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European Silver Sources from the 15th to the 17th Century: The Influx of “New World” Silver in Portuguese Currency

Rui Borges ^{1,2,3,*}, R. J. C. Silva ¹, Luís C. Alves ², M. F. Araújo ², António Candeias ³, Victoria Corregidor ⁴ and João Vieira ^{5,6}

- ¹ i3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology, Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal; rjcs@fct.unl.pt
- ² Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal; lcalves@ctn.tecnico.ulisboa.pt (L.C.A.); faraujo@ctn.tecnico.ulisboa.pt (M.F.A.)
- ³ Laboratório HERCULES, Universidade de Évora, Palácio do Vimioso, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal; candeias@uevora.pt
- ⁴ Instituto de Plasmas e Fusão Nuclear (IPFN), Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal; vicky.corregidor@ctn.tecnico.ulisboa.pt
- ⁵ Banco de Portugal, Museu do Dinheiro, Largo de São Julião, 1100-150 Lisboa, Portugal; jpvieira@bportugal.pt
- ⁶ Faculdade de Letras da Universidade de Lisboa, Centro de História da Universidade de Lisboa, Alameda da Universidade, 1600-214 Lisboa, Portugal
- * Correspondence: ruicamaraborges@sapo.pt

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Abstract: The circulation trading routes and the characterization of the silver metal used in the European continent in the 15–17th centuries are historical issues that are still open. This study aimed to bring an insight into the silver processed within a chronological framework in the Portuguese territory, relating the analytical data with the known historical information. This investigation developed on 230 high silver coins from two important Portuguese coin collections was based mainly on surface particle-induced X-ray emission (PIXE) analysis, complemented with a few energy-dispersive X-ray fluorescence (EDXRF) analyses. The silver processed in different timelines was discriminated based on the variation of the impurity contents, namely Au and Bi. European silver with high Au and Hg and low Pb and Bi contents supplied the 15th century chronologies, being replaced at the dawn of the 16th century by a new metal entering the Portuguese capital. This new metal, with low Au and high Bi contents, was probably derived from European argentiferous copper ores. By the end of the 1500s, the Philippine chronologies reveal the newly discovered Potosí silver, identified for the first time based on PIXE minor and trace element surface contents, distinguishable from the European silver in use until 1578 in the Portuguese territory, by Au contents <100 ppm and very low Bi contents.

Keywords: European silver; Potosí silver; argentiferous copper; PIXE; EDXRF

1. Introduction

1.1. Research Aims

The circulation of silver in Europe in the 15–17th centuries and the amount of American silver that was used on this continent in this period are historical issues that are still open, particularly regarding Portugal. Based on particle-induced X-ray emission (PIXE) and energy-dispersive X-ray

fluorescence (EDXRF) elemental analysis, silver surface enrichment was a major question for the initial investigation of 11 *dinheiros* Portuguese high silver coins (91.6% Ag). Surface silver analysis has revealed an overestimation of this element as high as 7%, due to a subsurface silver-rich layer of about 70 μm , where both analytical techniques have detected major, minor, and trace elements with the same order of magnitude [1]. Albeit both minor and trace element compositions do not represent the original contents of these alloys [1], their correlation allowed to discriminate 15th and 16th century Portuguese minting productions and to differentiate the silver bullion compositions received in the mints originated from European sources. Additionally, the Potosí Andean silver fingerprint was, for the first time, identified and assigned to the 16–17th Portuguese minted silver currency through correlations of minor and trace element surface contents. It was revealed that the new American silver was brought to Portugal by Dom Filipe I (Felipe II of Spain), being present in the Portuguese territory from 1580 onward, until at least 1640. The new American precious metal is discriminated from European silver alloys based on Au, Hg, Pb, and Bi contents and it seems to have locally distinct silver provenance contributions, which differ in their elemental compositions. This surface analytical investigation distinguishes Potosí and European silver in a similar manner to the earlier published neutron activation analysis results, mainly obtained on Spanish coins and reflecting the bulk average composition of coins [2,3].

1.2. European Sources of Silver in the 15th to 17th Centuries

From the Middle Ages until the 1530s, all European countries relied on silver supplies, which originated mostly from Germany and other parts of the former Roman Empire [4]. The most important points of the silver trade in Europe in the early years of the 1470s were Milan and Frankfurt, the latter fulfilling the silver needs of the Northern and Western European Mint Houses through Flanders [5,6]. Historically, the cities of Lisbon and Porto were frequent passage centers of ships linking Northern Europe, the Mediterranean, and North Africa [7]. In the second half of the 15th century, Flanders maintained a direct access to the Portuguese gold from Africa, this precious metal being brought by merchants and traders from the West coast of this continent to Europe via Lisbon, and then circulated by ship via Bruges [5].

In the early 15th century, Europe felt the scarcity of silver metal and coin, but the new sources of silver ores discovered mainly in Central Europe and Southern Germany in Erzgebirge, Saxony, and Tyrol, between 1460 and 1540 [5,8], and the technological improvements and innovations achieved from the mid-15th century, led to a major mining expansion of the silver-rich copper deposits quickly alleviating these difficulties [4–6,8,9]. The most important achievements were the modifications of furnaces to enhance higher smelting capacities, the introduction of drainage galleries and pumps for water drainage from deeper mines in stages to the surface, and the addition of lead to the argentiferous copper reduction process for silver recovery (Saigerprozess—liquation process). These practical advances in the field of mining and metallurgy were promoted and disseminated in specialized metallurgical treatises, *De la Pirotechnia* of Vanoccio Biringuccio [10] and *De Re Metallica* of Georg Bauer (Agricola) [11].

Initiated circa 1460, the argentiferous copper ores mining expansion would not lead to a large production of silver until 1510, reaching its peak in the decade of 1540 [4–6,8,9]. The European formerly richest older mines, such as Kutná Hora in Bohemia, Freiberg in Saxony, and Goslar in the Hartz, were reopened and processed silver along with the mines of Schwaz and Schneeberg [5,6,8].

New silver sources from the mines of Joachimsthal (1516) in Bohemia and of Annaberg in Saxony were discovered and exploited in the early 16th century, and the establishment of new continental trade routes or the revitalization of the existing ones would bring southern Germany and Hungary silver streams to Antwerp, turning it in an important financial and economic center [5,6,8]. Saxony, Bohemia, Slovakia, Thuringia, Hungary, and Tyrol annual silver production would grow five times until about 1540, with most of the mines reaching a greater prosperity between 1515 and 1540. The

silver extracted from these mines then decreased until the arrival of the American precious metal, at which point—in the early 1560s—it was exceeded by this new metal supply [4–6,9].

The large silver amounts from New World territories had Spain as the major destination in Europe just before the mid-16th century, and from there, silver moved with a constant and regular flow from West to East, counterbalanced in the opposite direction by exotic products. This South America silver influx substantially changed the 16th century European countries' economy [8], possibly representing in total the equivalent of half of all the existing European silver [12]. An increasingly number of silver ingots was then available from the international market for purposes of minting as the 16th century progressed, and silver replaced gold as the dominant metal [4,13].

In England, after 1540, almost all imported ingots arose from the new Spanish Silver, which by the end of this century had become a dominant Mint House silver supply [14]. The Cottington Treaty, signed by England and Spain in the next century (1630), restored trade relations between both countries and enabled the South American silver needed to sustain the Spanish Netherlands Government and the Spanish armies to pass by England, where two thirds of its amount were sent to the London Royal Mint [14,15]. London became one of the most active Spanish silver markets, strongly competing with Genoa and with Portuguese and Genoese bankers' profit by sending silver from the Atlantic Spanish ports of Corunna, San Sebastián, and Bilbao to the English ports [15].

In the second half of the 16th century, some European mines continued to prosper, like Freiberg and Goslar, but all Central European mining centers experienced a silver production decrease after the middle of the first quarter of the 17th century, with the silver production coming down to about one-third of the production from the 20s to 30s of the previous century [4,8].

1.3. The Silver Processed in Portugal

The exact origin of the silver supplies that reached Portugal during the 15th and 16th century is unknown. Despite the inexistence of historical documentation, it is assumed Portugal received this metal from Central and Northern Europe until the mid-15th century, once it was poor in silver [7]. The circulation of French coins was common in the country, some introductions of the English silver currency also existing in Portugal [7], and Portuguese monetary workshops would recast all the incoming silver in the form of these currencies, bars/bullions, or precious objects.

Copper was a current commodity in the Luso-Flemish trade during the 15th century and there are reports from the early 1440s of acquisitions of this metal in Flanders for minting in the Lisbon Mint House [16]. With copper, silver would probably also come. It seems that by the 1480s, the German copper inflows had 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 1500 to 2000 hundredweight of copper (88.1–117.5 t); the cork was to be shipped to the markets of Brittany and France [17,18].

By the 1490s and 1500s, 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 1515 marks (354.4 kg) in 1498–1505. In this last period, the Portuguese factory bought 639.7 hundredweight of copper (30 t) [19,20]. 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 3000 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 [21].

During the sixteenth century, Portuguese Mint Houses used principally South German silver [22]. From 1501 onwards, the Portuguese sought in Antwerp financial and commercial support from the bankers and traders of southern Germany, along with copper and silver metals, for trade with Asia [9,23]. From the beginning of the 16th century until the 1530s, the exportations of Hungarian copper to Antwerp strongly increased, and the Fugger–Thurzo families, who controlled the argentiferous copper of Neusohl, in Hungary, and a great part of that of Tyrol, were important copper suppliers to Spain and Portugal [9,23]. 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 7 May 1517 from Lourenço Lopes, a 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 [24].

Additionally, according to an historical notice, 299.6 silver marks, about 68.8 kg, arrived at Vila do Conde customs in the north of Portugal in the short period between 1504–1506 [25]. This imported silver came from unidentified harbors in Flanders, from Rouen and La Rochelle, and the major part was sent for minting in the Porto Mint House. During the first quarter of the 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 tons) to the Lisbon Mint House [23,26,27].

The first records of Peru (actual Bolivia) and Mexico Spanish gold and silver productions are found in the 1530s, as well as the first notice of the arrival of much “New World” gold in the north of Portugal to be minted in the Porto Mint House, dated 20 May 1537. The precious metal was bought on the Azores Islands from the Castilians returning from Peru, by Portuguese merchants in from the Entre Douro e Minho region [28].

Historically, in the last quarter of the 16th century, when Felipe II of Spain became King of Portugal (being known as Dom Filipe I of Portugal), American silver arriving to Seville was sent to the Lisbon Mint House to produce coins, and by the end of this century, the quick business developments with India and abroad drained the currency of the country, revealing that Spanish silver was not enough for the monetary needs [29].

During the beginning of the 17th century, in view of the positive commercial balance with Spain, Portugal continued to benefit from the large amount of American metal entering Europe through Seville to fulfil the monetary market needs, and its monetary stock increased with the maximum silver arrivals around 1627 [15]. This situation would change from 1630 to 1640, when the Lisbon Mint House became a minor buyer of American silver [15].

Later, after the Portuguese Restoration (1640), most of the Portuguese monetary production comprised a massive coin reminting operation of the Spanish currency circulating in the territory [15].

2. Materials and Methods

The silver coin emissions of the second and third dynasties of Portuguese Kings minted in Lisbon and Porto in the 15–17th century, stored in two important numismatic collections, respectively from the Imprensa Nacional-Casa da Moeda (INCM) and from Banco de Portugal (BdP), were studied within a chronological framework (Table 1). All the coins pertaining to the period from Dom Afonso V to Dom João III bear the monetary letter L (Lisbon) or P (Porto), which respectively identify the monetary workshop. Porto-minted coins of the Dom Sebastião I chronology are the only analyzed coins of this period which support the monetary letter, and all other coins, not marked, are historically assigned to a Lisbon production. During the Philippine chronologies, only the Lisbon monetary workshop produced coins.

The selection of coins considered the surface (preservation) condition of the coins made by visual inspection and the representativeness of each Portuguese king chronology to obtain statistical data enabling to infer reliable historical interpretations of the analytical data.

The available nondestructive and noninvasive analytical techniques were used in elemental composition analysis, as particle-induced X-ray emission (PIXE) and energy-dispersive X-ray fluorescence (EDXRF). The possible effects of surface contaminations and/or silver enrichment could not be minimized because of the impossibility of cleaning the surface of the coins before the analysis. The analytical compositional results were subject to statistical treatment and to principal component analysis (PCA) 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.

The C2TN 2.5 MV Van de Graaff accelerator produced a 2 MeV proton beam used to irradiate the coins in a vacuum and the accuracy of the PIXE quantification method was ascertained by analyzing the certified reference material 133X AGQ2 (batch C) from MBH Analytical Ltd., Barnet, England, using the conditions already disclosed in Reference [1]. The elemental data of a small number of coins in which only the EDXRF analysis was made complemented the previous data. In these coins, analysis by 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 with Ag and Gd secondary targets, using the same certified reference material and the experimental conditions also disclosed in Reference [1].

Table 1. Chronology and number of analyzed coins selected from the INCM and BdP numismatic collections.

Chronology	Number of Coins	Mint	
		Lisbon	Porto
Dom Afonso V (1438–1481)	9	5	4
Dom João II (1481–1495)	14	6	8
Dom Manuel I (1495–1521)	42	21	21
Dom João III (1521–1557)	46	26	20
Dom Sebastião I (1557–1578)	48	42	6
Dom Filipe I (1580–1598)	24	24	-
Dom Filipe II (1598–1621)	36	36	-
Dom Filipe III (1621–1640)	11	11	-

3. Results and Discussion

3.1. Silver Alloys of Joanine Dynasty Coins (1438–1578)

Apart from silver and copper, the Joanine dynasty coins consist primarily of six minor/trace elements: Nickel, zinc, gold, mercury, lead, and bismuth, with overall contents generally under 2 wt.%. Au and Pb form together the main impurity content of the coins, and Bi can be exceptionally important for the differentiation of the silver alloys, despite the normally low contents. Zn and Ni show high compositional heterogeneity in the coins sample and were not considered for statistical analysis.

Figure 1 shows the evolution of coins' silver alloy global impurity content by chronology and monetary workshop (Lisbon and Porto), from 1438 to 1578, permitting to compare the silver purity improvement from the 15th to 16th century. The silver metal minted in the 16th century has a better average purity than the metal previously used, with the exception of the Porto Mint House during the Dom Manuel I period, whose coins apparently continued to be minted mainly with the earlier metal sent through the Flanders route [25]. The increase in silver metal purity would certainly be related to the novel processing of silver bullions extracted from European argentiferous copper ore sources, emerging in the latter second half of the 15th century, and contrasts with the contents of the earlier silver bullions produced from galena silver-rich ores.

Portugal seems to have received this new source of silver in the earlier 16th century, well in accordance with the verified silver production growth and exploitation prosperity of argentiferous copper ores, namely, after 1510 [4–6,9,10]. The coinages were then made from better refined silver bullions produced in the European silver mining regions and used afterwards in the Portuguese mints, whose increased refining quality would have benefited from the new practical technological advances in the silver production processes and from the improved assaying methods, latter compiled and described in metallurgical treatises [10,11].

Gold and bismuth are important silver ore discriminators for fingerprinting ancient silver alloys, as both elements have been regarded as being solely associated with the silver sources [30–33]. The gold amount is not affected by the silver metallurgical processes being retained in the silver bullion in a quantity identical to that of the original ore. Silver sources from different silver artefacts have been successfully differentiated based on the concentration variability of this element [32,34–36]. The

Bi/Ag and Bi/Pb ratios can allow some differentiation between various silver origins/workshops, as the bismuth content is reduced by a factor of 5 during the silver cupellation process of argentiferous lead ores [33,37] and, in the case of finished objects, does not depend on its initial concentration in the smelted metal, but on the final progress of cupellation, the step in which the oxidation and the consequent removal of this element occurs [38].

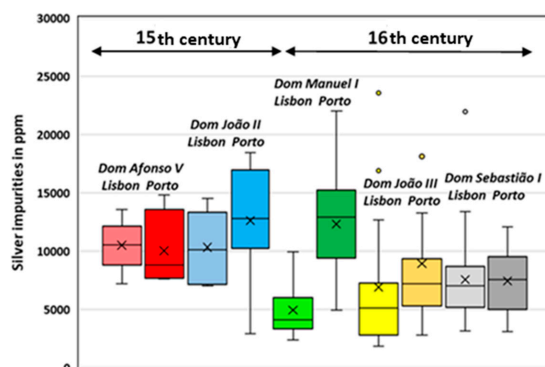


Figure 1. Evolution of silver impurities content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

On coins, where the geological signature is erased due to mixtures and the re-melting of metal, Au, Bi, and Pb will allow to judge on the composition of the produced silver ingots in each monetary workshop and may at least serve to discriminate different metallurgical production sites.

The silver coin alloys from the 15th century have higher Au and lower Bi average contents, as opposed to the following coinage periods with lower Au and higher Bi contents (Figures 2 and 3).

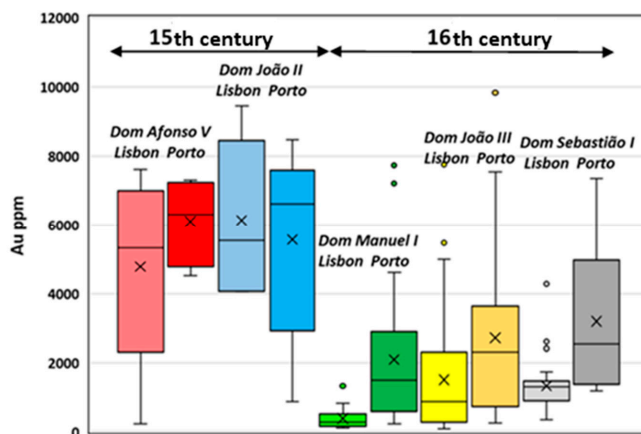


Figure 2. Evolution of Au content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

During the Dom Manuel I chronology, Lisbon Mint House operation seems to have not recycled the earlier circulating currency, as the coins were minted at the expense of fresh metal supplies. The decline of more than ten times in Au average content in the coinage is in fact consistent with the shift of the silver source, and the change from high gold/lower bismuth to low gold/high bismuth also suggests a sudden change of silver bullion source. The Porto coins minted during this reign have Pb (Figure 4), Bi, and global impurity contents, following the trends of the earlier chronologies, but their lower Au content also points to a change in the bullion origin of this mint. Pb dispersion is related with the presence of a significative number of coins with a higher content of this element, something that occurred in a lesser degree with Dom João II Porto-minted coins. This is possibly related with the

recycling of earlier silver metal through cupellation, and Porto mint seems to have relied much more on this practice than Lisbon mint during the 16th century.

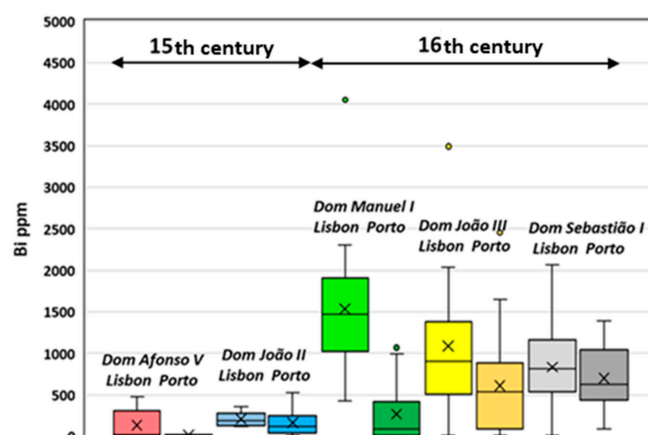


Figure 3. Evolution of Bi content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

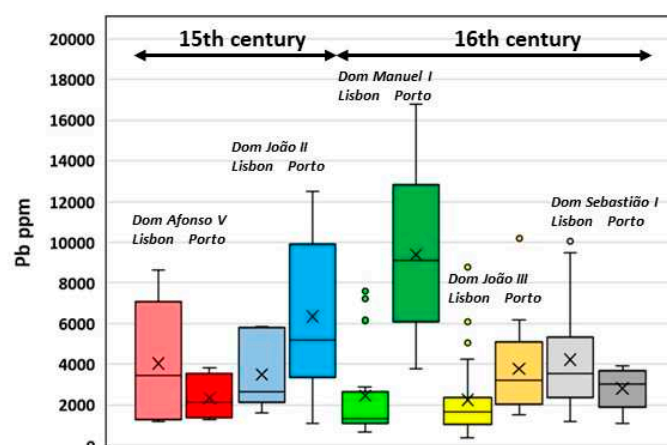


Figure 4. Evolution of Pb content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

Over the next 16th century chronologies, the higher Au and lower Bi contents of the coins point to the occurrence of a gradual dilution of the new introduced Lisbon silver source with the silver metal used in the previous century, resulting in a gradual increase of the gold content of the silver alloys. Additionally, the important Au dispersion verified in Porto coins seems to result from significant mixtures of both sources of metal that had involved earlier recycling and re-melting of currency, which have altered the elemental signature of Porto-minted silver. In fact, Dom João III minted alloys are historically influenced by an important recycling of earlier and older currency, due to the lack of silver metal in the kingdom and to major weight debasements of the silver coins, which were also responsible for the re-melting of some circulating coins [23,28,39], with a direct impact in the great Au dispersion observed in Figure 2.

Over the 16th century, each monetary workshop has distinct Au and Bi contents for the processed silver alloys, the trends of which run toward an homogeneity of the silver alloys composition of both centuries: Lisbon mint exhibits increasing Au and decreasing Bi content trends over the three analyzed chronologies, and Porto monetary workshop also presents an increasing Au tendency, on average, with higher contents than Lisbon, and by contrast, an increasing Bi trend.

The coins minted from the end of the 15th century reveal Hg contents with the same order of magnitude and do not define any compositional trend of this element (Figure 5).

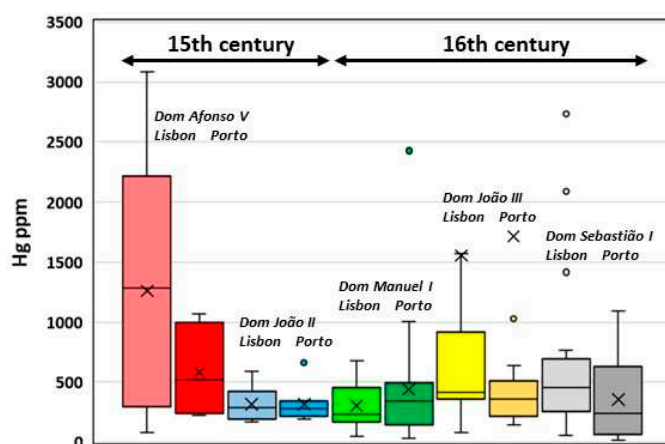


Figure 5. Evolution of Hg content in ppm in the Joanine dynasty silver alloys, discriminated by chronology and mint.

3.2. Silver Alloy of Philippine Dynasty Coins (1580–1640)

The silver coins of the Philippine Dynasty, which represent the silver alloy output of sixty years of monetary production under the rule of the Spanish kings from 1580 to 1640, reveal the same six minor/trace elements detected in the earlier coins, where gold and lead form the main impurity content, with bismuth having a very low contribution. Surprisingly, the global impurity contents point to a late 16th century silver supply change, occurring during the Dom Filipe I chronology.

Based mainly on Au and Bi contents (Figures 6 and 7), each of the Philippine chronologies reveals the presence of a distinct silver alloy group of coins, distinguishable from the compositions of the European silver alloys minted in the Portuguese territory before 1578 (death of Dom Sebastião I). At that time, large amounts of American metal had entered Europe through Seville [15,40] and 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 bullions to Portugal [29]. The impact of the new American silver source experienced in Portugal during the Dom Filipe I chronology is well in accordance with the inflow of Potosí silver in Spain during the reign of Felipe II of Spain (Dom Filipe I of Portugal), between 1565 and 1570 [41–43]. Additionally, the huge American silver production growth, attributed to the better accessibility to the American ore and to the introduction of innovative techniques for silver exploration in the American territories, occurring in Potosí about 1575 [40], a date very close to the beginning of the Dom Filipe I reign (1580) as well.

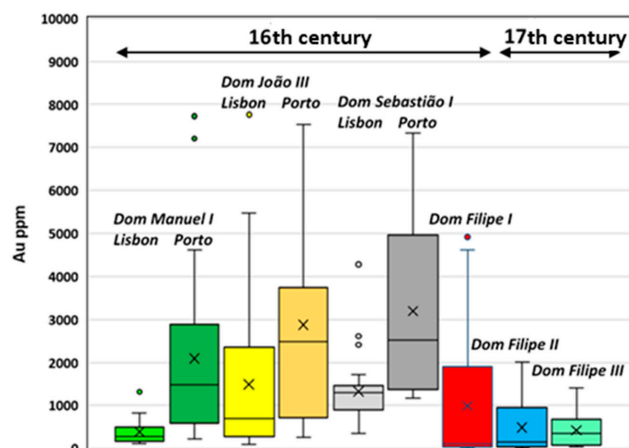


Figure 6. Evolution of Au content in ppm in the 16th and 17th century silver alloys, discriminated by chronology and mint.

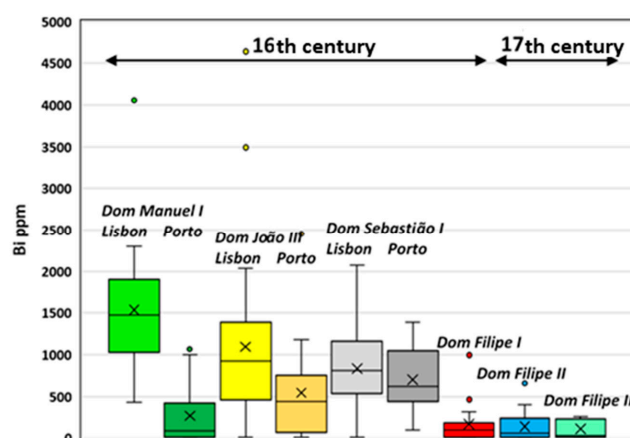


Figure 7. Evolution of Bi content in ppm in the 16th and 17th century silver alloys, discriminated by chronology and mint.

Philippine silver alloys present a very small decrease in Pb content when compared with the silver alloys of the previous Dom Sebastião I period (Figure 8), and their Hg content is similar to that observed in the previous 16th century chronologies (Figure 9).

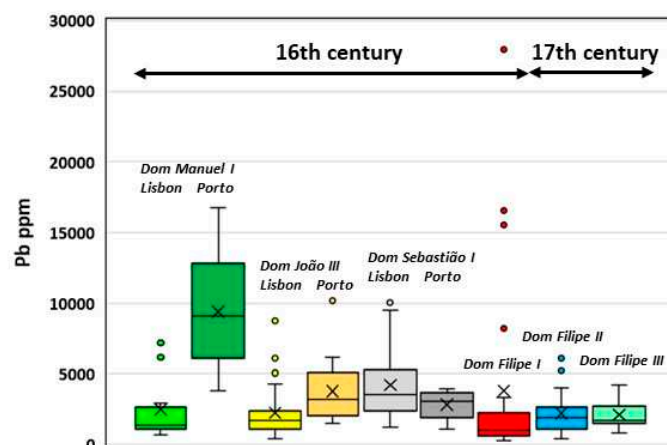


Figure 8. Evolution of Pb content in ppm in the 16th and 17th century silver alloys, discriminated by chronology and mint.

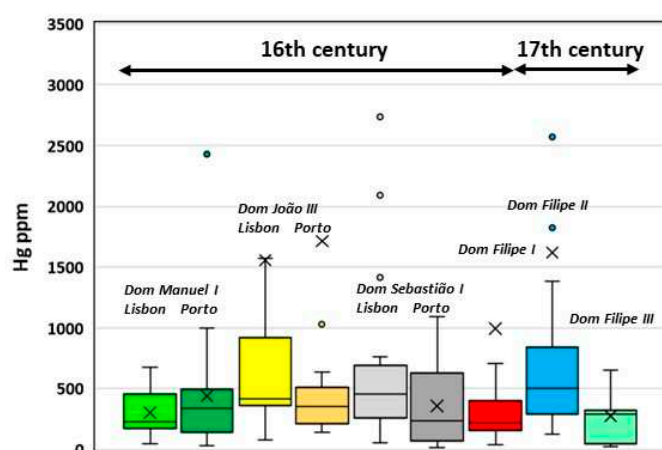


Figure 9. Evolution of Hg content in ppm in the 16th and 17th century silver alloys, discriminated by chronology and mint.

When analyzing in detail the Au contents of Dom Filipe I coins, an important multimodal dispersion is observed, suggesting the existence of three different compositional groups (Figure 10): (E) with greater Au contents, with the same order of magnitude as the previous chronology of Dom Sebastião I, where Au content is mostly higher than 500 ppm; (P1) characterized by very low Au contents, complying with the Au <100 ppm criteria proposed in Reference [2] for the silver source originating from Potosí [2,3,41,42]; and (P2) with a gold content ranging from more than 100 ppm to a little lower than 350 ppm. Moreover, most of the coins from the P1 and P2 groups have Bi contents under PIXE detection limits, typical of Andean silver mineral deposits, which are normally deprived of bismuth [44]. The reduced Au and Bi contents of P2 reject the assumption of this composition being obtained from an important recycling of E and P1, reinforcing the existence of another American silver source. With the exception of the Dom Filipe I chronology, Pb is on average under 0.2 wt.% in American silver alloys, generally about half the amount contained within the last Joanine silver alloys of Dom Sebastião I.

European coins minted with pure silver from Potosí, mostly from Spain and Italy and pertaining to the same timelines as the Portuguese Philippine coins, and Potosí-minted coins have been discriminated based on a gold content under about 100 and 50 ppm, respectively [2,3,41,42].

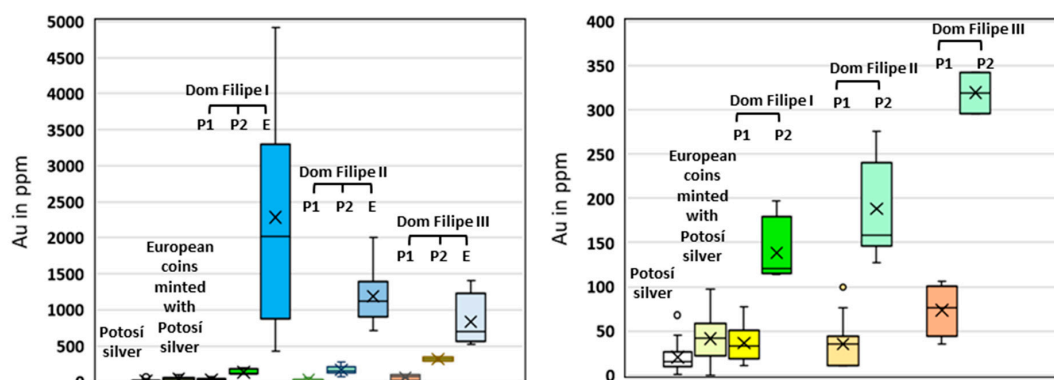


Figure 10. (Left) Comparison of Au contents in ppm of coins minted in Potosí [3], in Europe, with pure Andean silver [2,41,42] and in assigned subgroups of coins from Europe (E) and from Potosí (P1, P2) minted in Portugal by Dom Filipe I, Dom Filipe II, and Dom Filipe III. The first two groups of coins were minted during the Portuguese Philippine timelines. (Right) Magnification of previous graph in the range below 400 ppm of Au.

A two-factor PCA analysis was made based on the coins of Dom Filipe II (Figure 11 and Table 2), available in great numbers for investigation when compared to the other Philippine chronologies. Additionally, the coins from this chronology present a lower Au dispersion range than the preceding period, possibly reflecting a small influence of the previously used silver sources. This PCA analysis accounts for about 72% of the total variance in the original coins data and supports the attributed silver alloy contributions: The silver alloys assigned to Potosí silver, representing about 65% of the coins, and the earlier used European silver. In addition to Au and Bi, the PCA analysis includes as other significant discriminators the contents of Pb and Hg.

Surprisingly, in this case, American silver compositional groups, P1 and P2, discriminate from the assigned European silver alloys, E, also based on mercury content, probably due to the predominant amalgamation nature of the silver ore extraction processes implemented in the new territories of America. The European silver compositions of Philippine coins have Au, Pb, and Bi contents closer to the Dom Sebastião I coin compositions.

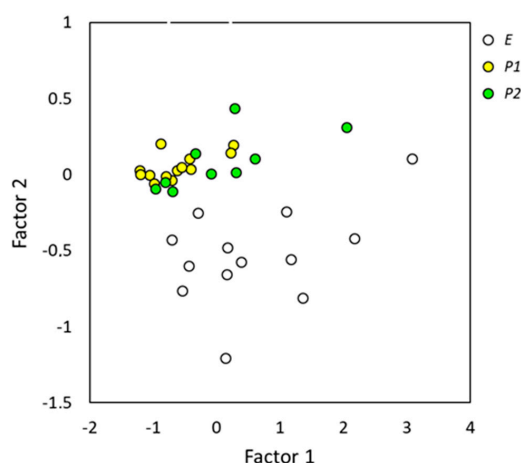
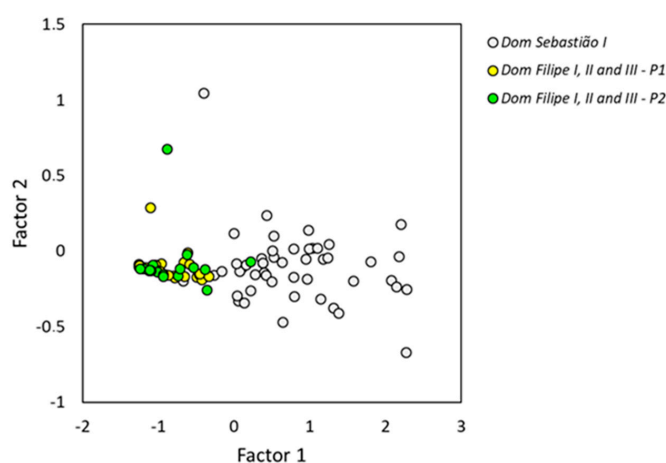


Figure 11. Factor 1 versus factor 2 principal component analysis plot considering Au, Hg, Pb, and Bi contents of Dom Filipe II coins. European coins (E) are discriminated from American silver (P1 and P2) based mainly on Hg contents (see factor loadings, Table 2).

Table 2. 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 PCA analysis of all the coins assigned to the American compositional groups (P1, P2) of all the Philippine chronologies and of the Dom Sebastião I coins (Figure 12 and Table 3) 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 coins minted during the 1557–1578 period.

**Figure 12.** Factor 1 versus factor 2 principal component analysis plot considering Au, Hg, Pb, and Bi contents of Dom Sebastião I coins, and Philippine coins assigned to American compositional groups (P1, P2). The group of Dom Sebastião coins is discriminated from Philippine coins based on Au, Pb, and Bi contents (see factor loadings, Table 3).**Table 3.** 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%

The American silver sources (P1, P2) represent together more than half of the silver processed at the end of 16th and early 17th centuries in Portuguese mints and were seemingly used without mixtures directly in the coin production process, separately from the simultaneous utilization of the silver metal/recycling from European origin. The lower trend of gold content over the last two Philippine chronologies and the reduced spreading of this element in the silver alloys seem to confirm the propensity for the utilization of “newer” fresh silver supplies, without recycling or carrying out important mixtures with the earlier silver metal in circulation.

When comparing the two latter Philippine chronologies with all the earlier timelines, it stands out that they show a reduced global silver alloy impurity content and spreading, and this increased silver purity would probably be related to the technological advances in the distinct silver extraction processes and to the effect of the amalgamation processes implemented in the new territories of America.

4. Conclusions

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 nonetheless allow to perceive differences in minting and to discriminate distinct silver sources.

Within this investigation, it was possible to determinate that Portuguese coin minting, which depended on European silver sources, relied 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 discrimination of the silver processed in each of the two mints is not evident.

This silver source 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 the Dom Manuel I period. Porto, the other mint in operation during this period, seems to have processed silver compositions proximate to the earlier century silver metal. It is unclear if this silver also originates 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 evolved over time towards compositional homogeneity and uniformity. The average main minor/trace elements contents comprised in each of the processed silver alloys, would reach later in this century the more uniform compositions observed in the Dom Sebastião I period. This evolution had probably arisen due to major recycling operations realized in each chronology of the earlier king minted currency.

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 elemental 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 to the European silver metal. It also seems that this American silver provenance could have different silver contributions with different elemental compositions.

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