(http://linkinghub.elsevier.com/retrieve/pii/S0305440307000878)

DOI: 10.1016/j.jas.2007.04.007

(http://dx.doi.org/10.1016/j.jas.2007.04.007)

CHEMICAL CHARACTERIZATION OF MAJOLICA FROM 14TH–18TH CENTURY PRODUCTION CENTERS ON THE IBERIAN PENINSULA: A PRELIMINARY NEUTRON ACTIVATION STUDY

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Journal of Archaeological Science, 35, 425-440 (2008)

Chemical characterization of majolica from 14th–18th century production centers on the Iberian Peninsula: a preliminary neutron activation study

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Abstract

Majolica pottery is one of the most characteristic tablewares produced during the Medieval and Renaissance periods. Majolica technology was introduced to the Iberian Peninsula by Islamic artisans during Medieval times, and its production and popularity rapidly spread throughout Spain and eventually other locations in Europe and the Americas. The prestige and importance of Spanish majolica was very high. Consequently, this ware was imported profusely to the Americas during the Spanish Colonial period. Majolica pottery is nowadays an important horizon marker at Spanish colonial sites. In order to make a preliminary study of Spanish-produced majolica, a set of 246 samples from the 12 primary majolica production centers located on the Iberian Peninsula were analyzed by neutron activation analysis (NAA) and the resulting data interpreted using an array of multivariate statistics. Our results show clear discrimination between the production centers, and even allow distinguishing amongst shards coming from the same production city suggesting different workshops or group of workshops of this pre-industrial pottery.

Keywords

Majolica, NAA, Provenance, Multivariate statistics, Iberian Peninsula, Medieval and Renaissance pottery

Introduction

Majolica is an earthenware pottery characterized by a creamy light-buff colored ceramic body and an opaque white tin-lead glaze that covers the entire outer surface of the vessel. The most characteristic feature of majolica pottery perhaps lies in the metallic oxide decorations that are applied on top of the opaque white glaze coat. The opaque white glaze which is characteristic of Majolica pottery is composed essentially of sand (e.g., quartz) and lead, which acts as a flux that decreases the temperature needed for melting SiO_2. The glaze is opacified with particles of tin oxide (SnO_2) and also by the action of extant quartz and feldspar inclusions. These inclusions, and the bubbles that result from the firing process, absorb, scatter, and/or reflect incident light, thereby giving the transparent glaze a white appearance. Due to this opacity, decoration is normally applied to the outer surfaces of the glaze coat (Molera *et al.* 1999, Garcia Iñañez *et al.* in press a, Garcia Iñañez *et al.* in press b, Garcia Iñañez *et al.* in press c, Garcia Iñañez in press).

The term Majolica is synonymous with *maiolica, mayólica, faience, delftware, loza,* and *pisa*. The origin of the word majolica and its derivations may originate from the earthenware production of Málaga (*Malica* during Medieval times) in southern Spain. Alternatively, the word may originate from the role that the Spanish Mediterranean island of Mallorca served in majolica trade with Italy during Medieval and Renaissance times. Irregardless of the origin, this philological aspect underscores the importance of Spanish majolica production (Farwell *et al.* 2003).

The antecedents majolica must be sought in the early glazed proto-earthenware productions of the Middle East, probably in Iraq, since the ninth century AD, although opacified glazed pottery making traditions existed in Mesopotamia as early as the fifth century BC (Mason i Tite 1997, Hill *et al.* 2004). The technological know-how of those productions, which were originally produced probably as coarse imitations of Chinese porcelain, was transferred to the Iberian Peninsula by Muslims. From there, majolica technology became widespread throughout the entire Iberian Peninsula during the Middle Ages, even in the New Christian kingdoms and principalities from the North and Northeast. Although an earlier tin-lead glazed earthenware existed, primarily in the Muslim *Al-Andalus*, the thirteenth century is generally considered as the starting point for majolica production in the Iberian Peninsula (Martínez-Caviró 1997). Majolica pottery from the Late Medieval Age usually was decorated using black and green motifs over a white background and with gold-like decorations referred to as lusterware. The most important production centers sampled from this period (the thirteenth to fifteenth centuries), were Teruel (Aragon), Manises, and Paterna (located in the Valencia region), and Barcelona (Catalonia).

By the sixteenth century Spanish majolica production flourished as Italian-influenced decorative styles diffused into the Iberian Peninsula. Consequently, black and green motifs (green was a color generally associated with Islam influences) were progressively replaced with blue patterns, sometimes mixed with other colors, especially yellow. By the end of the sixteenth and seventeenth centuries majolica polychrome was produced throughouth the Iberian Peninsula. At the same time the production of lusterware declined, both in quantity and quality. The most characteristic and important production centers from this period are Barcelona, Reus, Vilafranca del Penedès and Lleida in the Catalan area; Manises in the Valencian area; Muel and Villafeliche in Aragon; and Talavera de la Reina, Puente del Arzobispo and Sevilla in the Central and South Spain respectively (Figure 1). At the same time that the commercial trade with the Americas and Europe increased, the port of Seville became the most important port of trade for Spain. The increased importance of Seville occurred because this city's port served as the departure point and the final destination for most of the galleons that traded with the Americas in the so called "*Carrera de Indias*". Simultaneously, the importance of Sevillian majolica increased because of Seville's monopoly in the exportation of goods to the Americas. Whereas Seville became the primary production center for majolica exported outside of Spain, Talavera became the most important production center for majolica consumed within Spain—a consequence of Talavera being the official supplier of royal tableware.

In this paper, we summarize the results of a compositional analysis of 246 majolica shards obtained from the 12 primary production centers located on the Iberian Peninsula. These sites, which date from fourteenth to eighteenth centuries (Figure 2), have been involved in the manufacture of tin-lead glazed pottery since the Middle Ages, and continue to produce majolica even today. Consequently, majolica production of a few of these places achieved high prestige due to their high quality and asthetic value. The exportation of this pottery to the Americas, such is the case of the Seville and Talavera workshops, eventually resulted in the establishment of autochthonous workshops, such as Puebla or Mexico City, both in Mexico (Castro 1988, Gámez Martínez 2003, LaBrecque *et al.* 2003, Rodríguez-Alegría *et al.* 2003).

Our goal is to obtain a more precise understanding of majolica pottery production at the primary sites of the Iberian Peninsula dating from the fourteenth to eighteenth centuries or, in other words, from the appearence of majolica to the introduction of porcelain production in Spain at the end of the eighteenth century. By identifying compositional reference groups for majolica production within the Iberian Peninsula, we aspire, in future studies, to identify the provenance of majolica that was exported to areas outside of Spain, such as the Canary Islands and the Americas. The identification production centers for majolica recovered outside of Spain has important implications for understanding changing sociopolitical and economic relationships between Spain and the New World—relationships that may be at odds with historical documents of the era. The current archaeometric knowledge about tin-lead glazed pottery produced in the Iberian Peninsula is fractional and uneven. At the same time, many important works concerning majolica technology have been published, especially lusterware (Molera *et al.* 1993, Pérez-Arantegui *et al.* 2001, Fermo *et al.* 2002, Padeletti i Fermo 2003, Molera *et al.* 2005, Pradell *et al.* 2005, Roqué *et al.* 2006), there is a real lack of chemically defined reference groups that characterize the primary production sites. In that sense, there are just a few archaeometric works about these sites, such as Paterna (Molera *et al.* 1996, Molera *et al.* 2001), Barcelona, Reus and Vilafranca del Penedès (Garcia Iñañez in press) or Talavera, Puente and Seville (Buxeda *et al.* 2003, Garcia Iñañez *et al.* in press b). In addition, few works have previously studied the occurrence of Spanish majolica at overseas sites (e.g., the Americas), most of which refer primarily to Seville's production (Maggeti *et al.* 1984, Olin and Blackman 1989, Myers *et al.* 1992, Vaz *et al.* 1997). However, when most of these provenance studies were conducted on overseas majolica, there was a significant gap in the archaeological knowledge regarding the actual kiln sites at Seville. During the past several years, however, archaeological excavations have revealed a substantial number of such kiln sites—sites that can be used to establish the reference groups (Lorenzo Morilla *et al.* 1990, Mercado Hervás *et al.* 2001, Mesa Romero and Castañeda de la Paz 2001). On the other hand, the important role played by the Canary Islands in the Atlantic trade has also been assessed by Garcia-Iñañez *et al.* (in press d).

In addition, the archaeometric study of pre-industrial pottery production may provide insight into specific characteristics of a production center. For example, it is known from legal and commercial manuscripts that potters were organized in guilds that were responsible for the clay and other raw materials supply to their different unionized workshops. In that sense, a very standardized composition for each production center would be expected despite the existence of multiple workshops within a given city. As we discuss below, this scenario, however, is not always the case.

Methods

Table 1 lists a total of 246 majolica shards that were collected from the sites analyzed in this study. All of the specimens were sampled either from extant museum collections or from contemporary archaeological excavations. Our sampling strategy was strictly focused on kiln-related materials, in order to maximize the probability that materials belonged to the respective workshops and producing towns. In that sense, we mostly sampled ceramics from archaeologically and historically documented majolica kiln dumps; although in some cases we also sampled shards from other kinds of archaeological deposits, such as the roof vaults at the old *Hospital de la Santa Creu* in Barcelona. Most of these samples included in this study (113) were obtained from the *Museu de la Ceràmica de Barcelona*, which has large reference collections for most of the primary majolica production sites in Spain. In addition, we obtained 15 shards from the *Museu Comarcal Salvador Vilaseca de Reus* and 15 samples from the *Museu de Vilafranca del Penedès*. We also collected 30 majolica fragments from three different archaeological excavations within the city of Seville (Pureza, that is linked to the famous artist Niculoso Pisano's workshop, Valladares and Plaza de Armas), generously provided by the *Museo Arqueológico de Sevilla*, where the materials are curated. Finally, we obtained 15 specimens from the *Servei Arqueològic de la ciutat de Lleida* from three different archaeological sites (Obradors, St. Anastasi and Remolins) and 12 from Talavera de la Reina that were kindly provided by Mr. Sánchez Cabezudo.

In the present study about archaeometrical characterization of majolica ware, 10 g of each collected sample was powdered in a Spex Mixer (mod. 8000) tungsten carbide cell for 12 min. Prior to grinding, glazes and exterior surfaces were mechanically removed in order to minimize contamination of glaze materials and soil. Powdered specimens were stored polyethylene vials for transportation to the laboratory.

Chemical analyses were conducted by instrumental neutron activation analysis (INAA) at the Missouri University Research Reactor (MURR) Archaeometry Laboratory. Prior to analysis, the powdered pottery samples were oven-dried to a constant weight at 100ºC for at least 24 h. Approximately 150 mg of sample were weighed into small polyvials used for short irradiations. At the same time, 200 mg of each sample was weighed into high-purity quartz vials used for long irradiations. Along with the majolica samples, reference standards of SRM-1633a (coal fly) and SRM-688 (basalt rock) were prepared, as well as quality control samples of SRM-278 (obsidian rock) and Ohio Red Clay (an in-house standard treated as an unknown).

At MURR, INAA of pottery consists of two irradiations and a total of three gamma counts. Short irradiations involve a pair of samples being transported through a pneumatic tube system into the reactor core for a 5 s neutron irradiation using a flux of 8 X 10^{13} n cm^{-2} s^{-1}. After 25 min of decay, the samples are counted for 720 s using a high-resolution germanium detector. This count yields data for nine short-life elements: Al, Ba, Ca, Dy, K, Mn, Na, Ti and V. For the long irradiation, bundles of 50 or 100 of the encapsulated quartz vials are irradiated for 24 h at a flux of 5 X 10^{13} n $cm^{-2} \cdot s^{-1}$. Following the long irradiation, samples decay for seven days, and then are counted for 2000 s (known as "middle count") on a high-resolution germanium detector coupled to an automatic sample changer. This middle count yields determination of seven medium half-life elements: As, La, Lu, Nd, Sm, U and Yb. After additional two-week decay, a second count of 10.000 s is carried out on each sample. This measurement allows quantification of 17 long-life elements: Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn and Zr (Glascock 1992).

The statistical analysis of the data followed Aitchison's approach and Buxeda's observations on compositional data (Aitchison 1986, 1996, Buxeda 1999, Buxeda and Kilikoglou 2003). The statistical procedure consists of the use of ratios of logarithms obtained by dividing all the components, in this case chemical components, by the component that introduces the lowest chemical variability to the entire set of specimens taking into consideration, overcoming the compositional data problem called "close to unit sum", when data necessarily must sum 100%. Moreover, the use of logarithms compensates for differences in magnitudes between major elements, such as Al or Fe, and trace elements, such as lanthanide or rare earth elements (e.g. La, Ce, Sm or Dy) and log-transformed data serve to make the distributions of geochemical data more nearly normal. Moreover, dividing all components by the lower one in terms of variability also overcomes relative magnitudes problems of a given subcomposition, because after logratio transformation we tackle with the same relative magnitudes for each individual given that $s_i/s_j = x_i/x_j$ (Mateu *et al.* 2003). Finally, the logratio transformation also provides a better highlighting of possible perturbations in the chemical data as a result of diagenesis, contamination, or other alteration processes (Buxeda 1999).

The resulting data were examined using an array of multivariate statistical procedures. The application of multivariate statistical techniques to INAA data facilitate identification of compositional groups. Therefore, similarity of individuals, and subsequently their hypothetical provenance according to the provenance postulate (Weigand *et al.* 1977), was tested using squared Euclidian distance graphically represented by cluster plots that employed the centroid algorithm in the S-Plus program (MathSoft 1999). Stepwise Discriminant Analysis (DA) was performed to assess the archaeological classifications and the chemical groups proposed by cluster analysis. Performing DA was also an option to cluster unknown provenances of unclassified specimens. In addition, Mahalanobis distance was used to describe probabilistically, when group sizes permitted, the separation between defined groups and some of those individuals that remained unclassified. Mahalanobis distance takes into account variances and covariances in the multivariate group and is analogous to expressing distance from an univariate mean in standard deviation units. In that sense, Mahalanobis distance can also be converted into probabilities of group membership for each individual (Glascock 1992).

Although sample preparation was conducted under great care to minimize the analytical error, the potential for contamination exists nonetheless. In that sense, a conservative approach to data interpretation is warranted. For example, we considered that the element cobalt had to be removed from consideration during the statistical treatment because the tungsten carbide cell grinder exhibits traces of Co in its chemical composition (cobalt is a known binder in tungsten alloys). Additionally, Ni concentrations were below detection limits for many of the samples and subsequently had to be removed from consideration.

Conversely, a relevant number of the analyzed majolica shards exhibited a double process of alteration and contamination documented in previous studies (Garcia Iñañez *et al.* in press a, Garcia Iñañez *et al.* in press b, Garcia Iñañez *et al.* in press c, Garcia Iñañez in press). This process reports the leaching of potassium and, sometimes, rubidium, from the matrix, with a subsequent enrichment of sodium because of analcime crystallization (Schwedt *et al.* 2006, Garcia Iñañez in press, and references therein). Therefore, these alteration and contamination processes affect those components in the matrix composition, without any possibility of satisfactory correction by now. As a result, Na, K, and Rb were also removed from consideration during the statistical analysis.

Results and discussion

The variability of each chemical component was first taken into account in this study and assessed by the calculation of the variation matrix, which provides information about those components that introduce higher variability to the data set (Table 2). In that sense, the elements As, Sr and Sb were removed due to their high variability ($v\tau/\tau_i < 0.25$), which is presumably provided by possible contamination processes during burial, such is the case of As, or because many majolica exhibit yellow decoration that is essentially made of Sb. It must be pointed out that Cs was not removed despite its high variability because it plays an important role in the chemical discrimination between Talavera and Puente groups. As mentioned above, Rb, K and Na also were removed because they are involved in the previously cited alteration and contamination processes and because these elements exhibit high chemical variability ($v\tau/\tau_i < 0.46$). Following the exclusion of these elements, a logratio transformation was applied to the following subcomposition: Lu, Nd, Sm, U, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Ta, Tb, Th, Zn, Zr, Al, Ca, Dy, Mn, Ti and V, using La as divisor because it introduces the lowest variability ($v\tau/\tau_i = 0.9348$) according to the variation matrix.

The results can be summarized in the cluster analysis that was performed by the squared Euclidian distance and the centroid algorithm on the cited subcomposition using La as divisor in the logratio transformation.

Examination of the resulting dendrogram shows a clear 15-group structure that corresponds to the different production centers (Figure 3). Most of the groups show clear and defined cuts from the rest. Moreover, most of the samples belonging to a given cluster also exhibit a high degree of homogeneity within their chemical composition, as can be observed by their low fusion links, pointing to a similar composition.

However, upon further examination, the dendrogram also reveals that some of the production centers exhibit chemically differentiated productions that were made during the same chronological period. In that sense, the dendrogram also shows that Muel and Teruel productions can be split into two distinct groups for each respective center (Muel 1 and 2; Teruel 1 and 2). The Teruel subgroups exhibit clear differences between themselves, like higher amounts of Hf, Sb, Zr and Mn in shards of Teruel 1, whereas Teruel 2 shows higher values of U, Cs, Rb, Ba and K than the other (Table 3). On the other hand, subgroups of Muel also exhibit clear chemical differences, as can be seen by their differentiated position in the cluster. Muel 1 has slightly higher Cs, Fe, Al, Sc and Sr amounts than Muel 2 and Muel 2 has higher concentrations of Hf and, especially, Zr, whose higher content can be related to a higher sandy phase in their pastes. Moreover, there are multiple productions in Lleida and Barcelona. The city of Lleida, placed at the northeastern part of the Iberian Peninsula, exhibits a double and contemporary majolica production according to the chemical and archaeological data. Therefore, we can propose two chemical groups for Lleida: REM and OB/SA. Although the chemical group referred to as REM matches with those shards collected from the sixteenth and seventeenth century kiln site of *carrer Cardenal Remolins*, the chemical group named OB/SA clusters the shards from the seventeenth century kiln dump sites of *carrer Sant Anastasi* and the *carrer Obradors* (*Pati d'en Miqueló*'s lot). The latter groups are archaeologically linked and located very close to one another in the old quarter of the city. It must be pointed out that the name *obradors* means workshops in Catalan, revealing the importance of the ancient pottery activity in this neighborhood. Chemically, the REM group exhibits lower Ca values than OB/SA, whereas its concentrations of Fe and Al are higher than the other group. Additionally, those groups also have slight differences in their Cs, U and Ba concentrations, with those values slightly higher in the REM ceramics.

In a similar manner, pottery from Barcelona also shows a multiple group structure (Figure 3). Through the study of its materials at least two different groups can be suggested on the basis of their chemical composition: BCN-DR/PI and BCN-SC. The first group clusters pottery from two different sites with a diverse chronology. In that sense, although some of the ceramics were recovered at the vaults of the *Santa Maria del Pi* church, dating to the fourteenth century, the remaining samples were collected from the so-called *Drassanes* kiln dump, dated to the sixteenth and seventeenth centuries. Apparently, they seem to show slight chemical differences, as it has been noticed in previous studies by XRF (Garcia Iñañez *et al.* in press a, Garcia Iñañez *et al.* in press c, Garcia Iñañez in press), although their high homogeneity adds a complexity factor for effecting good discrimination between them. To the contrary, BCN-SC group clearly is differentiated from the mixed group of BCN-DR/PI, especially due to the presence higher of Ca amounts in its shards (Table 3).

A more complicated situation has the groups of TAL and Puente, corresponding respectively to the producing towns of Talavera de la Reina and Puente del Arzobispo. These cities are geographically very close to each other and have had a very similar majolica production history during the past four centuries. In that sense, there are many problems that hinder the discrimination of these production centers, especially on the basis of their decorative styles and typologies. Additionally, tableware production styles from Puente have traditionally been considered to be an imitation of the Talavera's (Sánchez-Pacheco 1997). In that sense, and related to their close proximity, chemical data generated for several shards analyzed from both sites exhibit a similar composition (Garcia Iñañez *et al.* in press b). This results in an overlapping structure by cluster analysis, labeled TAL-Puente, with all the specimens from both towns grouping together without unambiguous differentiation (Figure 3).

In addition to the clustered shards there are 12 specimens that initially do not cluster to any identified group: DIA317, DIA537, MJ0018, MJ0037, MJ0084, MJ0104, MJ0124, MJ0130, MJ0141, MJ0317, MJ0341 and TRI004.

In order to achieve a better discrimination of the groups previously identified by cluster analysis, a stepwise discriminant analysis was performed on the chemical data set using all of the analyzed samples. The most suitable components for running the discriminant analysis were the same as those used for the cluster analysis following the logratio transformation. Therefore, stepwise discriminant analysis were performed, using the Statgraphics Plus program, on the subcomposition Lu, Nd, Sm, U, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Ta, Tb, Th, Zn, Zr, Al, Ca, Dy, Mn, Ti and V, using La as the divisor in the logratio transformation (Table 2). Elements presumed to be problematic because of alteration or contamination processes, such as Na, Rb or K, and those components also dismissed in the cluster analysis because of their high variability (e.g., As, Sr and Sb), were not considered in the stepwise discriminant analysis.

Stepwise discriminant analysis (DA) provides a powerful tool to assess the groups identified by cluster analysis. Using a stepwise selection algorithm, it was determined that 16 variables (the logratio transformed components: Ca, Th, Cs, Sc, Sm, Al, Eu, Mn, Hf, U, Ta, Ba, Fe, Zn, Ce, Cr) are significant predictors of majolica groups. The 16 discriminating functions with P-values less than 0.05 are statistically significant at the 95% confidence level. In that sense, the evaluation of all the shards classified regarding to the previous dendrogram has shown a very high successful score: 94.72%, in which 233 out of 246 shards match their suggested group according to the cluster analysis and the archaeological information. In the latter sense, DA has operated in a successful way for those shards from different archaeological background, but with a similar chemical composition that results in a single chemical group in the dendrogram, such as the cases of BCN-DR/PI and TAL-Puente. Thus, unique groups for the producing towns of Talavera and Puente and the three different archaeological sites of Barcelona were identified according to their hidden chemical differences.

Therefore, 8 out of the 12 individuals labeled as unassigned (or non-clustered) were reclassified into some of the previously discussed groups. Consequently, it has been determined that DIA317 belongs to the Reus group, MJ0104 to the BCN-DR group, MJ0141 to the Manises group and MJ0341 to the Seville group despite their high amounts of Ba. Additionally, MJ0037 appears to belong to the Muel 1 group, whereas sample MJ0130 matches with the Paterna group. Moreover, the shards labeled as TRI004 and

MJ0317 apparently fit with the rest of the shards that form the Seville group. All these classifications agree with the expected results on archaeological grounds. Another situation is the one represented by the specimens MJ0043, MJ0089, MJ0161, TAL016 and TAL017. Those samples initially were grouped with specific reference groups according to their archaeological and chemical data. However, the stepwise DA has shown that they exhibit a better fitness with other groups, thereby being reclassified into their new ones. Thus, shard MJ0043 seems to be a better fit with the Muel 1 group than the Muel 2 group to which it was previously assigned, whereas MJ0089 matches the BCN-PI chemical group, instead of BCN-DR. Moreover, sample MJ0161 is linked archaeologically with the Puente group, but chemically is linked to the TAL one. In addition, the specimens TAL016 and TAL017, from the producing town of Talavera, apparently could be from the reference group of Puente. In any case, these small changes seem to be explained by the use of only 16 components, and not for all of them, as well as by the similarities existing between related productions. In no case they imply that the observed groups have no clear cut. On the contrary, four of the non-classified specimens, DIA537, MJ0084, MJ0124 and MJ0018, remain unclassified due to their compositional differences.

In order to assess the statistical strength of the groups suggested by the cluster analysis and confirmed by the stepwise DA, a probabilistic group assignment based on Mahalanobis distance calculations was performed. However, the low number of samples for each of the proposed groups precluded the possibility of employing all the chemical variables measured by NAA or the 16 most discriminating transformed variables for this dataset because most of the suggested groups are comprised of less than fifteen members. Thus, another scale reducing statistical technique is need to, such as Principal Components analysis (PCA). PCA was been performed in the same way as the stepwise DA and the cluster analysis: that is employing the subcomposition Lu, Nd, Sm, U, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Ta, Tb, Th, Zn, Zr, Al, Ca, Dy, Mn, Ti and V, using La as divisor in the logratio transformation (Table 2). Likewise, As, K, Na, Rb Sr, and Sb, were not included for reasons discussed above. The PCA indicated that 90% of the cumulative variation was accounted for in the first 6 principal components, resulting in a good estimation of the overall composition of the majolica shards. Given that the majolica production center groups identified by cluster analysis and DA are usually smaller in number than 16 and normally larger than 8, it was possible to calculate MD probabilities using the 6 first principal components to assess the membership probabilities for samples assigned to each group and to attempt to classify unassigned and problematic specimens. It must be highlighted that the only three groups do not agree with the number restriction rule were the chemical groups proposed for REM, BCN-SC and BCN-PI, having all of them less than 8 shards each one.

The MD calculations, once converted into membership probabilities, clearly confirm that the groups previously identified by cluster analysis and DA are statistically robust. In that sense, most of the shards are assigned with a higher probability of 5%, a theoretical limit of membership probability, to their respective chemical groups in the same way that they did by cluster analysis and DA. In the same sense, the provenance of the specimens that showed a discrepancy amongst the classification by cluster analysis of by DA are now in agreement with MD probabilities. Thus, sample DIA317 shows high membership probability with the chemical group of Reus as we would expect. At the same time, MJ0037 and MJ0043 belong to the Muel 1 group, whereas MJ0104 shows a clear membership in the BCN-DR group. Additionally, samples MJ0141 and MJ0341 exhibit high membership probability in their respective chemical groups: Manises and Seville. Moreover, the discussed provenance amongst the shards from Talavera and Puente shows a clearer panorama after MD calculations. Consequently, specimen MJ0161 from Puente del Arzobispo has been confirmed as Puente, whereas the samples TAL016 and TAL017 that where reclassified as Puente's by DA are now confirmed as Talavera products. As a result of the MD approach, sample MJ0084 is now clearly revealed as a Villafeliche product.

As is common with MD probabilities, some samples could not be assigned to any group. As a result of the number restrictions for MD calculations, DIA537 could not be compared with the rest of shards from the group of BCN-SC due to the low number of samples assigned to this group and remains unassigned. Contrariwise, MJ0317 and TRI004, both archaeological linked to Seville, exhibit a low membership probability with the reference group of Seville. Therefore, these shards must also remain unclassified. A different thing occurs with the MJ0124 and MJ0130 ceramics collected from Paterna. These samples have slight chemical differences when compared to the rest of majolicas from the same site. But, due to their geographically proximity, they showed some chemical similarities to the Manises group ceramics. The MD calculations suggest that MJ0124 belongs in fact to the Manises group, whereas sample MJ0130 remains as a Paterna product. However, this suggestion is in conflict with the archaeological data, especially about its decorative attributes (green and black) and its early chronology (fourteenth century). Hence, a conservative approach is to consider the MJ0124 shard as unclassified until such time that additional samples from this site are analyzed. Finally, the provenance of the MJ0018 ceramic is still ambiguous. The paste of this sample is lighter than the rest of the specimens analyzed from Teruel, which are redder and coarser. This aspect, translated in higher Ca amounts of the MJ0018, and might be related to a different technology process. Additionally, this shard is date to the seventeenth century, whereas the rest of the materials collected from Teruel are from the fourteenth century. Therefore, it does not seem improbable that a technological change occurred during the Renaissance in Teruel, and that potters started to produce majolica using a different paste recipe than that used by fourteenth century potters. In order to properly address this question it is necessary to increase the number of analyses and to include samples from from Teruel that span all historical periods.

Conclusions

The study of a representative sample of majolica pottery from the 12 primary production centers located in the Iberian Peninsula reveals a clear structure that allows the chemical differentiation of each majolica production. In some cases, more than one compositional group was identified for specifics centers, such as Teruel, Muel, Lleida or Barcelona. In these cases, two or three different productions according to their chemical characteristics were identified. A good chemical identification of Spanish majolica has been achieved in this paper given that most of the analyzed specimens can be linked to specific compositional groups. Following the statistical analysis only 5 of the 246 samples remain unclassified, clearly pointing to the need for a larger number of samples in order to better characterize all the variability existing in those production centers.

Pre-industrial pottery, such as majolica ware, reflects differentiate chemical behavior from other ancient pottery and other types of contemporary ceramics. In this sense, majolica ceramics exhibit high chemical homogenization as a result of the use of standardized raw materials and probably also recipes. Those materials were usually provided by the pottery guilds to the different workshops, then becoming their products highly chemically similar regardless the number of potters that are documented from any producing town. This could be summarized in the case of the city of Barcelona, from which are documented more than 600 potters from 1450 to 1650 (Cerdà 2001). This high density of potters and, consequently, of workshops, are not reflected in different chemical fingerprints of each production as a result of the homogenization of the raw materials provided by the guilds to their unionized workshops. Therefore, it has to be highlighted that dealing with majolica and, generically, with pre-industrial pottery other factors that just chemical analysis must be taken into account in order to differentiate different productions from a same producing city due to the role played by potters guilds during the Medieval and Renaissance periods.

Acknowledgements

The work presented here forms part of the project “Identification, Recovery and Improvement of ancient Mediterranean ceramic manufacturing technologies for the reproduction of ceramic artifacts of archaeological value (CERAMED)”, from the Research Directorate General, European Commission, European Community (ICA-3-CT-2002-10018). Javier Garcia Iñañez is also indebted to the support of *Departament d’Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya i Fons Social Europeu*. Authors are also indebted to the *Museu de la Ceràmica de Barcelona*, *Museo Arqueológico de Sevilla*, *Museu de Vilafranca del Penedès*, *Museu Comarcal Salvador Vilaseca de Reus* and to Mr. Sánchez Cabezudo for his collaboration and for providing some of the samples analyzed for this study. Special thanks are extended to Nicole Little for assistance with the laboratory work at MURR.

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Sites	Centuries	Green & Black	Blue	Lusterware	White plain	Polychrome	Non glazed	Total
Barcelona		15	4	16	-	-	-	35
Drassanes	16th-17th	4	4	9	-	-	-	17
H. Santa Creu	16th-17th	-	-	7	-	-	-	7
Sta. Maria del Pi	14th	11	-	-	-	-	-	11
Lleida		-	11	-	-	1	3	15
Obradors	16th-17th	-	2	-	-	1	2	5
St. Anastasi	16th-17th	-	5	-	-	-	-	5
Remolins	16th-17th	-	4	-	-	-	1	5
Manises	15th	-	-	15	-	-	-	15
Muel	16th-17th	-	26	-	-	-	-	26
Paterna	14th	15	-	-	-	-	-	15
Puente	16th-18th	-	13	-	-	1	1	15
Reus	16th-17th	-	-	3	12	-	-	15
Sevilla		-	21	1	9	5	-	36
Pureza	16th-17th	-	3	1	5	3	-	12
Valladares	16th-17th	-	8	-	2	-	-	10
Plaza Armas	16th-17th	-	8	-	2	-	-	10
Museu Ceràmica	15th-16th	-	2	-	-	2	-	4
Talavera		-	13	-	-	-	-	14
Mirasol	16th-17th	-	12	-	-	-	-	12
Museu Ceràmica	16th-17th	-	1	-	-	1	-	2
Teruel	13th-14th	30	-	-	-	-	-	30
Vilafranca	16th-17th	-	1	1	13	-	-	15
Villafeliche	17th-18th	-	15	-	-	-	-	15
Total		60	104	36	34	8	4	246

Table 1. Origin, chronology and decoration of the samples selected for the study

Components	As	La	Lu	Nd	Sm	U	Yb	Ce	Cr	Cs	Eu	Fe	Hf	Rb	Sb	Sc
As	0.000000	0.244651	0.263265	0.243504	0.245527	0.366413	0.254332	0.247945	0.251804	0.409604	0.241637	0.221365	0.300972	0.372576	0.346535	0.236091
La	0.244651	0.000000	0.009637	0.004047	0.002106	0.065571	0.004666	0.001122	0.033072	0.177263	0.002778	0.014501	0.034255	0.088022	0.252897	0.010168
Lu	0.263265	0.009637	0.000000	0.011302	0.006661	0.052122	0.009410	0.007770	0.049323	0.196291	0.012762	0.027057	0.035503	0.097829	0.270874	0.021311
Nd	0.243504	0.004047	0.011302	0.000000	0.002941	0.067549	0.006423	0.003752	0.044215	0.174955	0.007279	0.019610	0.036076	0.085420	0.268638	0.016301
Sm	0.245527	0.002106	0.006661	0.002941	0.000000	0.062136	0.003456	0.001460	0.041476	0.179533	0.004597	0.017340	0.030264	0.088105	0.269883	0.014687
U	0.366413	0.065571	0.052122	0.067549	0.062136	0.000000	0.073054	0.060021	0.124390	0.237414	0.079118	0.100893	0.115262	0.111917	0.348289	0.083212
Yb	0.254332	0.004666	0.009410	0.006423	0.003456	0.073054	0.000000	0.004688	0.045139	0.184582	0.006942	0.020274	0.027257	0.092420	0.268521	0.017782
Ce	0.247945	0.001122	0.007770	0.003752	0.001460	0.060021	0.004688	0.000000	0.036770	0.180014	0.003506	0.016392	0.034021	0.085788	0.255765	0.011553
Cr	0.251804	0.033072	0.049323	0.044215	0.041476	0.124390	0.045139	0.036770	0.000000	0.220120	0.025088	0.014460	0.090249	0.157230	0.219290	0.012944
Cs	0.409604	0.177263	0.196291	0.174955	0.179533	0.237414	0.184582	0.180014	0.220120	0.000000	0.201969	0.190927	0.275392	0.064273	0.528840	0.180337
Eu	0.241637	0.002778	0.012762	0.007279	0.004597	0.079118	0.006942	0.003506	0.025088	0.201969	0.000000	0.011544	0.030860	0.109036	0.240110	0.009254
Fe	0.221365	0.014501	0.027057	0.019610	0.017340	0.100893	0.020274	0.016392	0.014460	0.190927	0.011544	0.000000	0.066811	0.119442	0.230198	0.003998
Hf	0.300972	0.034255	0.035503	0.036076	0.030264	0.115262	0.027257	0.034021	0.090249	0.275392	0.030860	0.066811	0.000000	0.161719	0.302965	0.067333
Rb	0.372576	0.088022	0.097829	0.085420	0.088105	0.111917	0.092420	0.085788	0.157230	0.064273	0.109036	0.119442	0.161719	0.000000	0.426512	0.103702
Sb	0.346535	0.252897	0.270874	0.268638	0.269883	0.348289	0.268521	0.255765	0.219290	0.528840	0.240110	0.230198	0.302965	0.426512	0.000000	0.226805
Sc	0.236091	0.010168	0.021311	0.016301	0.014687	0.083212	0.017782	0.011553	0.012944	0.180337	0.009254	0.003998	0.067333	0.103702	0.226805	0.000000
Sr	0.500283	0.270001	0.268335	0.288763	0.277669	0.259916	0.297705	0.271054	0.211423	0.647991	0.255367	0.254420	0.318689	0.527408	0.425459	0.250199
Ta	0.252409	0.016950	0.020438	0.015322	0.012876	0.065570	0.018419	0.015069	0.063933	0.147498	0.023641	0.033152	0.052879	0.068516	0.326892	0.031440
Tb	0.247481	0.009504	0.011838	0.009584	0.006198	0.070977	0.008110	0.008641	0.050915	0.184817	0.012062	0.022797	0.035401	0.094085	0.272798	0.021324
Th	0.254808	0.005937	0.010321	0.006768	0.005393	0.049572	0.009631	0.004261	0.052350	0.156254	0.013805	0.024089	0.050391	0.064110	0.274039	0.017024
Zn	0.277075	0.060099	0.067437	0.063570	0.063588	0.138646	0.063591	0.061150	0.053811	0.211805	0.060419	0.039565	0.142081	0.135851	0.233777	0.035684
Zr	0.297867	0.034894	0.030982	0.036352	0.030570	0.096098	0.028998	0.033456	0.089129	0.277460	0.033048	0.064058	0.017423	0.158534	0.308027	0.063446
Al	0.237871	0.009994	0.021384	0.013017	0.011953	0.070687	0.018412	0.010407	0.029558	0.148460	0.013903	0.011598	0.068676	0.077454	0.270815	0.008019
Ba	0.363542	0.083125	0.103187	0.090558	0.091127	0.133271	0.098843	0.083117	0.108225	0.236728	0.085746	0.096723	0.146634	0.151189	0.304075	0.083779
Ca	0.358518	0.148228	0.136885	0.153204	0.143934	0.184613	0.155651	0.146063	0.132996	0.414789	0.139626	0.149285	0.185144	0.333798	0.365727	0.145907
Dy	0.242955	0.006159	0.009573	0.006739	0.003480	0.076856	0.006167	0.005806	0.043246	0.184833	0.007147	0.019715	0.028697	0.099154	0.275479	0.018311
K	0.358393	0.060310	0.076436	0.059229	0.064656	0.101692	0.069787	0.058887	0.115529	0.158888	0.071550	0.085813	0.120503	0.059896	0.395764	0.075236
Mn	0.276396	0.093565	0.098468	0.098705	0.094517	0.209334	0.091071	0.094978	0.080812	0.383493	0.079715	0.065810	0.123490	0.286466	0.221525	0.076652
Na	0.495475	0.324546	0.304262	0.331248	0.315389	0.422164	0.314381	0.322161	0.265397	0.584015	0.305986	0.276929	0.364485	0.530747	0.418656	0.283008
Ti	0.251251	0.011244	0.017078	0.015881	0.012899	0.081165	0.016040	0.011581	0.029212	0.201662	0.009209	0.019860	0.038167	0.116347	0.244042	0.016359
V	0.246275	0.046552	0.062732	0.055876	0.056001	0.135297	0.058301	0.050416	0.015840	0.206581	0.042747	0.021798	0.125145	0.154246	0.220443	0.019117
t.i	8.906823	2.125862	2.310474	2.236825	2.160426	4.043221	2.274054	2.127616	2.707947	7.546788	2.140450	2.260423	3.426746	5.021796	9.013636	2.160983
vt/t.i	0.223343	0.935749	0.860981	0.889329	0.920778	0.492002	0.874770	0.934978	0.734606	0.263592	0.929372	0.880045	0.580514	0.396128	0.220696	0.920541
r v,t	0.916753	0.994380	0.991460	0.990754	0.992480	0.947052	0.992003	0.993601	0.964105	0.877514	0.997284	0.991708	0.974376	0.864610	0.759244	0.994691

Components	Sr	Ta	Tb	Th	Zn	Zr	Al	Ba	Ca	Dy	K	Mn	Na	Ti	V
As	0.500283	0.252409	0.247481	0.254808	0.277075	0.297867	0.237871	0.363542	0.358518	0.242955	0.358393	0.276396	0.495475	0.251251	0.246275
La	0.270001	0.016950	0.009504	0.005937	0.060099	0.034894	0.009994	0.083125	0.148228	0.006159	0.060310	0.093565	0.324546	0.011244	0.046552
Lu	0.268335	0.020438	0.011838	0.010321	0.067437	0.030982	0.021384	0.103187	0.136885	0.009573	0.076436	0.098468	0.304262	0.017078	0.062732
Nd	0.288763	0.015322	0.009584	0.006768	0.063570	0.036352	0.013017	0.090558	0.153204	0.006739	0.059229	0.098705	0.331248	0.015881	0.055876
Sm	0.277669	0.012876	0.006198	0.005393	0.063588	0.030570	0.011953	0.091127	0.143934	0.003480	0.064656	0.094517	0.315389	0.012899	0.056001
U	0.259916	0.065570	0.070977	0.049572	0.138646	0.096098	0.070687	0.133271	0.184613	0.076856	0.101692	0.209334	0.422164	0.081165	0.135297
Yb	0.297705	0.018419	0.008110	0.009631	0.063591	0.028998	0.018412	0.098843	0.155651	0.006167	0.069787	0.091071	0.314381	0.016040	0.058301

Ce	0.271054	0.015069	0.008641	0.004261	0.061150	0.033456	0.010407	0.083117	0.146063	0.005806	0.058887	0.094978	0.322161	0.011581	0.050416
Cr	0.211423	0.063933	0.050915	0.052350	0.053811	0.089129	0.029558	0.108225	0.132996	0.043246	0.115529	0.080812	0.265397	0.029212	0.015840
Cs	0.647991	0.147498	0.184817	0.156254	0.211805	0.277460	0.148460	0.236728	0.414789	0.184833	0.158888	0.383493	0.584015	0.201662	0.206581
Eu	0.255367	0.023641	0.012062	0.013805	0.060419	0.033048	0.013903	0.085746	0.139626	0.007147	0.071550	0.079715	0.305986	0.009209	0.042747
Fe	0.254420	0.033152	0.022797	0.024089	0.039565	0.064058	0.011598	0.096723	0.149285	0.019715	0.085813	0.065810	0.276929	0.019860	0.021798
Hf	0.318689	0.052879	0.035401	0.050391	0.142081	0.017423	0.068676	0.146634	0.185144	0.028697	0.120503	0.123490	0.364485	0.038167	0.125145
Rb	0.527408	0.068516	0.094085	0.064110	0.135851	0.158534	0.077454	0.151189	0.333798	0.099154	0.059896	0.286466	0.530747	0.116347	0.154246
Sb	0.425459	0.326892	0.272798	0.274039	0.233777	0.308027	0.270815	0.304075	0.365727	0.275479	0.395764	0.221525	0.418656	0.244042	0.220443
Sc	0.250199	0.031440	0.021324	0.017024	0.035684	0.063446	0.008019	0.083779	0.145907	0.018311	0.075236	0.076652	0.283008	0.016359	0.019117
Sr	0.000000	0.314122	0.296976	0.297193	0.341808	0.297433	0.271591	0.340809	0.172882	0.286232	0.397096	0.290714	0.434549	0.250501	0.253066
Ta	0.314122	0.000000	0.018141	0.012335	0.089463	0.050654	0.014619	0.115857	0.175642	0.016124	0.056981	0.148330	0.374309	0.027692	0.075433
Tb	0.296976	0.018141	0.000000	0.011856	0.064832	0.037447	0.019641	0.104149	0.158161	0.009182	0.073902	0.094540	0.312365	0.019958	0.063423
Th	0.297193	0.012335	0.011856	0.000000	0.061214	0.045796	0.010076	0.085528	0.166407	0.011331	0.051568	0.115750	0.341127	0.021608	0.058308
Zn	0.341808	0.089463	0.064832	0.061214	0.000000	0.136972	0.056005	0.120974	0.174397	0.069161	0.132204	0.074868	0.225561	0.069489	0.041655
Zr	0.297433	0.050654	0.037447	0.045796	0.136972	0.000000	0.063220	0.144471	0.171626	0.030784	0.112343	0.125376	0.368134	0.038693	0.116106
Al	0.271591	0.014619	0.019641	0.010076	0.056005	0.063220	0.000000	0.087538	0.162941	0.016047	0.055829	0.112856	0.337771	0.019716	0.036439
Ba	0.340809	0.115857	0.104149	0.085528	0.120974	0.144471	0.087538	0.000000	0.228963	0.099763	0.116959	0.167369	0.409456	0.092547	0.113768
Ca	0.172882	0.175642	0.158161	0.166407	0.174397	0.171626	0.162941	0.228963	0.000000	0.143613	0.272362	0.152888	0.244258	0.133311	0.156351
Dy	0.286232	0.016124	0.009182	0.011331	0.069161	0.030784	0.016047	0.099763	0.143613	0.000000	0.072897	0.093035	0.310805	0.013624	0.059081
K	0.397096	0.056981	0.073902	0.051568	0.132204	0.112343	0.055829	0.116959	0.272362	0.072897	0.000000	0.223563	0.561270	0.081781	0.119263
Mn	0.290714	0.148330	0.094540	0.115750	0.074868	0.125376	0.112856	0.167369	0.152888	0.093035	0.223563	0.000000	0.187622	0.091783	0.084306
Na	0.434549	0.374309	0.312365	0.341127	0.225561	0.368134	0.337771	0.409456	0.244258	0.310805	0.561270	0.187622	0.000000	0.305100	0.269357
Ti	0.250501	0.027692	0.019958	0.021608	0.069489	0.038693	0.019716	0.092547	0.133311	0.013624	0.081781	0.091783	0.305100	0.000000	0.045443
V	0.253066	0.075433	0.063423	0.058308	0.041655	0.116106	0.036439	0.113768	0.156351	0.059081	0.119263	0.084306	0.269357	0.045443	0.000000
t.i	9.569654	2.654707	2.351107	2.288852	3.366751	3.339396	2.286497	4.488021	5.808170	2.265995	4.260588	4.337999	10.540535	2.303242	3.009364
vt/t.i	0.207873	0.749338	0.846101	0.869114	0.590859	0.595699	0.870009	0.443241	0.342496	0.877881	0.466901	0.458569	0.188726	0.863684	0.661028
r v,t	0.686610	0.964287	0.991683	0.979437	0.933639	0.974024	0.983339	0.980052	0.725588	0.992677	0.925300	0.780817	0.567605	0.996970	0.958884
vt	1.989273														

Table 2. Compositional variation matrix from the majolica production centers from the Iberian Peninsula. In each column i (i = 1,.,S) are the variances after a logratio transformation using the component x_i as divisor. vt = total variation. τ_i = total sum of variances in column i. vt/τ_i = percentage of variance in the logratio covariance matrix using the component $x_{.i}$ as divisor due to the total variation. $r_{v.\tau}$ = correlation between the values τ_{ij} ($i \neq j$) and the corresponding values τ_i (j = 1,.,i - 1,i + 1,.,S)

	BCN-DR (n=22)		BCN-SC (n=5)		BCN-PI (n=7)		Reus (n=15)		VdP (n=15)		Teruel 2 (n=14)		Teruel 1 (n=15)	
Components	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
As	20.22	11.29	34.57	16.76	16.91	1.79	16.15	2.27	18.56	3.95	17.94	2.00	84.90	174.01
La	38.78	1.53	35.32	1.53	41.40	0.78	30.31	1.36	42.10	0.95	39.13	1.53	39.79	3.22
Lu	0.40	0.03	0.35	0.02	0.43	0.02	0.30	0.03	0.43	0.03	0.35	0.02	0.38	0.03
Nd	33.51	2.08	31.24	2.87	34.77	1.65	25.54	1.60	36.93	2.01	34.20	1.38	33.69	3.17
Sm	6.84	0.29	6.26	0.31	7.35	0.13	5.15	0.24	7.34	0.15	7.00	0.26	6.75	0.53
U	3.38	0.34	2.42	0.21	3.41	0.26	3.21	0.65	3.77	0.26	3.31	0.54	2.74	0.34
Yb	2.96	0.18	2.68	0.26	3.32	0.27	2.03	0.10	3.11	0.11	2.78	0.15	2.95	0.22
Ce	77.15	3.58	71.31	3.68	85.03	5.01	60.05	2.76	83.85	1.82	78.60	3.21	75.17	6.24
Co	15.81	4.61	15.99	2.20	16.27	1.71	14.72	1.75	17.76	2.02	18.74	2.37	37.23	47.92
Cr	69.13	4.61	60.41	3.36	72.98	1.97	71.85	5.46	77.82	1.81	74.79	5.52	70.57	7.20
Cs	17.96	2.45	5.74	0.63	17.57	1.48	15.32	2.76	8.87	0.45	18.47	1.21	13.11	0.95
Eu	1.27	0.05	1.18	0.05	1.36	0.03	0.98	0.04	1.40	0.03	1.31	0.07	1.31	0.12
Fe (wt%)	3.52	0.22	3.08	0.20	3.77	0.09	2.98	0.11	4.25	0.09	3.89	0.30	3.59	0.27
Hf	5.07	0.34	4.97	0.26	6.60	0.39	3.14	0.23	5.03	0.36	4.94	0.26	6.83	0.39
Ni	27.95	27.34	19.61	27.16	31.11	24.21	32.59	23.35	34.80	25.75	23.61	26.32	38.28	28.60
Rb	223.78	21.00	103.17	3.80	210.25	9.25	113.42	12.13	148.61	7.58	221.25	13.41	131.09	9.86
Sb	3.15	2.26	2.53	0.29	2.24	0.12	2.08	0.73	3.05	0.46	1.67	0.09	2.66	0.16
Sc	13.55	0.65	11.81	0.54	13.90	0.39	11.66	0.69	15.89	0.37	13.71	0.95	12.75	1.21
Sr	165.17	40.41	219.53	26.92	127.15	13.65	495.61	70.29	229.18	33.15	257.40	50.79	250.19	36.06
Ta	1.21	0.08	1.02	0.06	1.27	0.03	0.92	0.04	1.27	0.06	1.54	0.05	1.22	0.08
Tb	0.93	0.09	0.80	0.04	0.99	0.10	0.66	0.06	1.02	0.08	0.92	0.09	0.91	0.10
Th	13.52	0.60	11.85	0.51	14.12	0.31	10.18	0.49	14.53	0.37	13.41	0.38	12.21	0.89
Zn	117.46	19.60	91.58	10.49	112.19	15.82	78.89	12.08	126.74	4.63	78.62	7.11	60.45	6.59
Zr	126.43	18.60	133.44	21.30	162.75	23.94	91.98	18.52	147.37	20.10	125.31	18.55	165.66	15.93
Al (wt%)	7.54	0.34	6.61	0.39	7.64	0.24	6.82	0.33	8.84	0.27	9.52	0.52	7.57	0.58
Ba	541.51	136.96	375.19	31.48	484.83	52.98	602.33	633.24	640.82	62.00	505.12	41.73	363.74	48.80
Ca (wt%)	10.84	1.08	17.16	1.07	8.30	0.83	17.82	0.76	8.61	0.61	6.88	0.90	6.32	0.67
Dy	4.88	0.26	4.43	0.42	5.06	0.19	3.58	0.21	5.08	0.27	4.80	0.17	4.96	0.45
K (wt%)	2.67	0.76	1.79	0.20	2.78	0.30	1.95	0.28	2.79	0.29	3.38	0.16	2.22	0.25
Mn	568.61	48.06	497.22	23.99	671.50	75.11	420.47	51.10	741.28	67.38	350.97	46.74	449.20	60.83
Na (wt%)	0.59	0.35	0.32	0.05	0.53	0.16	0.42	0.09	0.38	0.14	0.19	0.04	0.17	0.04
Ti	3750.42	492.31	3484.56	221.99	4012.19	293.06	3221.87	215.24	4145.82	228.52	3781.59	209.22	3862.80	391.95
V	94.57	7.49	82.90	12.33	99.68	8.69	97.50	8.64	118.68	9.92	88.33	7.65	88.61	9.02

Table 3

	Muel 1 (n=11)		**Muel 2 (n=15)**		**Villafeliche (n=15)**		**Paterna (n=14)**		**Manises (n=15)**		**OB/SA (n=10)**	
Components	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
As	28.39	10.16	16.65	1.61	10.46	5.56	18.44	1.96	18.60	1.34	26.41	10.93
La	39.99	0.99	37.98	0.85	39.27	1.72	35.13	2.20	35.92	0.98	34.81	2.72
Lu	0.36	0.02	0.38	0.03	0.44	0.04	0.37	0.03	0.36	0.03	0.36	0.04
Nd	34.87	1.67	32.29	1.72	32.47	2.18	31.03	2.32	31.26	0.82	28.43	1.96
Sm	6.91	0.16	6.59	0.13	6.81	0.28	6.37	0.39	6.41	0.18	5.76	0.43
U	3.34	0.36	3.40	0.35	6.93	1.35	3.32	0.32	3.30	0.34	3.28	0.21
Yb	2.72	0.08	2.77	0.08	2.75	0.19	2.61	0.16	2.58	0.17	2.43	0.21
Ce	80.11	1.93	78.18	3.35	80.84	2.56	72.09	4.64	70.39	2.41	69.63	5.66
Co	20.52	1.46	19.77	1.86	19.71	2.81	12.04	0.70	15.33	2.48	24.07	3.99
Cr	73.96	6.04	56.75	3.68	68.78	3.21	59.43	6.77	63.70	2.82	90.24	6.67
Cs	8.03	0.40	6.53	0.29	7.24	0.65	14.33	1.61	9.06	1.47	8.13	1.49
Eu	1.38	0.04	1.30	0.04	1.30	0.04	1.15	0.06	1.19	0.03	1.17	0.09
Fe (wt%)	3.76	0.33	2.98	0.08	2.92	0.13	2.92	0.11	3.20	0.13	3.99	0.35
Hf	5.32	0.31	6.93	0.28	5.86	0.33	5.31	0.32	4.88	0.32	3.92	0.32
Ni	30.89	22.81	15.03	20.40	26.27	26.27	22.62	22.39	36.61	13.04	41.78	22.95
Rb	132.34	6.18	115.19	4.41	161.64	11.72	182.46	18.11	128.88	10.11	118.04	16.94
Sb	3.53	0.11	3.40	0.18	2.35	0.69	1.16	0.08	1.42	0.33	4.94	2.39
Sc	13.37	0.57	11.10	0.29	12.67	0.65	11.14	0.78	11.20	0.42	14.49	1.20
Sr	370.55	43.35	312.93	32.66	635.66	44.54	183.92	50.92	355.56	42.13	606.37	51.16
Ta	1.17	0.04	1.13	0.04	1.19	0.04	1.54	0.13	1.22	0.05	1.18	0.11
Tb	0.85	0.05	0.89	0.07	0.84	0.06	0.84	0.10	0.83	0.06	0.76	0.04
Th	13.27	0.31	12.40	0.32	13.60	0.48	12.30	0.81	11.52	0.37	11.84	1.04
Zn	84.09	15.98	62.66	3.45	67.40	11.08	59.87	5.13	70.34	11.03	103.26	12.35
Zr	145.41	21.94	170.69	12.74	163.79	14.89	144.42	12.64	135.38	14.89	111.62	12.44
Al (wt%)	7.89	0.29	6.51	0.20	7.39	0.45	7.55	0.51	6.86	0.35	8.23	0.78
Ba	588.09	65.69	531.76	46.88	540.72	45.43	352.77	33.54	556.66	828.02	362.42	67.94
Ca (wt%)	11.24	0.55	10.69	0.29	12.01	0.69	10.25	1.15	15.88	1.01	14.37	1.61
Dy	4.62	0.23	4.63	0.26	4.51	0.26	4.59	0.32	4.47	0.27	4.08	0.44
K (wt%)	2.65	0.24	2.50	0.18	2.77	0.23	2.80	0.21	2.43	0.17	2.18	0.31
Mn	642.31	82.68	574.08	36.86	335.16	22.56	278.84	12.66	476.17	52.25	651.21	22.43
Na (wt%)	0.30	0.09	0.27	0.04	0.20	0.05	0.20	0.10	0.25	0.04	0.39	0.08
Ti	3859.31	418.97	3778.90	363.62	4014.24	273.30	3642.52	250.59	3339.24	236.62	3884.04	455.02
V	92.44	10.24	66.26	5.89	78.82	6.86	74.12	5.94	81.04	7.13	126.84	9.84

Table 3

	REM (n=5)		**Puente (n=15)**		**Talavera (n=14)**		**Sevilla (n=34)**		**MJ0018**	**MJ0124**	**MJ0317**	**TRI004**	**DIA537**
Components	mean	sd	mean	sd	mean	sd	mean	sd	concentration	concentration	concentration	concentration	concentration
As	38.80	7.76	21.56	2.43	22.47	9.85	18.67	11.20	15.28	11.22	10.71	17.53	30.97
La	41.60	0.29	38.15	0.85	38.77	1.69	30.94	1.75	40.93	33.35	30.30	33.18	39.03
Lu	0.43	0.03	0.47	0.02	0.44	0.03	0.33	0.02	0.34	0.38	0.30	0.34	0.40
Nd	33.23	0.95	34.58	1.46	35.80	2.92	26.22	2.48	35.63	29.15	24.57	27.81	31.69
Sm	6.87	0.05	7.42	0.16	7.44	0.32	5.63	0.29	7.07	6.02	5.44	5.89	6.88
U	4.44	0.84	5.24	0.37	4.83	0.47	2.44	0.29	3.32	3.32	2.44	2.42	3.45
Yb	2.83	0.22	2.97	0.11	3.01	0.21	2.35	0.18	2.51	2.39	2.32	2.58	2.82
Ce	83.59	0.98	79.98	1.64	79.88	3.61	61.92	3.46	84.42	69.09	60.60	64.89	77.39
Co	31.11	6.53	14.12	1.24	15.10	2.76	15.33	4.25	18.64	10.89	12.89	16.04	20.26
Cr	106.11	2.51	57.92	3.32	53.08	5.38	72.40	7.15	85.46	55.72	51.28	77.30	71.69
Cs	10.89	0.62	11.67	0.46	10.27	0.83	5.11	0.72	9.11	9.25	2.73	2.65	9.96
Eu	1.41	0.01	1.23	0.03	1.19	0.06	1.14	0.07	1.34	1.12	1.09	1.23	1.30
Fe (wt%)	5.01	0.08	3.55	0.19	3.27	0.29	3.21	0.25	4.19	2.62	3.16	3.28	3.39
Hf	3.75	0.06	5.45	0.48	5.85	0.76	5.35	0.48	4.65	5.36	5.07	5.59	4.97
Ni	58.44	34.85	17.04	19.74	15.30	31.86	18.53	18.67	0.00	37.98	52.27	40.60	0.00
Rb	168.83	8.01	165.03	9.42	157.10	18.76	74.49	11.54	173.64	119.88	46.79	39.26	151.39
Sb	5.15	0.22	1.86	0.69	1.76	0.78	3.09	3.30	1.75	1.26	2.74	1.48	15.64
Sc	18.50	0.31	12.64	0.59	11.83	0.82	11.22	0.99	15.34	10.60	10.75	12.29	13.72
Sr	750.22	213.22	353.97	45.64	329.46	40.15	456.15	63.98	383.28	296.94	424.31	436.71	191.32
Ta	1.32	0.04	1.50	0.06	1.47	0.15	0.93	0.06	0.98	1.25	0.89	1.06	1.18
Tb	0.95	0.08	1.03	0.15	1.02	0.10	0.75	0.06	0.82	0.80	0.68	0.80	0.92
Th	15.15	0.16	14.74	0.48	14.88	0.79	9.23	0.52	15.26	11.62	8.92	9.52	13.24
Zn	138.29	13.48	80.58	4.79	79.92	7.87	72.50	8.52	79.70	60.74	67.97	83.50	106.25
Zr	112.66	12.12	161.11	12.63	154.05	21.03	134.83	15.97	118.16	161.63	125.16	114.25	104.44
Al (wt%)	9.34	0.92	8.21	0.43	7.77	0.56	5.93	0.57	9.99	6.35	5.77	6.58	7.31
Ba	513.35	28.26	406.55	39.11	377.09	35.45	343.69	129.48	656.52	285.76	331.28	344.43	368.17
Ca (wt%)	8.89	0.42	12.63	0.74	13.02	0.98	14.83	1.22	9.30	15.02	11.86	14.14	14.84
Dy	4.51	0.34	5.17	0.24	5.20	0.34	4.11	0.32	4.64	4.35	3.67	4.75	4.78
K (wt%)	2.92	0.53	2.37	0.19	2.27	0.34	1.43	0.36	3.48	2.06	1.48	1.32	2.37
Mn	657.12	15.61	520.38	24.96	495.33	29.40	649.57	137.41	507.12	316.71	572.45	805.82	520.15
Na (wt%)	0.77	0.25	0.37	0.04	0.48	0.16	0.65	0.17	0.16	0.29	0.32	1.03	0.41
Ti	3652.23	370.75	3835.45	361.78	3500.05	277.22	3448.54	347.88	2418.39	3772.59	3253.86	3292.51	3576.24
V	166.99	12.41	79.68	8.24	68.23	5.36	81.65	11.31	111.10	65.13	64.11	103.19	108.47

Table 3. Mean and standard deviation (sd) of the different chemical groups characterized by NAA from 246 majolica shards from the main production centers of the Iberian Peninsula. All values are expressed as ppm (µg/g) except those expressed as weight % in brackets.

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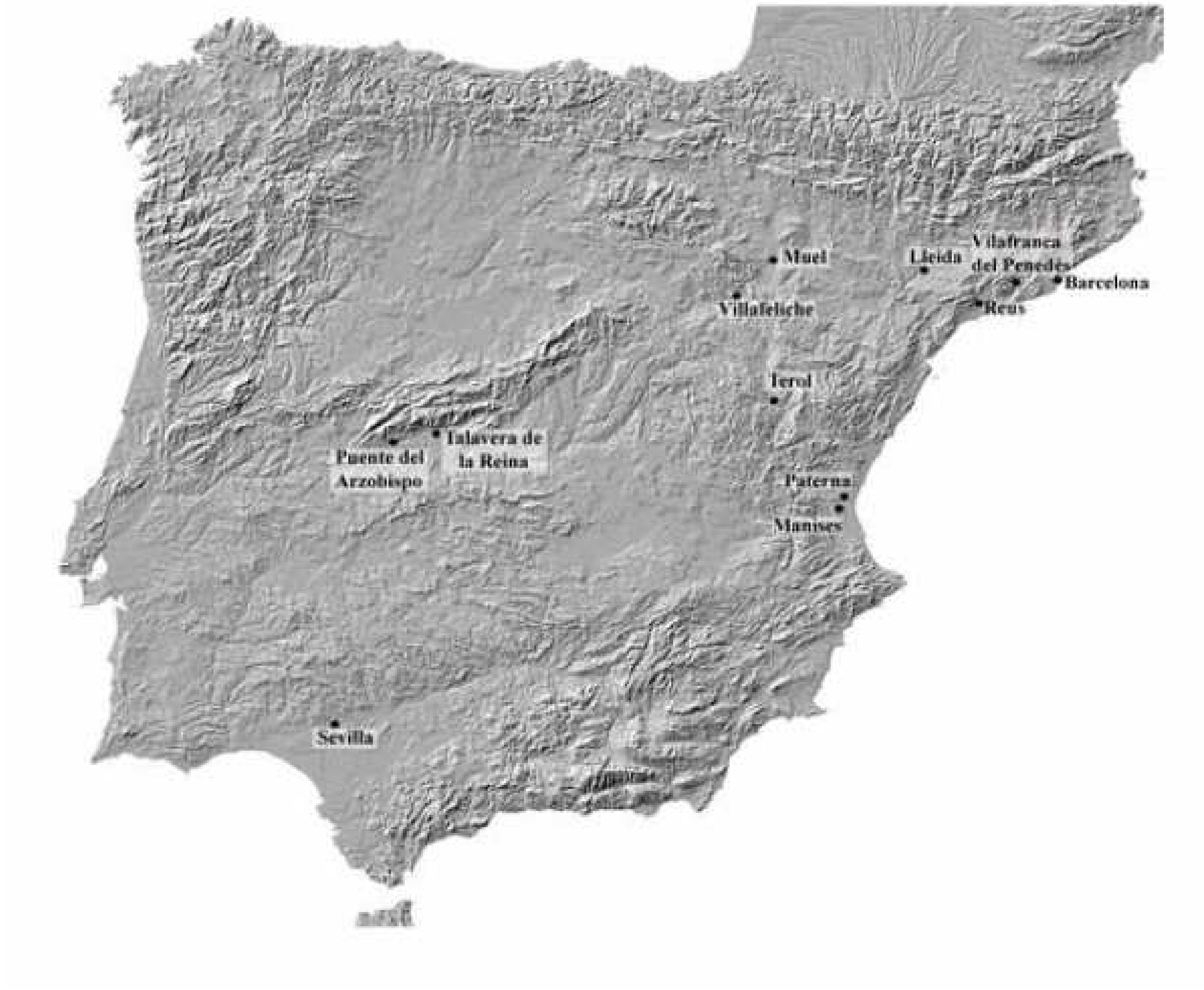

Figure 1. Main production center locations

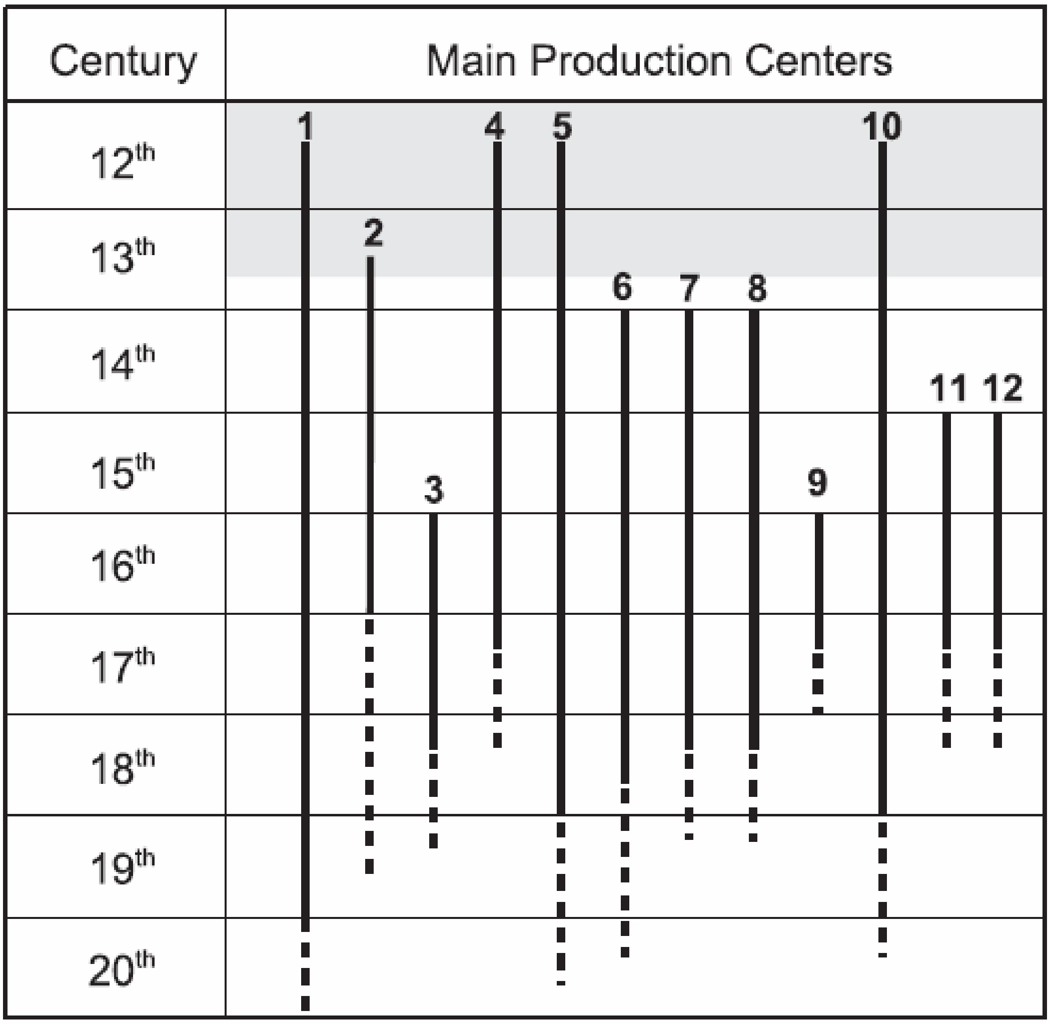

Figure 2. Chronological table of the main production centers from the Iberian Peninsula. Shaded area represents production activities during the Islamic period. 1, Seville; 2, Talavera de la Reina; 3, Puente del Arzobispo; 4, Paterna; 5, Manises; 6, Barcelona; 7, Reus; 8, Lleida; 9, Vilafranca del Penede`s; 10, Teruel; 11, Muel; 12, Villafeliche

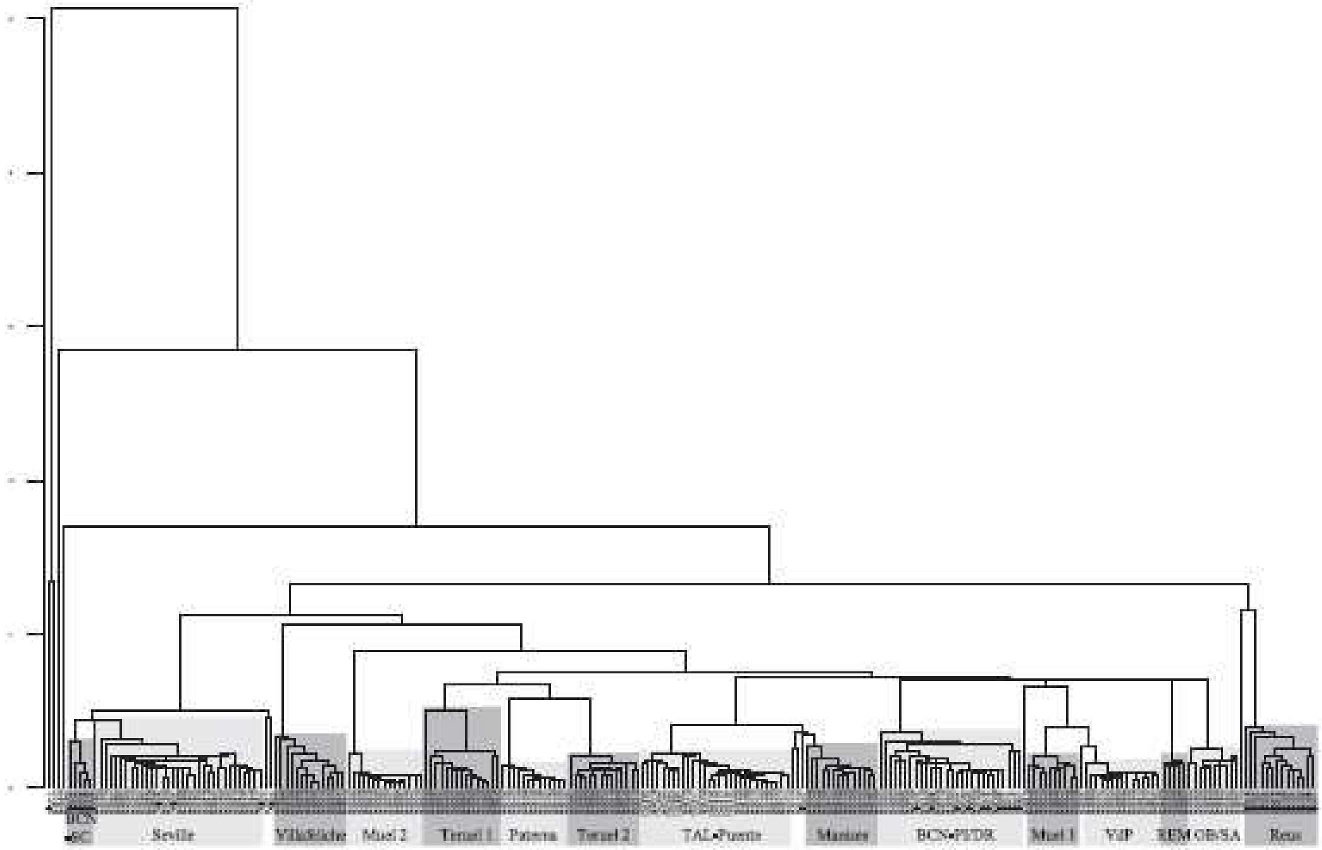

Figure 3. Dendrogram resulting of the cluster analysis of NAA data of the ceramics from the main majolica production centers from the Iberian Peninsula using the Square Euclidian Distance and the centroid algorithm on the subcomposition: Lu, Nd, Sm, U, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Ta, Tb, Th, Zn, Zr, Al, Ca, Dy, Mn, Ti and V, using La as divisor. BCN-SC, Barcelona Santa Creu; BCN-PI/DR, Barcelona Santa Maria del Pi and Barcelona Drassanes; TAL-Puente, Talavera de la Reina and Puente del Arzobispo; VdP, Vilafranca del Penede`s; REM, Lleida Remolins; OB/SA, Lleida Obradors and Sant Anastasi