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*Review*

# The Distinctive Role of Chemical Composition in Archaeometry. The Case of Apulian Red Figure Pottery

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**Abstract:** Correlation of the scientific approach to the archaeological investigation and vice versa is considered, for at least the past 30 years, as the best strategy to answer questions in cultural heritage. Many archaeological queries have merged archaeological and scientific studies and have been carried out with a multidisciplinary approach that uses complementary analytical techniques. Here, we focused our efforts on outlining the strong relevance of elemental composition in chemistry and mineralogical investigations to answer important archaeological questions in the case of Apulian red figure pottery. This ceramic class is the most important quantitative handcraft production group of figured pottery in Magna Grecia and the most widespread and commercialized production from the third quarter of the fifth century to the end of the next century. The results obtained indicate that, by exploring chemical elements in the ceramic mixture, it is possible to extract information about provenance, manufacturing processes, originality and restoration techniques.

**Keywords:** archaeometry; chemical analyses; multivariate statistical treatments; Apulian red figure pottery

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## 1. Introduction

The great contribution that scientific investigations, when applied to a well-selected and representative sample of finds and conducted according to a correct analytical method, provide to archaeological research is currently well established.

In case of ceramic finds, assessing provenance and technological features has almost always been represented as the main goal of archaeometric investigations.

Most archaeological questions can be solved using a combined mix of analytical techniques that can provide compositional and structural data about bulk and surfaces. For instance, the quantification of pottery pastes, followed by an appropriate data mining process, allows to trace the provenance [1–4] of the finds and/or of the raw materials, but also to disclose differences in the manufacturing process [5–11], to support an archeological classification [12–15], and to realize whether or not an attribution can be made [16,17].

The data mining used in the first archaeometric investigations involved scatter plots related to selected pairs of chemical elements or their combinations to extract the archeological information contained in the data set. Consequently, any type of information related to other measured variables was excluded. Over time, several multivariate statistical methods were used [18–21]. These techniques allow us to consider at the same time the contribution of a greater number of variables and possibly their synergistic effect, removing the spurious information and highlighting useful information. Among these, linear principal component analysis (PCA) and clustering analysis (CA and HCA) continue to be the widely used.

The actual origin of objects can be assessed comparing their chemical compositional data with reliable indicators of production (kiln dumps, wasters, etc.). However, if objects of a known provenance are not available, it is possible to hypothesize the origin of the finds through the compositional similarity of a statistically representative set of items, while directly correlating the provenance of the finds to the provenance of the clay alone is not immediate because the complexity of the manufacturing process used (possible mixing of clays with different mineralogical and chemical characteristics, intentional addition of tempers of various types and origins (grog, sand, etc.), firing, painting, glazing). It should also be considered the question of accessory minerals, often indicators of different clayey sedimentary basins, but those presence, because of the limited amount, does not influence the major elements chemical composition. However, their identification and the identification of their accurate composition allow us to recognize or to exclude the use of a given sedimentary deposit.

The chemical compositional analysis is not sufficient to fully clarify the manufacturing processes employed, which should always be supported by the identification of the mineralogical composition of pastes. In this respect, the determination of the maximum firing temperature, the duration of firing and the kiln atmosphere can be reconstructed through the identification of some newly formed phases related to firing [22–26]. Chemical and mineralogical data on ceramic pastes and coatings are also essential in restoration and forensic fields to recognize not recorded restoration action or forged vases (or part of them).

In this paper, the focus is on the Apulian (Southern Italy) red figure pottery (Figure 1) with the aim to integrate the data we obtained on finds from specific sites [8,11,27–32] into a more cohesive picture. Sections are assembled according to the type of information provided.


**Figure 1.** Apulian red figure samples analyzed coming from Arpi (**a**–**e**) and Taranto (**f**,**g**).

### 1.1. Archaeological Background

Apulian red figure pottery is the southern Italy variant of the renowned Attic production. In both cases, figures on the vase were obtained saving the ceramic body from the black glossy background, occasionally some accessory colors (white, yellow, brow, etc.) were present.

The production of Apulian red figure pottery took place in Apulia from the third quarter of the fifth century BCE to the end of the next century (three periods are formally recognized: Early (440–370 BCE), Middle (from 370 to 340–330 BCE) and Late Apulian (340–300 BCE)) [33–35]. As far as concerns red figure pottery produced in Magna Graecia, Apulian red figure pottery is the most numerically significant group, which was most widespread and available on the market. Its production also required great production skills and is of great quality.

The traditionally accepted date for the beginning of this type of manufacture is 440 BCE. Between 450 and 300 BCE a transitory transfer of skilled craftsmen and artists occurred from Taras (Taranto) to the wealthiest Apulian villages, so that these centres became branches of production outside the main polis (city).

The organization of production in workshops was complex and well planned. Production increased throughout the fourth century BCE, but mainly in the Late period, when iconographically and formally excellent handcraft pieces coexisted with low quality, mass production pieces. The Middle and Late periods are the most fascinating to be studied because a greater number of unsolved questions can be found [36].

Apulian red figure pottery has been extensively investigated by archaeologists and numerous studies are available in the literature (please refer to them for more detailed stylistic-typological information). Scientific papers are few, mainly dealing with Attic production and aimed at understanding the specific characteristics of each individual step in the overall production cycle, with particular attention being paid to the technique utilized to make black gloss, and they are fragmented into different investigation sectors [37–70]. A more limited number of papers have focused on Attic overpainting colors [47,58–62,67,71,72], especially white, yellow and red.

Fewer studies are available on pottery production in Magna Graecia and in Puglia particularly. Most part of them are devoted to assessing the provenance of finds [14,64,73–79] and fewer to identify technological features [8,11,28–32,36,56,78,80–84]. Often the items investigated were museum objects or seized material examined to verify their authenticity [27,85,86].

Although the Apulian red figure class has not been studied as thoroughly as Attic pottery, the picture emerging from archaeometric investigations is of great interest.

### *1.2. Analytical Methods and Multivariate Statistical Treatments*

Archaeological sampling surely represents a compromise between the safeguard of the priceless artworks under investigation and the requirement to obtain a representative sample for chemical and mineralogical analyses. In case of bulk analysis, we scrape off bulk ceramic powders from objects already fragmented or from hidden areas from inside or under the base of the vases, after eliminating the outermost external contaminated layer and without damaging the aesthetic of the object. Aliquots of about 60 mg of bulk ceramics [87] are then weighted and dissolved by acid digestion. The chemical dissolution of the ceramic bodies is carried out according to the procedure described in references [8,9]. Fragments, on the other hand, were sampled by collecting a few square millimeters wide shards from their edges. In addition to chemical investigations, we also perform minero-petrographic analyses to acquire info about technological production, possible integrations, etc.

Typically, bulk analyses to define the elemental chemical composition of ceramic bodies of this ceramic class are performed by atomic spectroscopies (AAS, ICP-OES, ICP-MS), X-ray fluorescence spectroscopy (XRF), laser ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). Compositional data (major, minor and traces elements) are generally treated by multivariate statistical treatments to find clusters distinguishable for provenance, manufacturing process and archaeological class.

Optical microscopy (OM), scanning electron microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) or Wavelength Dispersive X-ray Spectroscopy (SEM-WDS) and X-ray diffraction (XRD) are usually utilized to define the ceramic bodies mineralogical composition.

The multivariate statistical treatments proposed in this paper are NLPCA (nonlinear principal component analysis) and DA (discriminant analysis). NLPCA and DA are techniques based on the transformation of the original data [75,88]. NLPCA ignores class labels and finds directions of maximal variance and is used as an exploratory approach. DA gives a classification model, knowing a priori the classes in which the data set is divided, and attempts to find a feature subspace that maximizes class separability.

PCA graphic takes place plotting the score and loading vectors of the different parameters in the subplane of the first two or three principal components. However, the application of PCA to characterize data showed severe limitations because of its linear feature [75]. In this case, a nonlinear generalization of standard PCA by replacing linear surfaces with curved ones can be the right answer.

In this work, we consider hierarchical NLPCA based on Auto-Associative Neural network models. This method was already successfully tested on some Apulian red figure pottery [75]. To evaluate how good the model fits the data, two fitting parameters are considered: $R^2$ and the Lack of Fit (Lof). The Lof is the square root of the ratio between the sum of square of residuals and the total variance of the original dataset. The $R^2$ is the complement to 1 of the Lof square. The statistic $R^2$ is the fraction of variance explained by the analysis. The best model fitting of the experimental data is achieved when $R^2$ is closer to 1 and/or Lof to zero. When the noise is low, Lof provides more discrimination between models, otherwise when there is a larger noise contribution $R^2$ is preferred.

DA is a classification approach taking part of supervised techniques [88], less used in the archaeometric field, to discriminate samples based on different provenances [89,90] and styles [91]. It finds those directions that maximize the ratio between the between-class variance and the within-class. If the classes are separated by hyper-planes, the DA is linear (LDA), otherwise if the boundaries of the class are quadratic the method is named quadratic discriminant analysis (QDA). The validation of the model is carried out by cross validation (CV). All quality parameters, that describe the goodness of a model, are obtained from the confusion matrix (CF) -a square matrix of GxG dimension, where G is the number of classes-. The diagonal elements are the objects correctly classified; the off-diagonals are the wrongly classified ones. The non-error rate (NER) represents the percentage of elements correctly classified and it is the ratio between the diagonal element and the total number of objects. Data processing was performing by the R V3.3.3 software (R Core Team, Vienna, Austria) with the packages "MASS" [92] and "pcaMethods" [93].

## 2. Archaeological Questions/Archaeometric Answers

### *2.1. Authenticity: Original Versus Fake*

Research objectives can be addressed to:

(a) checking the nonauthenticity of a find or some parts of it, that could have been integrated during restoration (eventually, understanding where and when the integration was added); establishing the belonging of sporadic fragments to a single vase, when it is not possible based on well-known restoration procedures;

(b) identify undocumented repainting on the surface of the vases. As a matter of fact, understanding if the surface of the vase is original is essential if you want to use nondestructive techniques, that inevitably analyze the more superficial layers.

The above-mentioned aims are particularly important for this ceramic class, especially considering the high attention, since the end of the nineteenth century, museums and collectors have paid to it. This interest has led to an increase in excavations and sales of vases, making tomb robbing a business of colossal dimensions. Many objects have been sold on the domestic and international black markets, an illegal trade which is today worth over four billion dollars a year [94,95]. To put this into perspective, only the black-market trade in arms and drugs involve a higher turnover. Vases were often broken into small pieces to transport them more conveniently and then put back together without any kind of care for ancient and technological process. Sometimes, fragments were assembled from different vases or integrating the missing parts with parts specifically produced to increase the commercial value of the object. In this way, particularly in the case of artifacts excavated in more ancient times, important information such as the origin of the object and the context of excavation have been lost. Some vases acquired in the past, even by famous museums, have sometimes been assembled with original and nonoriginal pieces [96].

Some examples of information that can be obtained by archaeometric investigations to achieve the abovementioned objectives are reported below.

(a) Case study. Fragments: nonauthenticity or common origin.

Two important Apulian red figure vases (a krater and a loutrophoros) stored in the National Archaeological Museum of Naples (MANN) were investigated [27]. Both items were acquired from private collectors of Ruvo di Puglia in the nineteenth century and were subjected, through the ages, to several unrecorded restorations (the first ones probably carried out before the vases arrived at the MANN). The krater called dell'Amazzonomachia was attributed to Dario Painter (about 330 BCE) and the loutrophoros with the myth of Niobe to Varrese Painter (about 350–340 BCE). Doubts before archaeometric analyzes were focused exclusively on authenticity of a handle of the krater and both handles of the loutrophoros.

The archaeometric results have allowed to assess the nonauthenticity of the krater handle and the whole upper part of the loutrophoros (in addition to the handles).

Experimental results have supported the use of different raw materials for the body and the handle of the krater and body and the whole superior part of the loutrophoros—handles included. These hypotheses were based on differences in chemical (Table 1) and mineralogical composition of the pastes (silty-grain size and sintering degrees) and crystals shapes—especially quartz (Figure 2).

**Table 1.** Composition by ICP-MS of the ceramic bodies collected from the krater, the *cercine* and the loutrophoros.

| Sample | Fe | Al | Mg | K | Ti | Na | Ca | Mn | Pb | Ni | Sr | Cr | Ba | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (% *w*/*w*) | | | | | | | (ppm) | | | | | | |
| Krater basin | 5.17 | 9.96 | 1.48 | 2.38 | 0.55 | 0.72 | 6.70 | 959 | 192 | 78 | 316 | 131 | 407 | 131 |
| Krater handle | 2.96 | 9.24 | 0.55 | 2.56 | 0.32 | 0.62 | 7.55 | 865 | 1256 | 28 | 123 | 51 | 364 | 43 |
| *Cercine* | 4.20 | 10.89 | 1.93 | 2.57 | 0.43 | 0.74 | 7.89 | 740 | 811 | 63 | 386 | 141 | 295 | 99 |
| Loutrophoros foot | 5.01 | 8.99 | 1.37 | 2.26 | 0.51 | 0.54 | 6.99 | 1267 | 57 | 68 | 280 | 102 | 350 | 119 |
| Loutrophoros basin | 5.04 | 8.89 | 1.39 | 2.26 | 0.51 | 0.51 | 6.54 | 1126 | 34 | 88 | 310 | 133 | 388 | 117 |
| Loutrophoros neck | 3.91 | 5.70 | 1.66 | 1.87 | 0.33 | 1.91 | 11.41 | 658 | 183 | 142 | 745 | 343 | 328 | 137 |
| Loutrophoros neck edge | 3.90 | 7.09 | 1.85 | 2.15 | 0.38 | 0.60 | 8.92 | 956 | 10,869 | 70 | 456 | 103 | 422 | 164 |

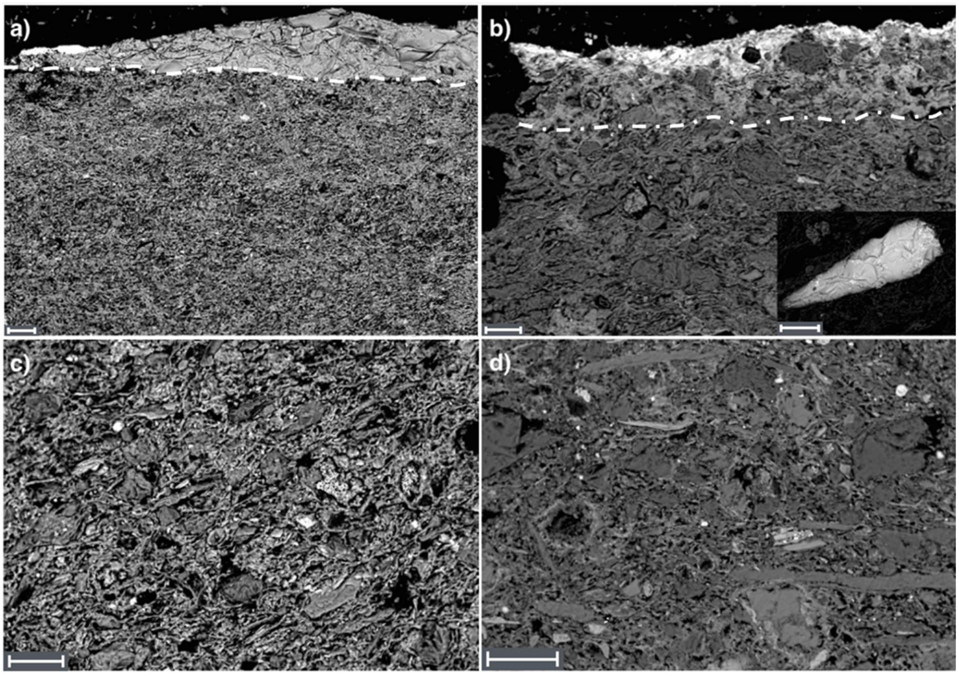



**Figure 2.** SEM-BSE photomicrographs of thin sections of the ceramic body of the krater dell'Amazzonomachia: basin (**a**), handle (**b**) (Inset: crystal of lead silicate inside the paste.), the *cercine* (**c**) and the neck of Loutrophoros (**d**). Scale 30 micron. Dashed lines separate the ceramic body and the surface decoration: the traditional black gloss and the repaintings on it (brighter) (**a**), the layer based on Pb newly formed silicates, Mn and Sn simulating the traditional black gloss (upper) (**b**).

In the mixture of the handle of the krater, numerous crystals of lead silicates—inevitably linked to the raw material used to create the surfaces of the nonauthentic pieces—have been observed (Figure 2). Moreover, the similarity of the material used (Figure 2c) for the cercine (the ceramic support used to transport the vase and therefore reasonably made in the same place where the object was found) and for the handle of the krater support the hypothesis regarding the addition of the krater handle after its recovery and suggests that this restyling was carried out in Ruvo (where the krater came from) and not, after the purchase, in Naples.

Although the nonauthenticity of the neck of the loutrophoros had not been highlighted by autoptic examinations, it was suggested by restorers during the dismantle phase of parts [97], which observed the lack of congruence in shape between the neck and the body. It must, therefore, be assumed that this part has been made in modern times (nineteenth century BCE) and added during restoration. As a matter of fact, a joint band between the neck and body was added to fix the shape inconsistence. The camouflage was completed thanks to a decoration seamless between the figurative scenes, observable in the first photographs, and later succeed by an achromatic integration, as shown in the more recent images. Both handles of the loutrophoros, as it had already been assumed during the first restorations, were not authentic and were made with a paste based on glue and plaster. Although the black surfaces of the nonauthentic parts, for both vases, are lead-based, the diversity in the materials mixed to lead in the two cases could indicate a manufacturing in different workshops.

An example of determining the common origin of sporadic fragments to a single find is hereafter illustrated.

The fragments analyzed come from the residual edges of a tomb filling, which underwent a clandestine excavation in the past and recently it was excavated by the Commission for the Architectural and Landscape Heritage for the Provinces of Barletta-Andria-Trani and Foggia (Puglia, Southern Italy). Independent investigative activities related to criminal affairs had led to the seizure by the Guardia di Finanza of Foggia of a group of highly artistic and manufactured Apulian red figure vases, dating back to the fourth to third century BCE, in excellent state of conservation. Since during the excavation, ceramic fragments similar based on archaeological studies with the seized finds were found, archaeometric analyzes were carried out to verify their relevance to the same context. Results pointed out strong chemical, shown in Figure 3, and mineral-petrographic similarities among seized vases and fragments recovered from the tomb, made it possible to verify the relevance of a large part of seized vases to the tomb complex under investigation.

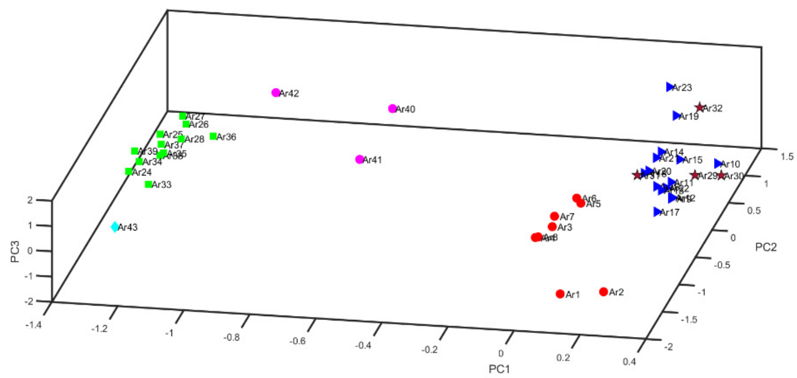



**Figure 3.** Scores plot (PC1, PC2, and PC3) of the NLPCA model for samples from Arpi (blue triangles and magenta circles: vases seized by the Guardia di Finanza of Foggia, red stars edged in black: sporadic fragments from ONC28 tomb of Arpi, green squares: vases from tomb of Niobids, red circles: vases from Tomba 5/2005, cyan diamond: vase from Tomba 4/2005). The fitting values obtained are 0.84 and 0.40 for $R^2$ and Lof, respectively. The parameter $R^2$ is closer to 1 than Lof to zero, confirming a high noise contribution.

(b) Case study. Surfaces: undocumented repainting.

Reintegration examples involving Apulian red-figure vases are numerous and almost never documented.

Most common materials used in most ancient restorations are based on Pb, added with Ba, sometimes Sb, Sn and C (Figure 4a,b) [27,28] to obtain the black coloring of the surfaces and with Hg sometimes added with Sn to paint the red ones [98].

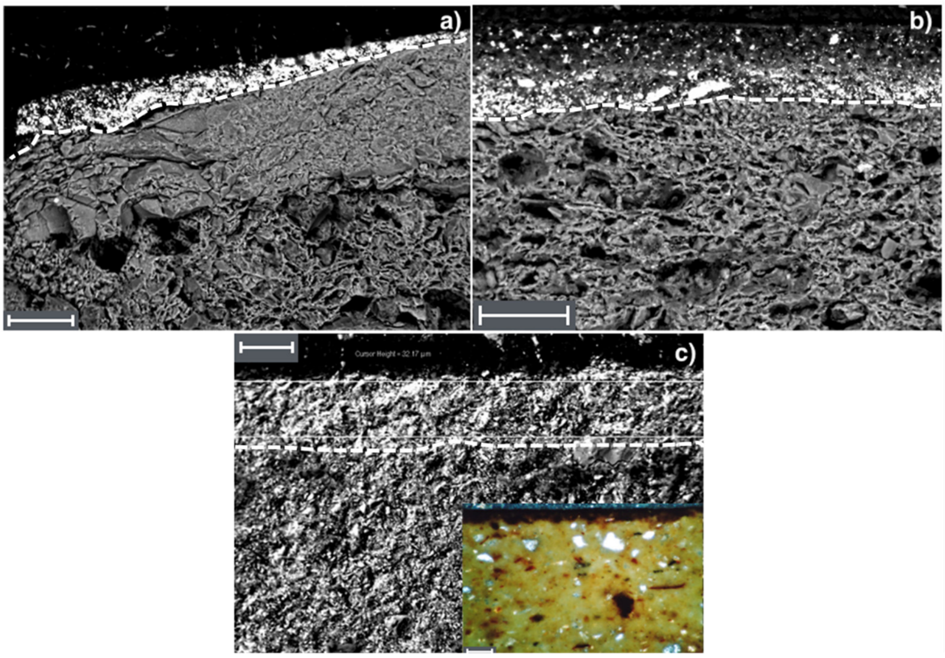



**Figure 4.** SEM-BSE photomicrograph of thin sections of samples of Caputi-Intesa Sanpaolo Collection [28] (**a**,**b**) and tomb of Niobids (**c**, inset: OM image of the same area.). Dashed lines highlight the repaintings on the black gloss (**a**), on the ceramic body (**b**) and a layer applied instead of the traditional black (**c**). Layers are based on: (**a**) Pb (small grains) and Sr+ Ba (large grains) in organic matrix, (**b**) upper layer: Pb (large grains) and Ba (small grains) in organic matrix and lower layer: Pb (large grains) and Pb + Sb (small grains) in organic matrix; (**c**) Mn and Fe. Scale 30 micron. Inset scale 85 micron.

Repainting based on Mn and Fe was highlighted on the black surface of vases of the tomb of the Niobids (Arpi, Foggia) (Figure 4c) [98] and are attributable to a more recent restoration (around 1960).

It is noteworthy to mention that any restoration action, even if merely performed on the surface of the find, can lead to the contamination of the original material of the underlying ceramic body, characterized by a non-negligible porosity, even in its innermost part. This could make chemical analyses to assess the provenance of finds/raw materials worthless. The gluing operations of fragments should be adequately documented because they can lead to a contamination of the ceramic body too. For instance, Figure 5 shows NaCl contamination highlighted in depth in the ceramic body. This is the result of a treatment performed on the surface of a vase from the tomb of the Niobids in Arpi during the restoration.

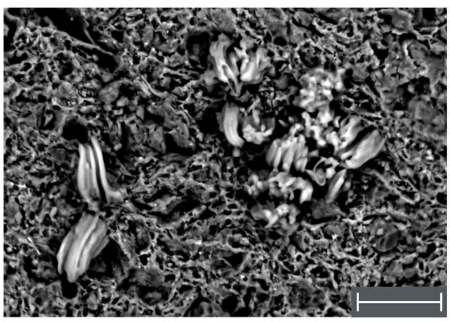


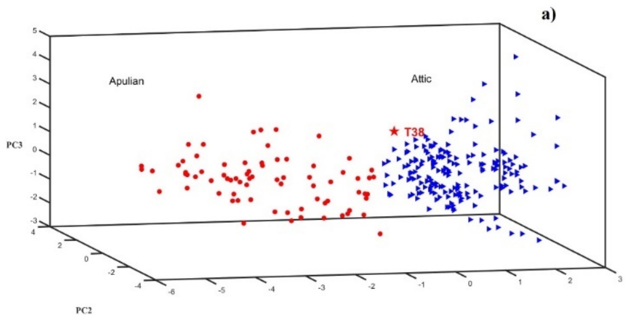
**Figure 5.** SEM-BSE photomicrograph of thin sections of a sample of tomb of Niobids (Arpi) highlighting the contamination of the ceramic body by NaCl. Scale 20 micron.

*2.2. Provenance: Importation Versus Local Production*

As previously said, the aim of this paper is to integrate the data on the Apulian red figure pottery obtained on finds from specific sites into a more cohesive picture.

The chemical data obtained for each archaeological site have been then assembled into a single matrix and analyzed using traditionally (DA) and innovative (NLPCA) multivariate statistical analysis techniques. Preliminary investigations were conducted on the original matrix of 30 chemical elements (Fe, Al, Mg, K, Ti, Na, Ca, Mn, Co, Cu, Pb, Ni, Sr, Cr, Ba, Sn, Zn, Li, V, Zr, Cs, La, Ce, Sn, Tb, Yb, Lu, Eu, Nd, Dy). Statistical technique, based on comparing the means and the variances of the different variables, was applied as a criterion to reject those chemical elements that introduce noise and make more difficult the exploratory analysis and the subsequent classification. Therefore, statistical treatment was performed on a concentration matrix of 11 chemical parameters (Fe, Al, Mg, K, Ti, Na, Ca, Mn, Ni, Sr, Cr).

To clarify if Apulian items were locally produced or imported, a bibliographic research on compositional data of Attic red figure finds has been carried. The statistical treatment comparison to detect similarities and/or differences has been performed regards Attic samples coming from different Greek sites -Atene, Perati, Rafti, Thorikos, Aigina, Megara- [51], whose chemical bulk data have been obtained by applying Atomic Spectroscopy techniques and are thus immediately comparable to our Apulian ones. Common parameters are Fe, Al, Mg, Ti, Na, Ca, Ni, Cr, which unfortunately implies that useful information obtainable by other minor and trace elements contents are missing. Results (Figure 6a) highlight a strong compositional diversity of ceramic bodies of finds from Apulian sites and Greek ones, so making it possible to discriminate between Apulian and Attic production, allowing to identify imported and locally produced objects. For example, it was possible to confirm the importation of a sample (code T38, inventory number 227208), excavated in Taranto which, based on archaeological investigations, was believed to be made in Greece. Its score position, in fact, inside the Attic cluster and far from the Apulian one, shows a greater compositional similarity to the Attic samples than to the Apulian ones.




b)

| | | Predicted (CV) | |
|---|---|---|---|
| | | Apulian | Attic |
| Actual | Apulian | 185 | 1 |
| | Attic | 0 | 76 |
| | NER | 99.62% | |

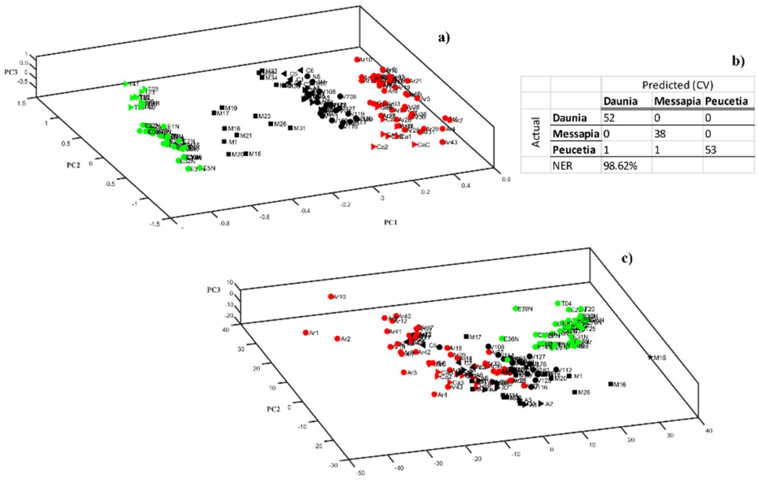
**Figure 6.** (**a**) Scores plot of the NLPCA model related to finds from Apulia (red) and Greece (blue), ($R^2$ 0.89 and Lof 0.34). Sample T38 is marked with a star. (**b**) Confusion matrix and NER value obtained with the application of QDA on data.

The same conclusion can be deduced using a QDA model computed by considering the Attic and Apulian classes a priori. In the table (Figure 6b), the parameters evaluating the quality of the model are summarized. The NER shows that the 99.62% of the total samples are correctly classified. Output analysis highlights that only the sample T38 is classified in another class.

The mineral-petrographic investigations [29], highlighting for T38 a mineralogical composition dissimilar to Apulian samples, strengths the hypothesis of a sample importation.

Excluding samples of suspected imports, all the analyzed Apulian samples have been treated by NLPCA. The results highlight three different clusters that follow the ancient division of Apulia (Peucetia, Messapia and Daunia) (Figure 7a), proving the existence of a polycentric production [99]. The fitting values in the terms of $R^2$ and Lof, 0.96 and 0.19, respectively, indicate that the better model fitting is achieved when at least the first

3 principal components are considered. Compositional data matrix included data relating to finds which historical sources indicate to come from Ruvo di Puglia: the samples of the Caputi-Intesa Sanpaolo collection, kept at Gallerie d'Italia Leoni Montanari [28] in Vicenza (Italy) and the two vases kept at MANN [27]. LDA application shows that the 98.62% of the samples are correctly classified. All 52 Daunian and 38 Messapian samples are recognized to be belonged to the a priori classes. Only 2 of 55 Peucetian samples are classified as Daunian and Messapian ones (Figure 7b). The same dataset was already analyzed by applying the linear PCA. Unsatisfactory values of Lof and $R^2$ (0.54; 0.70) are achieved when the first three PCs are considered. This condition can arise when the nonlinear effects and the contribution of the noise are relevant. The score plot is shown in Figure 7c.




| | | Predicted (CV) | | |
|---|---|---|---|---|
| | | **Daunia** | **Messapia** | **Peucetia** |
| Actual | **Daunia** | 52 | 0 | 0 |
| | **Messapia** | 0 | 38 | 0 |
| | **Peucetia** | 1 | 1 | 53 |
| | NER | 98.62% | | |

**Figure 7.** (**a**) Scores plot (PC1, PC2, and PC3) of the NLPCA model for samples belonging to three different areas of Apulia (Peucetia (black: triangles Conversano, squares Monte Sannace, circles Ruvo di Puglia, diamonds Altamura), Messapia (green: triangles Taranto, circles Egnazia) and Daunia (red: circles Arpi, triangles Canosa). (**b**) Confusion matrix and NER value for the LDA model built considering as priori classes Daunia, Messapia, and Peucetia. (**c**) Scores plot (PC1, PC2, and PC3) of the PCA model. Samples labelled as NLPCA model (**a**).

As concern Taranto finds, the availability of some indicators of production -a probable firing tester [100] and two stick of clayey raw material- coming from a coeval pottery workshop located in Taranto, producing black gloss and plain ware [101] made it possible to confirm the Tarentine manufacture of a group of finds excavated in the town, which on a stylistic basis were attributed to painters considered to be among the major exponents of the local school -Tarporley, Truro, and Hoppin- (Figure 8) [29].

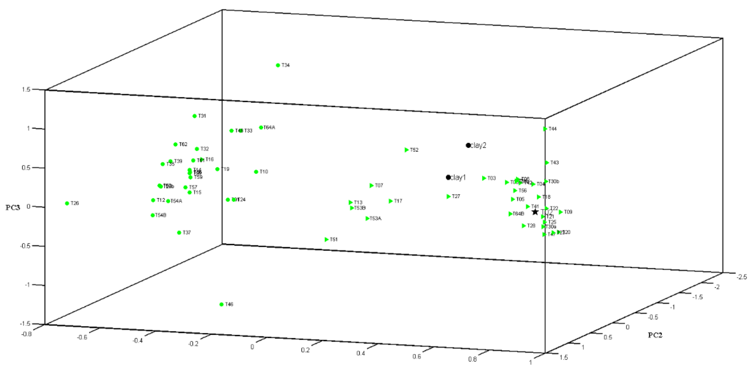



**Figure 8.** NLPCA scores plot related to finds from Taranto. The fitting parameters with 3 PCs are $R^2$ = 0.81 and Lof = 0.43. Taranto finds: green triangles Apulian manufacture, green circles traditional manufactures. Black star: a probable firing tester. Black circles: clayey raw materials from a coeval pottery workshop located in Taranto [100,101].

*2.3. Workshops Location: Painters Transfer Versus Vases Transfer*

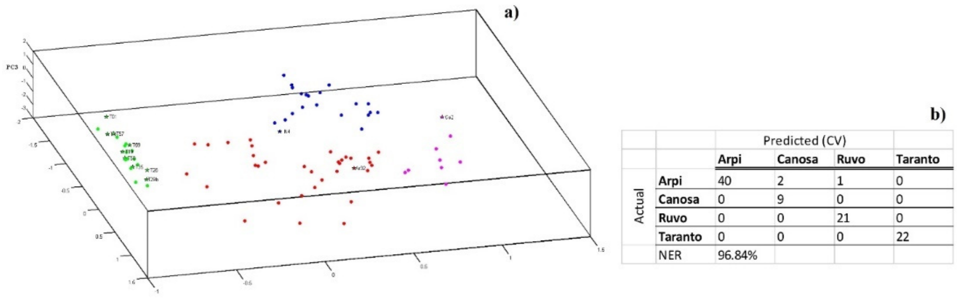
The workshop locations of different painters and the question of whether it was objects or the painters themselves who moved among Apulian sites represent an aspect of considerable relevance in the study of Apulian red figure productions.

A first attempt to answer this question was made by analyzing nine vases stylistically attributed to Dario Painter, excavated in various sites (tomb of Niobids in Arpi [102], hypogeum of Varrese in Canosa [103], military arsenal area at Taranto). The analysis included the krater of the Amazzonomachia supposed coming from Ruvo di Puglia [104], Table 2.

**Table 2.** Apulian red figure vases stylistically attributed to Dario Painter analyzed.

| Code | Inv. n° | Description | Site |
|---|---|---|---|
| Ar2 | 132734 | Oinochoe, Tomb of Niobids | Arpi |
| Ca2 | 8925 | Deinos, Hypogeum of Varrese | Canosa |
| T1 | 51381 | Volute krater with Frisso on the ram | Taranto |
| T19 | 227162 | Pelike with quadriga | Taranto |
| T26 | 227196 | Krater with Athena's head | Taranto |
| T29 | 227199 | Krater with quadriga driven by a Nike with standing | Taranto |
| T35 | 227205 | Fragment with seated Athena leaning on her shield | Taranto |
| T36 | 227206 | Fragment with body of a paniskos holding a flute in his right hand | Taranto |
| N4 | 81667 | Krater of the Amazzonomachia | Ruvo di Puglia |

The NLPCA model was built with 5 PCs with a $R^2$ of 0.92 and a Lof of 0.29. A good fitting is graphically seen with 3 PCs ($R^2$ of 0.83). The results of the treatment of data by NLPCA are shown in Figure 9, illustrating the scores plotted on to the first three principal components subspace. Markedly distinct groups can be identified. The classification model created with a LDA shows a NER of 96.84%. Almost all samples are assigned to the a priori classes. It was not possible to build a QDA model due to the low number of the Canosa samples in the dataset.




| | | Predicted (CV) | | | |
|---|---|---|---|---|---|
| | | Arpi | Canosa | Ruvo | Taranto |
| Actual | Arpi | 40 | 2 | 1 | 0 |
| | Canosa | 0 | 9 | 0 | 0 |
| | Ruvo | 0 | 0 | 21 | 0 |
| | Taranto | 0 | 0 | 0 | 22 |
| | NER | 96.84% | | | |

**Figure 9.** (**a**) NLPCA scores plot for the first three PCs related to the finds from Arpi (red), Canosa (magenta), Taranto (green), and Ruvo (blue). The $R^2$ and Lof of the model with 3 PCs were 0.83 and 0.41, respectively. The samples attributed to Dario' painter, found in the same sites, are labelled by stars. (**b**) Confusion Matrix and NER value for the classification model built with LDA considering as a priori classes Arpi, Canosa, Taranto, and Ruvo.

It can be observed in Figure 9 that the scores of the samples relating to vases attributed to the same painter but coming from different sites are not in the same cluster, but in the cluster containing red figure vases coming from the same site.

Although the number of items analyzed have to be enlarged to increase the significance of the statistical processing, it would seem reasonable to assume that the distinction among finds is mainly derived from the geographical origin of the vessels, so making more reasonable to hypothesize the transfer of painters rather than of artifacts between the main Apulian sites, by reason of demand from local customers, in a context of fragmented local production.

### *2.4. Manufacture: Tradition Versus Innovation*

As concerns production technology, scientific studies, as mentioned above, have highlighted that two different manufacturing procedures were used in Apulia during the fourth century BCE. Some vases were produced using classic Attic technology, others with a previously unknown and different process that involved the application of a red engobe layer on the ceramic body before the application of black gloss (Figure 10) [8].

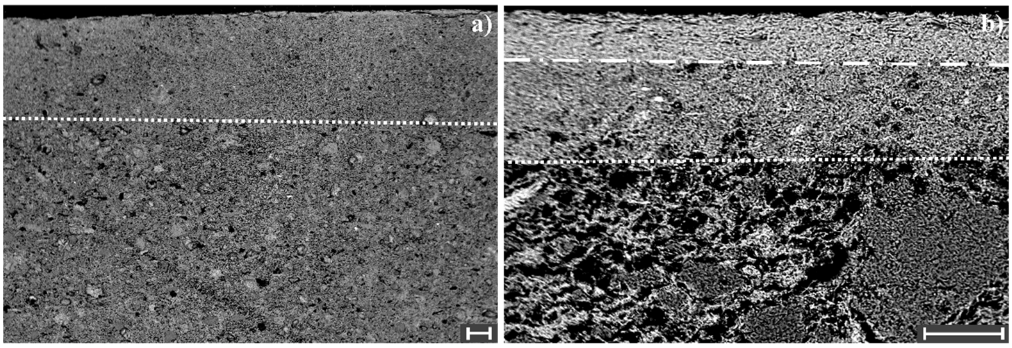



**Figure 10.** SEM-BSE photomicrographs of thin sections of fragments from Taranto (**a**) and Monte Sannace (**b**). The dashed lines separate red engobe layer (upper) from ceramic body (lower), showing the more compact and finer paste of engobe layer with respect to the ceramic body. Scale 100 micron.

Experimental data have suggested that the coarse fraction of clay -generally discarded by Attic potters- was used for the ceramic body, with the elutriated fraction being used for the red engobe. This hypothesis can be deduced from the comparison between the morphological and minero-petrographical characteristics of the ceramic body and the engobe. The engobe layer with respect to the ceramic body is more compact and finer, richer in matrix and poorer in silt. The same minerals are present, but their quantitative ratio is different: more quartz and feldspars in the body, more micas (biotites and muscovites) and clayey minerals in the engobe.

Chemical analysis allows to discriminate samples from the same site, according to the employed production technology [8]. Figure 11 shows the results obtained from the NLPCA analysis for the samples of three sites—Monte Sannace, Egnazia and Taranto—in which the presence of the two different production technologies has been highlighted. It is evident that the samples differ in provenance and, in case of the same origin, in production technology. The $R^2$ value of 0.86 and the Lof of 0.37 show that the best fitting model is built with 3 PCs.

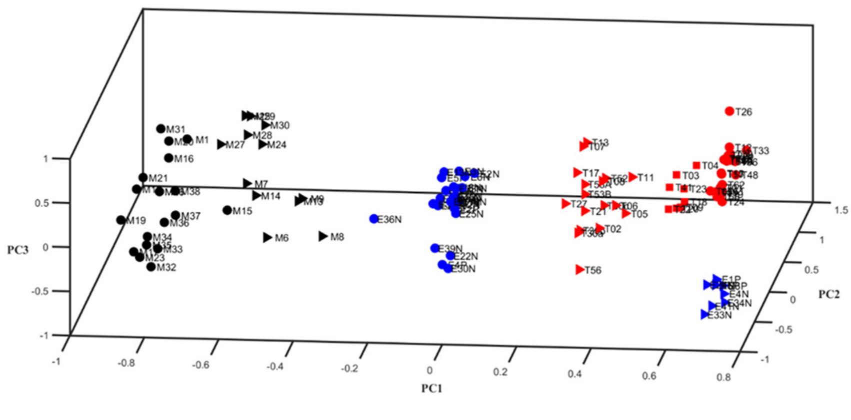



**Figure 11.** NLPCA scores plot of the samples belonging to Monte Sannace (black), Egnatia (blue) and Taranto (red). Circles and squares: classical Attic technology, triangles: Apulian technology.

The causes leading to the development of this new technology during the fourth century BCE are yet unclear. Was it the need for a more suitable raw material for the manufacture of the monumental vases which were typical of late production or was it to reduce manufacturing costs of items aimed at less well-off customers? This second hypothesis seems more likely since red engobe has not up to now been found on vases attributed to famous painters and/or coming from tombs referable to the aristocratic classes [28,30,31].

It is noteworthy to underline the presence of engobe on the firing tester [100] from Tarantine workshop mentioned in paragraph 2.2 and, based on the results obtained from the analysis of the paste, manufactured in the town.

## 3. Concluding Remarks

While stressing that the best methodological approach to the study of archaeological finds not only has to merge morphological–stylistic studies to scientific ones, but also to embrace a coordinate instrumental strategy, the results here outlined strongly highlight the relevance of metallic elements investigation in case of archaeological ceramic study. Their presence and/or quantification have shown their relevance, replying a high number of archaeological queries.

It has been highlighted, for example, how the presence of certain elements in the ceramic body, in larger quantities than trace ones, can provide important clues to the non-originality of pieces, probably integrated during an undocumented "restoration" and that the specific element can also supply information about the period this integration occurred. In the ceramic class here investigated, e.g., the presence of Pb in quantities higher than 200 ppm in the clay material used to produce the nonoriginal parts of the vessels has proved to be an indication of a contamination due to the materials used to obtain the black coating. The use of Pb, instead of Fe, to realize the black coating simulating the original black gloss is characteristic of nineteenth century restorations, which took place before the ferrous nature of the original black coating (black gloss) was determined.

It has been also pointed out how the potential information resources in the matrix of compositional data are not limited to the provenance of finds but it can also provide indications on manufacturing period [8] and production technology.

From an analytical point of view, it has been confirmed that the use of the NLPCA -nonlinear generalization of standard PCA by replacing linear surfaces with curved ones and considering hierarchical NLPCA based on the autoassociative neural network model method is more appropriate than PCA to treat archaeometric data, allowing to extract a greater amount of information from them.

It has been shown how it is possible by a single analysis to discriminate samples from the different production areas and manufactured with two different technologies. Excellent results have been obtained also with the application of LDA and QDA for the creation of classification models. The NER values obtained are always bigger than the 96%, so the samples are correctly classified in the class previously assigned. The models built could be used in future applications as a training set using for projecting unknown samples, as a test set, and for predicting the belonging class.

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