

Article

Double-Relief Silver Coins Minted in the Greek Colonies (444–390/340–280/270 BC) of Southern Italy Analysed by XRF

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Abstract: A sample of 18 double-relief coins from different poleis of Magna Graecia and ancient Italy has been analysed using a handheld XRF spectrometer directly inside the Museo Provinciale Campano (Capua, Italy). The data analysis shows that (i) the main elements are Ag and Cu, indicating that the coins are of high fineness (average Ag 95.7%), (ii) trace elements can help to characterise the coins, (iii) a superficial chemically altered layer (corrosion) is absent, (iv) the values of ratio Ag $K\alpha/L\alpha$ evidence the presence of an enrichment layer on the surface of silver or subaerata in some coins. Multivariate statistical analysis and graph analysis allowed the coins to be assigned to different groups with the highest possible accuracy on the basis of the chemical data obtained and models to be constructed to classify the coins according to their historical periods.

Keywords: silver double-relief coins; XRF spectroscopy; numismatic analysis; multivariate analysis; graph analysis; poleis of Magna Graecia; Oscan-Campanian community



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1. Introduction

Coinage is one of the main sources for the study of political and economic history, especially when other information is lacking. In fact, its detailed analysis makes it possible to study coins scientifically, to classify them over time and to place them in the economic and social context of the historical period. Each coin is minted by means of two dies (obverse and reverse), which are worn at different times. Generally, the “hammer”—the reverse die (the upper one)—has to be replaced before and more often than the obverse die. The number of the dies and how they fit together is important in studying the minting process. The characteristics of the metals used, and their sources are the subject of much research and interest.

The XRF (X-ray Fluorescence) technique has become a recurring elemental characterisation technique for obtaining specific sample data [1–4], including historical data. It is non-destructive and requires no sample preparation. In addition, it is a multi-element, sensitive and quantitative technique that can be obtained without the need for certified reference materials or can be derived by comparing the sample spectrum with spectra of sufficiently similar standard samples of known composition. XRF has proven to be the basic analytical technique in cultural heritage studies [5–8] because it provides key information about the objects under study in a reliable, rapid and non-invasive manner. It is now recognised that XRF spectrometry could have a wider application in studies of metal objects [9–11] and ancient coins [12,13]; also, if its results are not sufficient, it can help to carry out a preliminary screening to determine which artefact should be subjected to other more expensive and invasive analyses [14]. The XRF technique also allows the determination of the concentration, depth distribution and trace elements, which are useful for quantifying many features of an object [15,16]. In particular, it is also widely used in the

study of ancient coins [17–29]. As part of a project to study the ancient coins in the collection of the Museo Provinciale Campano (Capua, Italy), a series of ancient coins (incuse) has already been studied using this technique, as well as with numismatic analysis [3,30]. In [31], numismatic and historical studies were combined with metallurgical research based on non-destructive neutron diffraction, neutron structure analysis and neutron tomography to provide an overview of the minting of incuse coins.

In the present work, coins which were double-relief minted in the Greek colonies of southern Italy and in some cities and communities of ancient Campania (444–390 BC; 340–280/270 BC) are analysed by XRF. The coins were chosen to represent characteristic samples from different cities. In our recent work [32], eight double-relief silver coins belonging to southern Italian poleis and dated between the late 5th and early 3rd centuries BC were analysed. Non-invasive in situ analyses were carried out using point XRF and MA-XRF measurements and digital microscopic photographs. These results, combined with numismatic studies, provided information on the historical context, the alloy used and cases such as subaerata and restored coins. In other projects [33], the corrosion and protection of Ag coins from Greek colonies in southern Italy (6th century BC) were studied using in situ electrochemical and spectroelectrochemical methods.

The aim was to investigate the fineness and source of the silver alloy, as well as other peculiarities such as overstriking or subaerata. For these purposes, the sample was selected from the Coin Collection of Museo Provinciale Campano (Capua). The analyses on these coins were carried out non-destructively on both the obverse and reverse sides of the surface due to the well-known and documented problems arising from corrosion effects and surface treatments [34–36]. These represent a serious limitation in achieving a reliable quantification of their bulk composition. To overcome these problems, the Ag $K\alpha/L\alpha$ ratio and Ag $K\alpha/CuK\alpha$ are also analysed [37–41].

1.1. The Coin Sample: An Historical Background

1.1.1. I Section 444–390 BC ca.

This sample of ancient coins consists of some issues of the most important poleis of Magna Graecia and one of the most interesting communities in the Campanian-Samnitic world, as well as two Latin colonies are represented. This coin sample can be divided into two groups: (A) the older one includes coins dated from 444 BC to 390 BC ca., issued by Sybaris, Croton, Metapontum, Greek poleis in Magna Graecia, and by Hyria, which was an Oscan-Campanian community (Figure 1).



Figure 1. A map of Italy showing the city of Rome and the corresponding cities of the analysed coins shows that the location of Hyria is still uncertain: Campania or Sannio are the most likely areas.

The second group (B) consists of coins from the second half of the 4th century BC until 290/280–270 BC ca. More details on the chronology and numismatic classification are given in Table 1. It must be said, however, that the same coinages of ancient Italy have yet to be properly studied, and many questions, first chronological ones, await more in-depth studies.

Table 1. Chronology and classification of the analysed coins.

Sybaris	Croton	Metapontum	Heraclea	Hyria	Cales	Suessa
			450–425 BC			
11–12; triobol 446–440 BC						
7–8; triobol post 440 BC	I 10; stater 430–420 BC					
			425–400 BC			
	5–6; stater 425–350 BC					
			400–375 BC; 400–340 BC			
	19–20; stater 425–350 BC	15–16; stater 400–340 BC		1–2; 3–4; 5–6 staters 400–395 BC ca.		
	15–16; stater 400–325 BC	17–18; stater 400–340 BC				
			340–330 BC			
		7–8; 11–12; staters 340–330 a.C.				
			325–275 BC			
		13–14; fraction				
			290/280–240 BC ca			
		9–10; stater 290–280 BC	Meta 21 o 19–20; stater 281–278 BC		Cales 9–10; stater 265–240 a.C.	Suessa 3–4; stater H.N.I. n. 447 265–240 BC

These coins can be referred to as a really important epoch that is difficult to study because of the complexity of the political background and its sources, both literary and archaeological-numismatic ones.

In the second half of the 5th century BC, Magna Graecia was the scene of many relevant processes that were intertwined with other events. Only the essential elements of this historical situation will be discussed here in order to place the coin sample in its context.

Firstly, with regard to this coin sample, in the second half of the 5th century, three new poleis were founded: Magna Graecia, Thurium, Sybaris on Traeis, and Heraclea.

Thurium was founded on the ashes of ancient Sybaris, well-known as one of the most prestigious Greek towns. Sybaris was destroyed by Croton in 510 BC, but its inhabitants tried to rebuild it several times thanks to alliances with other Greek poleis, in 476 BC, in 453 BC, in 444/3 BC, and finally in 443/442 BC [42].

In 446 BC, Athens accepted the invitation of the Sybarites to participate in the refoundation of their polis, and the Attic metropolis led an expedition with members from many poleis of Greece to achieve this purpose and to strengthen the polis of Sybaris.

This expedition in the West and its aims were in line with Pericles' policy towards foreigners but had unforeseen consequences in southern Italy. This community (Sybaris the 4th), composed of the descendants of the Sybarites and the new colonists from Greece,

was troubled by internal contrasts and soon the newborn polis was divided: the site of the ancient Sybaris was firmly held by the new Panhellenic colonists, who founded the polis of Thurium there, while the Sybarites had to leave their home. They founded a new polis along the Traeis river called Sybaris on the Traeis.

These events established a new political equilibrium in Magna Graecia, initially in line with the needs and interests of the Achaean communities, especially of Croton, but a few years later, this equilibrium was broken, and new alliances were born. On the one hand, Thurium broke the agreement with Croton and reached a new agreement with Tarentum; on the other hand, the heirs of the ancient Achaean communities of Croton, Caulonia, and Sybaris (Sybaris on Traeis) formed a political and military union, the Achaean union, around 430 BC, with the aim of defending their own interests [42,43].

Later, the Greek communities of Italy and Sicily were engaged in epochal events, such as the Peloponnesian War, which we will neglect here.

Subsequently, when the theatre of the Peloponnesian war moved towards the eastern Mediterranean Sea, from the last decades of the 5th century BC, the Greek poleis of Magna Graecia had to deal with two new and demanding enemies, Dionysius I of Syracuse and the Lucanians: the Italiots (i.e., the Greek polity/citizens of southern Italy) no longer had to struggle among themselves, but against these two threatening and powerful common enemies.

So, the former Achaean Union, reserved until those events to the Achaean *poleis* of Bruttium, was then extended and included other Greek communities in various areas of Southern Italy from Elea, on the Tyrrhenian coast, to Regio on the Stretto and Thurium on the Ionian coast, and it became the Italiote League. This league was probably founded in 393/2 BC, as Diodorus tells us and as historical research confirms [42].

The Italiote League fought against Dionysius and his allies during the first Italic War (391–388 BC ca.), but the war ended with the victory of Dionysius, who dissolved the league after conquering Caulonia, Hipponium and Regio.

In the Bruttium (Calabria), only Croton and Thurium survived as independent *poleis* and were involved in a new conflict against Dionysius, the Second Italic War (383–374 BC ca.).

This chain of events had relevant effects on the poleis of Magna Graecia, as evidenced to some extent by their coinage.

1.1.2. The Oldest Coins in the Sample (A) with Regard in the Historical Context

In this paragraph, coin sample A is considered in relation to the historical events that have just been recalled.

Sybaris (coins nn. 11/12 and 7/8): Following the chronological order of the coins, the Sybaris coins (nn. 11/12 and 7/8) are triobols minted by Sybaris 4th and Sybaris 5th, respectively [44]: they, therefore, bear witness to the Athenian policy towards the western Greeks, and Sybaris in particular, and some of its consequences, as it has just briefly recalled.

The piece no. 11/12 has on the obverse the portrait of the goddess Athena, wearing an Attic helmet: she was the Athenian goddess par excellence, and she is portrayed with typical Attic iconography. The portrait of Athena is a new type of coin in the coinages of Magna Graecia, and it recalls the role of Athens in the refoundation of Sybaris and Thurium in 446–444/443 BC ca. On the reverse, the type is a bull with an iconographic attitude that recalls the most ancient issues of Sybaris in the sixth BC: on the incuse staters of Sybaris (I) of the sixth century, a bull with its head turned back stands out against the background, both on the obverse and on the reverse: the type is in relief on the obverse side of the coin, but on the reverse it is incuse, i.e., carved inwards in the flan.

Later, after the defeat of Croton (510 BC), the bull is often matched with other types that are historically significant, such as the tripod of Croton, the peculiar type of the polis that defeated Sybaris. The ethnic (legend) of no. 11/12 is ΣΥΒΑ. This coin, therefore, has to be assigned to Sybaris 4th and witnesses the first steps of the new community, made up of

the descendants of the ancient Sybarites and the new colonists coming from Greece under the control of Athens.

The other triobol (n. 7/8), with Poseidon on the obverse and a bull (the head is now in profile) on the reverse with the ethnic ΣΥ, was minted by Sybaris on the Traeis: the type of Poseidon recalls the ancient links between Sybaris and Poseidonia, a sub-colony of Sybaris on the Tyrrhenian Sea. Poseidonia had already tried to give a new life to its metropolis (Sybaris) in 453 BC. Differently, the bull on the reverse stems from the ancient sybaritic tradition.

These types definitely explain the break with Thurium, which kept the head of Athena on the obverse as a tribute to Athens, and on the reverse, a bull in a different pose, with its head down, ready to hit with the horns, while the ethnic had become ΘΟΥΡΙΩΝ.

Croton (coins nn. I 10; 5/6; 19/20; 15/16): The silver double relief coinage of Croton has not yet been definitively studied; nevertheless, the pieces of this sample can be dated from the last decades of the 5th century BC to the first decades of the 4th. Century BC [45].

Croton was a prominent member of the Achaean Union and, together with Thurium, also of the Italiote League.

It has been noted that on the eve of the first Italic war against Dionysius, Croton was powerful, and its coinage was consistent with its demographic and military resources [42].

In this sample, some of the meaningful types of double relief coinage are represented: first of all, the traditional emblem, the tripod, is matched with an eagle (nn. 5/6, 19/20), a type with political implications that recalls prestigious issues, such as those of Olympia. The political meaning of the coin types is particularly emphasised by the issues with the portrait of Hera Lakinia on the obverse and Herakles on the reverse (nn. 15/16). The portrait of Hera Lakinia is related to the sanctuary of Cape Lacinio, under the control of Croton: in this sanctuary the Italiote League held its meetings and councils, and Croton had the leadership of the league, at least during some periods. This series, and particularly the type of Hera Lakinia, represents a meaningful historical source on the league and political dynamics of the time: the head of Hera Lakinia was also adopted for their coinages by Pandosia and Thurium, other members of the league, suggesting that the worship of Hera Lakinia was shared by the allied Italiote. It is worth noting that Hera Lakinia was also chosen as a coin type by some Osco-Samnitic communities, i.e., Hyria and Fenserni [42,45,46].

Metapontum (coins nn. 15/16 and 17/18): During the second half of the 5th century, Metapontum also stopped incuse issues and began a huge double relief coinage, which is also one of the most important testimonies to the historical and institutional life of the period, although historical sources are rather scarce.

The double relief issues of Metapontum were rich in new types for the obverse, while the traditional badge—an ear of barley—appears on the reverse: it reminds us that Metapontum was founded as an agricultural colony and its barley crops were a relevant resource for its wealth.

Among the new types, first of all, gods and goddesses, Demeter, who was also important in relation to the cycle of the seasons, of birth and death, plays a prominent role: in this sample, Demeter is the obverse type of the coin no. 17/18, while Persephone is portrayed on the obverse of no. 15/16. Here, the inscription “ΨΥΤΙΕΙΑ” describes her as “health-giving” [47].

Hyria (coins nos. 1/2; 3/4; 5/6): This first group of coins, dating between the last decades of the 5th century and the first ones of the 4th century, includes three staters of Hyria (nos. 1/2, 3/4, 5/6): they pertain to an Oscan-Campanian coinage, a topic which still deserves a great deal of attention, especially in the case of Hyria and some other communities such as Phistelia and the Fenserni.

It should be noted that coinage is the only testimony of this native community. It is only thanks to its coins that we know of its existence: the features of its coinage, such as types, weights, the technical procedure of minting, and its diffusion in ancient Italy, tell us that Hyria was an Oscan-Campanian community, but we do not know its exact location.

Notwithstanding this, Hyria was a relevant community of people in the Campanian context if we consider its coinage, which was sometimes richer than that of Neapolis: the Hyrian coinage was huge and consisted of staters, i.e., high denominations [48].

1.1.3. II Section 340–280/270 BC ca.

In the second half of the IV century BC and in the first decades of the following century (III), many other events happened, such as the Latin war and Samnite wars, with serious consequences on the political balance of ancient Italy. In this respect, we need only remember that Rome managed to bond firm ties with Campanian communities and towns by means of several proper diplomatic, administrative, and juridical institutions, such as the alliance with Neapolis (326 BC) and the institution of the Latin colonies (*coloniae iure latino*) in Cales (334 BC) and Suessa Aurunca (304 BC).

These political and administrative relationships had a fundamental role in the historical dynamic of the period and had meaningful effects on the coinages of Rome and the Campanian communities.

The second half of the 4th century BC is still interested in the struggle of the Greek poleis against the indigenous peoples, but this time, foreign princes coming with their armies from Laconia or the Balkans played a leading role. They were invited by Tarentum, which, after the conquest of Croton by Dionysius, had become the main Greek polis of Magna Graecia and had compelled the allied poleis to defend themselves against the indigenous, particularly the Lucanians, Apulians, Messapians and to defeat them.

Then, in 340 BC, a new epoch began in Magna Graecia, the epoch of the “Condottieri” foreign princes or chiefs of mercenary armies: in 340 BC, Archidamus arrived from Sparta, in 334–331 BC, Alexander the Molossian from Epirus, in 315 BC Acrotatus, in 302 BC Cleonimus again from Sparta, in 280–272 BC Pirrhus, king of Epirus [49].

They led the armies on behalf of the Greek towns, and the military actions had many, sometimes unpredictable, effects on the political situation in southern Italy.

These wars were relevant for the relationships of Greek poleis not only with native people but also with Rome, as the last expedition of the “condottieri” effectively demonstrates.

Pirrhus was the last foreign military chief called by Tarentum on behalf of the Greek poleis of southern Italy, and he led the so-called “Tarentine War”: he fought with his armies against Rome with its colonies and allies.

Rome was successful in the Tarentine War (272 BC ca), and its role became even more prominent in Magna Graecia.

1.1.4. Magna Graecia: Metapontum (Nos. 7/8; 11/12; 13/14); Heraclea (Nos. 19/20)

In this sample, the remaining coins of Metapontum and Heraclea can be assigned to this epoch when, in general, the Greek poleis of Magna Graecia had to increase the number of coin issues, especially because of the wars.

Coins nos. 7/8 and 11/12, two staters minted by Metapontum in the age of Alexander the Molossian, stand out in relation to this period: this polis then added new types to the traditional ones (barley ear; Demeter) from a military point of view and among these was Leukippus, portrayed here on coins nos. 7/8 and 11/12 [49–51].

The coin of Heraclea (nos. 19/20, see Table 1) [44,52] also dates back to the Tarentine War or immediately before (see Table 1).

1.1.5. Campania: Latin Colonies of Cales (Nos. 9/10) and Suessa (Nos. 3/4)

Cales and Suessa became Latin colonies in 334 BC and 313 BC, respectively, and their institution as Latin colonies (*coloniae iure latino*) was a primary step in the Roman plans of political development: the coinages of Cales and Suessa are intertwined with other main coinages, such as those of Neapolis and Rome itself.

The didrachms, silver coins of high value, of Cales (nos. 9/10) and Suessa Aurunca (nos. 3/4) [53] date back to the first half of the III century BC, most probably to the years of the Tarentine war.

Notwithstanding this, the didrachms of Campanian Latin colonies and of the Roman allies (Cales, Suessa, Teanum) are still the subject of debate as to their chronology and destination: on the one hand, some scholars date them to the years of the Pyrrhic war (280–270 BC ca.) and they should have been issued by Latin colonies and Roman allies to fund the war and support the Roman efforts [53–58]. On the other hand, by other scholars, these coinages have been dated later, during the First Punic War [58] or after the end of this conflict, in a completely different perspective [59]: such issues should have been minted for repaying Roman allies and Latin colonies for their help in the war against the Carthaginian enemy.

2. Materials and Methods

Eighteen double-relief representative coins from the Campano Museum (Capua, Italy) are analysed using the XRF technique. The analysed coins in double relief belong to the poleis of southern Italy: Hyria (3), Croton (4), Metapontum (6), Heraclea (1), Sybaris (2), Cales (1), and Suessa (1). Table 2 shows a photo of a representative coin (observe and reverse side) and the corresponding weight for each of the polis or communities involved. The coin code is the same as that used in the Museum's classification.

Table 2. Photo of the two sides of a representative coin for each polis and the corresponding mass.

Mint (Coin No.)	Obverse Side	Reverse Side	W(g) d(mm)
Hyria (3–4)			7.0 ± 0.1
			20.9 ± 0.1
Croton (5–6)			7.8 ± 0.1
			20.0 ± 0.1
Metapontum (15–16)			7.8 ± 0.1
			20.8 ± 0.1
Heraclea (1–2)			6.6 ± 0.1
			21.3 ± 0.1

Table 2. Cont.

Mint (Coin No.)	Obverse Side	Reverse Side	W(g) d(mm)
Sybaris (11–12)			1.1 ± 0.1
			12.0 ± 0.1
Cales			6.8 ± 0.1
			21.2 ± 0.1
Suessa			5.3 ± 0.1
			20.4 ± 0.1

2.1. Instrumentation and Method

A handheld ED-XRF spectrometer (XSORT XHH03, 47,533 Kleve-Germany) equipped with a Rh anode was used. The x-ray tube was operated with an anodic voltage of 50 kV and a current of 125 μ A and irradiated a surface of 10 mm diameter. Experimentally, it was found that the instrument does not examine uniformly across the measurement window, so the size of the investigated area (approximately 7 mm²) and its position within the investigation window must be considered. A CCD camera is available to check the measured area. The fluorescent x-rays were detected by a silicon drift detector. The energy resolution on the K α line of the Mn value (5.9 keV) is about 160 eV. Spectra were collected for 20 s. This instrument has an internal calibration for metal alloys based on the fundamental parameter method. The acquisition and analysis of XRF spectra are carried out using XRF Analyzer CE and XRF Analyzed PRO. This instrument is available at the CIRCE laboratory (<http://www.circe.unicampania.it>) and was used directly in the museum to carry out these measurements. The XRF measurements are made on both sides of each coin, where the surface can be considered “locally homogeneous”. This analytical procedure is applied for surface irregularities and their possible compositional inhomogeneity. The average percentage concentration of the elements and spectra detected by the XRF measurements on the two sides of the coins are considered.

The data obtained are examined using multivariate statistical analysis to study the relationships among elements and spectra detected by XRF analysis. The analysis and representation methods used are boxplot, Principal Component Analysis (PCA), Graph Analysis (GA), diagram and Hierarchical Cluster Analysis (HCA) [60–64].

The ratio of the characteristic lines of AgK α /L α and the cross ratio AgK α /CuK α are determined and compared with those of a standard [3,36,62,63] to unmask the possible presence of enrichment on the surface [65]. PyMca software 5.6.3(Copyright (c) 2004–2022 European Synchrotron Radiation Facility (ESRF)) is used to calculate the net area of characteristic elements of Ag and Cu. PyMca provides full control over background/continuum

modelling, peak shape modelling (including long, short, and stepped tails), feature line group modelling, energy calibration and pile-up and runaway peak modelling. It also features control over the modelling of the energy emitted from polychromatic X-ray sources, which is important for reliable quantitative analysis and research in art and archaeology [66,67].

Standard

Comparable standards (private seller, 81100 Caserta, Italy) to coins are analysed to test the effectiveness of the quantitative method based on x-ray instruments. They are used in previous works [3,68,69]. The concentrations of the elements and the ratio of the characteristic lines of $AgK\alpha/L\alpha$ and the cross ratio $AgK\alpha/CuK\alpha$ were deduced by comparing the spectrum of the coin with the spectra of sufficiently similar standard samples of known composition (82.0, 92.5, 99.9% silver concentrations).

3. Results and Discussion

The coins are made of a natural alloy of silver with copper as a minor element. The concentration of these two elements, which makes the mixture variable over time, depends on the financial availability. The alloy also contains trace elements (Au, Pb, Bi) collected from the primary minerals during the extraction process [19–23] and related to the fineness of the silver, mine, and production technologies. Other trace elements (such as Fe, Si, and S) are due to the products of contamination present in the environment to which the coins were exposed during their use and subsequent burial period. They could be present in the superficial patinas and in the incrustations [24,70–72]. The patina is due to the surrounding soil, the external environment, the exhibition environment, the marine environment, and artificial surface treatments.

The set of samples examined appears visually quite heterogeneous: the colour of the coins varies from silver grey to dark grey. Different XRF measurement points on the same coins showed different percentage concentrations at fractures or disintegrated points. For this reason, some of these coins were excluded from the statistical analysis and will be further investigated later (i.e., Heraclea 1–2).

A summary of the concentration results is shown in Figure 2, where silver is rescaled by a factor of ten, and the red “+” sign marks the coins that do not fall within the interquartile range. The ranges of concentration variability for the detected elements are: Ag (92.32–97.73)%; Cu (0.04–4.66)%; Au (0.04–0.54)%; Pb (0.03–1.35)%; Bi (0.03–0.20)%, Fe (0.04–1.43)%. and Si (0.10–2.16)%.

The high concentration of Ag does not seem to have been affected by the issuance in different historical periods and, in this sample, by problems of historical and economic nature (except for Heraclea 1–2, Croton 15–16 and Meta 17–18).

What changes in different historical periods is the use of Ag and Cu. The fineness (i.e., the purity of the content of the precious metal) is higher. Coins dated to the period from 450 to 350 BC were minted from high-grade silver (varying in fineness from 950 to 980) with a mixture of copper (0.10–3.00%—Figure 3a); the presence of other indigenous impurities is also recorded in silver: gold, lead, bismuth, and other elements, whose content, with some exceptions, does not exceed 1.5% (Figure 2). The silver content of coins dated 325 to 270 BC proved to be different. Coins from the Latin colonies in Campania, for example, were minted from high-grade silver (920–950 fineness) with a mixture of copper (1.5–5%), as well as lead and gold as trace impurities.

The trace elements indicate that silver from the same sources was most likely used for the minting of the coins. This is indicated by the similar content in several coins of the ‘original’ gold and bismuth impurities that characterise certain genetic groups of deposits. It should be noted that the sample studied demonstrates the constant presence of gold impurities in the metal of the coins, which suggests the use of silver from the gold-silver deposit group Figure 3b. Based on the results of the study of the elemental composition of silver, it can be concluded that during the manufacture of the coins of the

450–350 chronological group, silver coins were minted with high-quality silver. At the same time, the silver used as a raw material for minting coins in the 280 s was diluted with copper.

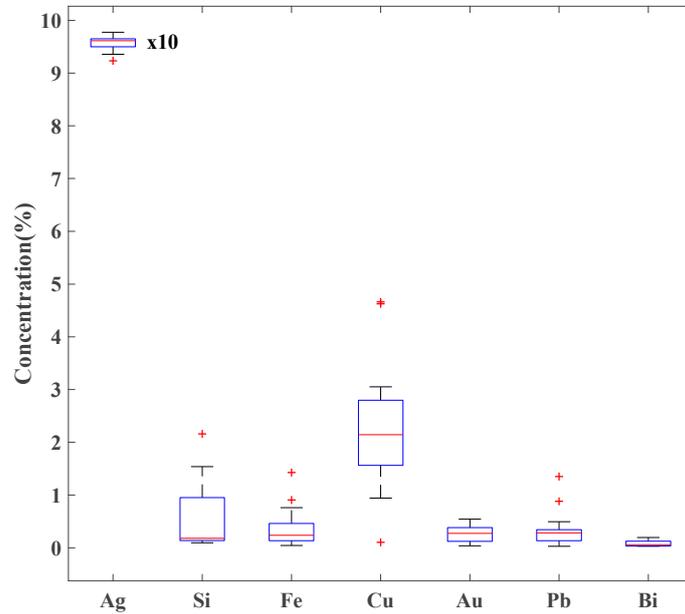


Figure 2. Box plot of the concentration values of the elements detected by the XRF. Silver values have been rescaled by a factor of 10.

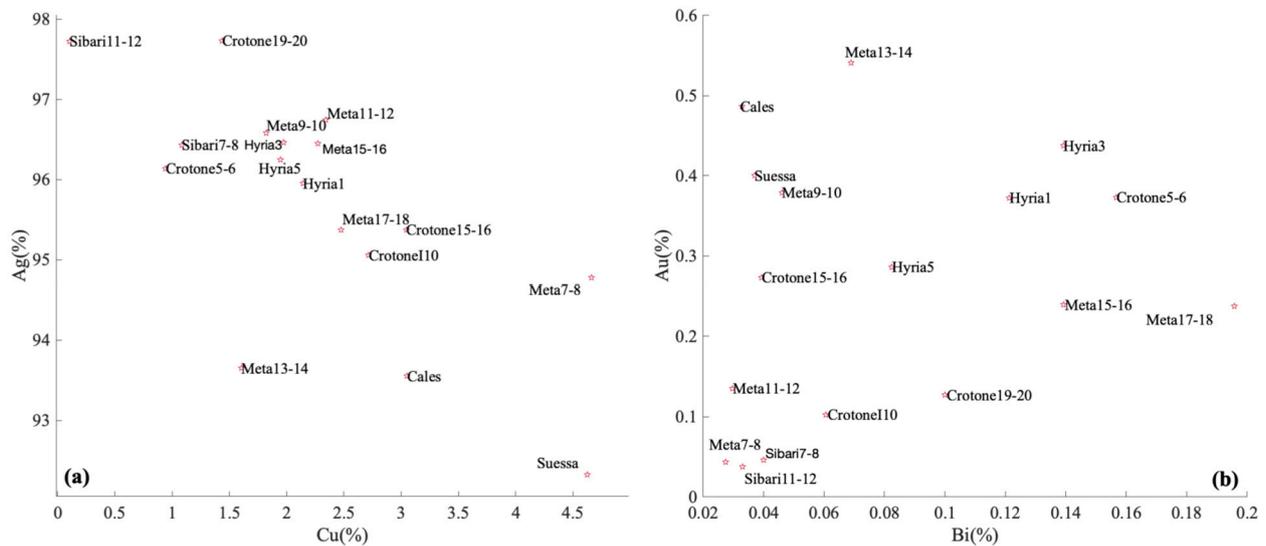


Figure 3. The concentration of Ag vs. Cu (a) and concentration of Au vs. Bi (b) of all coins analysed.

3.1. Ratio of Characteristic Lines of Ag and Cu

For ancient silver alloy coins, the presence of thick silver-enriched surface layers [26,65] is quite common. In this case, XRF analysis may overestimate the silver content as it is unable to analyse the inner core, and therefore, no accurate quantification of fineness (precious metal) can be obtained for debased coins. Mc Kerrel and Stevenson [72] argue that a concentration of Cu greater than 3% in silver is deliberately added, i.e., it is not part of the silver matrix. Other researchers also indicated that the enrichment of Ag can be deliberately performed during the production process. Hence, Crotona 15–16, Cales, Suessa, Meta 7–8 and Meta 17–18 should have been enriched (Figure 3a).

In the coins of Cales and Suessa, belonging to a ‘more recent’ coinage and to a different area than the others, copper could have been added intentionally to dilute the Ag concentration. From the different XRF measurement points analysed, it appears that they have not undergone an enrichment process.

The XRF measurements of Meta 7–8 are quite homogeneous, so in this case, it is not a surface enrichment but an intentional addition of Cu.

In the case of suberate, corroded or surface-enriched coins, an important disadvantage of EDXRF is its low depth of information, which is a function of the energy of both primary and fluorescent radiation, as well as the chemical composition of the sample itself. Surface results may not reflect the chemical composition of the nucleus. Therefore, the main question that arises is to what extent the chemical composition in the current state corresponds to that at the time of production [34]. To overcome this, the ratios and cross-ratios of the characteristic lines of Ag and Cu were studied. Quantitative data were not used for these measurements, but simply the intensities (counts) of the peaks were considered to perform the data analysis. Here, only a few significant XRF measurements of Heraclea, Croton 15–16 and Meta 17–18 coins were considered. These are those relating to a flat surface and to breaks or disintegrated points.

The analysis of $\text{AgK}\alpha/\text{L}\alpha$ and $\text{AgK}\alpha/\text{CuK}\alpha$ ratios of these coins is shown in relation to the net area of the characteristic line of Ag $\text{K}\alpha$ (Figure 4). It can be observed that the $\text{K}\alpha/\text{L}\alpha$ ratios of Ag (Figure 4a) are significantly altered (compared to the standard) due to the greater attenuation of the characteristic lines $\text{L}\alpha$, which are absorbed by the most superficial part. The cross-ratio $\text{AgK}\alpha/\text{CuK}\alpha$ (Figure 4b), on the other hand, increases exponentially as the Ag concentration increases and the Cu concentration decreases.

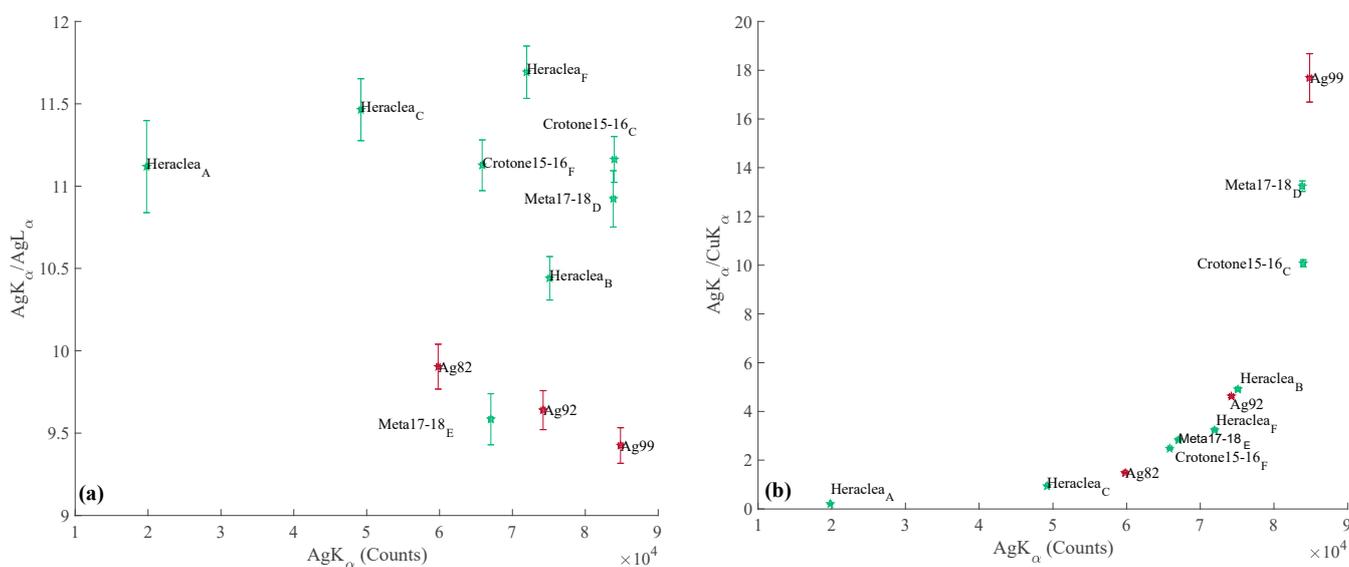


Figure 4. (a) Comparison of the ratio of silver $\text{K}\alpha/\text{L}\alpha$ characteristic lines to the net area of Ag $\text{K}\alpha$; (b) Comparison of the cross-ratio of silver $\text{K}\alpha$ characteristic line to copper $\text{K}\alpha$ vs. net area of Ag $\text{K}\alpha$.

Figure 4a,b show the inhomogeneity of these coins at the different measuring points. These results could be useful to confirm the surface enrichment or subaerata hypothesis, especially in the Heraclea coin, where there is a clear difference between the XRF measurement in the crack and that in the intact surface. Further analysis will be carried out to determine exactly whether these are enriched or subaerata cases.

3.2. Principal Component Analysis (PCA)

PCA was used to distinguish the different groups of the coins studied. For this analysis, the average percentage concentrations of 17 measurements (observations) of the selected elements (input variables) were selected. The data were first standardised since

the measured concentrations are of different orders of size. The elements considered are those most representative of the silver coins [3]. They were based on information found in the literature [17–20].

The first three principal components (PCs) were taken into account, achieving a cumulative variability of 79%.

In the biplot, each variable is shown as a blue vector, whose modulus indicates the contribution of the variable to each principal component; the observations are represented as red crosses and grouped in the plane according to the relationship between the elements.

The biplot suggests that the largest contribution to the definition of PC1 is given by Ag, as opposed to Cu. On PC2, the largest contribution is given by Au and Bi, which derive from a raw material supply (mining). On PC3, Pb (technological process) is opposed to Fe and Si are correlated (same direction and modulus) depending on the surface pollution (Figure 5a). The score plot allows us to identify the subdivision of the objects according to these characteristics (Figure 5b).

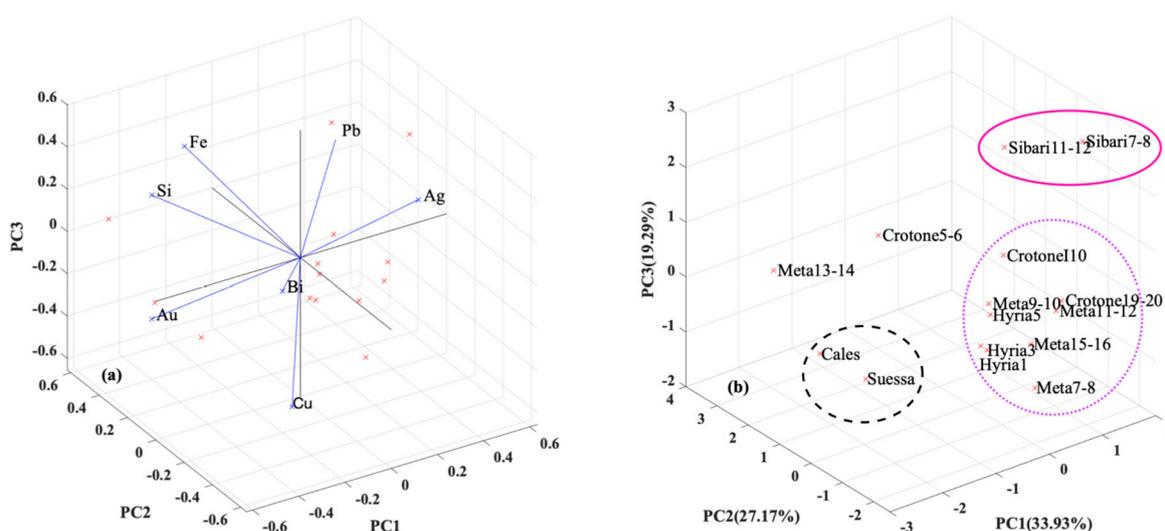


Figure 5. (a) The selected elements among those detected are shown in the biplot. (b) The three principal component results obtained from PCA (PC1, PC2 and PC3) are presented in the score plot.

Cales and Suessa could belong to the same mine (dashed black ellipse). Most of the coins (Metaponto, Crotona e Hyria) have similar concentrations of Ag and Cu, and the raw materials for their production and the technological process could be the same (dotted purple ellipse). The coins from the city of Sybaris are quite distinct (fuchsia ellipse) because they contain more lead.

The measurements on Crotona 5–6 and Meta 13–14 could be influenced by the burial site and the state of preservation of the coins.

The average spectra of the XRF measurements were also used in PCA analysis (Figure 6a).

On PC1, the largest contribution is from Cu opposite $AgK\alpha$, while on PC3, the largest contribution is from Pb opposite $AgL\alpha$, Fe and Au. Figure 6b shows PC1 vs. PC3 and that most coins have rather similar Ag and Cu concentrations.

Crotona 19–10 and Sibari 11–12 have the highest Ag concentration, about 98% (dotted black ellipse). In the same ellipse, there are Crotona 5–6 and Sibari 11–12, the coins with the most Fe ($1.4 \pm 0.5\%$) and ($0.91 \pm 0.01\%$), respectively. Suessa and Meta 7–8 are the samples with the highest concentration of Cu ($5 \pm 2\%$) and ($5 \pm 1\%$), respectively (dashed green ellipse). Sibari 7–8 and Crotona I10 are the samples with the highest concentration of Pb ($1.35 \pm 0.03\%$) and ($0.9 \pm 0.1\%$), respectively. Coins with similar concentrations and elements are also grouped in the red ellipse.

PCA analyses of concentrations and spectra can provide a variety of information, such as the identification of the main elements of the coin alloys and trace elements indicating the production and extraction processes of the raw materials. Indeed, most coins were grouped according to the same concentrations of the main elements (Ag and Cu) circled in red. Furthermore, isolated groups are highlighted that show a different coin production process for the Crotone I 10 and Sibari 7–8 coins, the presence of contaminating elements on the surface, for Crotone 5–6 and Sibari 11–12, and the use of Cu in the alloy, for Meta 7–8 and Suessa.

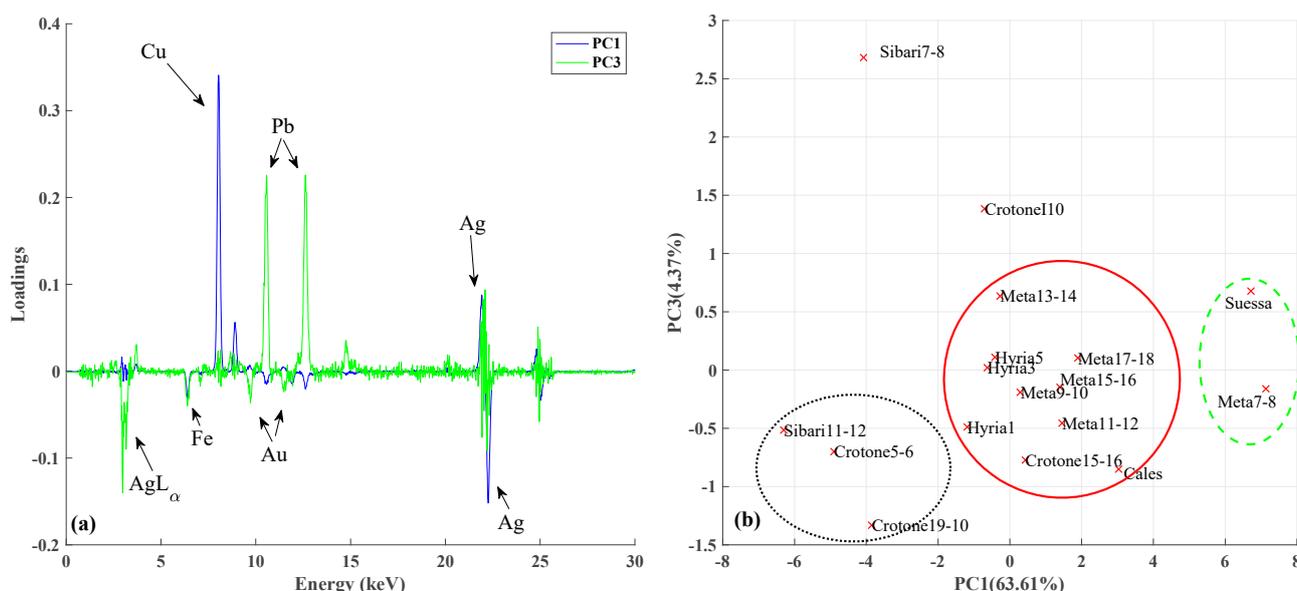


Figure 6. Loadings as a function of energies (keV) to determine which fluorescence peaks contribute most to the PCs. PC1 and PC3 give 68% cumulative variance.

3.3. Graph Analysis (GA)

Further classification of the XRF spectra of all 17 samples based on all 4096 channels was performed using Graph Analysis (GA). It is performed by constructing the symmetric correlation matrix (17×17) of the spectra to reduce the computational burden associated with the statistical analysis of the spectra. The matrix can be interpreted as an adjacency matrix in which the correlation values, appropriately weighted, define the presence or absence of links between the different nodes. The elements of the matrix vary between 0 (completely uncorrelated spectra) and 1 (identical spectra). The graph is divided into classes in which the XRF spectra are strongly correlated with each other and weakly correlated with those of other classes.

An edge weighting filter was applied to speed up the process of finding communities and to obtain the optimal number of classes and their best separation. This filter neglects weak correlations and is not known in real applications. The correct value of the filter to be applied must be found by searching for the maximum of the modularity parameter [73]. The modularity of the untreated correlation matrix is rather low, and the spectra are embedded in a large cluster Figure 7a. The optimal modularity parameter correlates with the edge weight filter values around 0.36. The low modularity parameter suggests that the spectra are uncorrelated. When this filter is applied to the graph, a very clear separation into classes is obtained, as shown in Figure 7b.

The graph is used to confirm the chronology of the coins.

Sibari 7–8, Sibari 11–12 and Crotone I 10 belong to the historical period from 450 to 425 BC [74] and are joined by Crotone 5–6, which belongs to the later period (425–400 BC).

Crotone 19–20, Meta 15–16, Meta 17–18, Hyria1, Hyria3, and Hyria5 belong to the historical period from 400 to 340 BC, but Crotone 15–16 are not connected to them because

the ratios of the characteristic lines show surface anomalies (see Figure 4) so it could be surface enriched or subaerata.

Meta 7–8 and Meta 11–12 are connected and belong to the historical period from 340 to 330 BC.

Meta 13–14 belongs to the historical period from 375 to 325 BC.

Meta 9–10 belongs to the historical period from 290 to 280 BC.

Cales and Suessa belong to the historical period from 280 to 270 BC.

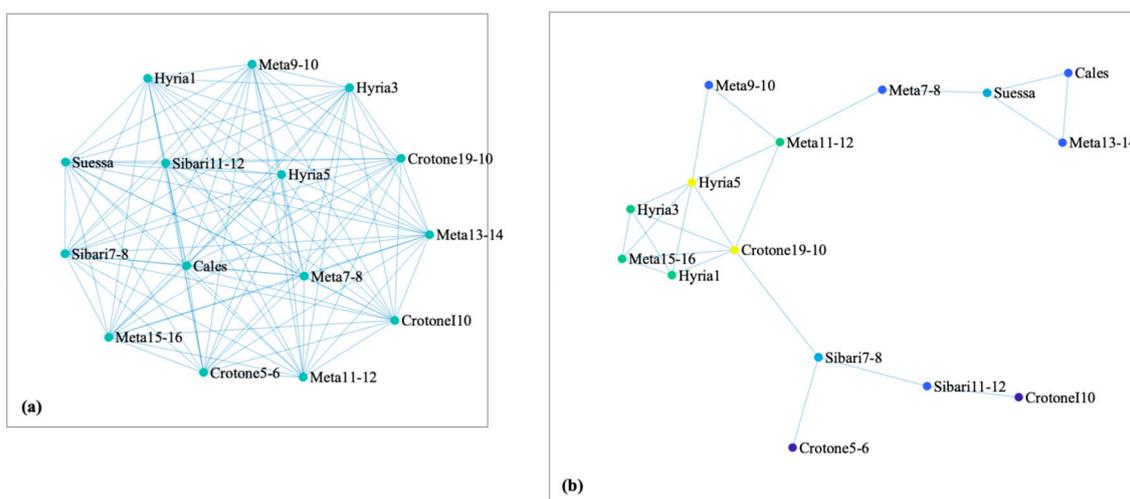


Figure 7. (a) The graph obtained from the correlation matrix. Blue edges (weights) link XRF spectra (nodes, blue dots). (b) The graph obtained after applying the edge weights corresponding to 0.36.

3.4. Hierarchical Cluster Analysis (HCA)

HCA was used to find similarities between samples. It works as a bottom-up procedure based on the distances between objects: the first cluster is assigned to the two closest objects, the second to two of the remaining objects with the shortest distance, and so on.

The method used to calculate the distances for HCA is the Euclidean distance, while among all possible clustering methods, the Complete Linkage method was used (the distance between two clusters is the maximum distance between an observation in one cluster and an observation in the other cluster). Distance values in HCA can be strongly influenced by differences in scale between the dimensions from which the distances are calculated, so the percentage concentration matrix was standardised.

The quantitative results obtained from the HCA applied to the percentage concentrations of the elements are shown in Figure 8. It was expected to obtain a series of clusters corresponding to the number of home cities, each connected to larger clusters based on different characteristics. However, the partitioning shows three main clusters corresponding to three different historical periods.

The cluster in red corresponds to the period from 340 to 270 BC, excluding Crotona 15–16; the cluster in light blue and purple corresponds to the period from 450 to 400 BC; and finally, the green cluster corresponds to the period from 400 to 340 BC.

Despite the chain of turbulent historical events (as described in Section 1.1), the coins of the polis of Sybaris maintained a rather high Ag content, especially the coin Sibari 11–12.

Although the Crotona coin series, and in particular the Hera Lakinia type (Crotona 15–16), represents a significant historical source on the league and the political dynamics of the time, the Crotona 15–16 coin shows surface anomalies, as illustrated in Figure 4; it could therefore be surface-enriched or subaerata. Moreover, it should be included in the green cluster because it is dated to 390 BC.

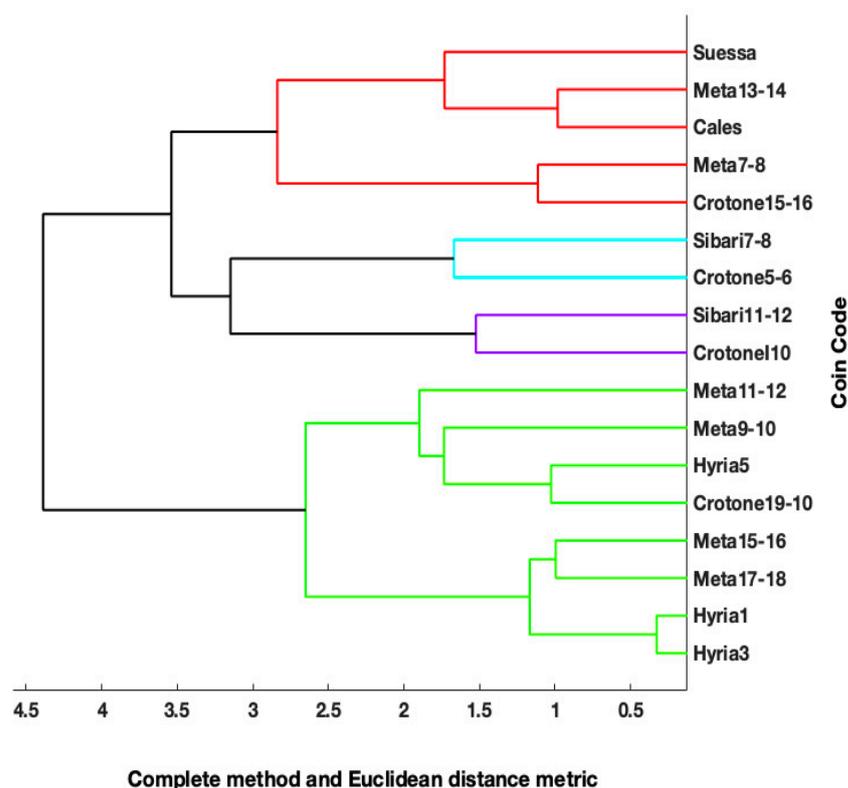


Figure 8. HCA on the XRF dataset using the complete linkage algorithm and the Euclidean metric.

Regarding the coinage of Hyria, it is the only witness or evidence on this community. As already mentioned, the characteristics of its coinage, such as the types, the weights, the technical procedure of minting, and its distribution in ancient Italy, show us that Hyria was an Osco-Campanian community, but we do not know its exact location. Its coinage, therefore, consisted of staters with a high denomination and a fineness of around 960. It falls within the historical period of the coinage of Metapontum (with the exception of Metapontum 13–14, 7–8—Figure 8).

Some historical and numismatic hypotheses or suggestions were considered for some coins.

Regarding the oldest group, it is interesting to note that the coins from Sybaris stand out clearly from the others. The absence of Au and Bi may suggest a different source of raw material compared to the other coins from the Achaean poleis of Magna Graecia that have been analysed. This difference could be even more significant if one considers that these coins were issued by or on behalf of two newly constituted political authorities: Sibarys IV and Sibarys V (on Traeis): as far as Sybaris 11–12 (Sybaris IV) is concerned, it has already been pointed out that this polis also consisted of new citizens coming from Greece, especially from Athens. It would be interesting to extend the sample and test whether other exemplars from Sybaris IV and V, and in particular from Thurii, the new polis of Greek origin which replaced ancient Sybaris (cf. 1.1.1), show these characteristics, i.e., whether the peculiarity of the alloy found here is accidental or regular.

The high Pb concentrations, depending on the technological process, could be significant, especially about Sibari 7–8. It could be considered from two points of view: on the one hand, it should be remembered that it was minted by or for a new polis, probably in uneasy technical conditions, but on the other hand, it could be considered whether a higher level of Pb could be related to the minting of divisional, coins of lower weight and value than the staters. If a higher level of Pb in fractions were confirmed, one could wonder whether it was due to the need to keep the weight balanced, saving Ag and Cu. In this context, it may be useful to mention another Sybaris fraction from the same collection, an incuse drachma

with Pb = 0.99% and without Au. It is tempting to wonder whether Sybaris used different alloys or parameters for divisional [30,74].

The results of these analyses showed similar concentrations of Ag and Cu in most of the coins in the sample, suggesting that the source of Ag and technical procedures were shared by different poleis or communities in ancient Italy.

The exemplars from Hyria also have similar characteristics to those of the Greek series from southern Italy: this may offer some clues about this still relatively unknown community, or at least about its mint and technical minting procedures, especially considering that its coinage suggests an Oscan-Campanian context or site.

It is also necessary to focus on the Ag/Cu ratio in the examined coins. A higher level of Cu was detected, especially in the group of coins consisting of Croton 15–16 and Meta 17–18, and it could be related to an enrichment process. These coins are related to the relevant historical situation. Croton 15–16 (390 BC ca.) refers to the Italiote League, to the leadership of Croton in it and to the political dynamics of the period when the Italiote poleis were threatened by the Lucanians and Dionysius of Syracuse. Metaponto 17–18 (340 BC ca.) marks the eve of a long series of wars and military expeditions in southern Italy when foreign armies and mercenaries were engaged by Greek poleis.

Furthermore, a higher percentage of Cu could also indicate cases of subaerata, i.e., coins consisting of an inner core of Cu covered by a layer of silver, and this seems to be the case of the Heraclea coin. The historical situation is also relevant for Heraclea (281–278 BC ca.); it dates back to the war between the Greek poleis, led by King Pyrrhus, and Rome: the data on the Heraclea stater seem to be consistent with a few other on the Tarentine coinage, more or less contemporary, and could suggest that when several Italiote *poleis* lightened their silver coins, during the Pyrrhic war, they could also have reduced the fineness [75,76]. These data should be investigated further and, if confirmed by more extensive evidence, could shed new light on the financial conditions of the Greek poleis of Magna Graecia during a crucial period. The group of coins consisting of Meta 7–8, Cales and Suessa also showed a high percentage of Cu, but under different technical conditions since, in this case, there is no evidence of enrichment, and the Cu may be due to an intentional act. The historical context of these coins and their series is also relevant. Metapontum 7-8 dates from around 340 BC, at the beginning of the military expeditions to Magna Graecia led by foreign princes or mercenary armies. The Cales and Suessa coins were later and were coined in the first half of the 3rd century BC: they are still quite controversial from a chronological and historical point of view, as already mentioned (cf. I.1.3–5).

It has been suggested that they were minted to finance the Roman military effort during the war against King Pyrrhus and his allies in Magna Graecia (280–273 B.C.) [58]. According to another theory, they should have been minted after the First Punic War (264–242 B.C.) in order to distribute the spoils among Rome's victorious allies [59].

Either way, the results obtained, and in particular the ratio Ag/Cu, could be very significant, providing new and more accurate elements for a monetary mosaic of ancient Italy when Rome was at its leading role.

4. Conclusions

Eighteen ancient double-relief coins from the collection of the Museo Provinciale Campano (Capua, Italy) have been analysed; they were coined by the Greek colony of southern Italy (Metapontum, Croton, Sybaris), by an Oscan community (Hyria), by two Campanian poleis that were Latin colonies (Cales and Suessa) between the 5th century BC and the 4th century BC/beginning of the 3rd century AD. It must be said that the same coinages of ancient Italy have not yet been properly studied, and many questions, especially chronological ones, await more in-depth studies.

The coins were analysed by means of a completely non-invasive XRF analysis in the same museum where they are kept. The study of the composition of their silver alloy provides a great deal of information, thanks to the conspicuous production and use of this precious metal in this period. In fact, the coins are of high fineness, and

the concentration ranges of the elements found are as follows: Ag (92.32–97.73%); Cu (0.04–4.66%); Au (0.04–0.54%); Pb (0.03–1.35%); Bi (0.03–0.20%); Fe (0.04–1.43%) and Si (0.10–2.16)%. Although no cleaning of the coin surfaces was done, the coins were found not to have an altered surface layer (corrosion). Fractures or cracks present in some coins were carefully analysed with targeted measurements in order to evaluate the elemental content in more detail. The values of the concentrations and the Ag $K\alpha/L\alpha$ and Ag $K\alpha/CuK\alpha$ ratios indicate the presence of an enrichment layer on the silver surface in some coins, which deserves further study. Multivariate statistical analysis, using GA, PCA, and HCA, made it possible to group the coins as accurately as possible based on the chemical information and spectra acquired and build models that organised the coins according to historical periods. The different methods agree sufficiently to identify some coins with anomalies. Most of the coins (Metapontum, Croton and Hyria) show similar concentrations of Ag and Cu, and the raw materials for their production and the technological process could be the same. In particular, Croton 19–20, Meta 15–16, Meta 17–18, Hyria1, Hyria3, and Hyria5 belong to the historical period from 400 to 340 BC. Although the Hera Lakinia type (Crotone 15–16) is an important historical source on the league and the political dynamics of the time, it shows surface anomalies, as illustrated in Figure 4; it could therefore be surface-enriched or subaerata.

As for the Hyrian coin, it is the only evidence or indication of this community. Hyria was an Oscan-Campan community, but we do not know its exact location. Its coinage, therefore, consisted of staters with a high face value and a fineness of around 960. It falls within the historical period of the coinage of Metapontum (except for Meta 13–14, 7–8).

The coins of the city of Sybaris (450–425 BC) are distinguished by their higher lead content. Despite the chain of turbulent historical events, the coins of the polis of Sybaris retain a rather high Ag content. The absence of Au and Bi may indicate a different source of raw material than the other coins analysed from the Achaean poleis of Magna Graecia.

The higher Cu content was mainly found in the group of coins consisting of Croton 15–16 and Meta 17–18 and could be related to an enrichment process. These coins are related to the respective historical situation. There are also cases of subaerata, i.e., coins consisting of an inner core of Cu covered by a layer of silver, and this seems to be the case with the coin from Heraclea.

The measurements on Crotone 5–6 and Meta 13–14 could be influenced by the burial site and the state of preservation of the coins.

The group of coins consisting of Meta 7–8, Cales and Suessa also show a high Cu content, but in different technical conditions, as in this case, there is no evidence of enrichment, and the Cu could be due to an intentional act. The historical context of these coins and their series is also relevant.

Cales and Suessa belong to the historical period from 280 to 270 BC, and they may belong to the same mine.

A detailed numismatic analysis and other characterisations will be carried out in the near future.

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References

1. Robbiola, M.; Blengino, J.M.; Fiaud, C. Morphology and mechanisms of formation of natural patinas on archaeological Cu–Sn alloys. *Corros. Sci.* **1998**, *40*, 2083–2111. [[CrossRef](#)]
2. Constantinides, I.; Adriaens, A.; Adams, F. Surface characterization of artificial corrosion layers on copper alloy reference materials. *Appl. Surf. Sci.* **2002**, *189*, 90–101. [[CrossRef](#)]
3. Brocchieri, J.; Vitale, R.; Sabbarese, C. Characterization of the incuse coins of the Museo Campano in Capua (Southern Italy) by X-ray fluorescence and numismatic analysis. *Nucl. Instr. Meth. Phys. Res. B* **2020**, *479*, 93–101. [[CrossRef](#)]
4. Brocchieri, J.; Scialla, E.; D’Onofrio, A.; Sabbarese, C. Combining XRF, Multispectral Imaging and SEM/EDS to Characterize a Contemporary Painting. *Quantum Beam Sci.* **2023**, *7*, 13. [[CrossRef](#)]
5. Corsi, J.; Lo Giudice, A.; Re, A.; Agostino, A.; Barello, F. Potentialities of X-ray fluorescence analysis in numismatics: The case study of pre-Roman coins from Cisalpine Gaul. *Arch. Anth. Sci.* **2018**, *10*, 431–438. [[CrossRef](#)]
6. Liss, B.; Stout, S. Materials Characterization for Cultural Heritage: XRF Case Studies in Archaeology and Art. In *Heritage and Archaeology in the Digital Age*; Springer: Cham, Switzerland, 2017; pp. 49–65.
7. Francis, A.D.A.; Nardes, R.C.; Hamilton Filho, S.G.; dos Santos, R.S.; de Araujo, O.M.; Machado, A.S.; Calgam, T.; Bueno, R.; Canellas, C.; Gonçalves, E.A.S.; et al. Characterization of a sacred statuette replica of “Nossa Senhora da Conceição Aparecida” using X-ray spectrometry techniques. *Rad. Phys. Chem.* **2020**, *167*, 108266.
8. Ager, F.J.; Respaldiza, M.A.; Scrivano, S.; Ortega-Feliu, I.; Kriznar, A.; Gómez-Tubío, B. Cultural heritage science at CNA (Seville, Spain): Applications of XRF and IBA techniques to art and archaeological objects. *Rad. Phys. Chem.* **2020**, *167*, 108324. [[CrossRef](#)]
9. Scialla, E.; Improda, P.; Brocchieri, J.; Cardinali, M.; Cerasuolo, A.; Rullo, A.; Zezza, A.; Sabbarese, C. Study of ‘Cona degli Ordini’ by Colantonio with IR and XRF Analyses. *Heritage* **2023**, *6*, 1785–1803. [[CrossRef](#)]
10. Brocchieri, J.; Sabbarese, C. Thickness determination of the gilding on brass materials by XRF technique. *Nucl. Instr. Meth. Phys. Res. B* **2021**, *496*, 29–36. [[CrossRef](#)]
11. Sabbarese, C.; Brocchieri, J.; Scialla, E. Gold-coating thickness determination on Ag, Cu, Fe, and Pb using a handheld X-ray instrument. *X-ray Spect.* **2021**, *50*, 1–11. [[CrossRef](#)]
12. Italiano, A.; Torrisi, L.; Cutroneo, M.; Gentile, C.; Torrisi, A. A comparative analysis of old and recent Ag coins by XRF methodology. In Proceedings of the 3rd Workshop-Plasmi, Sorgenti, Biofisica ed Applicazioni, July 2013; pp. 23–28.
13. Abramzon, M.G.; Saprykina, I.A.; Chugaev, A.V.; Presnyakova, N.N.; Tereshchenko, E.Y. Chemical and Pb-Isotopic Characteristics of Metal of Silver Coins of the Bosphorus and Ionia Dated from the 5th to 1st centuries BC. *Nanobiotech. Rep.* **2021**, *16*, 616–622. [[CrossRef](#)]
14. Fulminante, F.; Unavane, M. “Community practices” and “communities of practice” in smelting technology by XRF analysis of Archaic bronze votive figurines in central Italy (6th–5th centuries BC). *Arch. Sci. Rep.* **2020**, *31*, 102266. [[CrossRef](#)]
15. Kantarelou, V.; Ager, F.J.; Eugenidou, D.; Chaves, F.; Andreou, A.; Kontou, E.; Katsikosta, N.; Respaldiza, M.A.; Serafin, P.; Sokaras, D.; et al. X-ray Fluorescence analytical criteria to assess the fineness of ancient silver coins: Application on Ptolemaic coinage. *Spectrochim. Acta B Atom. Spect.* **2011**, *66*, 681–690. [[CrossRef](#)]
16. Cruz, J.; Manso, M.; Corregidor, V.; Silva, R.J.C.; Figueiredo, E.; Carvalho, M.L.; Alves, L.C. Surface analysis of corroded XV–XVI century copper coins by μ -XRF and μ -PIXE/ μ -EBS self-consistent analysis. *Mat. Charact.* **2020**, *161*, 110170. [[CrossRef](#)]
17. Buccolieri, A.; Buccolieri, G.; Filippo, E.; Manno, D.; Sarcinelli, G.; Siciliano, A.; Vitale, R.; Serra, A. Nondestructive Analysis of Silver Coins Minted in Taras (South Italy) between the V and the III Centuries BC. *J. Arch.* **2014**, *171243*, 12. [[CrossRef](#)]
18. Klockenkämper, R.; Bubert, H.; Hasler, K. Detection of near-surface silver enrichment on Roman Imperial silver coins by X-ray spectral analysis. *Archaeometry* **1999**, *41*, 311–320. [[CrossRef](#)]
19. Borges, R.; Alves, L.; Silva, R.J.C.; Araújo, M.F.; Candeias, A.; Corregidor, V.; Valério, P.; Barrulas, P. Investigation of surface silver enrichment in ancient high silver alloys by PIXE, EDXRF, LA-ICP-MS and SEM-EDS. *Microchem. J.* **2017**, *131*, 103–111. [[CrossRef](#)]
20. Romano, F.P.; Garraffo, S.; Pappalardo, L.; Rizzo, F. In situ investigation of the surface silvering of late Roman coins by combined use of high energy broad-beam and low energy micro-beam X-ray fluorescence techniques. *Spectrochim. Acta B Atom. Spectr.* **2012**, *73*, 13–19. [[CrossRef](#)]
21. Pronti, L.; Felici, A.C.; Alesiani, M.; Tarquini, O.; Bracciale, M.P.; Santarelli, M.L.; Pardini, G.; Piacentini, M. Characterisation of corrosion layers formed under burial environment of copper-based Greek and Roman coins from Pompeii. *App. Phys. A* **2015**, *121*, 59–68. [[CrossRef](#)]
22. del Hoyo-Meléndez, J.M.; Świt, P.; Matosz, M.; Woźniak, M.; Klisińska-Kopacz, A.; Bratasz, Ł. Micro-XRF analysis of silver coins from medieval Poland. *Nucl. Instr. Meth. Phys. Res. B* **2015**, *349*, 6–16. [[CrossRef](#)]
23. Davenport, W.G.; King, M.; Schlesinger, M.E.; Biswas, A.K. *Extractive Metallurgy of Copper*; Elsevier: Amsterdam, The Netherlands, 2002.
24. Canovaro, C.; Calliari, I.; Asolati, M.; Grazzi, F.; Scherillo, A. Characterization of bronze Roman coins of the fifth century called nummi through different analytical techniques. *App. Phys. A* **2013**, *113*, 1019–1028. [[CrossRef](#)]
25. Davis, G.; Gore, D.B.; Sheedy, K.A.; Albarède, F. Separating silver sources of Archaic Athenian coinage by comprehensive compositional analyses. *J. Archae. Sci.* **2020**, *114*, 105068. [[CrossRef](#)]
26. Martorelli, D.; Bortolotti, M.; Lutterotti, L.; Pepponi, G.; Gialanella, S. Characterization of the mistura alloy used for Venetian sesino coins: 16th century. *X-ray Spect.* **2019**, *48*, 8–20. [[CrossRef](#)]

27. Darling, A.S.; Healy, J.F. Micro-probe Analysis and the Study of Greek Gold–Silver–Copper Alloys. *Nature* **1971**, *231*, 443–444. [[CrossRef](#)]
28. Birch, T.; Kemmers, F.; Klein, S.; Seitz, H.; Höfer, H. Silver for the Greek colonies: Issues, analysis and preliminary results from a large-scale coin sampling project. *Metal. Numis.* **2020**, *6*, 101–148.
29. Sheedy, K.A.; Blet-Lemarquand, M.; Weisser, B.; Gore, D. Elemental Composition of Gold and Silver Coins of Siphnos. *Metal. Numis.* **2020**, *6*, 149–164.
30. Vitale, R.; Brocchieri, J.; Sabbarese, C. Gli incusi della Collezione Numismatica del Museo Campano: Presentazione preliminare. *AIIN* **2018**, *64*, 33–75.
31. Salvemini, F.; Sheedy, K.; Olsen, S.R.; Avdeev, M.; Davis, J.; Luzin, V. A multi-technique investigation of the incuse coinage of Magna Graecia. *J. Arch. Sci. Rep.* **2018**, *20*, 748–755. [[CrossRef](#)]
32. Brocchieri, J.; Vitale, R.; Sabbarese, C. MA-XRF analysis of ancient silver coins minted in southern Italy. *X-Ray Spectr.* **2023**, 1–12. [[CrossRef](#)]
33. Bozzini, B.; Giovannelli, G.; Mele, C.; Brunella, F.; Goidanich, S.; Pedferri, P. An investigation into the corrosion of Ag coins from the Greek colonies of Southern Italy. Part I: An in situ FT-IR and ERS investigation of the behaviour of Ag in contact with aqueous solutions containing 4-cyanopyridine. *Corros. Sci.* **2006**, *48*, 193–208. [[CrossRef](#)]
34. Linke, R.; Schreiner, M.; Demortier, G.; Alram, M. Determination of the provenance of medieval silver coins: Potential and limitations of x-ray analysis using photons, electrons or protons. *X-Ray Spectr.* **2003**, *32*, 373–380. [[CrossRef](#)]
35. Linke, R.; Schreiner, M. Energy dispersive X-ray fluorescence analysis and X-ray microanalysis of medieval silver coins. *Microchim. Acta* **2000**, *133*, 165–170. [[CrossRef](#)]
36. Beck, L.; Bosonnet, S.; Réveillon, S.; Eliot, D.; Pilon, F.J.N.I. Silver surface enrichment of silver–copper alloys: A limitation for the analysis of ancient silver coins by surface techniques. *Nucl. Instr. Meth. Phys. Res. B* **2004**, *226*, 153–162. [[CrossRef](#)]
37. Cesareo, R.; Bustamante, A.; Azeredo, S.; Lopes, R.T.; Franco, R.J.; Fernandez, A. Analytical studies on pre-Columbian gold and silver from the North of Peru. *Rend. Lincei Sci. Fis. Nat.* **2020**, *31*, 473–484. [[CrossRef](#)]
38. Cesareo, R.; Buccolieri, G.; Castellano, A.; Lopes, R.T.; De Assis, J.T.; Ridolfi, S.; Brunetti, A.; Bustamante, A. The structure of two-layered objects reconstructed using EDXRF-analysis and internal X-ray ratios. *X-Ray Spectr.* **2015**, *44*, 233–238. [[CrossRef](#)]
39. Bolewski, A.; Matosz, M.; Pohorecki, W.; del Hoyo-Meléndez, J.M. Comparison of neutron activation analysis (NAA) and energy dispersive X-ray fluorescence (XRF) spectrometry for the non-destructive analysis of coins minted under the early Piast dynasty. *Rad. Phys. Chem.* **2020**, *171*, 108699. [[CrossRef](#)]
40. Cesareo, R.; Rizzutto, M.A.; Brunetti, A.; Rao, D.V. Metal location and thickness in a multilayered sheet by measuring $K\alpha/K\beta$, $L\alpha/L\beta$ and $L\alpha/L\gamma$ X-ray ratios. *Nucl. Instr. Meth. Phys. Res. B* **2009**, *267*, 2890–2896. [[CrossRef](#)]
41. Hložek, M.; Trojek, T. Silver and tin plating as medieval techniques of producing counterfeit coins and their identification by means of micro-XRF. *Rad. Phys. Chem.* **2017**, *137*, 234–237. [[CrossRef](#)]
42. Mele, A. Crotona greca negli ultimi due secoli della sua storia. In *Crotona e la sua Storia tra IV e III Secolo a. C.*; Università degli Studi di Napoli Federico II, Dipartimento di Discipline Storiche, Centro studi per la Magna Grecia: Naples, Italy, 1993; pp. 235–291.
43. Mele, A. Atene e la Magna Grecia. Atene e l’Occidente. I grandi temi. Le premesse, i protagonisti, le forme della comunicazione e dell’interazione, i modi dell’intervento ateniese in Occidente. In *Proceedings of the Atti del Convegno Internazionale, Athens, Greece, 25–27 May 2006*; Emanuele Greco e Mario Lombardo, Ed.; pp. 239–267.
44. Rutter, N.K. *Historia Numorum. Italy*; The British Museum: London, UK, 2001.
45. Stazio, A. La monetazione argentea di Crotona nel IV–III sec. a.C. *Crotona E La Sua Stor. Tra IV E III Secolo a.C* **1993**, 103–109.
46. Parise, N.F. Era Lacinia in Campania. I limiti della documentazione numismatica. In *Proceedings of the culti della Campania antica, Atti del Convegno Internazionale di Studi in ricordo di Nazarena Valenza Mele, Napoli, Italy, 15–17 May 1995*; pp. 89–96.
47. Johnston, A. *The Coinage of Metapontum*; Pt. 3; (NNM 164); The American Numismatic Society: New York, NY, USA, 1990.
48. Rutter, N.K. *Campanian Coinages*; Amazon: Edinburgh, UK, 1979.
49. AA VV. Alessandro il Molosso e i “Condottieri” in Magna Grecia. In *Proceedings of the Atti del XLIII Convegno di studi sulla Magna Grecia, Taranto–Cosenza, Italy, 26–30 September 2003*; Istituto per la Storia e l’Archeologia della Magna Grecia–Taranto: Taranto, Italy, 2004.
50. Mele, A. Alessandro il Molosso e le città greche d’Italia. In *Alessandro il Molosso e i “Condottieri” in Magna Grecia*; Giorgio Bretschneider Editore: Roma, Italy, 2004; pp. 283–320.
51. Taliercio Mensitieri, M. La documentazione numismatica. In *Alessandro il Molosso e i “Condottieri” in Magna Grecia*; Giorgio Bretschneider Editore: Roma, Italy, 1998; pp. 401–435.
52. Van Keuren, F. *The Coinage of Heraclea Lucaniae*; Giorgio Bretschneider Editore: Roma, Italy, 1994.
53. Sambon, A. Les monnaies antiques de l’Italie. Tome Premier. In *Étrurie–Ombrie–Picenum–Samnium–Campanie (Cumes et Naples)*; Giorgio Bretschneider Editore: Roma, Italy, 1903.
54. Cantilena, R. La monetazione di un centro campano alleato di Roma. Riflessioni su Teanum. In *Atti del XII Congresso Internazionale di Numismatica*; Springer: Berlin, Germany, 2000; pp. 28–37.
55. Taliercio Mensitieri, M. Le emissioni romano-campane di bronzo. La monetazione romano-campana. In *Proceedings of the Atti del X Convegno del Centro Internazionale di Studi Numismatici, Napoli, Italy, 18–19 June 1993*; pp. 49–140.
56. Pantuliano, S. La monetazione della colonia latina di Cales. In *Atti del XIII Congresso Internazionale di Numismatica*; Ministerio de Cultura: Madrid, Spain, 2005; pp. 357–365.

57. Vitale, R. La monetazione di Suessa: Alcuni dati ed interpretazioni. In *La Monetazione di Suessa, X*; Fabrizio Serra Editore Pisa: Roma, Italy, 2009; pp. 1000–1039.
58. Crawford, M.H. *Coinage and Money under the Roman Republic: Italy and the Mediterranean Economy*; University of California Press: Berkeley, CA, USA, 1985; Volume 3.
59. Burnett, A.M. Reflections on the San Martino in Pensilis hoard. *Rev. Numis.* **2006**, *6*, 37–50. [[CrossRef](#)]
60. Renda, V.; Nardo, V.M.; Anastasio, G.; Caponetti, E.; Vasi, C.S.; Saladino, M.L.; Armetta, F.; Trusso, S.; Ponterio, R.C. A multivariate statistical approach of X-ray fluorescence characterization of a large collection of reverse glass paintings. *Spectroch. Act. B Atom. Spectr.* **2019**, *159*, 105655. [[CrossRef](#)]
61. Rácz, A.; Héberger, K.; Rajkó, R.; Elek, J. Classification of Hungarian medieval silver coins using x-ray fluorescent spectroscopy and multivariate data analysis. *Herit. Sci.* **2013**, *1*, 1–9. [[CrossRef](#)]
62. Odelli, E.; Palleschi, V.; Legnaioli, S.; Cantini, F.; Raneri, S. Graph clustering and portable X-Ray Fluorescence: An application for in situ, fast and preliminary classification of transport amphoras. *Spectroch. Act. B Atom. Spectr.* **2020**, *172*, 105966. [[CrossRef](#)]
63. Brocchieri, J.; Scialla, E.; Manzone, A.; Graziano, G.O.; D’onofrio, A.; Sabbarese, C. The gilding technique on lead objects of the Royal Palace of Caserta (Italy) studied using XRF analysis. *MAA* **2021**, *22*, 29–43. [[CrossRef](#)]
64. Brocchieri, J.; Scialla, E.; Manzone, A.; Graziano, G.O.; Sabbarese, C. Gouache gilding on lead and wood objects studied by multivariate and graph analyses applied to XRF spectra. *J. Archae. Sci. Rep.* **2022**, *42*, 103382. [[CrossRef](#)]
65. Hrnjić, M.; Hagen-Peter, G.A.; Birch, T.; Barfod, G.H.; Sindbæk, S.M.; Leshner, C.E. Non-destructive identification of surface enrichment and trace element fractionation in ancient silver coins. *Nucl. Instr. Meth. Phys. Res. B* **2020**, *478*, 11–20. [[CrossRef](#)]
66. Solé, V.A.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J.A. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. *Spectroch. Act. B Atom. Spectr.* **2007**, *62*, 63–68. [[CrossRef](#)]
67. Heginbotham, A.; Solé, V. ACHARMed PyMca, Part I: A Protocol for Improved Inter-laboratory Reproducibility in the Quantitative ED-XRF Analysis of Copper Alloys. *Archaeometry* **2017**, *59*, 714–730. [[CrossRef](#)]
68. Brocchieri, J.; Scialla, E.; Sabbarese, C. Estimation of Ag coating thickness by different methods using a handheld XRF instrument. *Nucl. Instr. Meth. Phys. Res. B* **2021**, *486*, 73–84. [[CrossRef](#)]
69. Brocchieri, J.; Scialla, E.; Ambrosino, F.; Terrasi, F.; Sabbarese, C. Ag X-ray fluorescence on different thickness and concentration layers. *Il Nuovo C. C* **2018**, *41*, 1–8.
70. Reale, R.; Plattner, S.H.; Guida, G.; Sammartino, M.P.; Visco, G. Ancient coins: Cluster analysis applied to find a correlation between corrosion process and burial soil characteristics. *Chem. Cent. J.* **2012**, *6*, 1–9. [[CrossRef](#)] [[PubMed](#)]
71. Shreir, L.L.; Jarman, R.A.; Burstein, G.T. *Corrosion*, 3rd ed.; Butterworth-Heinemann: Woburn, MA, USA, 1994; Volume 1—Metal/Environment Reactions.
72. Mackerrel, H.; Stevenson, R.B. Some analysis of anglo-saxon associated oriental silver coinage. In Proceedings of the Methods of Chemical and Metallurgical Investigation of Ancient Coinage—A Symposium Held by the Royal Numismatic Society in London, London, UK, 9–11 December 1970; pp. 195–209.
73. Grifoni, E.; Legnaioli, S.; Lorenzetti, G.; Pagnotta, S.; Palleschi, V. Application of Graph Theory to unsupervised classification of materials by Laser-Induced Breakdown Spectroscopy. *Spectroch. Act. B Atom. Spectr.* **2016**, *118*, 40–44. [[CrossRef](#)]
74. Spagnoli, E. *La Prima Moneta in Magna Grecia: Il Caso di Sibari*; Diogene Edizioni: Pomigliano d’Arco (Na), Italy, 2013.
75. Manno, D.; Serra, A.; Micocci, G.; Famà, L.; Filippo, E.; Siciliano, A.; Vitale, R.; Sarcinelli, G.; Calcagnile, L.; Quarta, G.; et al. Tecniche di indagine morfologiche e microanalitiche nello studio della monetazione di Taranto, in Studi di Antichità. *STUDI DI ANTICHITÀ* **2008**, *12*, 225–238.
76. Vitale, R. “Appendix 1” in Buccolieri, A.; Buccolieri, G.; Filippo, E.; Manno, D.; Sarcinelli, G.; Siciliano, A.; Vitale, R.; Serra, A. Nondestructive analysis of silver coins minted in Taras (South Italy) between the V and the III centuries BC. *J. Archae.* **2014**, *2014*, 171243.

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