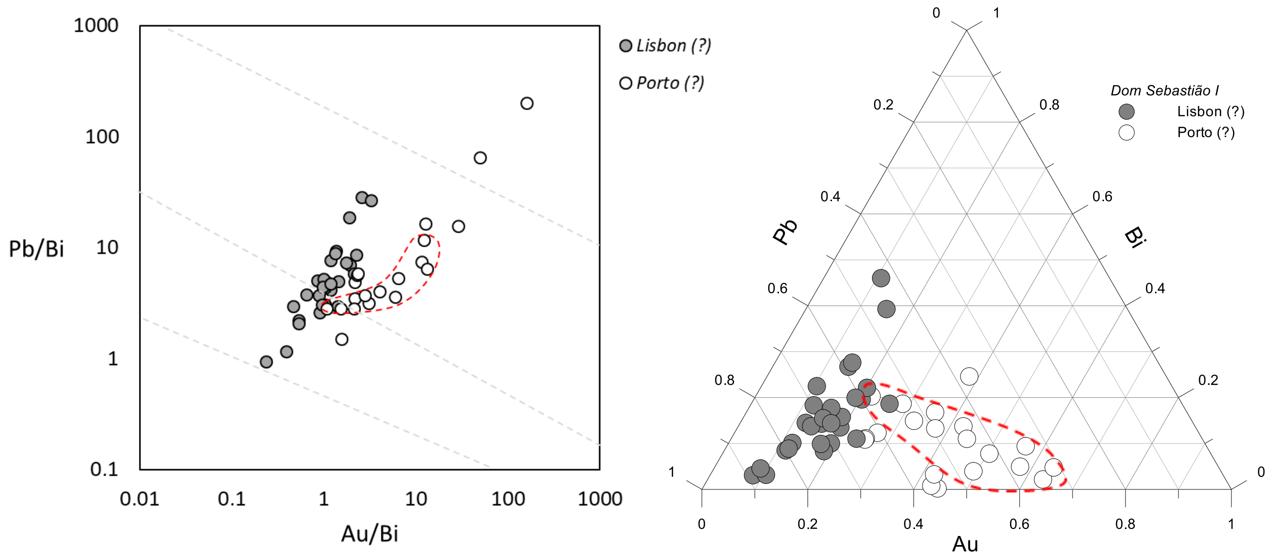

Figure 3.38 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Sebastião I* coins, proposing Lisbon and Porto compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb contents in ppm of *Dom Sebastião I* coins, proposing Lisbon and Porto compositional groups. The previous Porto Tostão coins group contour is presented in both graphs.

The first thing that stands out when correlating *Dom Sebastião I* coins with the coins from the previous chronology, is that the compositional ratios of the major part of *Dom Sebastião I* coins situates all the monetary production in the range of the previous Porto silver alloys, even for the Lisbon emissions which clearly differentiates from the earlier Lisbon emissions (Figure 3.39).

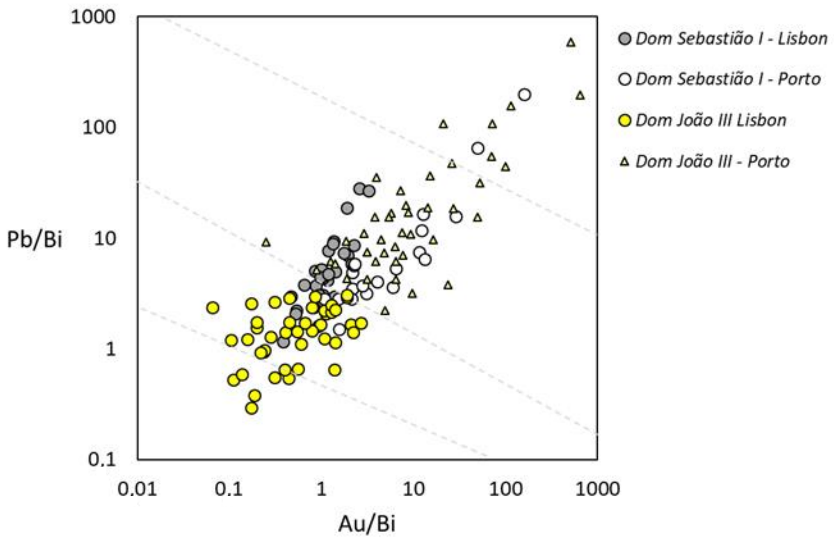

Figure 3. 39 – Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom João III* and *Dom Sebastião I* chronologies. The coins are discriminated by Lisbon and Porto proposed compositional groups. Logarithmic scale on abscissas and ordinates axis.

As presented in 3.2.1, it was already expected a compositional evolution of the silver alloys during the sixteenth century based in the global trend of the Au and Bi contents. The compositional issues, already identified in these sixteenth century chronologies, seems to concern more to the operational procedures implemented by each one of the two monetary workshops in each timeline, and could only be clarified through a profound numismatic and historical study of the coins, as well as of the contemporaneous historical information linked to the work organization and to the work relationships between both mints.

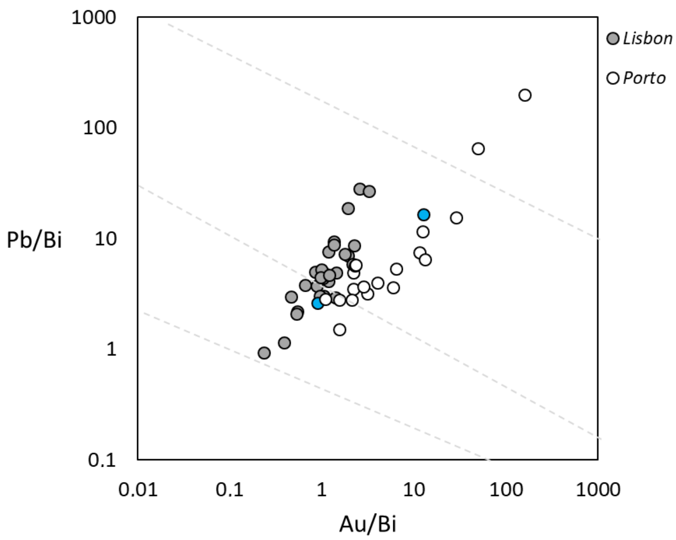

Figure 3.40 – Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom Sebastião I* coins, proposing Lisbon and Porto compositional groups, identifiying the high mercury content coins with blue color. Logarithmic scale on abscissas and ordinates axis.

As occurred in the previous chronology, minting processes seem to probably involve amalgamation procedures that can in this case justify the occurrence of two higher mercury content coins (5.7 wt.% and 41.2 wt.%) (Figure 3.40).

3.2.6 *Results summary*

The compositions of the 84 coins belonging from *Dom Afonso V* to *Dom Manuel I* chronologies were addressed with Principal Components Analysis (PCA) taking into consideration four initial variables as Au, Hg, Pb, and Bi contents, originating a two-factor analysis responsible for about 69 % of the total variance in the original data set (Figure 3.41, Table 3.6).

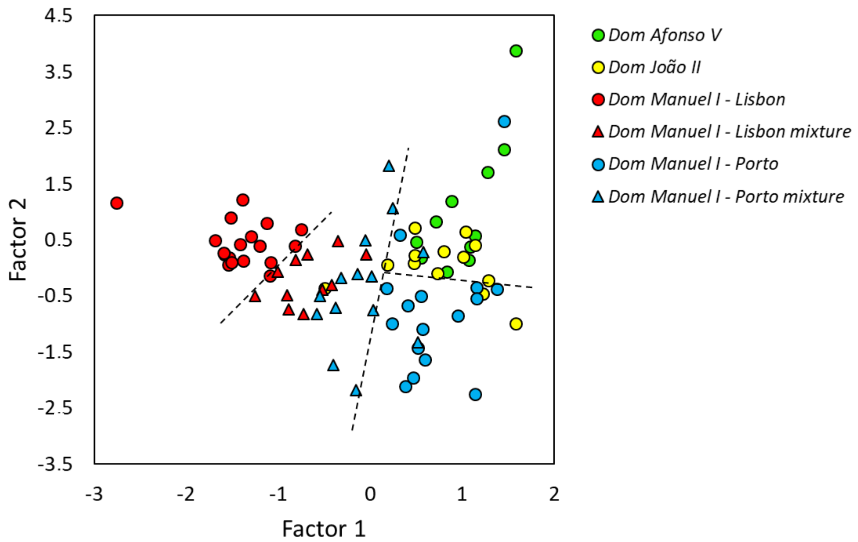

Figure 3.41 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Afonso V* to *Dom Manuel I* coins.

Figure 3.41 shows four well-defined groups, consisting of (i) *Dom Afonso V* and *Dom João II* silver alloys, *Dom Manuel I* silver alloys from (ii) Lisbon and (iii) Porto, and (iv) mixtures between Lisbon and Porto silver alloys.

Table 3.6 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Afonso V* to *Dom Manuel I* coins, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.794**	0.185
Hg	0.273	**0.702**
Pb	0.418	**-0.705**
Bi	**-0.905**	0.170
Explained variance	42.5 %	26.3 %

In this PCA analysis it is quite clear that *Dom Manuel I* Lisbon compositions stands out, confirming that in the beginning of 16th century the Portuguese capital received a precious metal not related with the silver metal source that was supplying the minting processes in the previous century. In this case, the Au and Bi impurity contents are important silver alloys discriminators: the low Au and high Bi contents of *Dom Manuel I* Lisbon silver alloys contrasting with the high Au and low Bi contents from the Porto silver alloys and the earlier chronologies of *Dom Afonso V* and *Dom João II*. It remains unclear if this Lisbon silver metal was derived from an argentiferous copper source.

Also, it is quite evident that during *Dom Manuel I* period Porto silver supplies involved a material source with a compositional distinctiveness closer to the silver alloys previously minted by *Dom João II* and *Dom Afonso V*, being discriminated from these based on the lower Hg and higher Pb contents. It remains unclear whether Porto compositions come from a new silver source or if they result from important technical improvements on the upstream silver ore extraction and/or on the upgrading quality of the coin minting process of this mint. Further, there exists a mixture range composed of Lisbon and Porto *Dom Manuel I* "unadultered" silver alloys, showing that during this whole reign silver bullions transferences between Porto and Lisbon had occurred in time periods of a great need.

A similar statistical treatment of the coins compositional data from *Dom Manuel I* with that from *Dom João III*, and from this later king with that from *Dom Sebastião I*, shows overlaid scattered ranges of data, confirming the previous assumptions derived from the above presented trace elements ratio analysis. During the second and third quarter of the 16th century, the silver alloy coin compositions of both Lisbon and Porto mints evolve over time towards a homogenization and uniformization of the average main minor/trace elements contents, til reaching the more convergent compositions found in *Dom Sebastião I* period. This evolution arised probably due to the major recycling operations of the earlier king minted currency, which was realized in each chronology. This fact is better understood through Figure 3.42, which shows the two factor PCA analysis of the minor/trace contents of 84 coins from the Lisbon and Porto compositional groups of *Dom Manuel I* and *Dom Sebastião I* chronologies, responsible for about 70 % of the total variance in the original data set (Table 3.7).

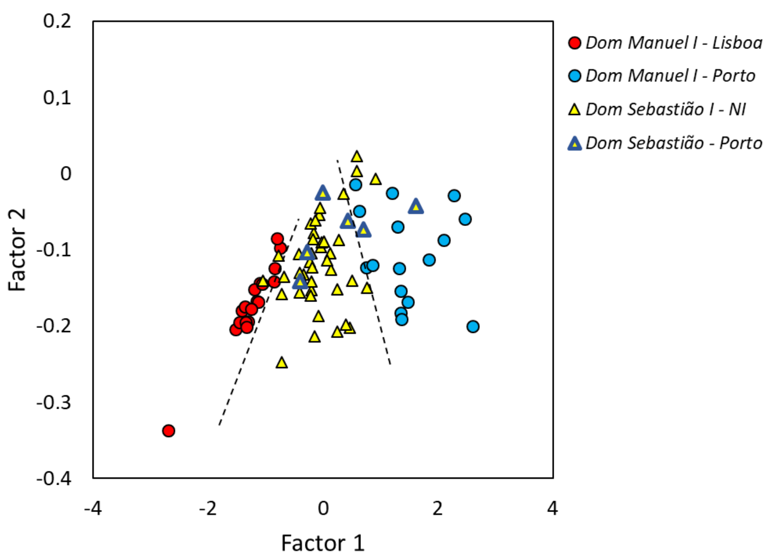

Figure 3.42 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of Lisbon and Porto compositional groups of *Dom Manuel I* and *Dom Sebastião I* coins.

From this PCA analysis it is quite clear that *Dom Sebastião I* compositional groups are standing inbetween the *Dom Manuel I* Lisbon and Porto mint compositional groups in the span of the silver alloys mixtures made of both Manueline compositions (compare with Figure 5.1), and Hg could be an important discriminator of Lisbon and Porto mints of *Dom Sebastião I* period with four of the six coins of the later mint havng a higher content of this element.

Table 3.7 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of Lisbon and Porto compositional groups of Dom Manuel I and Dom Sebastião I coins, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.752**	-0.014
Hg	-0.027	**0.998**
Pb	**0.737**	-0.073
Bi	**-0.853**	-0.028
Explained variance	45.9 %	25.0 %

3.2.7 *Counterfeited coins*

Some coins well below the legal 11 dinheiros silver fineness and with very high copper contents were detected.

A *Real Grosso* coin of *Dom Afonso V* (BdP 9002340400, 4 in Appendix 1) was coined in Porto mint, present a surface analysis of about 24 wt.% copper, and compositional correlations well according the remaining set of coins from this chronology (Figure 3.43). It will represent an intentional (?) contemporaneous counterfeiting produced under the organizational structure of this mint, realized aside from the established manufacturing steps and assay procedures.

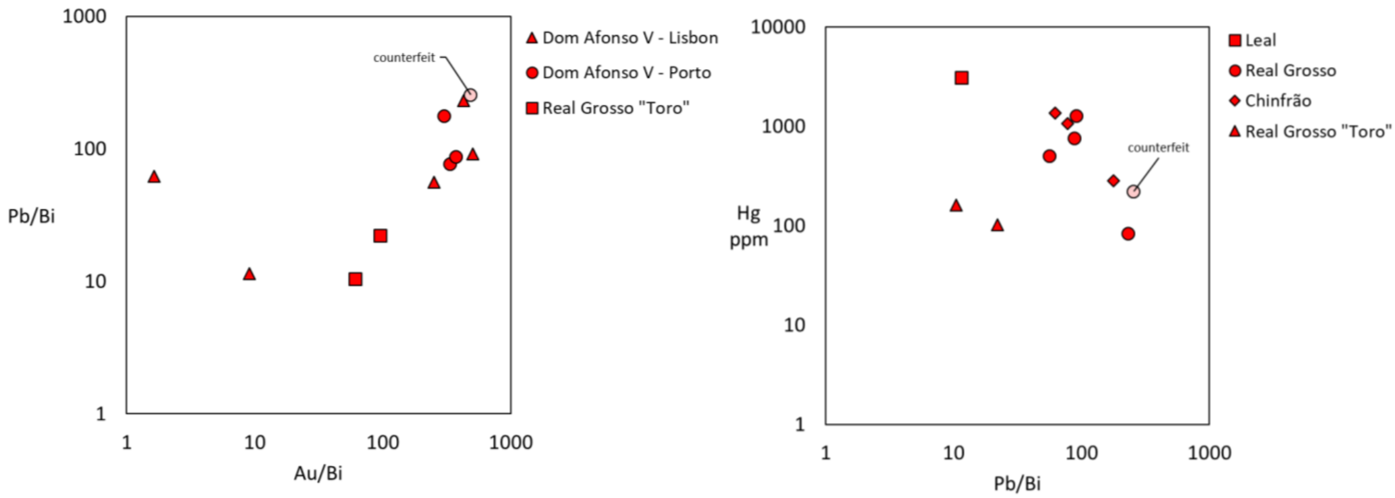

Figure 3.43 – Left, scatterplot of Au/Bi against Pb/Bi ratios, and right, scatterplot of Pb/Bi ratio against Hg content of *Dom Afonso V* coins identifying a contemporaneous counterfeited coin marked in pink colour. Logarithmic scale on abscissas and ordinates axis.

Also, a few coins of *Dom Manuel I* chronology were detected having lower silver and higher copper contents than the monetary law: three *Vintém* coins, INCM 9422, INCM 13178 and INCM 13179, and a *Tostão* coin, INCM 9405 (Figure 3.44).

The *Vintém* coins reveal, respectively, a copper superficial analysis of about 16, 17 and 12 wt.% and were minted in Porto. The *Tostão* coin was minted in Lisbon and has on surface a 10 wt.% copper content. All the *Vintém* coins constitute also contemporaneous adulterations of the coins silver fineness, whose responsibility could pertain to the mint itself.

The alarms of the existence of counterfeited currency and of non-authorised coin production, even if this were according the legal alloys and types, were already an important concern of the king in April of 1506. Years later, in 1509, there is a notice indicating that a great number of counterfeited *Tostão* coins have been spread near Guarda, being the coins very difficult to tell apart from the legal ones and telling that their contrafractors have been arrested in Spain. Could these *Vintém* coins be related to northern coin counterfeiting operations during *Dom Manuel I* reign and not to Porto mint intentional malpractices?

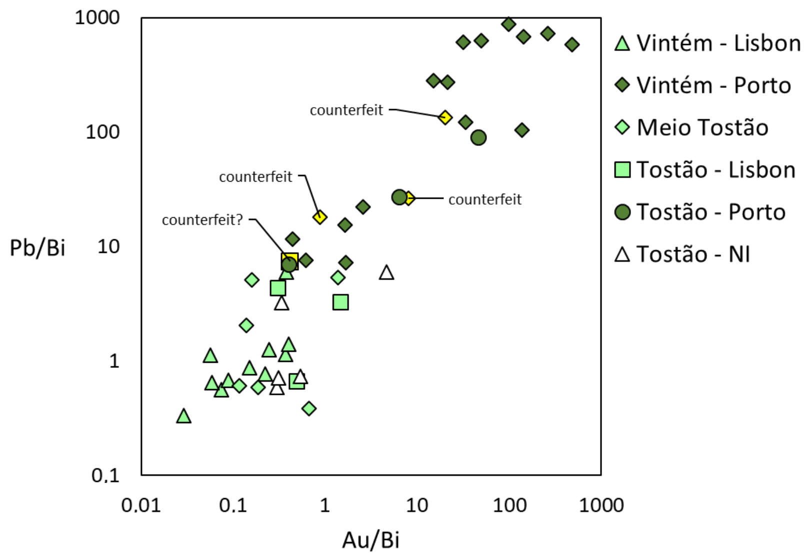

Figure 3.44 – Scatterplot of Au/Bi against Pb/Bi ratios of *Dom Manuel I Vintém*, *Meio Tostão* and *Tostão* coins identifying contemporaneous counterfeited coins marked in yellow. Logarithmic scale on abscissas and ordinates axis.

According to Gambetta, A.F., 1978 (see 1.6.1.ii)) the silver fineness was determined through the touchstone test assay using silver touch-needles and allowed to determine a silver fineness within an accurateness range of approximately 6 grains, a value that would correspond today to about two parts in one hundred. Also, Craig, J., 1953, points out an exactness of more than one part in one hundred, when using this procedure for determining the silver fineness. Considering the above stated, the *Dom Manuel I Tostão* coin composition with a surface bullion content of 89.96 wt.% (constituted by all the elements contents making part of alloy analysis but copper) may simply be close to the lower limit of silver fineness variation and could be considered as not resulting from a counterfeiting malpractice.

The *Dom João III Cinquinho* coin minted in Lisbon (BdP 9004800300, 36 in Appendix 1) is an example of an actual counterfeiting detected by this investigation. Its surface analysis has 99.93

wt.% silver and 0.04 wt.% copper, free of mercury and pratically free of gold and bismuth, indicating the use of a very pure silver alloy for producing this coin.

3.3 | Coins from the Philippine Kings dynasty

Please refer to the Table 2.2 for the identification of the number and type of analysed coins from each chronology, as well as to the mint workshop coin identification, and to Appendix 4 for the elemental compositional analysis of each coin. All the coins from this dynasty have been numismatically attributed to a Lisbon production.

3.3.1 Evolution of silver alloys purity

The coins from the Philippine Dynasty represent the silver alloy output of sixty years of monetary production under the rule of the Spanish kings from 1580 to 1640. The impurities of the silver alloys consist of the same six minor/trace elements as detected in the former Joanine Dynasty, niquel, zinc, gold, mercury, lead and bismuth, whose global contents generally show much lower values than the ones detected for the former sixteenth century timelines (Figure 3.45).

Surprisingly, the analysis of global impurities contents points out to a late sixteenth century silver supply change, occurring during *Dom Filipe I* chronology. In fact, the differences between median and average silver impurities contents in this chronology would appear to be related to the jointly processing, in a simultaneous but separate way, of the earlier silver alloys together with a new silver alloy from a different source/origin.

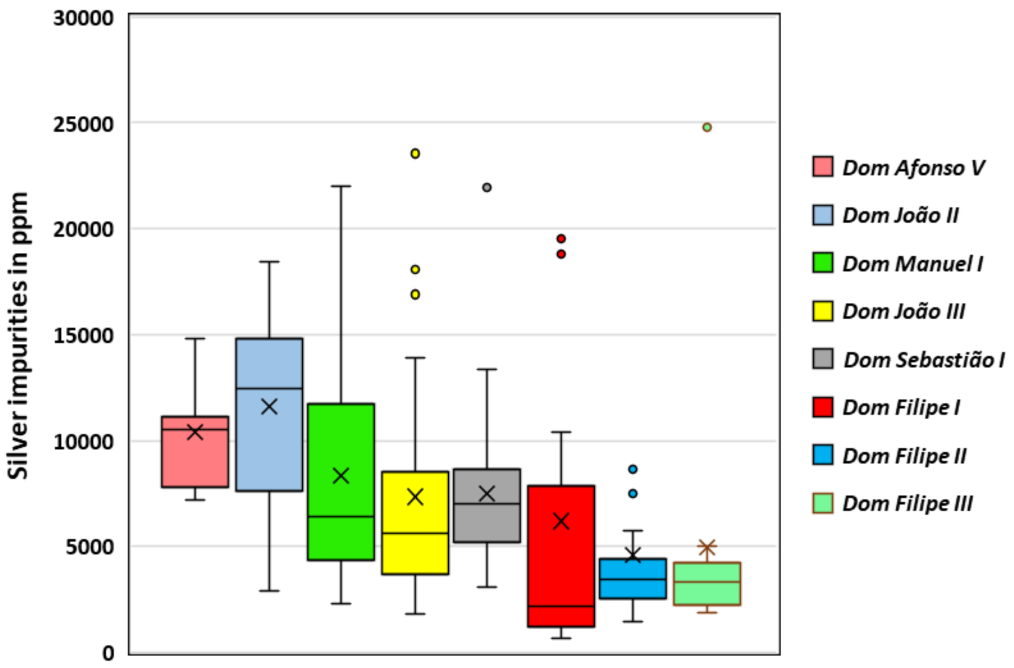

Figure 3.45 – Evolution of silver impurities content in ppm during the Joanine and Philippine king's dynasties silver alloys. Important Hg outliers of *Dom Sebastião I* coins were removed for clearness of the results in terms of average and median values, and an outlier (30454 ppm) from *Dom Filipe I* is not graphically represented.

When comparing the two latter Philippine chronologies with all the earlier timelines, it stands out that they show a reduced silver alloy impurities content and spreading. Their silver alloys present a much better cleanliness with highest values of approximately 0.5 wt.%, a figure about half the content found on the other sixteenth century silver alloys.

This increased silver cleanliness is probably related to the introduction in the last quarter of the sixteenth century of American silver bullions in Portuguese territory (Mauro, F., 1997). In this time, large amounts of American metal have entered Europe through Seville (Garner, R.L., 1988; Marsilio, C., 2015) and the detected compositional variations could represent a strong evidence of this metal have been incorporated into Portuguese currency. If this was the case, this increased silver metal cleanliness would reflect the impurities content obtained by the amalgamation processes implemented in the new territories of America.

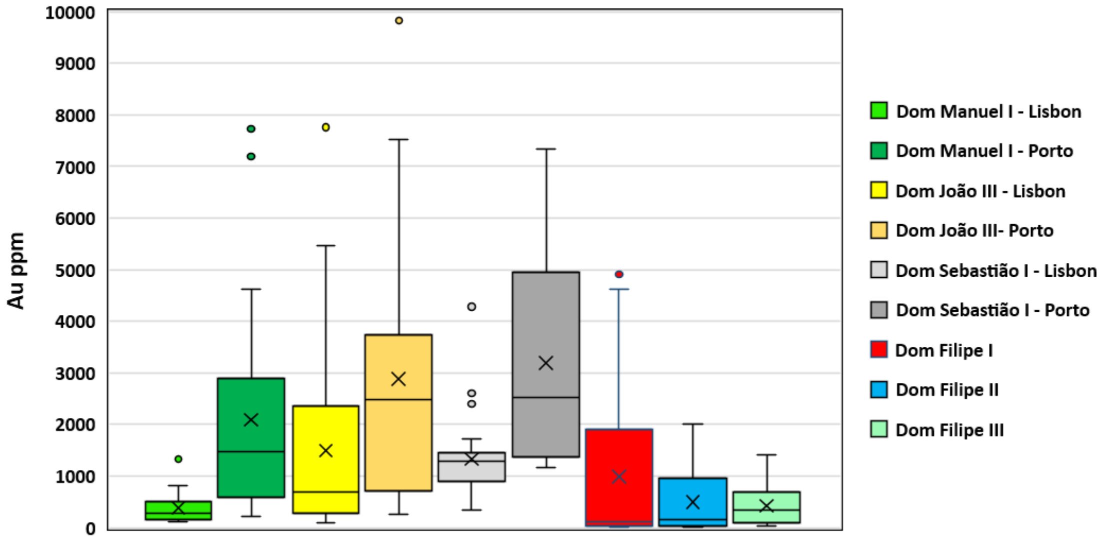

Figure 3.46 – Evolution of Au content in ppm in the sixteenth century silver alloys, discriminated by chronology and mint.

The introduction in Portugal of the new American silver source during *Dom Filipe I* chronology is well in accordance with the introduction of Potosí silver in Spain during the reign of *Felipe II* of Spain (*Dom Filipe I* of Portugal), between 1565 and 1570 (Guerra, M.F., 1990; Le Roy Ladurie, E. et al., 1990; Barrandon, J.-N. et al., 1992). It also should be noted, that the huge American silver production growth, attributed to the better accessibility to the American ore and to the introduction of the innovative techniques for silver exploration in the American territories, occurred in Potosí about 1575 (Garner, R.L., 1988), a date also very close to the beginning of *Dom Filipe I* reign (1580).

It seems in this dynasty, that gold and lead form together the main impurity content of the coins, with bismuth having a very low contribution (Figures 3.46 to 3.48). When looking for *Dom Filipe I* global gold analysis (Figure 3.46) an important deviation of the average and median gold values is observed, evidencing the presence of two different compositional groups. Coins elemental analysis in Appendix 4 corroborate the existence of two gold compositional groups: one with higher gold contents with more or less the same order of magnitude as the previous chronology of *Dom Sebastião I*, and another with very small gold contents. The lower trend of gold content over the last two Philippine chronologies, and the reduced spreading of this element in the silver alloys, probably shows a propensity for the utilization of “newer” fresh silver supplies, without recycling or carrying out important mixtures with the earlier silver metal in circulation.

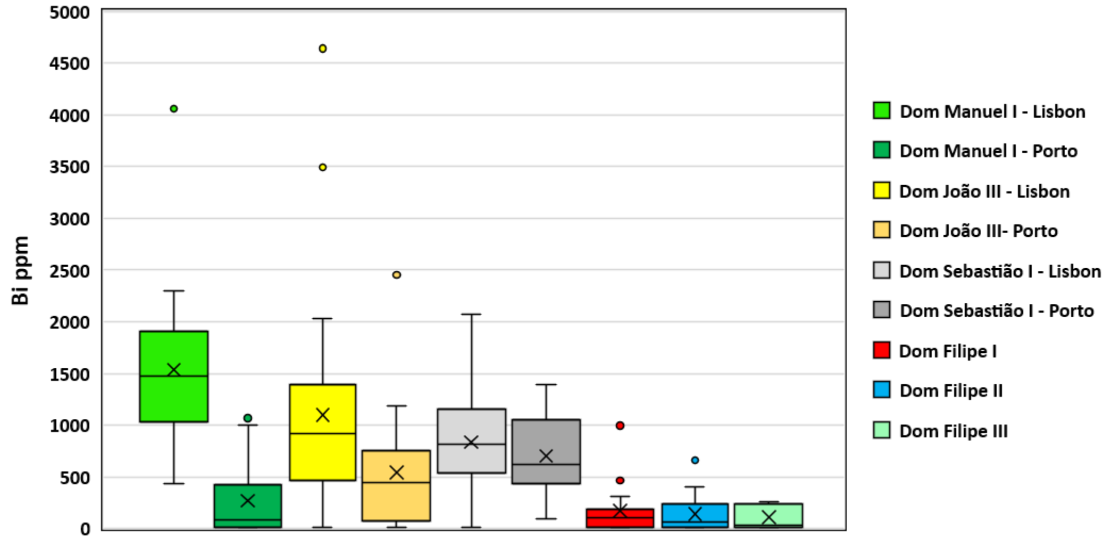

Figure 3.47 – Evolution of Bi content in ppm in the sixteenth century silver alloys, discriminated by chronology and mint.

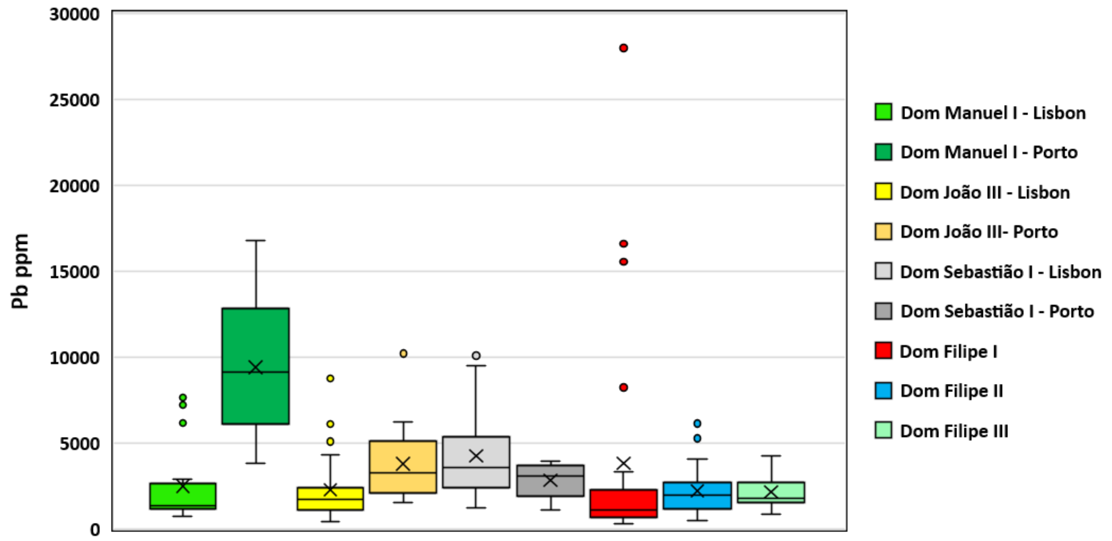

Figure 3.48 – Evolution of Pb content in ppm in the sixteenth century silver alloys, discriminated by chronology and mint.

In addition to the great number of coins where gold is present in very low quantities, a great number of coins where bismuth is under PIXE detection levels or have very low contents (see Appendix 4 and Figure 3.45) is also consistent with a sudden shift in silver alloy utilization. Gold and bismuth elements have been regarded as being associated solely to the silver sources and are considered important silver ores discriminators for fingerprinting ancient silver alloys (Mckerrell, H. and Stevenson, R.B.K., 1972; Metcalf, D.M. and Northover, J.P., 1986; Gitler, H. *et* *al.*, 2009; Pernicka, E., 2013), corroborating both elements herein the utilization of a new silver source.

As for lead content a small decrease in this element is observed in Philippine minted coins (Figure 3.48), when compared with the previous periods, possibly related to the technological advances and the differences verified in the silver extraction processes (refer to 1.2 and 1.3).

3.3.2 Au contents of the coins minted in Peru - Potosí and Lima - and in Europe with pure Andean silver

Gordus, A. and Gordus, J., 1988, have reported Au in Ag contents for forty Potosí Spanish coins minted in Peru during *Felipe II* to *Felipe IV* of Spain chronologies (the same kings that have reigned in Portugal as *Dom Filipe I* to *Dom Filipe III*), to which other results available from Guerra, M.F., 1990 and published also by Le Roy Ladurie, E. *et al*., 1990, could be added. Guerra, M.F., 1990 and 2004, also published NAA Au elemental contents of five Lima coins minted during the late eighteenth century, that could be taken herein as a reference for this location.

Also, thirty-two European coins, mostly from Spain and Italy and pertaining to the same timelines as the Portuguese Philippine dynasty, have been distinguished as having been minted with pure Andean silver based on their Au contents (Gordus, A. and Gordus, J., 1988, and Guerra, M.F., 1990).

Gold content in Potosí and European minted coins is not higher than 100 ppm (median and average below 50 ppm) (Figure 3.49), satisfying the criteria established by Gordus, A. et al. 1972, and Gordus, A. and Gordus, J., 1988, for Potosí silver differentiation.

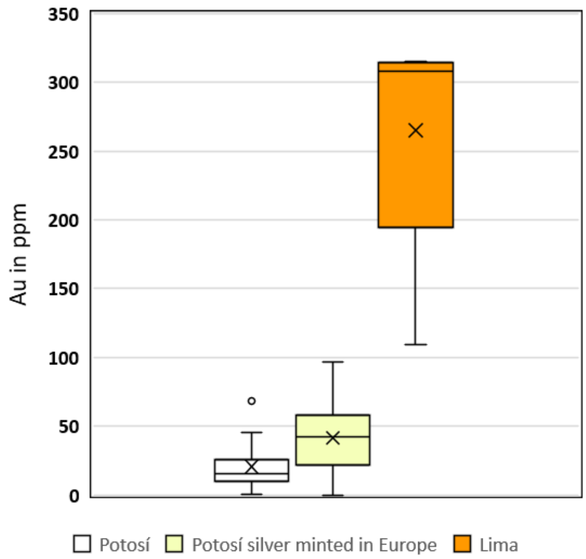

Figure 3.49 – Au content in ppm of coins minted in Europe with pure Andean silver and in Peru – Potosí and Lima. European and Potosí coins were minted during the studied Portuguese Philippine timelines, and Lima coins were produced in the eighteenth century. The depicted data were taken from Gordus, A. and Gordus, J., 1988; Guerra, M.F., 1990 and 2004; Le Roy Ladurie, E. *et al*., 1990.

However, the coins minted in Lima in the eighteenth century present much higher gold values, revealing a silver source distinct from that of Potosí.

3.3.3 The coins minted by Dom Filipe I (1580-1598)

A total of 24 coins from five types (see Table 2.2) pertaining mainly to BdP collection were investigated: *Vintém* or *20 Reais* (e.g., 66-68 in Appendix 1), *40 Reais* (e.g., 69-71 in Appendix 1), *Meio Tostão*, *80 Reais* (e.g., 72-74 in Appendix 1), and *Tostão* (e.g., 75-80 in Appendix 1). All coin's emissions have been numismatically considered to have been carried out in Lisbon mint.

By the law of 1 February 1581, *Dom Filipe I* instructs that all new silver coins would have a weight equal to those minted in the time of *Dom Sebastião I*, and on 4 February 1581 he ordered the collection of the coins minted previously by *Dom António*, to be cut and recycled (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880).

On November 15, 1582 the weight of the silver coins was reduced, keeping however the same silver fineness, making the silver value equal to that minted in Seville, and the new coins of *40 Reais* and *80 Reais* were introduced. The lack of silver coin originates again on November 21, 1588, a new weight reduction of the silver coins, namely on *Tostão* and *80 Reais*, and later on December 7, 1595, a Royal Charter reduces once more the *Tostão*, *Meio Tostão* and *Vintém* coins weight (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880).

When observing *Dom Filipe I* analytical results making part of Appendix 4, it stands out the existence of two silver alloy compositional groups: (i) one with very low Au contents, apparently according to the Au compositional criteria proposed by Gordus, A. et al. 1972, for Potosí silver, also characterized by Bi contents under PIXE detection limits in a majority of the coins, which grouping in the following discussion will be termed as "P" (from Potosí), and another group (ii) with higher Au and Bi contents in the order of magnitude of the previous used Portuguese silver alloys compositions, hereinafter denoted as "E" (as being probably originated from European silver metal).

As in all other previous results discussions, all the graphically outlined silver alloys groups are tentatively proposed for clearness of understanding, being not strictly established at least in the groups margins were undetected mixtures could inevitably exist.

According to Figure 3.50, Au and Bi correlation discriminates three groups of *Dom Filipe I* coins, a similitude being found between the E group (n=10 coins) and the silver alloys used in the previous *Dom Sebastião I* chronology. Remarkably, all the *Vintém* coins have been produced with this silver alloy.

P1 and P2 groups were discriminated based in the Au<100 ppm content criteria established by Gordus, A. et al. 1972, and Gordus, A. and Gordus, J., 1988, for Potosí silver differentiation. P1 group (n=10) has a very low gold content similar to the group of European coins minted purely with Potosí's silver presented in Figure 3.49 and will be considered thereafter as being of Potosí origin (Figure 3.51). Also, a Portuguese coin (BN K1182/3) from *Dom Filipe I* chronology analysed by Gordus, A. and Gordus, J., 1988, presented a gold in silver content of 84 ppm, well according to the coins analysed included in this group.

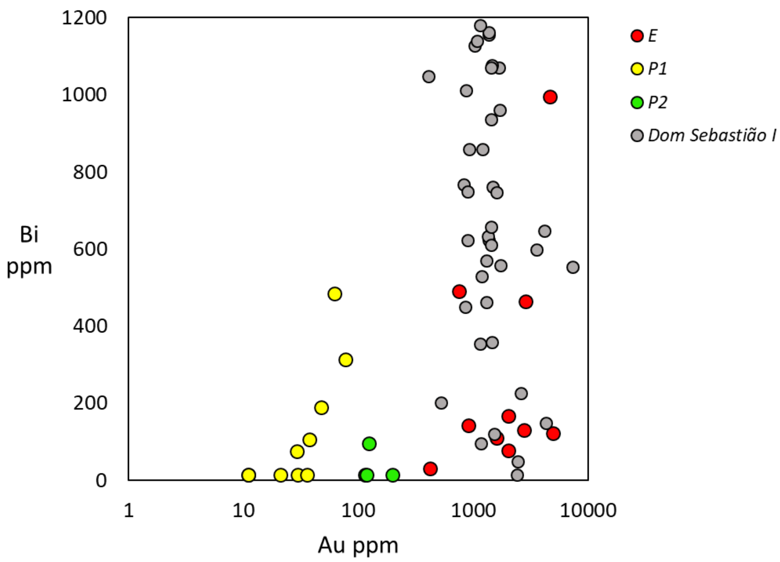

Figure 3.50 – Scatterplot of gold against bismuth in ppm of *Dom Filipe I* (E, P1, P2) and *Dom Sebastião I* coins, identifying different compositional groups. Logarithmic scale on abscissas axis.

Further, Philippine dynasty coins discussion will show that the P2 group (n=4) silver source should be considered distinct from the two previous origins, being closely related with the American origin of P1 silver source. It seems to not merely to correspond to a silver alloy mixture based on Potosi silver and on the silver alloys previously used in Portuguese territory, as evidenced by Bi contents mainly under PIXE detection limits.

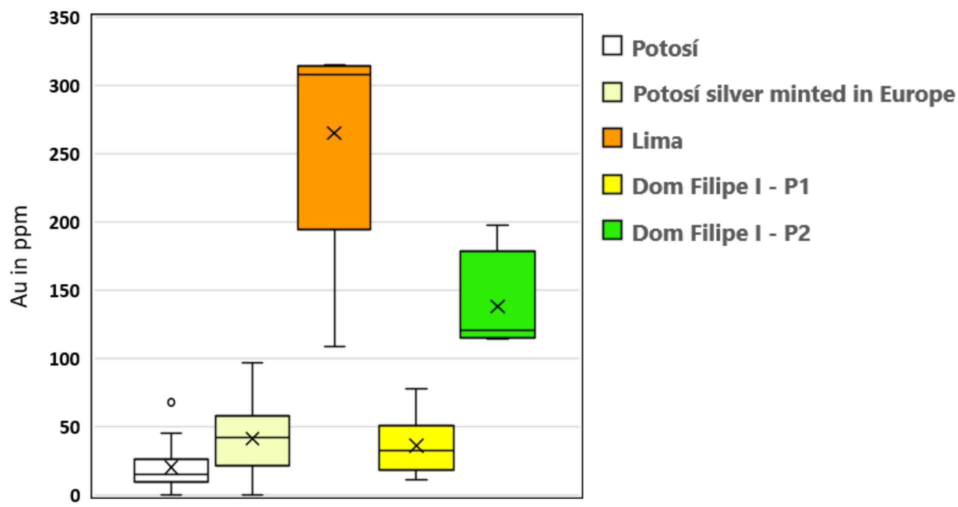

Figure 3.51 – Comparison of gold contents presented in Figure 3.49 with that from coins minted in Portugal by *Dom Filipe I* and belonging to P1 and P2 compositional groups.

Surprisingly, in this case, P2 and E compositional groups discriminate better using a Au/Bi versus Hg/Bi ratio correlation instead of Pb/Bi (Figure 3.52, left), being this probably related to the predominant amalgamation nature of the American silver ore extraction. This ratio correlation allows to differentiate all the three compositional silver groups.

The analytical results of an *8 Reales* Potosí silver coin from *Felipe II* of Spain (see Appendix 5), that as been tentatively attributed to a minting from 1576-1586(?) were included in the graphic representations of Figure 3.52, standing within the spreading range of P1 data.

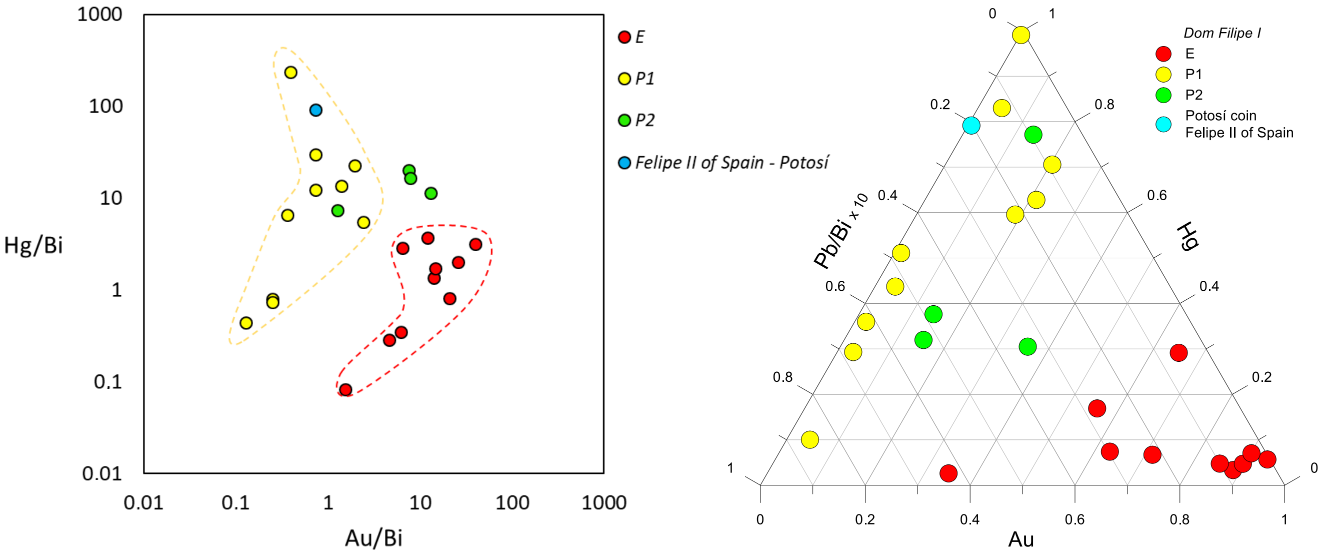

Figure 3.52 – Left: Scatterplot of Au/Bi ratio against Hg/Bi content of *Dom Filipe I* coins, discriminating E, P1 and P2 compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb/Bi x10 contents in ppm of *Dom Filipe I* coins, discriminating E, P1 and P2 compositional groups. Both graphic representations exhibit the elemental analysis of a Potosí coin minted by *Felipe II* of Spain (BdP4240051173).

As expected, the European nature of *Dom Filipe I* E group of coins is revealed in Figure 3.53, standing these coins within the elemental compositional variation ranges of the earlier coins of *Dom Sebastião I*, being divided between the two previously assigned Lisbon and Porto groups. *Dom Filipe I* P1 group of coins attributed to Potosí discriminates also quite well from *Dom Sebastião I* coins.

To obtain a possible relationship of the minting compositions produced in the different coin silver depreciation periods, it will be necessary a previous numismatic study which allow to differentiate the coins according these silver debasement's, something not addressed by this investigation.

The number of coins minted in Portugal exclusively with silver coming from Potosí is quite high, amounting for almost 42 %, just like the verified in Spain during the same kingdom and reported by several authors (33 % according to Gordus, A. et al., 1972 and 43 % according to Guerra, M.F., 1990, Le Roy Ladurie, E. et al., 1990 and Barrandon, J.-N. et al., 1992), indicating that the silver from this source was also used directly in the striking of a great part of the Portuguese coins, playing thereafter an important role on the economy of this country. However, no extensive distinct compositional group of American and European silver sources mixtures have been detected in the Portuguese coins of this period, contrary to the verified with the Spanish coins where this group accounts for 50 % of the analised coins (Guerra, M.F., 1990; Le Roy Ladurie, E. et al., 1990; Barrandon, J.-N. et al., 1992).

Even if *Dom Filipe I* P2 group would constitute an intermediary compositional group between Potosí and European silver sources, it would represent a small global percentage (17 %).

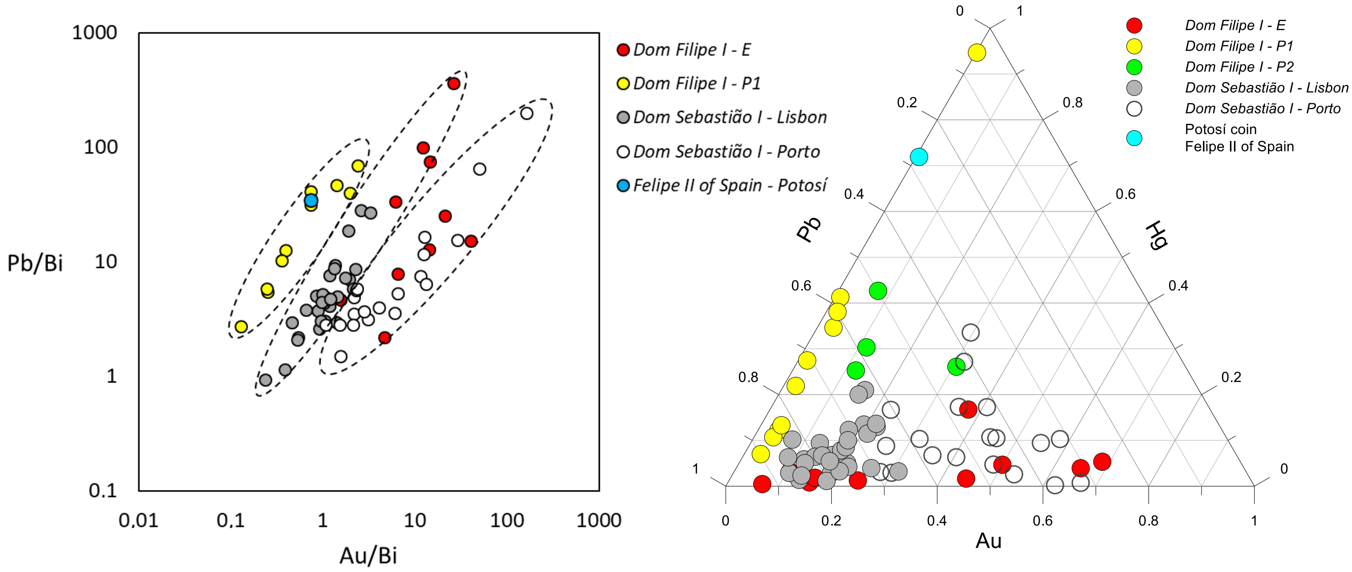

Figure 3.53 – Left: Scatterplot of Au/Bi ratio against Pb/Bi content of *Dom sebastião I* and *Dom Filipe I* coins, discriminating E and P1 compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Hg and Pb contents in ppm of *Dom Sebastião I* and *Dom Filipe I* coins. Both graphic representations exhibit the elemental analysis of a Potosí coin minted by *Felipe II* of Spain (BdP4240051173).

3.3.4 The coins minted by Dom Filipe II (1598-1621)

The investigated thirty-six coins of *Dom Filipe II* from three types (see Table 2.2), *Vintém* or *20 Reais*, *Meio Tostão*, and *Tostão,* pertain globally to INCM collection, and their description can be accessed on Catálogo descritivo das moedas Portuguesas – Museu Numismático Português, C.M. Almeida do Amaral, Lisboa, Imprensa Nacional Casa da Moeda, 1977. All coin's emissions have been numismatically considered to have been carried out in Lisbon mint. The coins were minted with the same fineness and weight as that from the final period of *Dom Filipe I*.

As in *Dom Filipe I* chronology, the same silver alloy compositional groups were detected being here denoted as "E" from Europe, and "P" from Potosí.

Figure 3.54 discriminates three groups of Dom Filipe II coins based in Au and Bi correlation, and as for *Dom Filipe I*, the same matching occurs between the E group (n=13 coins) and the silver alloys used in the earlier Dom Sebastião I chronology.

P1 group (n=14) show a gold content of a similar order of magnitude as the group of European coins minted purely with Potosí's silver presented in Figure 3.49, confirming its Potosí origin (Figure 3.55). P2 group (n=9) silver source should be considered as being from the same origin as that from *Dom Filipe I* P2 coins group, having similar gold and bismuth contents closely related with the American origin of P1 silver source.

As seen from Figure 3.56, the proposed distribution of P2 coins group, based in their Au content, encompasses four coins, on the lower left of Au/Bi versus Hg/Bi scatterplot, made with a silver alloy composition which seems to be related to the European group of coins. The analytical results of an *8 Reales* Potosí silver coin minted in 1613-1617 period by *Felipe III* of Spain (see Appendix 5) were included in the graphic representations of this Figure, standing this coin within the spreading range of P1 and some of P2 data.

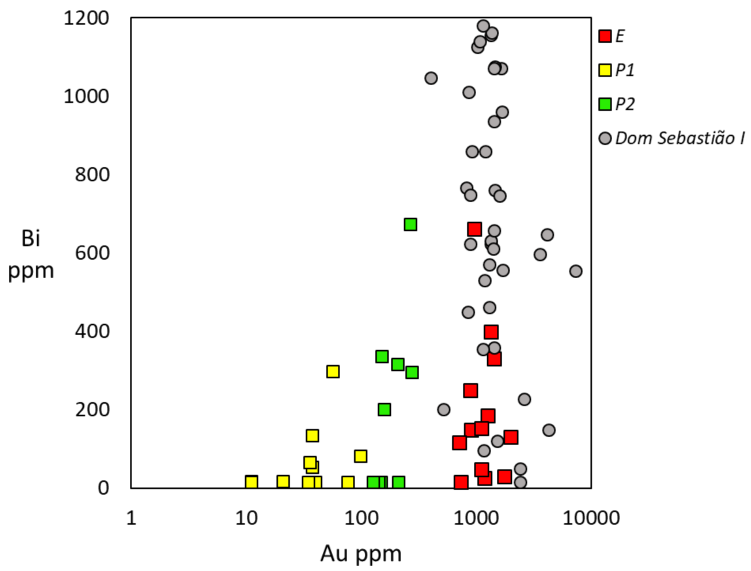

Figure 3.54 – Scatterplot of gold against bismuth in ppm of *Dom Filipe II* (E, P1, P2) and *Dom Sebastião I* coins identifying different compositional groups. Logarithmic scale on abscissas axis.

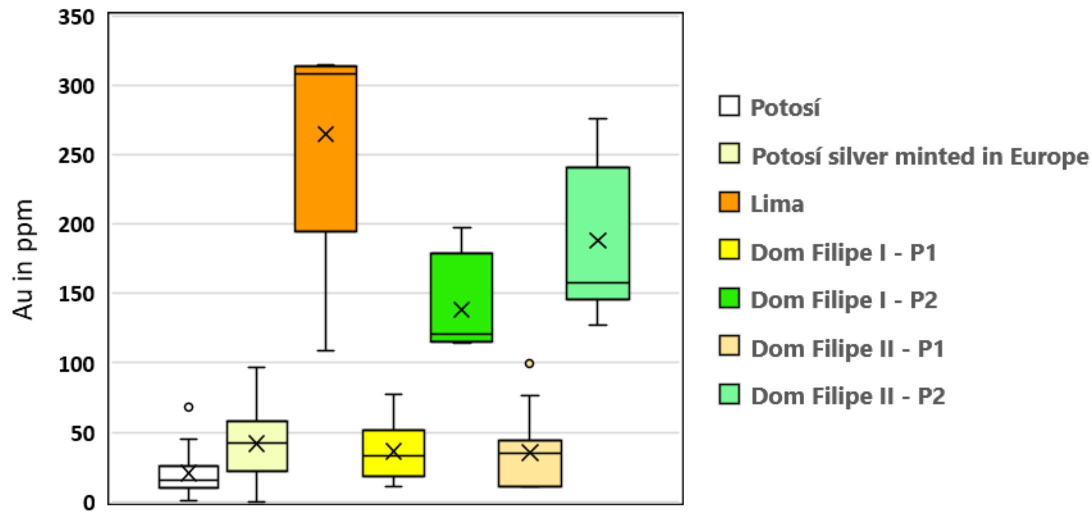

Figure 3.55 – Comparison of gold contents presented in Figure 3.49 with that from coins minted in Portugal by *Dom Filipe I* and *Dom Filipe II* and belonging to P1 and P2 compositional groups.

In this chronology, the number of coins assigned to Potosí's silver origin is also higher, about 40 %, still revealing the important presence of this silver in Portugal and the coins assigned to P2 group would represent at least about 25 % of their global number. Gordus, A. et al., 1972 recognize one out of the five analysed coins (20 %) of *Filipe III* of Spain as being minted with Potosí silver, and Guerra, M.F., 1990, Le Roy Ladurie, E. et al., 1990 and Barrandon, J.-N. et al., 1992, identify three out of the four analised coins (75 %) as being produced with this silver, assuming that the other coin constitutes a mixture of American and European silver sources.

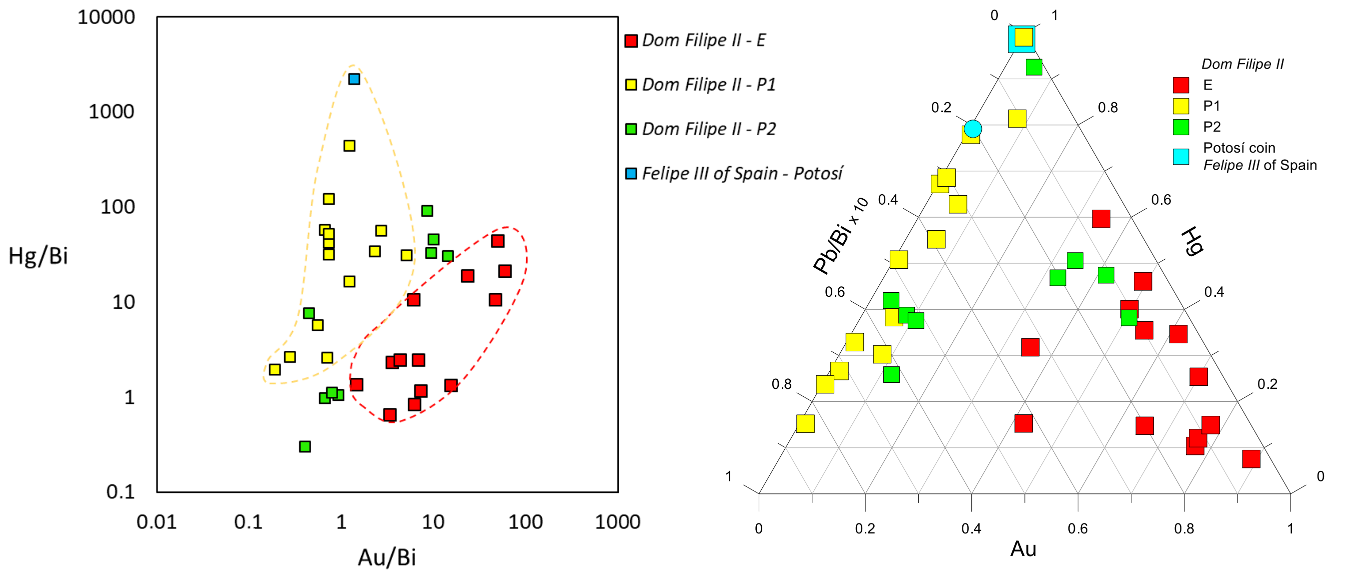

Figure 3.56 – Left: Scatterplot of Au/Bi ratio against Hg/Bi content of *Dom Filipe II* coins, discriminating E, P1 and P2 compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb/Bi x10 contents in ppm for *Dom Filipe II* coins, discriminating E, P1 and P2 compositional groups. Both graphic representations exhibit the elemental analysis of a Potosí coin minted by *Felipe III* of Spain (BdP 4240046814).

The coins belonging to *Dom Filipe I* and to *Dom Filipe II* chronologies could not be differentiated in Figure 3.57, but the discrimination of the two main silver compositional groups are enhanced when relating both chronologies.

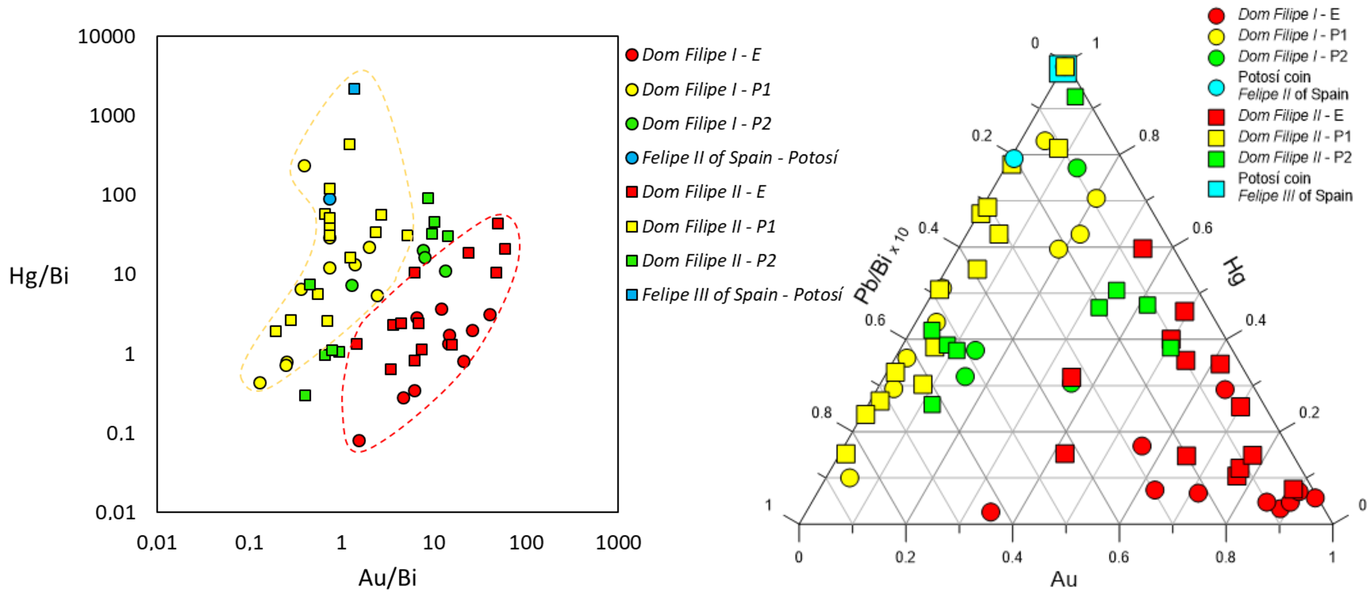

Figure 3.57 – Left: Scatterplot of Au/Bi ratio against Hg/Bi content of *Dom Filipe I* and *Dom Filipe II* coins, discriminating E, P1 and P2 compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb/Bi x10 contents in ppm of *Dom Filipe I* and *Dom Filipe II* coins, discriminating E, P1 and P2 compositional groups. Both graphic representations exhibit the elemental analysis of two Potosí coins minted by *Felipe II* and *Felipe III* of Spain.

3.3.5 The coins minted by Dom Filipe III (1621-1640)

The investigated eleven coins of *Dom Filipe III* from two types (see Table 2.2) pertain globally to BdP collection: *Meio Tostão* (81-84 in Appendix 1), and *Tostão* (85-91 in Appendix 1). As for the other Philippine chronologies, all coin's emissions have been numismatically considered to have been carried out in Lisbon mint.

The monetary legislation of this period is not identified (Fernandes, M.B.L., 1856; Aragão, A.C.T., 1875-1880), but the coins were minted with the same wheight and fineness as those from *Dom Filipe II* period.

As in the former Philippine chronologies, the same silver alloy compositional groups were detected being indicated by the same reference letters, "E" from Europe, and "P" from Potosí.

Figure 3.58 discriminates three groups of *Dom Filipe III* coins based in Au and Bi correlation, and the same matching occur between the E group (n=5 coins) and the silver alloys used in *Dom Sebastião I* chronology, showing that silver metal of European origin was still being processed.

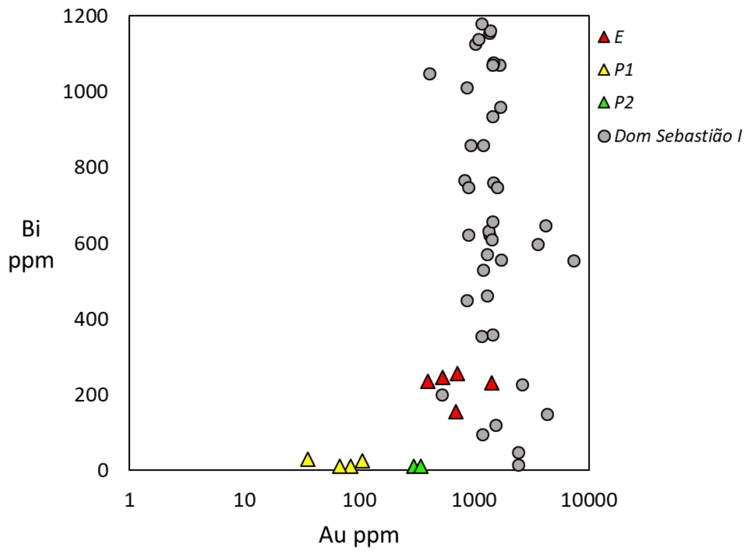

Figure 3.58 – Scatterplot of gold against bismuth in ppm of *Dom Filipe III* (E, P1, P2) and *Dom Sebastião I* coins identifying different compositional groups. Logarithmic scale on abscissas axis.

Potosí origin of P1 group (n=4) stands out once more, with a similar gold content following the trend verified in the earlier Philippine chronologies (Figure 3.57). Also, the silver source of P2 group (n=2) with very low bismuth content as in P1 group, could be inferred to the earlier P2 chronological compositional groups of an American origin.

American silver sources and European silver sources are well discriminated using Au/Bi versus Hg/Bi ratios (Figure 3.608), and the number of coins assigned to Potosí's silver origin is still important in the second half of the Philippine Dynasty, amounting for more than one third of the analysed coins.

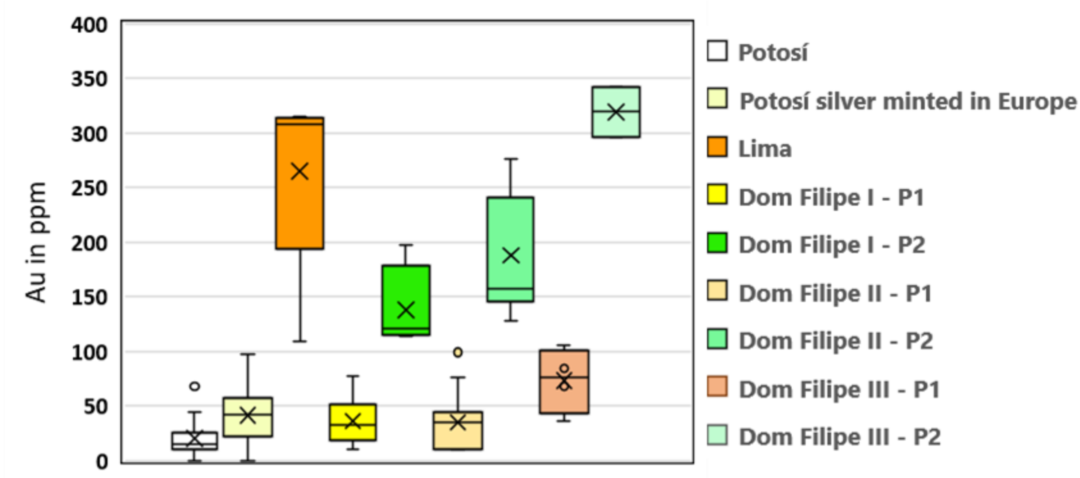

Figure 3.59 – Comparison of gold contents presented in Figure 3.49 with that from coins minted in Portugal by *Dom Filipe I*, *Dom Filipe II* and *Dom Filipe III* and belonging to P1 and P2 compositional groups.

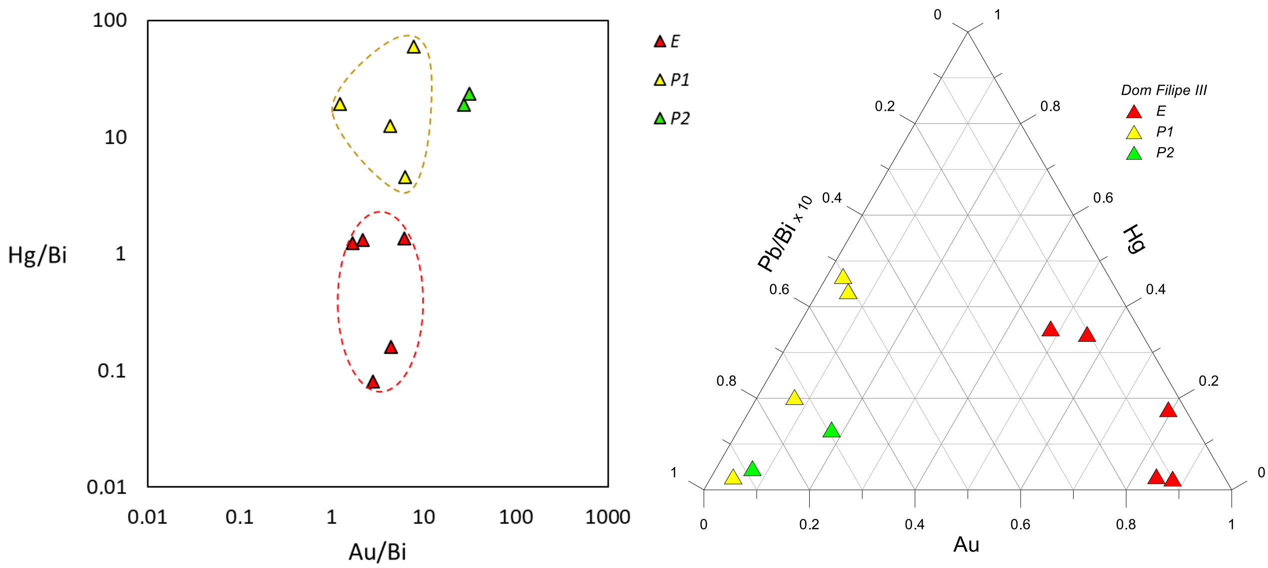

Figure 3.60 – Left: Scatterplot of Au/Bi ratio against Hg/Bi content of *Dom Filipe III* coins, discriminating E, P1 and P2 compositional groups. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb/Bi x10 contents in ppm of *Dom Filipe III* coins, discriminating E, P1 and P2 compositional groups.

Discrimination of the two main silver sources compositional groups can be identified when comparing the coins from *Dom Filipe II* and *Dom Filipe III* chronologies (Figure 3.61), but their correlation does not allow a differentiation of the minting production of both chronologies.

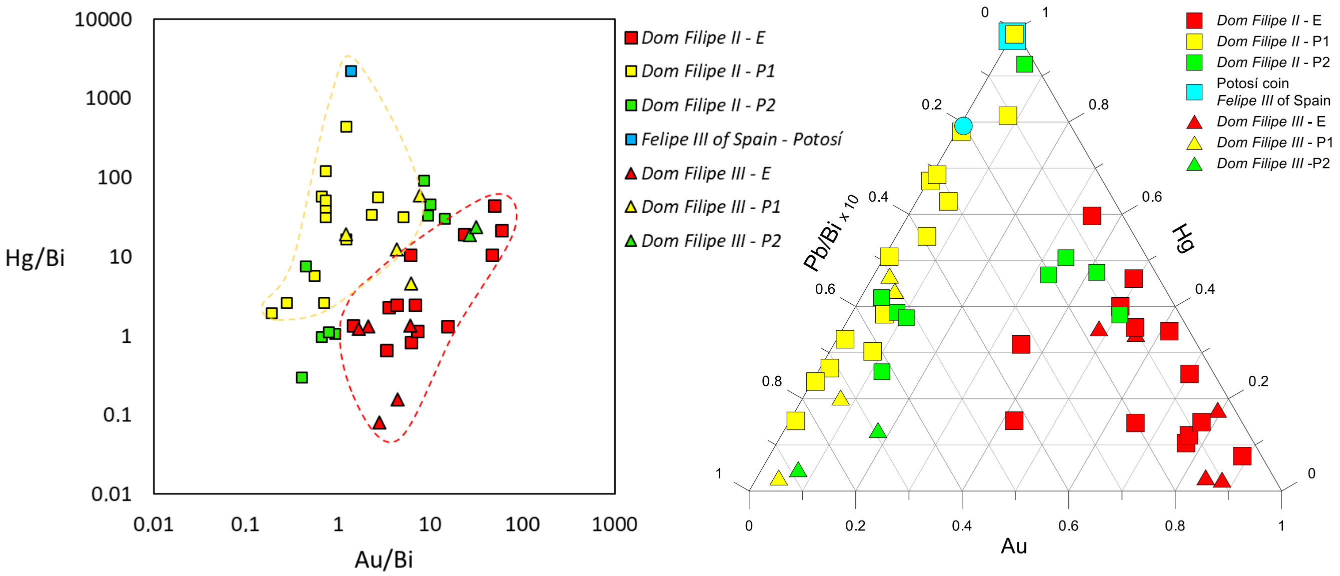

Figure 3.61 – Left: Scatterplot of Au/Bi ratio against Hg/Bi content of *Dom Filipe II* and *Dom Filipe III* coins, discriminating E, P1 and P2 compositional groups, and of a Potosí coin minted by *Felipe III* of Spain. Logarithmic scale on abscissas and ordinates axis. Right: Ternary diagram of Au, Bi and Pb/Bi x10 contents in ppm of *Dom Filipe II* and *Dom Filipe III* coins, discriminating E, P1 and P2 compositional groups.

3.3.6 American silver versus European silver - Results summary

Based mainly on Au and Bi contents, the elemental analytical results of each of the Philippine chronologies reveal the presence of two possible silver alloys groups, P1 and P2, distinguishable from the compositions of the silver alloys used until 1578 in the Portuguese territory.

It is known that at the final quarter of the 16th century, the determination of *Dom Filipe I* (*Felipe II* of Spain) brought American silver to Portugal (see 1.2.1), hereinabove identified as P1, whose composition seems to originate mostly from Potosí as they are characterized above all by Au contents < 100 ppm. The Au together with Bi content allow to discriminate American and European silver sources when correlated with Hg or Pb (Figure 3.62).

However, an explanation about the nature of the other silver alloy contribution that was processed in the Portuguese mints during the Philippine period, denoted as P2, e.g., in Figures 3.57 and 3.61, is needed. It is important to clarify whether this compositional group constitutes a mixture of European and Potosí's silver sources or not, or in fact it forms a second American contribution, necessarily from a different location with Au, Bi, Hg, and Pb contents proximate to Potosí silver.

Based on the coins of *Dom Filipe II*, in greater quantity when compared to the other Philippine chronologies, apart from P1 and E compositional groups, P2 coins group appears as two different silver alloys contributions in Figure 3.56. In the righthand of this Figure, a subgroup of these coins stands out, and as for 3 out of the 4 coins of *Dom Filipe I* and 2 coins of *Dom Filipe III*, is characterized by a Bi content under the PIXE detection limit. The other left-hand P2 subgroup has a similar Au content but a higher Bi composition of a few hundred ppm. For these coins a similar general distribution occurs when relating Au/Bi versus Pb/Bi ratios (Figure 3.63).

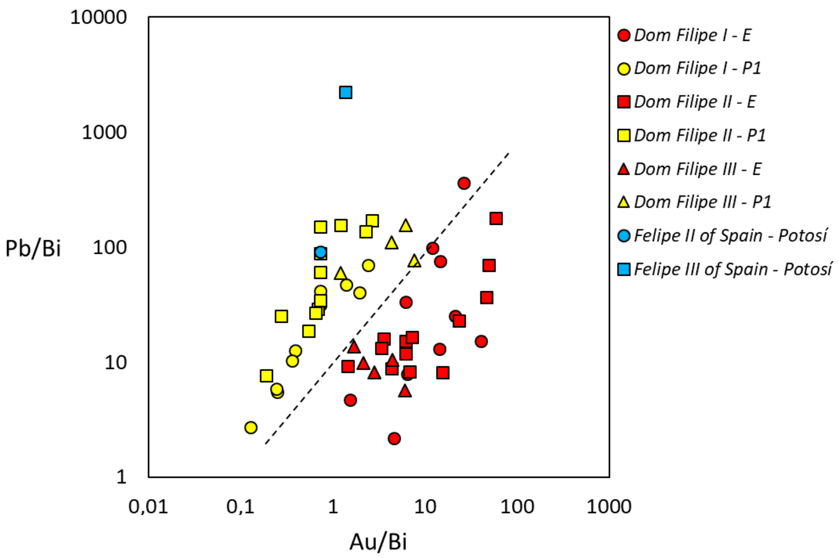

Figure 3.62 – Scatterplot of Au/Bi ratio against Pb/Bi content of E and P1 silver groups of Philippine chronologies, and of two coins minted in Potosí. Logarithmic scale on abscissas and ordinates axis.

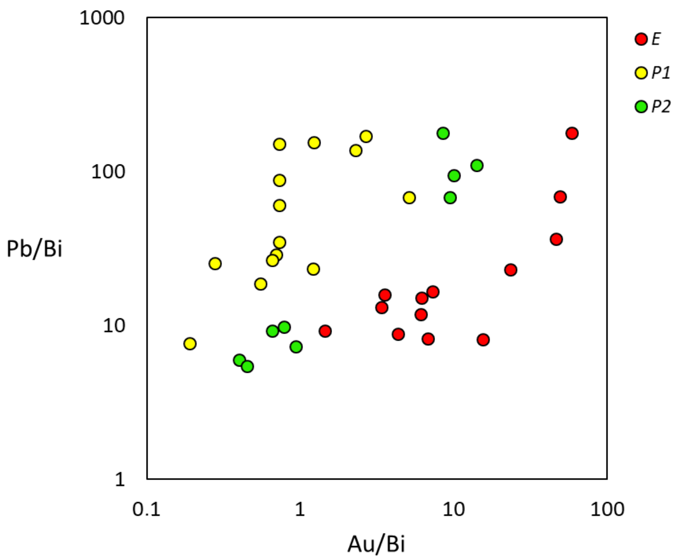

Figure 3.63 – Scatterplot of Au/Bi ratio against Pb/Bi content of E, P1 and P2 silver groups of *Dom Filipe II* coins. Logarithmic scale on abscissas and ordinates axis.

A two factor PCA analysis of all *Dom Filipe II* coins (Figure 3.64) accounting for about 72 % of the total variance in the original coins data, seems to predict that the coins assigned to P1 and P2 groups have in fact a proximate silver origin. In addition, this analysis confirms that Hg can be an important discriminator of American and European silver sources (Table 3.8).

Based on its Au content, P2 silver alloy group may represent a different gold-enriched silver alloy probably from auriferous deposits in Peru (see above 1.5.2) and has in the case of *Dom Filipe I* and *Dom Filipe II* a gold content ranging from 114 to 212 ppm, closer to the example of the late eighteenth century Lima silver coins. Also, the Andean silver mineral deposits are normally deprived of bismuth (see 1.5.2), a premise satisfied for example by the major part of the coins belonging to P2 and P1 groups of the two earlier Philippine chronologies, with the higher number of coins, where the Bi contents is under the PIXE detection limits, but gold-bismuth associations may occur in some mineral deposits, a condition verified in the remaining coins.

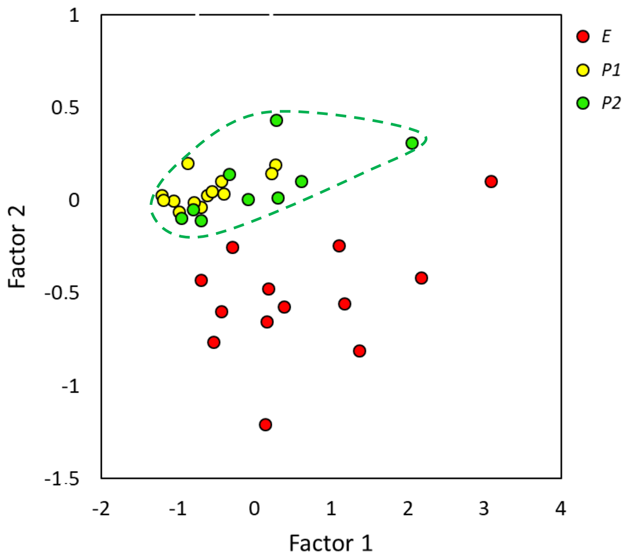

Figure 3.64 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Filipe II* coins.

Table 3.8 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Filipe II* coins, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.508**	**-0.422**
Hg	0.032	**0.942**
Pb	**0.895**	-0.020
Bi	**0.865**	0.005
Explained variance	45.2 %	26.6 %

Another two factor PCA analysis of the minor/trace contents of 94 coins of *Dom Sebastião I* chronology and of all the coins assigned to the American compositional groups (P1, P2) of all the Philippine chronologies, accounts for about 70 % of the total variance in the original data set and seems to confirm that American silver was not present in the minted coins of the 1557-1578 period and was thereafter latter introduced by Dom Filipe I.

These American silver sources (previously referred as P1 and P2) represents together more than half the silver (about 60 %) processed at the end of 16th and early 17th centuries in the mints, and seemingly have been used directly in the coin production process, subsisting with the separate but simultaneous utilization of silver metal/recyclings from European origin.

Potosí silver (P1) has also a lower impurity content on silver when compared with the European silver sources used in the Joanine and Philippine Dynasties, a fact indiciating likewise that this silver source would have been used directly in the coin minting process (Figure 3.66).

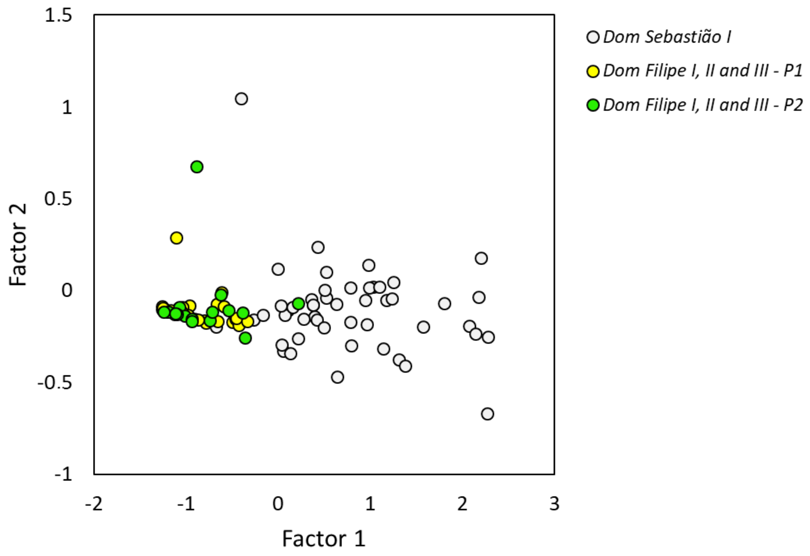

Figure 3.65 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Sebastião I* coins, and Philippine coins assigned to American compositional groups (P1, P2).

Table 3.9 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Sebastião I* coins, and Philippine coins assigned to American compositional groups (P1, P2), with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.625**	-0.064
Hg	0.009	**0.992**
Pb	**0.841**	-0.037
Bi	**0.832**	0.171
Explained variance	44.7 %	25.5 %

Gold content is present in P2 silver alloy under 212 ppm in the two earlier timelines but can go up to about 300 ppm in the two coins from *Dom Filipe III*, being this element in P1 silver alloy under 100 ppm (Figure 3.67). Bismuth also decreases on P1 silver alloy, from the highest values observed in the mintings of *Dom Filipe I* to the lowest amounts verified in *Dom Filipe III* coins, showing the contribution off different silver ores over time.

In American silver alloys, exceptuating *Dom Filipe I* timeline, Pb is present on average under 0.2 wt.%, representing generally about half the amount contained within the last Joanine silver alloy (Figure 3.68). When comparing the Pb content of Philippine E silver alloy groups with that *of Dom Sebastião I* coins, a small average decrease over time is noticed.

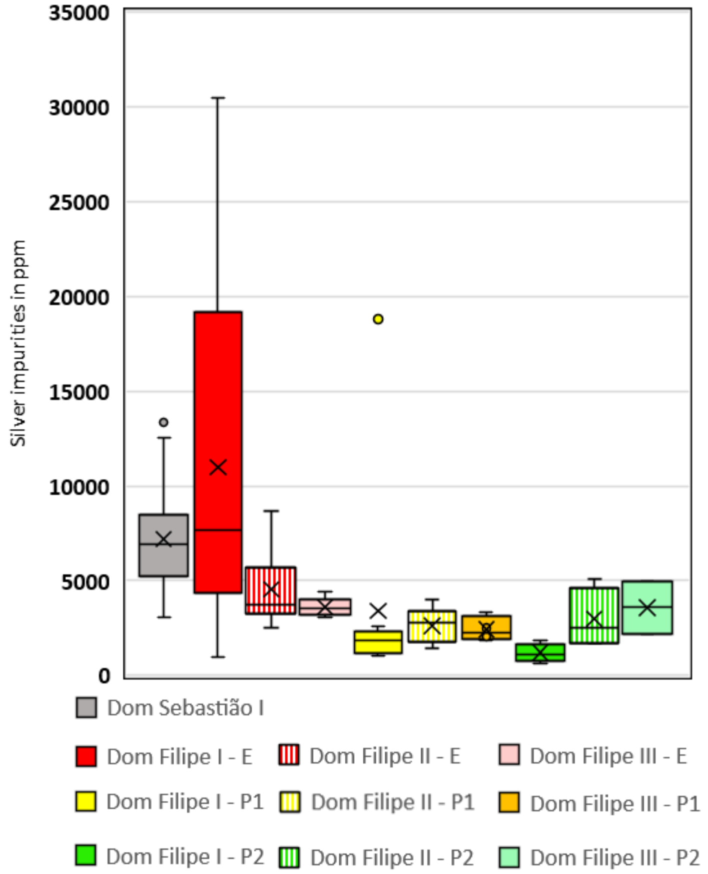

Figure 3.66 –Evolution of silver impurities content in ppm in the silver alloys minted by *Dom Sebastião I* and by the Philippine chronologies.

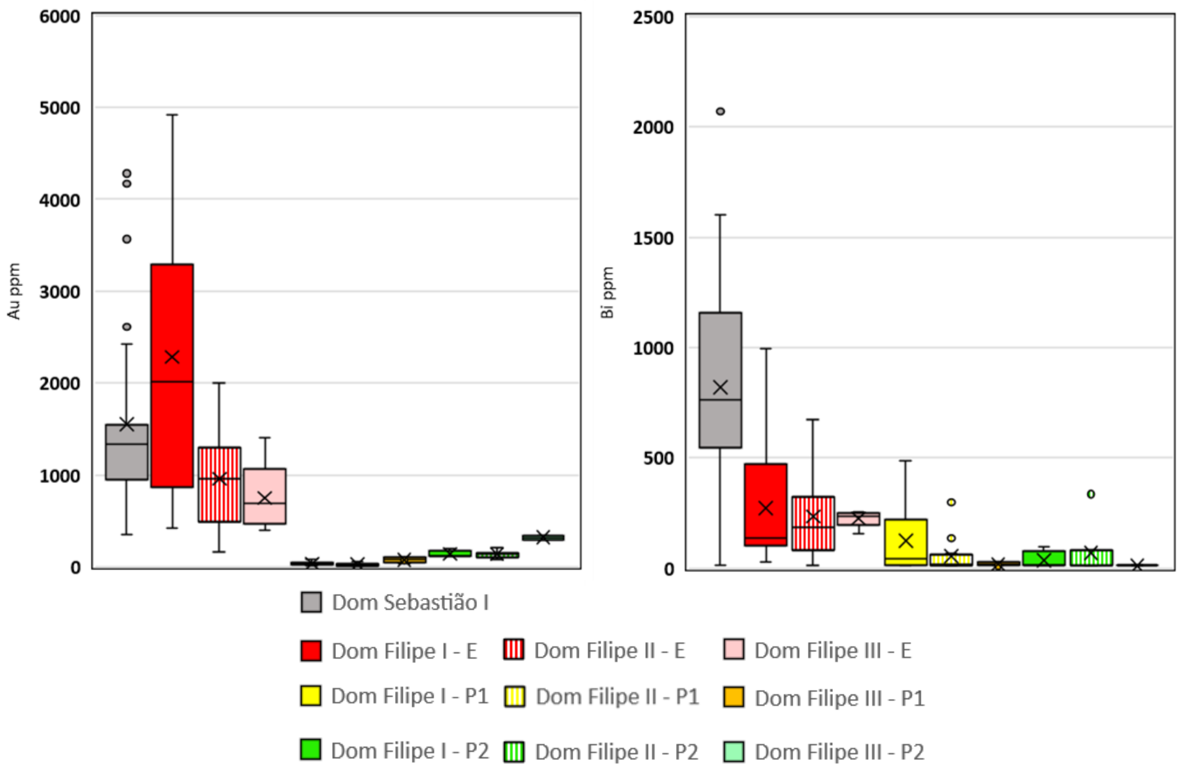

Figure 3.67 – Evolution of Au (left) and of Bi (right) content in ppm in the silver alloys minted by *Dom Sebastião I* and by the Philippine chronologies.

The high range spreading of *Dom Filipe I* E silver alloy group is due to at least three coins, having respectively 1.6, 1.7 and 2.8 wt.% Pb. This circumstance also occurred in *Dom Manuel I* Porto chronology, and because of the lack of silver in the Portuguese territory during Dom Filipe I kingdom could be related to the successive recyclings of this precious metal, carried out to accomplish the coin weight depreciations motivated by the consecutive coins silver debasement's. Also, the higher Au content of a great number of coins belonging to this European silver alloy group, lead to assume that gilded silver artefacts were used likewise in the production of currency.

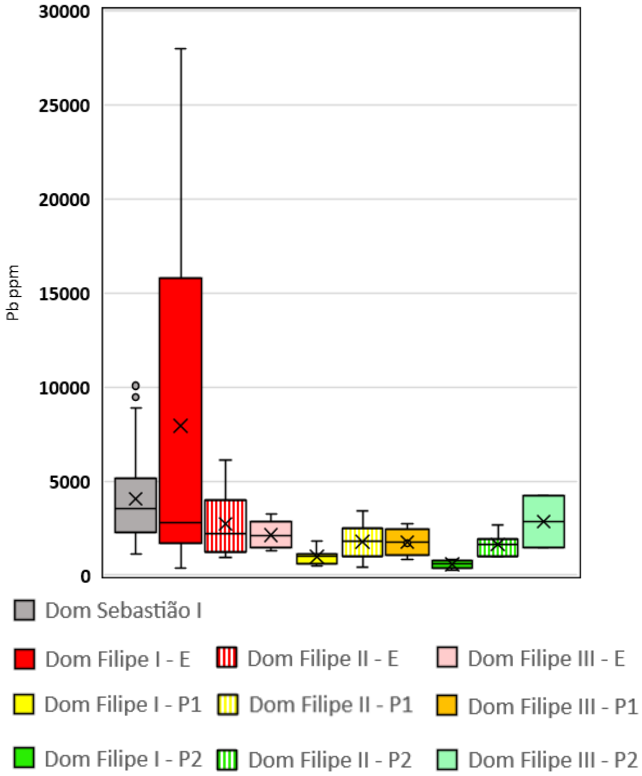

Figure 3.68 –Evolution of Pb content in ppm in the silver alloys minted *by Dom Sebastião I* and by the Philippine chronologies.

European silver compositions of Philippine coins appear to have Au, Pb and Bi contents closer to Dom Sebastião I coin compositions.

3.4 | Coins correlations with contemporaneous silverware objects

From a charter of April 7, 1506, in addition to what was ordered concerning the currency, we know of the necessity of the silverware works produced by the silversmiths having to be subjected to a rigorous assay and control of their silver alloy, avoiding falsehoods and adulterations in their fineness. At that date, *Dom Manuel I* instructed and decreed that no silversmith should make falsehood in the works that he carried out to sell, in which the silver alloy is lowered, and that he must fulfil what the owners of the said works want in the respect of the silver fineness (Aragão, A.C.T., 1875-1880).

This situation was also of great concern to *Dom João III* that on September 16, 1534, addressed the silversmiths, stipulating that only the assayer of the currency could assay the silver and that this later must put a respective hallmark on the tested silver (Peres, D., 1957).

Both previous informations permit to infer that for the compositional silver alloy investigation of the silversmith's production of this period in Portugal, it is necessary to develop a study of the sources/supplies of the worked silver metal used by these masters, as well as concerning the silversmith's relationships/obligations to the existing minting silver metal regulations. All these matters, together with the historical knowledge of each of the silversmith produced objects, are of added importance for the characterization of the used silver alloys and could allow to unravel an association between ceremonial and/or domestic apparatus objects and their production chronological period.

To perceive if besides the context of numismatic studies, coins results would have the potential to establish chronologically valid silver alloy compositions references in the context of Portuguese silversmith produced pieces, some of the above obtained coins compositional correlations were verified with the compositional results of a few silverware objetcs contemporaneous of the coins (see Appendix 6). Please refer to 2.1.2 for the identification of the objects.

Figure 3.69 – Dragon salver being analysed by PIXE external beam on the ungilded dish rear surface.

The compositional results of a salver presenting a Porto silversmith hallmark, historically attributed to a *Dom Manuel I* kingdom period production, identified in this investigation as the "dragon salver" (Figure 3.69), has been correlated with the coins results of *Dom Manuel I* and earlier chronologies (Figures 3.70 and 3.71).

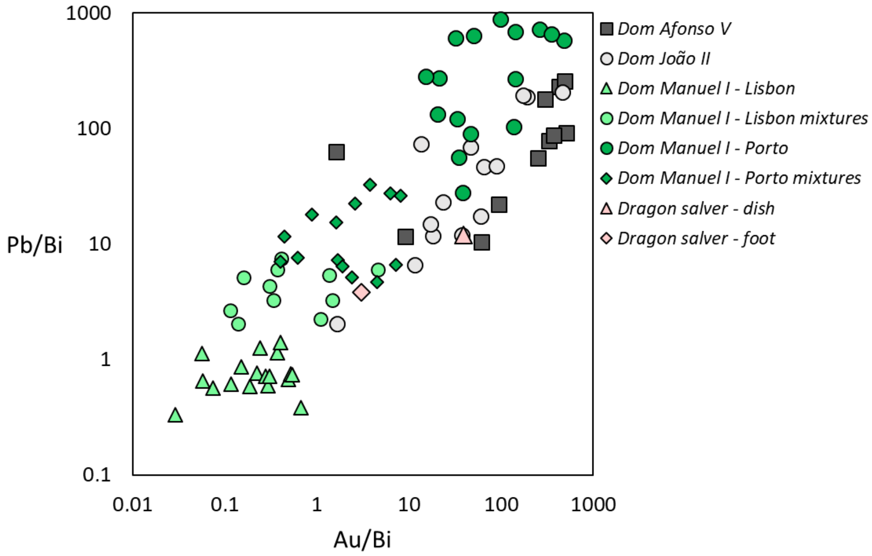

Figure 3.70 – Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom Afonso V*, *Dom João II* and *Dom Manuel I* chronologies, plus the compositional data of the dish and foot of the dragon salver. Logarithmic scale on abscisssa and ordinates axis.

The Au/Bi versus Pb/Bi ratios correlation seems to indicate that this salver was formed with a silver alloy more related to that produced in the minting processes previous to *Dom Manuel I* kingdom. Correspondingly, the two factor PCA analysis based on all the coins belonging from *Dom Afonso V* to *Dom Manuel I* chronologies (Figure 3.71) seems also to suggest that the silver alloy composition is closer to that used in *Dom João II* period, being discriminated based on the higher Au and Hg and lower Pb and Bi contents. This analysis considered the Au, Hg, Pb, and Bi contents as initial variables, and is responsible for about 69 % of the total variance of the original data (Table 3.10).

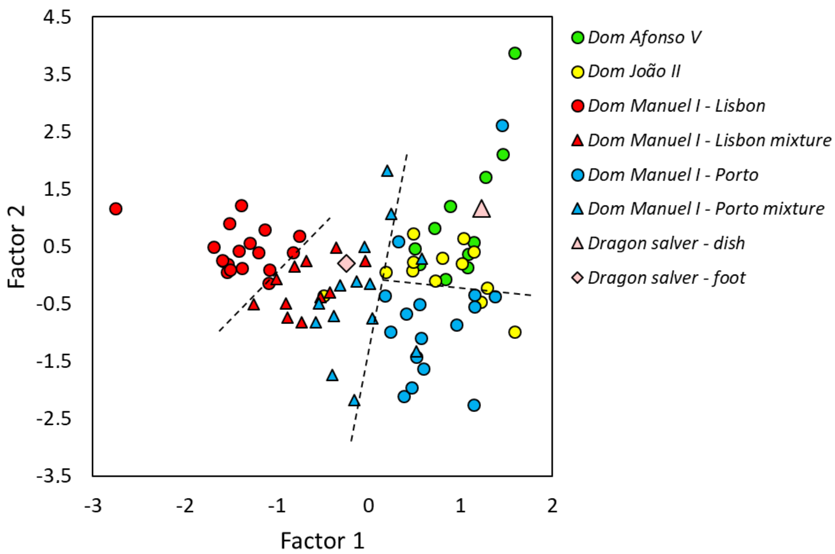

Figure 3.71 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Afonso V* to *Dom Manuel I* coins and of the dragon salver.

Table 3.10 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Afonso V* to *Dom Manuel I* coins, plus the dragon salver, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.809**	0.193
Hg	0.302	**0.633**
Pb	0.366	**-0.768**
Bi	**-0.897**	0.214
Explained variance	42.1 %	26.8 %

The compositional results of two salvers dated respectively from 1548 and 1551 (Figure 3.72) and produced thereafter during *Dom João III* kingdom, were correlated with the coins from this period.

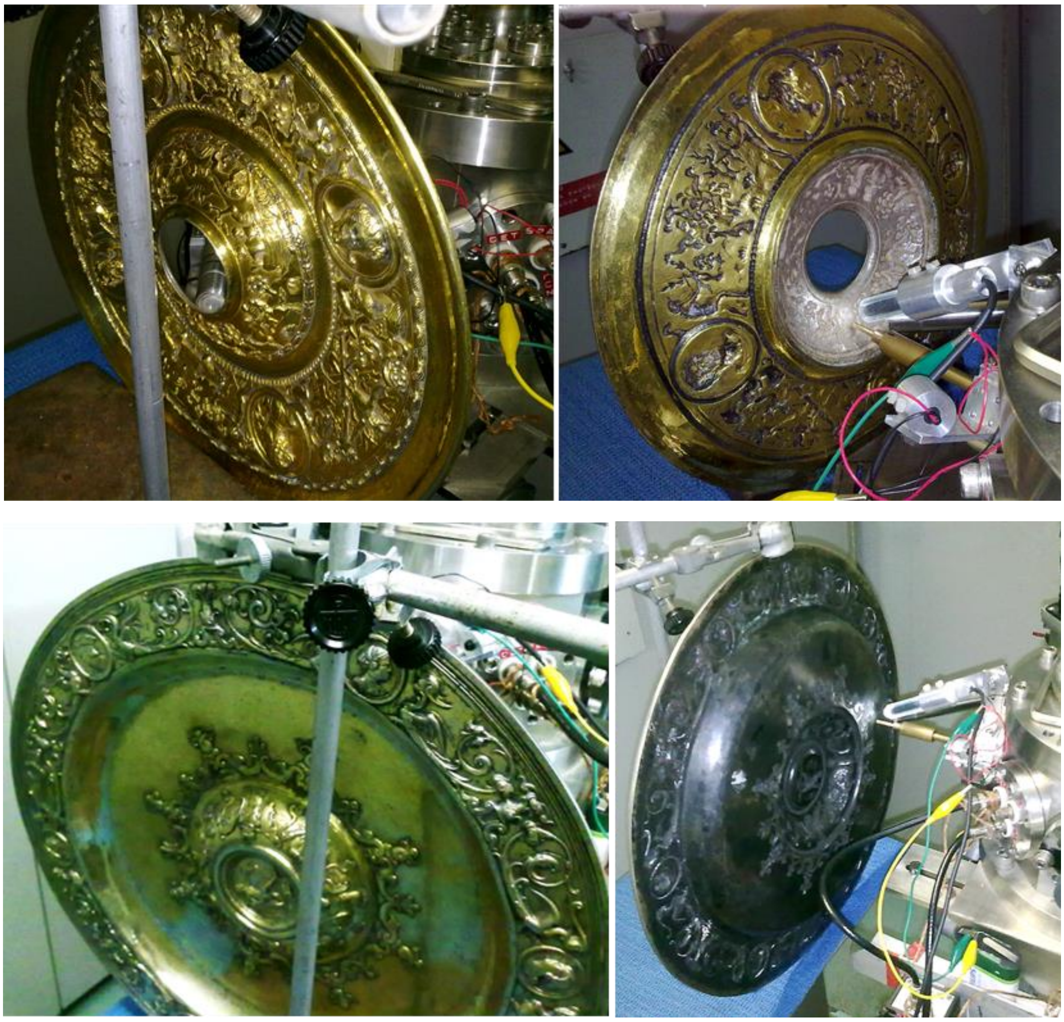

Figure 3.72 – 1548 salver (top) and 1551 salver (bottom) being analysed by PIXE external beam on the ungilded dish rear surface.

Based on the proposed Au/Bi versus Pb/Bi ratios correlation of *Dom João III* coins from Figure 3.31 (left), it seems that these salvers were formed with a silver alloy more related to that produced in the Porto minting process (Figure 3.73). Can this indiciate that both salvers have been produced in a northern silversmith production center?

Also, both salvers present very proximate ratio results probably because they were produced with a 3 years time lapse.

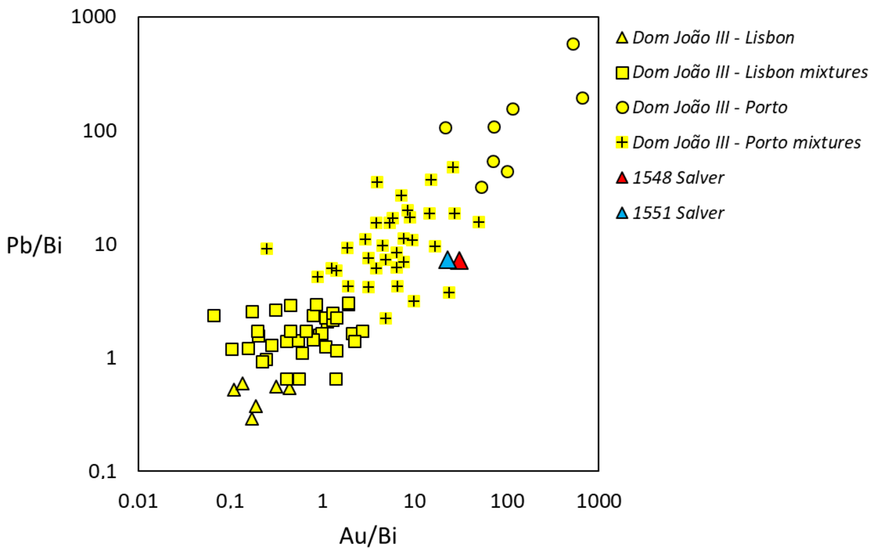

Figure 3.73 – Scatterplot of Au/Bi ratio against Pb/Bi content of all the coins pertaining to *Dom João III* chronology (Figure 3.31, left), plus the compositional data of 1548 and 1551 salvers. Logarithmic scale on abscisssa and ordinates axis.

A two factor PCA analysis of all the coins belonging from *Dom João III* chronology and of these salvers (Figure 3.74), confirms the above discrimination based on the elemental ratio correlation, at least for the 1551 salver locating it closer to Porto silver alloy compositions with higher Au, Pb and Hg and lower Bi contents. This analysis considered the Au, Hg, Pb and Bi contents as initial variables, and is responsible for about 70 % of the total variance of the original data (Table 3.11).

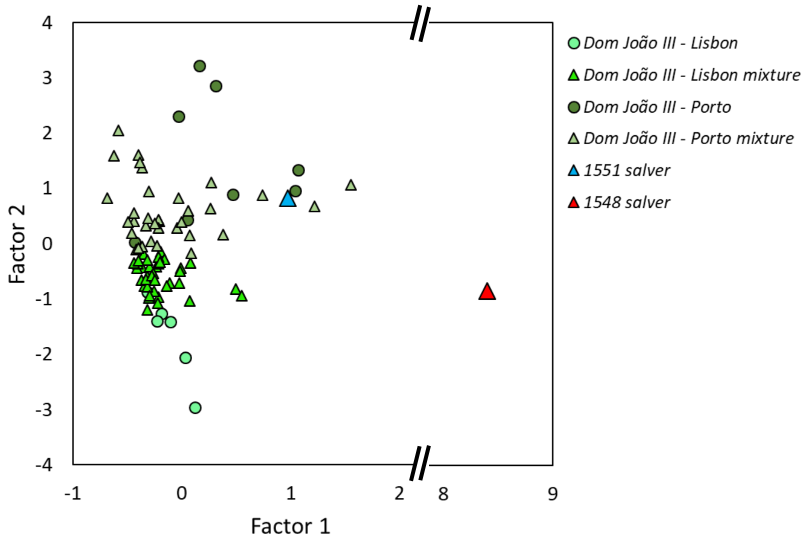

Figure 3.74 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom João III* coins and of the 1548 and 1551 salvers.

Table 3.11 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom João III* coins, plus 1548 and 1551 salver, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.716**	0.517
Hg	**0.940**	-0.074
Pb	0.029	**0.788**
Bi	-0.095	**-0.700**
Explained variance	35.1 %	34.6 %

According to PCA statistical analysis, Au and Hg contents (factor 1) are largely the responsibles for the data deviation of the 1548 salver. This great divergence is due probably to the 19th century reworks to which this salver was submitted, since it was further gilded using a gold and mercury amalgam through the known process of firegilding. The extremely high Hg surface content of 11.7 wt.% supports this fact, and gold content could also have been altered during the gilding new process.

The compositional results of the jug and of the MNAA salver (Figure 3.75), historically attributed to the time span from the end of the 16th to the beginning of 17th century, respectively, were correlated with the coins from *Dom Sebastião I* to *Dom Felipe II* (*Felipe III* of Spain) period.

Figure 3.75 – Jug (left) and MNAA 1021 salver (right) being analysed by PIXE external beam on the ungilded surface.

A first two factor PCA analysis of all these coins and objetcs (Figure 3.76), locates the jug in the the distribution range of *Dom Sebastião I* (the jug marker overlays a point from this chronology) and *Dom Filipe I* – European silver, and assigns MNAA 1021 salver to a production made with American silver. This analysis considered the Au, Hg, Pb and Bi contents as initial variables, and is responsible for about 62 % of the total variance of the original data (Table 3.12).

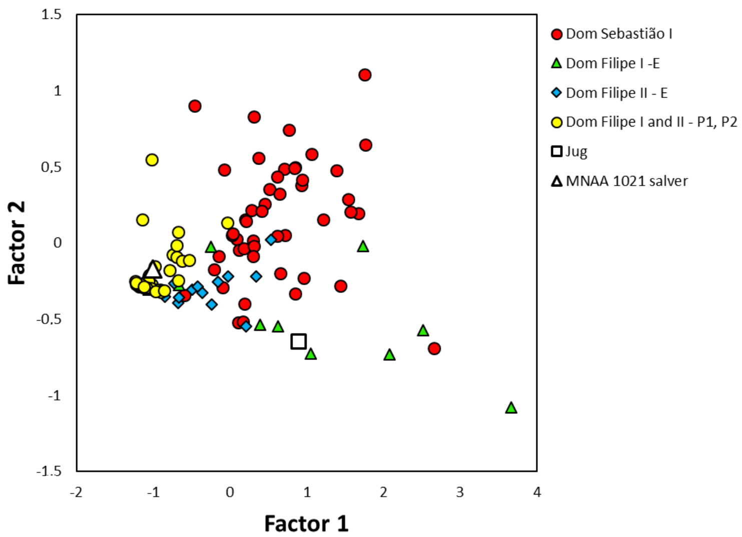

Figure 3.76 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Sebastião* I, *Dom Filipe I* and *Dom Filipe II* coins, and of the jug and the MNAA 1021 salver.

Table 3.12 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Sebastião I*, *Dom Filipe I* and *Dom Filipe II* coins, and of the jug and the MNAA 1021 salver, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.693**	-0.092
Hg	-0.082	**0.933**
Pb	**0.756**	-0.045
Bi	**0.611**	0.426
Explained variance	35.8 %	26.6 %

However, a more restrictive PCA analysis by chronology shows that the jug seems to be more related with the silver alloys from *Dom Sebastião I* coins (Figure 3.77 and 3.78), locating it within the range of the above proposed Porto compositional group (see above 3.2.5).

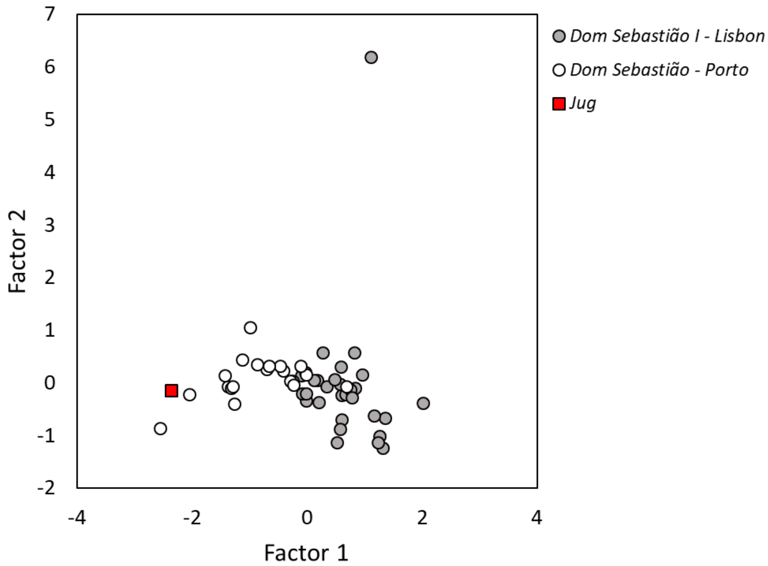

Figure 3.77 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Sebastião I* coins, with proposed Lisbon and Porto compositional groups, and of the jug.

Table 3.13 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Sebastião I* coins and of the jug, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.693**	-0.092
Hg	-0.082	**0.933**
Pb	**0.756**	-0.045
Bi	**0.611**	0.426
Explained variance	35.8 %	26.6 %

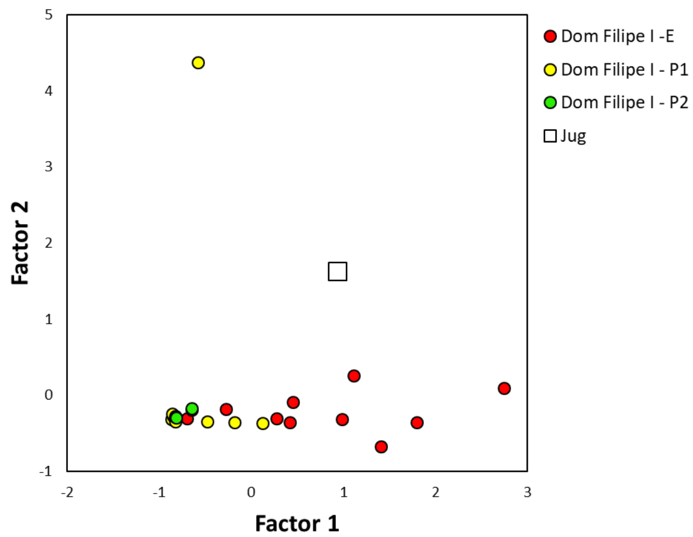

Figure 3.78 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Filipe I* coins and of the jug.

Table 3.14 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Filipe I* coins and of the jug, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.856**	0.126
Hg	-0.063	**0.983**
Pb	0.572	-0.180
Bi	**0.710**	-0.077
Explained variance	39.2 %	25.5 %

As for the MNAA 1021 salver, a conjoined PCA analysis with *Dom Filipe II* coins (Figure 3.79, Table 3.15) confirms its former American silver indexation and sustains its historical classification of a production from this period.

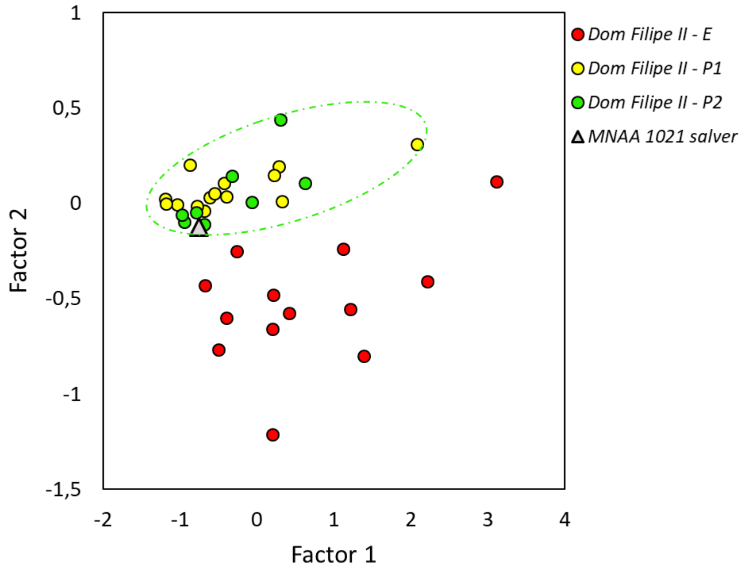

Figure 3.79 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Filipe II* coins and of the MNAA 1021 salver.

Table 3.15 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Filipe II* coins and of the MNAA 1021 salver, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	0.515	-0.417
Hg	0.031	**0.943**
Pb	**0.888**	-0.011
Bi	**0.857**	0.006
Explained variance	44.7 %	26.6 %

Concerning the Vidigueira treasure from the MNAA collection, when correlating the missal lectern, the oratory-reliquary and the pax data through a PCA analysis with the coins data corresponding to *Dom Sebastião I* and *Dom Filipe I*, their silver alloys seems to be well correlated with the compositions of the European silver alloys from these periods (Figure 3.80, Table 3.16), and not with the American silver, being this analysis responsable for about 61 % of the total variance of the original data.

Again, a more restrictive PCA analysis by chronology shows that the Vidigueira treasure objects seems to be more related with the silver alloys from *Dom Sebastião I* coins (Figure 3.81, Table 3.17), and not from *Dom Filipe I* (Figure 3.82, Table 3.18), locating these objects within the range of the above proposed Porto compositional group (see above 3.2.5).

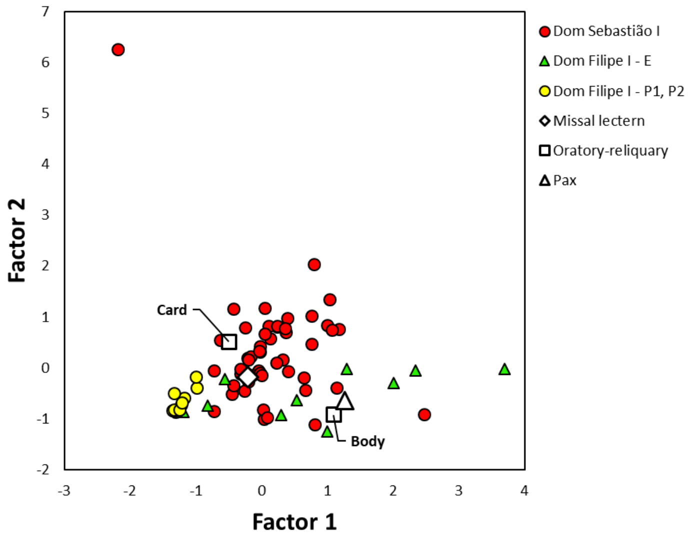

Figure 3.80 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Sebastião I* and *Dom Filipe I* coins and of the Vidigueira treasure objects.

Table 3.16 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Sebastião I* and *Dom Filipe I* coins and of the Vidigueira treasure objects, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.708**	0.362
Hg	-0.299	-0.368
Pb	-0.075	**0.909**
Bi	**0.852**	-0.155
Explained variance	33.0 %	27.9 %

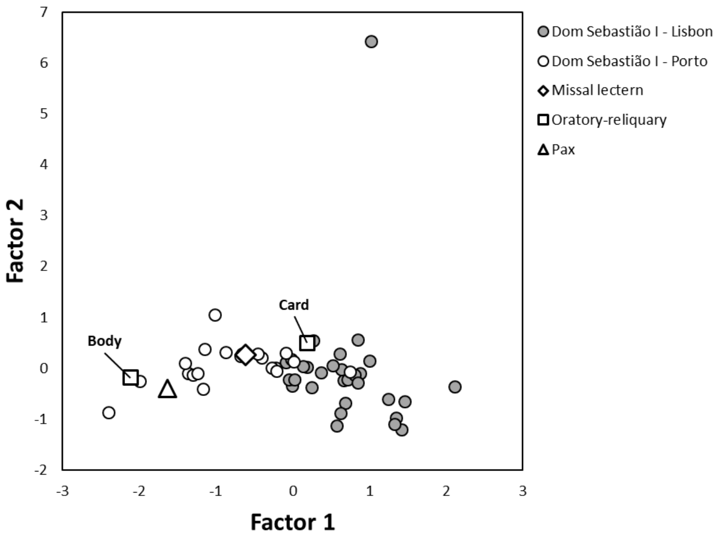

Figure 3.81 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Sebastião I* coins and of the Vidigueira treasure objects.

Table 3.17 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Sebastião I* coins and of the Vidigueira treasure objects, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**-0.721**	-0.180
Hg	0.121	**0.906**
Pb	0.609	-0.447
Bi	**0.809**	0.033
Explained variance	39.0 %	26.3 %

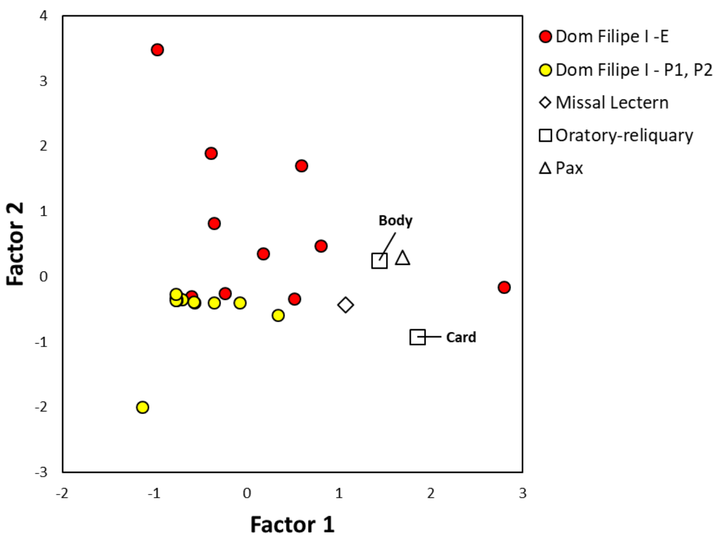

Figure 3.82 – Factor 1 versus factor 2 principal component analysis plot of Au, Hg, Pb and Bi contents of *Dom Filipe I* coins and of the Vidigueira treasure objects.

Table 3.18 – Factor loadings of Au, Hg, Pb and Bi contents of principal components analysis of *Dom Filipe I* coins and of the Vidigueira treasure objects, with important factor loadings in bold.

Variable	Factor 1	Factor 2
Au	**0.726**	0.429
Hg	-0.214	-0.394
Pb	-0.078	**0.916**
Bi	**0.902**	-0.070
Explained variance	34.8 %	29.6 %

In summary, the potential of PIXE elemental compositional analysis of coins as a chronological silver alloy reference that could be correlated with the elemental compositional data of silverware contemporaneous objects, should be further evaluated. The above correlations between coins and objects seems to disclose new useful information for a better knowledge of the silver objects, however, they should be deployed together with an in-depth historical investigation of each of them, something beyond the scope of this thesis. This field seems nevertheless to constitute a promising area of knowledge development associated with these objects.

3.5 | General Conclusions

Elemental analysis of high silver alloys

The elemental analysis investigation of high silver alloys focused on the microstructural and compositional characterization of Portuguese 11 dinheiros silver coins, has shown the existence of an important surface silver enrichment in these coins.

Until now, the extent in which the surface elemental composition analytical results were influenced by surface silver enrichment in coins alloys with silver finenesses greater than the silver content indexed to the maximum value of copper solid solubility in silver, i.e., 91.2 wt.%, had been disregarded. Accordingly, surface elemental analysis presenting high silver contents have been considered as reliable for original bulk composition of high silver coins which in some cases have been referred as being produced from very pure silver alloys.

In these high silver alloys, the coin manufacturing process induces a subsurface microstructurally modified layer resulting from intergranular dry and wet corrosion in the annealing operations, primarily related to the preferential leaching of the Cu-rich phase in the subsurface layer depth, with a different proportion of copper and silver rich phases than the core of the coins and with an unknown elemental compositional gradient and depth. In the case of the Portuguese *11 dinheiros* silver alloys, this layer can extend to about 70 µm.

PIXE and EDXRF analysis of this subsurface layer originates a silver overestimation 4 to 7 % higher than the bulk of the coins, and the copper depletion gradient as identified by LA-ICP-MS represents as much as 50 % less copper on surface than on the bulk of the coins.

This investigation shows however through the combination of different methods of analysis, EDXRF, PIXE, SEM-EDS and LA-ICP-MS, that important metallurgical information resulting from the minting process may be missed when analyzing high silver alloys relying only on the judgment of surface analysis.

The results obtained by surface analytical techniques may differ from the original bulk compositions for these high silver content alloys incurring in potential erroneous interpretations of the coins fineness, and thereafter should be taken cautiousness together with numismatic and economic historical context and information.

Albeit the existing minor/trace elements compositional gradients between the bulk and the surface of the coins, the correlations of their surface contents obtained by PIXE analysis allow to discriminate historical periods (chronologies) and differences of mints (Lisbon and Porto). In this sense, the gold/bismuth ratio related to the initial composition of the processed silver and the lead/bismuth ratio related to the silver metallurgical processes, are important discriminators of these high silver alloys. Hg appears also to be an important element for the discrimination of different alloys sources.

In addition, PIXE surface results had allowed for the first time, through minor and trace chemical elements, to distinguish the silver alloy "signature" or "fingerprint" of the Potosí silver, contrasting with the so far achieved by NAA multielement global analysis that reflects the average composition of coins.

Silver sources and silver minting in the Portuguese 15th to early 17th centuries

Albeit the minor/trace impurity contents determined by PIXE are indicative, since they do not represent global values of the alloys, but values obtained on a very proximate surface layer, they allow nonetheless to perceive minting's differences and to discriminate distinct silver sources.

Within this investigation, it was possible to determinate that the Portuguese coin minting, who depended on European silver sources, have relyed on different silver alloys during the 15th to 17th centuries.

One silver source characterized mainly by high Au and Hg, and low Pb and Bi contents, supplied the earlier chronologies of *Dom Afonso V* and *Dom João II* during the 15th century, being processed in both minting houses of Lisbon and Porto. However, the composition discrimination of the silver processed in each of the two mints is not evident.

This silver was replaced during the end of the 15th century and/or beginning of the 16th century by a new silver metal entering the Portuguese capital, probably derived from the processing of argentiferous copper ore sources, characterized by low Au and high Bi contents and whose dissemination in the country was made through Lisbon in *Dom Manuel I* period.

Porto, the other mint in operation during this period, seems to process silver compositions proximate to the earlier century silver metal. It is unclear if this silver originates also from a new provenance or if it resulted from the important technical improvements on the upstream silver ore extraction introduced during this century in the European silver processing.

In the second and third quarters of the 16th century, Lisbon and Porto silver alloy coin compositions evolve over time towards compositional homogenization and uniformization. The average main minor/trace elements contents comprised in each of the processed silver alloys, will reach later in this century the more uniform compositions observed in *Dom Sebastião I* period. This evolution probably had arisen due to major recycling operations realized in each chronology of the earlier king minted currency.

Lisbon and Porto processed compositions seems to be well discriminated during Dom Manuel I chronology, but the homogeneization of the silver alloys that will verify over time together with the precious metal bullion movements between both mints will render problematic the identification of the processed silver of each mint, at least for the mint unidentified coins.

The Philippine chronologies reveal the presence of another silver source distinguishable from the silver compositions used until 1578 in the Portuguese territory: the new Potosí American silver brought to Portugal by *Dom Filipe I* (*Felipe II* of Spain). The elementary compositions of Potosí and of European silver alloys are for the first time differentiated through a superficial analytical method, such as PIXE, based mainly on Au and Bi contents. This new source provenance is characterized by Au contents < 100 ppm and very low Bi contents when compared with the European silver metal. It seems also that this American silver provenance could have different silver contributions with different elemental compositions.

Numismatic historical issues

Two Dom Afonso V Real Grosso coins numismatically assigned to Toro minting place and produced between May 1475 and June 1476, were analised in the present investigation. From the elemental correlations found, it seems that these coins have been produced with a silver metal only used during the upcoming chronology. This fact and a composition distinct to Lisbon and Porto mints, leads to assume that they could have been produced in a different location. However, more investigation is needed on the Dom Afonso V coins.

The Manueline Meio Vintém coins produced with a gotic letter Π have compositions that correlate with Porto silver alloys, agreeing to Gomes, A., 2003, previous presumption that this kind of lettering should have been used in the Porto mint. A new fact is that Meio Vintém coins were produced with Lisbon and Porto alloys supposedly making part of the production of both mints.

Something to be explained is the local production of the coins that do not bear a monetary letter, whose clarification depends on the development of new numismatic and historical investigations of the coins. It remains the question of these coins having been simultaneously minted in Lisbon and Porto mints, or only in Lisbon, as numismatically accepted, but with processed Porto silver bullions that were transferred to the capital. The latter case had occurred for example with Dom João III Tostão coins, as attested by the monetary L letter beared by the related coins, confirming the movimentation of silver processed ingots between both mints.

From the correlations of coins analytical results, it appears that Porto monetary production had relied more on “older” silver supplies, either in the form of bullions or of earlier circulating coins, and that its mint operation depended more of silver metal recycling.

Some Porto coins with a silver fineness well below the legal 11 dinheiros and with very high copper contents were detected, being probably produced within the organization structure of this mint. They represent intentional contemporaneous counterfeitings, being the result of a malpractice aside from the established manufacturing steps and assay procedures.

This investigation allowed also to detect an actual counterfeiting of a Dom João III Cinquinho coin minted in Lisbon (BdP 9004800300, 36 in Appendix 1), based on the use of a very pure silver alloy, free of the major impurities that are always presented in the coins of this period.

Contemporaneous silver objects issues

PIXE elemental compositional analysis of coins could establish potential chronological silver alloy references to be used in elemental compositional correlations with silverware contemporaneous objects, bringing new useful information/knowledge about their material constitution. However, due to the objects history, to further alterations/modifications and to the complexity of their execution in some cases, any correlation analysis should be deployed together with an in-depth historical investigation of the same

.

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Appendices

Appendix 1 – Portuguese silver coins from the Money Museum

1. *Dom Afonso V – Leal* – Lisbon – 9003625800

2. *Dom Afonso V – Chinfrão* – Lisbon – 9002340100

3. *Dom Afonso V – Chinfrão* – Porto – 9002340300

4. *Dom Afonso V – Chinfrão* – Porto – 9002340400

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5. *Dom Afonso V – Real Grosso* – Lisbon – 9002340500

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6. *Dom Afonso V – Real Grosso* – Porto – 9002340700

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7. *Dom Afonso V – Real Grosso* – 9002830100

8. *Dom Afonso V – Real Grosso* – 9003473800

9. *Dom Afonso V – Real Grosso* – Lisbon – 9003507100

10. *Dom Afonso V – Real Grosso* – Lisbon – 9003573500

11. *Dom Afonso V – Real Grosso* – Porto – 9003625900

12. *Dom João II* – *Vintém* – Lisbon – 9000995900

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13. *Dom João II* – *Vintém* – Lisbon – 9001029700

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14. *Dom João II* – *Vintém* – Lisbon – 9002342400

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15. *Dom João II* – *Vintém* – Lisbon – 9002342600

16. *Dom João II* – *Vintém* – Lisbon – 9002342700

17. *Dom João II* – *Vintém* – Lisbon – 9002343200

18. *Dom João II* – *Vintém* – Porto – 9002344000

19. *Dom João II* – *Vintém* – Porto – 9002344100

20. *Dom João II* – *Vintém* – Porto – 9002344300

21. *Dom João II* – *Vintém* – Porto – 9002344400

22. *Dom João II* – *Vintém* – Porto – 9002344500

23. *Dom João II* – *Vintém* – Porto – 9002344600

24. *Dom João II – Vintém* – Porto – 9002344800

25. *Dom João II – Vintém* – Porto – 9002529300

26. *Dom Manuel I – Vintém* – Porto – 9000989200

27. *Dom Manuel I – Vintém* – Porto – 9002350100

28. *Dom Manuel I – Vintém* – Porto – 9002350300

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29. *Dom Manuel I – Vintém* – Porto – 9002350700

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30. *Dom Manuel I – Vintém* – Porto – 9002350800

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31. *Dom Manuel I – Vintém* – Porto – 9002350900

32. *Dom Manuel I – Vintém* – Porto – 9002351100

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33. *Dom Manuel I – Tostão* – Porto – 9002352200

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34. *Dom Manuel I – Tostão* – Porto – 9002943100

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35. *Dom João III – Cinquinho* – 9002354300

36. *Dom João III – Cinquinho –* Lisbon – 9004800300

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37. *Dom João III – ½ Vintém* – 9002354500

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38. *Dom João III – ½ Vintém* – 9002354600

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39. *Dom João III – Vintém –* Lisbon – 9002354700

40. *Dom João III – Vintém –* Lisbon – 9002354800

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41. *Dom João III – Vintém –* Lisbon – 9002354900

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42. *Dom João III – Vintém –* Porto – 9002357700

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43. *Dom João III – Vintém –* Porto – 9002358000

44. *Dom João III – Real Português* – 9002358800

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45. *Dom João III – Real Português* – 9002358900

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46. *Dom João III – Real Português* – 9002359300

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47. *Dom João III – Real Português* – Porto – 9002359600

48. *Dom João III – ½ Tostão* – 9001019000

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49. *Dom João III – ½ Tostão* – 9002359900

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50. *Dom João III – ½ Tostão* – 9002360000

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51. *Dom João III – Real Português Dobrado* – 9002360200

52. *Dom João III – Tostão* – Porto – 9000199400

53. *Dom João III – Tostão* – 9001030100

54. *Dom João III – Tostão* – Porto – 9001172700

55. *Dom João III – Tostão* – Lisbon – 9002360700

56. *Dom João III – Tostão* – Porto – 9002360800

57. *Dom João III – Tostão* – Porto – 9002360900

58. *Dom João III – Tostão* – Lisboa – 9002361400

59. *Dom João III – Tostão* – 9002362000

60. *Dom João III – Tostão* – Porto – 9003573700

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61. *Dom João III – Tostão* – Lisbon – 9004131500

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62. *Dom Sebastião I – Tostão* – Porto – 9001172800

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63. *Dom Sebastião I – Tostão* – Porto – 9002366700

64. *Dom Sebastião I – Tostão* – Porto – 9002366900

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65. *Dom Sebastião I – Tostão* – Porto – 9004910400

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66. *Dom Filipe I – Vintém* – Lisbon – 9002371200

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67. *Dom Filipe I – Vintém* – Lisbon – 9002371300

68. *Dom Filipe I – Vintém* – Lisbon – 9002371400

69. *Dom Filipe I – 40 Reais* – Lisbon – 9002371500

70. *Dom Filipe I – 40 Reais* – Lisbon – 9002371600

71. *Dom Filipe I – 40 Reais* – Lisbon – 9004199400

72. *Dom Filipe I – 80 Reais* – Lisbon – 9002371700

73. *Dom Filipe I – 80 Reais* – Lisbon – 9004189300

74. *Dom Filipe I – 80 Reais* – Lisbon – 9004199500

75. *Dom Filipe I – Tostão* – Lisbon – 9002371800

76. *Dom Filipe I – Tostão* – Lisbon – 9002371900

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77. *Dom Filipe I – Tostão* – Lisbon – 9002372000

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78. *Dom Filipe I – Tostão* – Lisbon – 9002372100

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79. *Dom Filipe I – Tostão* – Lisbon – 9002372200

80. *Dom Filipe I – Tostão* – Lisbon – 9004912100

81. *Dom Filipe III – ½ Tostão* – Lisbon – 9002373200

82. *Dom Filipe III – ½ Tostão* – Lisbon – 9002373500

83. *Dom Filipe III – ½ Tostão* – Lisbon – 9004050800

84. *Dom Filipe III – ½ Tostão* – Lisbon – 9004924400

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85. *Dom Filipe III – Tostão* – Lisbon – 9000068700

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86. *Dom Filipe III – Tostão* – Lisbon – 9002372700

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87. *Dom Filipe III – Tostão* – Lisbon – 9002373700

88. *Dom Filipe III – Tostão* – Lisbon – 9002373800

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89. *Dom Filipe III – Tostão* – Lisbon – 9002373900

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90. *Dom Filipe III – Tostão* – Lisbon – 9002530500

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91. *Dom Filipe III – Tostão* – Lisbon – 9004800400

Appendix 2 – Colonial Spanish silver coins from the Money Museum

1. *Felipe II – 8 Reales* – Potosí – 4240051173

2. *Felipe III – 8 Reales* – Potosí – 4240046814

Appendix 3 – Portuguese silver coins used in invasive analysis

1. *Dom João II – Vintém –* Lisbon – C1

2. *Dom João II – Vintém –* Porto – C2

3. *Dom Manuel I – Vintém –* Lisbon – C3

4. *Dom Manuel I – Vintém –* Porto – C4

Appendix 4 – Compositional data of Portuguese *11 dinheiros* coins

PIXE compositional data

Where data are missing in the tables, this is because the elements were under the detection limits.

Table A4.1 – PIXE elemental compositional data of *Dom Afonso V* coins

***Dom Afonso V* (1438-1481)**

			%		**ppm**						
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**As**	**Au**	**Hg**	**Pb**	**Bi**
Leal	BdP 9003625800	Lisbon	95.56	3.09	120			4346	3082	5500	478
Chinfrão	BdP 9002340100	Lisbon	91.86	7.06	173		207	227	1348	8647	139
	BdP 9002340300	Porto	96.19	2.83	82		32	6996	1071	1621	21
	BdP 9002340400	Porto	94.13	5.10	55		106	4515	281	2663	
Real	BdP 9002340500	Lisbon	96.91	2.05	92	32		7600	1280	1368	
Grosso	BdP 9002340700	Porto	74.53	23.99	619	779	2022	7303	220	3833	
	BdP 9002830100		95.28	3.62	32	54		9021	162	1545	148
	BdP 9003473800		96.96	1.92	14	456		8507	102	1970	89
	BdP 9003507100	Lisbon	97.42	1.86	139			5335	504	1178	21
	BdP 9003573500	Lisbon	96.53	2.41	52	532		6395	84	3461	
	BdP 9003625900	Porto	96.76	2.47	86			5594	761	1308	

Table A4.2 – PIXE elemental compositional data of *Dom João II* coins

***Dom João II* (1481-1495)**

			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Vintém	BdP 9000995900	Lisbon	97.75	0.96	61	202	9443	363	2712	156
	BdP 9001029700	Lisbon	93.15	6.14	44	73	5094	196	1605	134
	BdP 9002342400	Lisbon	94.84	3.93	21		6004	244	5854	255
	BdP 9002342600	Lisbon	95.75	2.79	39	101	8112	325	5817	125
	BdP 9002342700	Lisbon	97.24	2.06	20	76	4064	167	2324	354
	BdP 9002343200	Lisbon	96.11	3.11	98	204	4063	591	2631	224
	BdP 9002344000	Porto	96.77	2.16	144	96	7015	340	3080	
	BdP 9002344100	Porto	94.57	4.17	29	189	7775	267	4176	88
	BdP 9002344300	Porto	95.45	3.25	49	112	6387	195	6252	34
	BdP 9002344400	Porto	96.86	2.85	45	82	873	286	1076	531
	BdP 9002344500	Porto	95.31	3.68	40	513	4867	208	4185	282
	BdP 9002344600	Porto	92.87	5.56	53	41	2284	659	12486	170
	BdP 9002344800	Porto	92.32	5.84	50	115	8477	345	9377	49
	BdP 9002529300	Porto	93.65	4.61	75		6846	226	10105	147

Table A4.3 – PIXE average elemental compositional data of *Dom Manuel I* coins

***Dom Manuel I* (1495-1521)**

			%	ppm						
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
½ Vintém	INCM 9426		96.86	2.19	61	4714	993	421	1421	1902
	INCM 13182		91.42	7.95	86	104	184	75	4261	1610
	INCM 13183		95.47	3.63	85	56	2398	329	5153	1002
	INCM 13184		97.77	1.56	35	283	2154	189	4044	
	INCM 13185		95.10	4.27	53	194	2510	917	2254	344
	INCM 13186		96.06	3.44	118	68	1123	370	2305	1031
	INCM 13187		95.09	4.27	176	146	2428	534	2517	540
	INCM 13188*		95.28	4.13	235	107	2827	574	2075	74
	INCM 13189*		95.86	3.60	69		784	1558	2600	409
	INCM 13190*		96.74	2.86	50	59	524	125	1359	1894
	INCM 13191		96.52	2.40	100	79	3934	232	6329	114
	INCM 13192		95.84	2.44	156	155	1639	631	14199	435
	INCM 13193		94.79	3.61	141	211	5320	510	9769	
Vintém	INCM 13175	Porto	95.89	3.06	174	254	1683	227	7213	999
	INCM 13180	Porto	91.09	7.27	60	129	7200	405	8665	
	INCM 13181	Porto	93.89	3.91	301	68	4616	137	16772	138
	INCM 13506	Porto	95.49	3.89	113	178	499	493	4693	305
	BdP 9000989200	Porto	95.76	3.47	154	217	674	580	5786	260
	BdP 9002350100	Porto	94.03	4.54	44	171	474	160	12414	1069
	BdP 9002350300	Porto	91.32	7.67	93	59	478	402	9110	
	BdP 9002350700	Porto	94.01	4.70	82		2153	372	10299	
	BdP 9002350800	Porto	92.81	5.66	21		3917	491	10812	
	BdP 9002350900	Porto	94.22	4.68	102		751	650	9503	
	BdP 9002351100	Porto	92.83	5.65	71	56	1478	362	13234	
Tostão	INCM 9405	Lisbon	88.96	10.04	52	195	423	619	7615	1023
	INCM 13134	Lisbon	94.83	4.60	41	1487	820	578	1123	1680
	INCM 13136	Lisbon	91.56	7.51	180	561	450	315	6400	1471
	INCM 13137	Lisbon	98.39	1.29	13	238	633	516	1413	432
	INCM 13143		91.16	8.29	7	603	678	630	1347	2288
	INCM 13144		96.61	2.91	22	185	657	225	1521	2136
	INCM 13145		95.25	4.01	13	682	2489	443	3208	536
	INCM 13146		92.82	6.54		63	1302	847	1783	2428
	INCM 13147		90.55	8.25		5400	442	532	4252	1306
	INCM 13149	Porto	96.41	2.73	172	122	1489	195	6386	235
	BdP 9002352200	Porto	97.28	2.23	25	222	216	123	3786	538
	BdP 9002943100	Porto	94.68	4.06	120	56	3383	2427	6566	73

*One analysis only

Table A4.4 – PIXE average elemental compositional data of *Dom João III* coins

***Dom João III* (1521-1557)**										
			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Cinquinho	BdP 9002354300		95.91	3.25	28	100	4816	365	2796	291
	BdP 9004800300	Lisbon	99.93	0.04		8	68		289	15
½ Vintém	BdP 9002354500		96.01	2.86	16	104	1707	36	8445	909
	BdP 9002354600		96.78	2.19	11	121	7608	88	2357	152
Vintém	INCM 9436	Lisbon	94.37	5.12	194	488	273	390	2385	1381
	INCM 9438		96.01	2.28		76	397	15254	727	655
	INCM 9440	Lisbon	90.97	8.43	59	229	2298	409	1816	1104
	INCM 9441	Lisbon	94.56	4.83		31	2939	210	1859	1089
	INCM 9443	Lisbon	95.11	4.19	31	197	878	913	4266	699
	INCM 9475		96.49	3.23	26	65	43	497	1548	656
	INCM 9476		96.22	3.28	34	87	322	436	2508	1613
	INCM 13265		94.27	4.80		141	6132	297	2702	61
	INCM 13266		94.57	4.17	47	133	1232	7435	3511	228
	INCM 13267		98.25	1.42	62	138	566	200	919	1408
	INCM 13268		96.49	3.16		104	815	374	1376	834
	INCM 13273	Porto	97.05	2.03		91	2571	149	6068	307
	INCM 13274	Porto	94.55	3.64	41	79	7532	182	10198	66
	INCM 13276	Lisbon	97.63	2.09	87	196	350	646	1394	91
	INCM 13277	Lisbon	95.42	3.32		3734	2527	159	6090	167
	INCM 13330	Lisbon	95.41	4.02	9	215	1584	553	2457	835
	BdP 9002354700	Lisbon	96.85	2.43	31	24	4983	81	1611	510
	BdP 9002354800	Lisbon	95.80	3.73	18	88	274	511	2110	1743
	BdP 9002354900	Lisbon	96.20	2.59	106	248	2783	362	5059	3493
	BdP 9002357700	Porto	95.83	3.78	40	109	260	1027	2318	66
	BdP 9002358000	Porto	95.20	3.83	26	322	2404	414	5700	760
Real Português	INCM 9455	Porto	95.51	3.28		384	5657	143	5148	739
	INCM 13282	Porto	97.77	1.95		141	697	249	1508	156
	INCM 13283	Porto	95.99	3.17		52	3808	325	3677	594
	INCM 13291		95.17	3.98	25	86	2005	319	4153	1857
	INCM 13299	Porto	92.68	6.68	12	84	3274	396	2143	504
	BdP 9002358800	Lisbon	95.93	3.63	23	124	184	338	2700	1061
	BdP 9002358900	Lisbon	92.43	6.18	128	30	5286	539	7854	73
	BdP 9002359300	Lisbon	96.97	2.50	21	60	1558	441	3005	176
	BdP 9002359600	Porto	96.20	2.48	13	279	9824	202	2920	
½ Tostão	INCM 9474		93.56	5.85	40		2010	605	2986	266
	BdP 9001019000		97.68	2.00	22	211	284	233	1189	1291
	BdP 9002359900		97.61	2.09	4	82	1260	68	594	908
	BdP 9002360000		95.75	3.74	15		1948	216	2568	307
Real Português Dobrado	INCM 13308		93.31	5.94	19	169	1050	975	1864	3363
	BdP 9002360200		96.55	2.90	5	128	1866	694	1511	1315
Tostão	INCM 9433	Lisbon	97.44	2.29	67	115	378	426	986	691
	INCM 9434	Lisbon	97.28	2.54		79	91	365	432	826
	INCM 9437	Lisbon	90.32	8.87	59	127	871	653	1753	4643
	INCM 9471	Porto	92.63	6.61	40	1093	741	1205	2852	1647

Table A4.4 (cont.) – PIXE average elemental compositional data of Dom João III coins

***Dom João III* (1521-1557)**

			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Tostão	INCM 13253	Lisbon	95.60	4.05	172	163	242	1094	410	1409
	INCM 13254	Lisbon	97.75	1.72	4	246	1346	932	1567	1258
	INCM 13257	Lisbon	95.16	2.48	6444	350	873	13409	1517	949
	INCM 13260	Lisbon	96.48	3.07	16	60	894	401	1097	2034
	INCM 13323		90.01	8.81	45	434	2286	212	8475	315
	INCM 13324	Porto	95.95	3.27	31	129	1220	515	5029	866
	INCM 13325	Porto	94.15	5.30	40	402	1365	575	2154	959
	INCM 13326	Porto	95.07	4.58	28	176	293	488	1888	653
	BdP 9000199400	Porto	95.68	3.47	39	226	2014	634	4574	1068
	BdP 9001030100		90.83	8.53	49	247	1547	356	2964	1203
	BdP 9001172700	Porto	96.32	3.09	17	148	3416	249	2055	65
	BdP 9002360700	Lisbon	97.61	2.21		116	262	360	758	320
	BdP 9002360800	Porto	95.34	4.06	59	225	254	144	2948	2457
	BdP 9002360900	Porto	95.62	3.93	28	98	788	356	2037	1184
	BdP 9002361400	Lisbon	94.17	5.35	13	200	1057	638	1960	938
	BdP 9002362000		95.57	3.75	12	37	824	344	4726	921
	BdP 9003573700	Porto	96.50	3.21	34	129	346	320	1191	847
	BdP 9004131500	Lisbon	92.51	7.13	99	63	435	1224	1285	546

Table A4.5 – PIXE average elemental compositional data of *Dom Sebastião I* coins

***Dom Sebastião I* (1557-1580)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Vintém	INCM 9494		97.10	2.08	21	67	2405	2736	3000	
	INCM 9495		95.30	3.90	25		1463	366	5341	761
	INCM 9496		98.13	1.35			890	620	3082	623
	INCM 9497		97.46	2.04			2608	451	1695	227
	INCM 9498		96.75	2.88			350	465	1396	1490
	INCM 13432		97.21	2.01		273	4282	763	2331	150
	INCM 13436		97.02	0.79		17515	1352	258	2178	622
	INCM 13437		97.47	1.77		40	1351	274	4793	1155
	INCM 13438		94.41	4.38	31	546	1369	150	8883	1162
	INCM 13439		96.13	2.75		652	1654	265	7049	1602
	INCM 13440		97.15	2.32			821	53	3572	767
	INCM 13441		95.64	3.70		038	1190	198	4595	530
	INCM 13442		97.54	1.98		107	1198	126	2536	859
	INCM 13443		97.24	2.12	13		923	378	4201	860
	INCM 13513		98.51	1.01		22	1718	730	1768	557
	INCM 13514		95.52	3.85	38	66	796	574	3284	1492
	INCM 22726		95.28	4.01		115	1591	249	4391	747
½ Tostão	INCM 9486*		98.20	1.33	113	168	1337	656	1784	632
	INCM 9487		97.05	2.24			1296	764	3820	1251
	INCM 9489		95.94	2.72		34	1453	723	10064	1076
	INCM 9490		95.97	2.98	13	56	1687	744	6996	960
	INCM 9491		97.94	1.70			1442	347	1439	359
	INCM 9492		97.84	1.61			1432	143	3221	658
	INCM 13422		94.97	4.26	110		857	621	5082	1011
	INCM 13424		56.63	1.66			1021	412086	2934	1127
	INCM 13430		97.82	1.81			1293	204	1703	461
	INCM 13431		96.25	2.62		54	1153	324	9478	354
Tostão	INCM 9481		97.80	1.66		128	1296	148	3244	570
	INCM 9483		96.04	3.11		173	1066	1415	4572	1221
	INCM 9485		95.20	3.77			853	628	8426	450
	INCM 13402		92.48	1.45			1530	57172	1976	120
	INCM 13403		94.24	5.13			1083	593	3472	1140
	INCM 13406		94.36	4.38			1428	584	9482	1071
	INCM 13407		98.46	1.23		218	405	256	1211	1048
	INCM 13408		93.55	5.42			1321	601	6969	1329
	INCM 13409		95.77	3.76			644	300	2552	1222
	INCM 13411		93.37	5.84			1147	373	5259	1181
	INCM 13412		97.74	1.64		90	1416	483	3566	610
	INCM 13417		98.36	1.19			1659	164	1615	1071
	INCM 13418		94.75	4.68			891	497	3544	749
	INCM 13419		94.92	4.15			959	173	6160	2072
	INCM 13401	Porto	96.62	2.51	18	188	4167	207	3457	648
	INCM 13410	Porto	89.33	10.37	44	391	1170	268	1109	95
	BdP 9001172800	Porto	92.92	6.25	69	277	1494	1093	3947	1388
	BdP 9002366700	Porto	96.73	2.07		493	7342	85	3573	554
	BdP 9002366900	Porto	96.55	2.89	45	102	1428	470	2639	935
	BdP 9004910400	Porto	96.98	2.34	23	396	3565		2156	598

*One analysis only

Table A4.6 – PIXE average elemental compositional data of *Dom Filipe I* coins

***Dom Filipe I* (1580-1598)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Vintém	INCM 9527		95.37	2.72	58	23	2852	161	15529	464
	INCM 9528		96.91	2.05	8	279	1595	188	8210	109
	BdP 9002371200		98.23	1.50	24	57	911	408	1111	142
	BdP 9002371300		98.41	0.95	14	155	2746	105	3304	130
	BdP 9002371400		94.35	2.60	124	122	2004	154	27973	77
40 Reais	BdP 9002371500		96.75	3.13	8	120	114	303	580	
	BdP 9002371600		97.11	2.78	62	61	118	249	618	
	BdP 9004199400		95.21	4.30	37	1299	752		2297	490
½ Tostão	INCM 9531		98.36	0.91	22		4917	386	1872	122
80 Reais	INCM 9529		96.30	3.58	76	27		444	620	
	INCM 13525		97.61	2.19	16	840	36	82	1044	
	INCM 13526		92.65	7.17	75	34	123	707	825	96
	INCM 13527		96.55	3.22	44	148	62	214	1325	485
	BdP 9002371700		97.04	2.80		201	48	151	1040	190
	BdP 9004189300		98.00	1.93			197	169	280	
	BdP 9004199500		95.64	4.26	11	95	423		383	30
Tostão	INCM 9525		95.09	4.71	17	99	38	688	1080	105
	INCM 13524		94.94	3.18	114	119	29	17514	945	75
	BdP 9002371800		95.17	2.87		146	2024	615	16569	167
	BdP 9002371900		96.56	3.33	57	77	21	203	702	
	BdP 9002372000		97.33	2.56	124	80	29	336	604	
	BdP 9002372100		95.97	3.77	7	112	78	230	1833	314
	BdP 9002372200		95.02	4.86	30	490		184	473	
	BdP 9004912100		93.59	5.60			4616	281	2188	996

Table A4.7 – PIXE average elemental compositional data of *Dom Filipe II* coins

***Dom Filipe II* (1598-1621)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
20 Reais	INCM 9546		94.96	4.69	24	51	40	855	2550	
	INCM 9547		96.16	3.53	20	30	276	316	2169	297
	INCM 9548		96.86	2.80	22	232		1826	1317	
	INCM 13556		94.46	5.02	37		268	203	4043	674
	INCM 13558		94.40	5.33	58	100	34	512	2057	
	INCM 13560		95.65	4.04	59	59	21	283	2651	17
	INCM 22727		98.03	1.62	75	83	912	124	2241	148
½ Tostão	INCM 9539		94.81	4.41	21		1767	642	5349	30
	INCM 9540		97.43	2.32	47	72	1189	270	930	25
	INCM 9541		96.63	3.18	32	99	38	142	1567	54
	INCM 9542		97.79	1.83	64	22	207	307	2915	316
	INCM 9544		96.24	3.19		82	889	577	3967	249
	INCM 9545		94.32	5.54	17			980	448	17
	INCM 13544		97.61	2.03		135	1257	457	1518	185
	INCM 13545		92.71	3.47	11		99	36162	1918	82
	INCM 13546		94.23	5.49	52	19		476	2269	
	INCM 13547		97.47	2.27	231	124	150	694	1418	
	INCM 13548		95.77	3.97	72	38	737	668	1039	
	INCM 13553		97.27	2.35	43	319	2004	172	1050	129
	INCM 13555		96.48	3.34	20	29	142	497	1024	
Tostão	INCM 9535		97.91	1.74	38	28	710	1227	1377	116
	INCM 9537		92.96	6.17	30		961	902	6111	662
	INCM 13528		96.70	3.11	47	131	36	375	1213	65
	INCM 13529		95.34	4.41		82	212	460	1654	
	INCM 13532		92.29	7.54	92	85		635	904	
	INCM 13533		95.56	4.02	24	190	1117	177	2538	153
	INCM 13534		96.28	3.57	68	44		784	520	
	INCM 13535		96.14	3.54		43	57	586	2293	298
	INCM 13536		95.91	3.64	57	214	128	1386	2681	
	INCM 13537		98.78	0.85	90	423	1112	898	1087	47
	INCM 13538		97.34	2.40	14	60	158	226	1971	201
	INCM 13539		97.18	2.07	66	159	1347	260	5249	399
	INCM 13540		93.74	5.75	100	105	151	2568	1836	336
	INCM 13541		96.99	2.84	57	106	77	473	1025	
	INCM 13542		95.36	4.08		118	1441	812	2915	331
	INCM 13543		93.60	6.00	15	45	37	359	3429	135

Table A4.8 – PIXE average elemental compositional data of *Dom Filipe III* coins

***Dom Filipe III* (1621-1640)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
½ Tostão	BdP 9002373200		97.49	2.17	76	107	106	307	2703	25
	BdP 9002373500		96.79	3.01	72	374	84	653	842	
	BdP 9004050800		97.25	2.44	77	512	687	25	1624	156
	BdP 9004924400		96.58	3.09	27	217	716	21	2077	255
Tostão	BdP 9000068700		96.55	2.95	187	74	296	208	4222	
	BdP 9002372700		89.31	10.33	92	197	1407	314	1312	232
	BdP 9002373700		96.70	2.93	49	100	528	324	2426	247
	BdP 9002373800		91.66	8.09	85	54	36	557	1740	29
	BdP 9002373900		90.52	9.26	75		343	259	1484	
	BdP 9002530500		97.35	2.21	109	138	396	292	3227	235
	BdP 9004800400		96.47	3.34	43		68	50	1710	

EDXRF average compositional data

Where data are missing in the tables, this is because the elements were under the detection limits.

Table A4.9 – EDXRF average elemental compositional data of *Dom Manuel I* coins

***Dom Mnauel I* (1498-1521)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Vintém	INCM 9416	Lisbon	97.73	1.93			<220	<220	1103	1956
	INCM 9417	Lisbon	92.47	6.91			<220	674	1352	4057
	INCM 9418	Lisbon	95.96	3.75			363	395	1108	972
	INCM 9419	Lisbon	95.95	3.71			228	376	1313	1515
	INCM 9420	Lisbon	96.01	3.76			<220	564	694	906
	INCM 9421	Porto	94.23	4.31			1044	<220	13414	<170
	INCM 9422	Porto	82.24	16.36			1802	320	11811	<170
	INCM 13154	Lisbon	97.41	2.25			<220	<220	1205	1858
	INCM 13157	Lisbon	95.98	3.10		1495	388	<220	6159	1032
	INCM 13159	Lisbon	95.62	3.97			551	231	1937	1376
	INCM 13166	Lisbon	95.41	4.30			281	<220	1453	1152
	INCM 13167	Lisbon	95.82	3.72	<300		<220	<220	2204	1954
	INCM 13174	Porto	94.30	4.17			764	284	14205	<170
	INCM 13176	Porto	97.65	1.74			410		5023	659
	INCM 13177	Porto	95.72	2.91			7726	<220	5819	<170
	INCM 13178	Porto	81.68	17.17			2405	1002	7815	298
	INCM 13179	Porto	86.42	12.05			684	<220	13825	775
½ Tostão	INCM 9412	Lisbon	95.67	3.42			223	254	7211	1402
	INCM 9413	Lisbon	94.24	5.33	<300		740	<220	2895	539
	INCM 9414	Lisbon	95.02	4.54			431	358	1351	2302
	INCM 9415	Lisbon	96.79	2.92			<220	<220	979	1601
	INCM 13151	Lisbon	97.84	1.77			<220	<220	2391	1169
	INCM 13153	Lisbon	95.79	3.78			1323	229	757	1985

Table A4.10 – EDXRF average elemental compositional data of *Dom João III* coins

***Dom João III* (1521-1557)**

			%		ppm					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
½ Vintém	INCM 9444		97.33	2.26		<300	1307	272	2363	<170
Vintém	INCM 9439		95.09	4.19			<220	686	5730	626
	INCM 9442	Lisbon	95.75	3.93			<220	415	1863	701
	INCM 13256	Lisbon	97.95	1.82			528	<220	621	949
	INCM 13263		95.86	3.02			2457	1048	7221	428
	INCM 13264		96.27	3.22			820	435	2858	968
	INCM 13269	Lisbon	94.67	3.65			7761	365	8762	
	INCM 13270	Lisbon	96.90	2.86			<220	412	878	904
	INCM 13271	Porto	97.94	1.72		957	320	519	1609	
	INCM 13272	Porto	92.66	3.49			4803	27171	6204	332
	INCM 13275	Lisbon	97.42	2.38			357	<220	1360	<170
	INCM 13278	Porto	96.55	2.89		376	2709	467	1856	<170
	INCM 13279		96.98	2.66			267	287	1151	1952
	INCM 13280	Lisbon	94.51	3.11			5469	14096	4164	<170
Real	INCM 9454	Porto	95.18	3.98			3563	356	4064	378
Português	INCM 13281		97.03	2.69		359	708	241	1142	373
	INCM 13289	Porto	93.75	5.58		<300	2202	261	3504	569
	INCM 13296		96.11	3.41			2204	<220	1403	998
½ Tostão	INCM 4965		96.94	1.85			9881	311	1555	413
	INCM 13255		97.42	2.05			3006	307	1352	613
Real Português Dobrado	INCM 13312		92.63	6.99			1251	345	1902	260
Tostão	INCM 9467		95.37	4.13		<300	1353	292	2255	1048
	INCM 13258	Lisbon	96.55	2.81			520	1571	2391	1860
	INCM 13320		94.91	4.67			1501	252	2001	476

Table A4.11 – EDXRF average elemental compositional data of *Dom Sebastião I* coins

***Dom Sebastião I* (1557-1580)**										
			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
½ Vintém	INCM 13444		96.30	2.97		204	519	708	5702	202
Vintém	INCM 9494		95.83	3.42			1052	336	5111	991
	INCM 9495		93.81	5.27			1601	<220	6306	1051
	INCM 9496		96.37	2.76			892	241	6281	1206
	INCM 9497		97.21	2.28			2769	412	1790	<170
	INCM 9498		96.36	3.32			338	<220	1259	1410
	INCM 13432		97.00	2.43			3152	552	1851	<170
	INCM 13434		96.39	2.84			2419	2090	3173	<170
	INCM 13436		96.47	0.88		21855	1464	291	2373	486
	INCM 13437		96.89	2.41			1055	<220	4980	790
	INCM 13438		94.34	4.47			1403	<220	8917	1503
	INCM 13439		94.38	3.25		1803	1182	<220	18999	1555
	INCM 13440		96.19	3.26			771	<220	3754	834
	INCM 13441		93.47	5.57			1152	<220	7210	1135
	INCM 13442		96.29	3.13			1004	<220	3564	1155
	INCM 13443		97.56	1.87			952	281	3687	739
	INCM 13513		97.67	1.70			1203	<220	4008	905
	INCM 13514		96.35	2.93			1853	936	3956	475
	INCM 22726		94.76	4.34			1401	<220	6454	1051
½ Tostão	INCM 9486		96.78	2.56			912	676	4014	969
	INCM 9487		96.69	2.66			1155	672	3764	914
	INCM 9489		94.75	3.96			1352	362	9864	1352
	INCM 9490		95.88	3.07			1251	3022	5404	877
	INCM 9491		97.56	2.01			1511	286	2015	516
	INCM 9492		96.71	2.50			1451	<220	5353	966
	INCM 13422		94.46	4.51			920	430	7559	1352
	INCM 13424		71.16	2.34			2131	258922	3541	473
	INCM 13430		97.42	2.14			1504	<220	2179	515
	INCM 13431		95.91	2.93			1259	<220	9911	255
Tostão	INCM 9480		95.98	3.33			781	370	4561	1203
	INCM 9481		97.40	1.93			1102	<220	4607	919
	INCM 9483		95.85	3.37			746	621	5167	1254
	INCM 9485		94.40	4.25			831	360	11459	806
	INCM 13402		93.74	1.90			1504	38236	3458	380
	INCM 13403		93.74	5.64			1001	377	3705	1152
	INCM 13406		94.59	4.44			1202	448	6963	1112
	INCM 13407		98.12	1.58			300	<220	1351	1251
	INCM 13408		93.32	5.51			814	302	8959	1652
	INCM 13409		95.51	3.25		7411	544	224	3210	1043
	INCM 13411		92.92	6.21			939	243	6057	1402
	INCM 13412		96.89	2.32			1104	299	5470	999
	INCM 13417		97.39	2.14			1413	228	2217	879
	INCM 13418		93.75	5.61			798	408	4305	865
	INCM 13419		94.84	4.12		607	839	<220	6636	2213

Table A4.12 – EDXRF average elemental compositional data of *Dom Filipe I* coins

***Dom Filipe I* (1580-1598)**										
			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
½ Tostão	INCM 9531		98.37	0.93			5155	285	1501	<170

Table A4.13 – EDXRF average elemental compositional data of *Dom Filipe II* coins

***Dom Filipe II* (1598-1621)**										
			%		**ppm**					
Coin	**Reference**	**Mint**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
20 Reais	INCM 9547		96.28	3.40	<300		307	223	2317	257
½ Tostão	INCM 9541		96.34	3.47			<220	<220	1506	<170
	INCM 9542		96.97	2.61			<220	<220	3314	460
	INCM 9544		95.89	3.48			777	223	4875	433
Tostão	INCM 9535		97.56	2.13			717	582	1654	<170
	INCM 13529		94.54	5.24			267	<220	1563	<170
	INCM 13536		95.68	3.63	<300	<300	<220	4112	2160	<170
	INCM 13543		94.33	5.30			<220	428	3003	179

Appendix 5 – PIXE compositional data of colonial Spanish coins

Where data are missing in the tables, this is because the elements were under the detection limits.

Table A5.1 – PIXE average elemental compositional data of colonial Spanish coins

				%		ppm					
King	**Coin/Reference**	**Mint**	**Date**	**Ag**	**Cu**	**Ni**	**Zn**	**Au**	**Hg**	**Pb**	**Bi**
Felipe II	*8 Reales* BdP4240051173	Potosí	1576-1586?	96,07	3,74	22			1363	520	
Felipe III	*8 Reales* BdP4240046814	Potosí	1613-1617	91.87	5.38	31			24405	341	

Appendix 6 – PIXE compositional data of Portuguese silverware objects

Where data are missing in the tables, this is because the elements were under the detection limits.

Table A6.1 – PIXE elemental compositional data of Portuguese silverware objects

Denomination	Date/Atribution period	Production center	Analysis location	% Ag	Cu	ppm Ni	Zn	As	Au	Hg	Pb	Bi
Dragon salver	c. 1490-1500	Porto	Dish	95.94	2.66		2970		7790	725	2372	200
			Foot	94.82	4.31		476		3060	390	3806	998
1548 salver	1548	—	Dish	83.88	2.64	41	350	250	13625	116970	3250	450
1551 salver	1551	—	Dish	95.83	2,77	60	350	100	8225	2361	2634	362
Jug	end of 16th century	Portugal(?)	Body	92.68	6.01	58	850	100	4675	5525	2000	50
MNAA 1021 salver	last quarter of 16th - beginning of 17th century	—	Dish	96.22	3.52	14	589	38	409	1239	84	155