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Application of chemical, physical and chemometric analytical techniques to the study of ancient ceramic oil lamps

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Abstract

A chemical, mineralogical and morphological characterization of 54 fragments of oil lamps found in two Spanish archaeological sites (*Cordoba* and *Herrera de Pisuerga* (*Palencia*)) has been performed. Flame atomic absorption and emission spectrometry were used for the determination of Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O and TiO_2 as major constituents and Cu, Cr, Ni, Pb and Zn as minor and trace selected elements. Physical, mineralogical and morphological analyses were made by using dilatometry at constant heating rate for the thermal behaviour, X-ray diffraction spectrometry for the mineralogical composition and, in a group of selected samples, scanning electron microscopy and polarizing petrographic microscopy for the observation of thin layers and mineral identification. Separations of light and heavy minerals were carried out with bromoform and X-ray diffraction analysis was applied to both fractions. Multivariate statistical analysis was used to establish correlations between variables and to deduce factors which allow the gathering of oil lamp samples in groups as a function of their composition.

The results of these analyses allow the comparison among pieces and the establishment of conclusions about several aspects of their manufacture, the origin of the raw materials and the provenance of the oil lamps (local or imported). They provide information supporting certain archaeological hypothesis. For example, some oil lamps found in *Herrera de Pisuerga* showed a clearly different physicochemical composition. They were probably brought from *Italy* by the Roman Legions together with their initial furniture household.

Keywords: Archaeometry; Ceramics; Multivariate analysis

1. Introduction

Traditional methods with a largely archaeological and typological basis did not enable us to obtain enough information about several aspects regarding the nature and origin of ancient ceramic materials. This is the reason why a large number of articles have recently emerged devoted to study these materials using physical and chemical analyses. Among these studies, geological and ceramic reference materials have been used [1,2] to establish decomposition procedures and analysis schemes using different techniques, such as ICP-AES, NAA, XRF and results, were statistically evaluated. Other large number of appeared articles introduce us into the importance of physicochemical and chemometric data for classification of ceramic pieces within archaeological realm. In these sense, tile fragments [3,4], amphorae sherds and fine ware [5–10], ancient bricks [11], figure vases [12], etc. were analyzed by different techniques and data were subjected to statistical treatment by multivariate analyses in order to classify ceramic pieces into compositional groups, where the obtained results often supported archaeological hypothesis previously established.

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During the last decades, ancient roman pottery oil lamps have been one of the ancient ceramic types studied in great profusion due to the interest of scientists to reach a better knowledge of Roman society through the investigation of these ceramic objects [13,14]. The main objectives of these studies were the following: (i) the determination of chronological data. Roman pottery oil lamps present a well known morphological evolution that allows us to date archaeological quarries with a quite precision. (ii) The establishment of geographical origin of the ceramic paste and the technology used in their manufacture process. (iii) The location of production centres and the commercial ties that link these centres with the different Roman Empire cities. Although the first item has been well studied in this type of archaeological objects [15], the others require a most deep research in the field of the physicochemical characterization of these materials, the interpretation of the data and statistical study of the results that help us to classify them in groups sharing a similar composition.

Iberian Peninsula constitutes one of the most important places where Roman archaeological sites containing pottery oil lamps were discovered. Among others, Morillo [15] is one of the scientists that studied complete series of *Hispanic workshops* and looked into the military policy of Augustus in the Norwest of the Iberian Peninsula. An example of these archaeological quarries is the ancient Roman military settlement sited in *Herrera de Pisuerga* (*Palencia*, Spain) where the Third Macedonian Legion remained from the 20–15-year B.C. to about the 39-year A.D., during the Augustus and Tiberius commands. A great number of pottery oil lamps were found there [15,16], most of them corresponding to *Vogelkpoflamper* or *Dressel 4* type (so called "bird headed type") [17].

The purpose of this paper was to discern if pottery oil lamps found during the archaeological excavation in the area of *Herrera de Pisuerga* (*Palencia*, Spain) were manufactured by the local military settlement workshop or maybe they were imported from *Italy* either through the Hispanic Mediterranean and the *Ebro Valley* ports or through Roman Legions together with their initial furniture.

The analytical chemistry is an essential and indispensable discipline to tackle these studies. Therefore, a chemical, mineralogical and physical characterization of pottery oil lamps from *Herrera de Pisuerga* was made to carry out this investigation. The composition of these oil lamps was compared with those of the clay materials from the surrounding areas of the archaeological site in order to support the theories exposed above. In the same way, a physicochemical comparison with pottery oil lamps from another Roman settlement discovered in the south of the Iberian Peninsula, specifically in *Cordoba* (Spain) [18], was carried out. Owing to the large number of chemical and mineralogical results, several multivariate statistical studies were additionally performed in order to obtain relations among pottery oil lamps with similar characteristics and to establish significant differences among them that might help to shed more light on the manufacture technology and the use of these oil lamps.

2. Experimental

2.1. Description of the samples

Samples consisted of fragments of 54 different pottery oil lamps from archaeological deposits located in two Spanish provinces: *Palencia* and *Cordoba* (see Fig. 1A). They were selected from an archaeological point of view; 32 of them were collected in the archaeological excavations of *Herrera de Pisuerga* (*Palencia*, Spain) and dated from 10 B.C. to 40 A.D. [15] and 22 were collected in another archaeological excavation sited in *Cordoba* together with *Hispanic terra sigillata* pottery, and as a consequence they are dated in the Julius–Claudius period [19]. All samples are Late Republicans. As an example, a photograph and a scheme of their different parts are included in Fig. 1B and C.

Samples were obtained by taking a minimum part of the archaeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. These samples were ground in an agate mortar and pestle before analyses, in order to reduce the particle size and to secure homogeneity.

2.2. Physicochemical analyses

Flame atomic absorption spectroscopy (FAAS), using a Perkin-Elmer 503 spectrometer, was employed for determining several major and minor elements, including Al, Ca, Cu, Cr, Fe, Mg, Mn, Ni, Pb, Ti and Zn. K and Na were measured using the same instrument in flame emission mode. Silica content was deduced by difference. The previous sample dissolution was carried out in the following way: a minimum amount of sample was treated with hydrofluoric acid in an open vessel and heated on a hot plate. It was followed by addition of aqua regia, heating again until dryness. The residue was dissolved with 1 ml of concentrated hydrochloric acid and diluted with water to the mark in Teflon volumetric flasks. Care was taken to keep the contamination to a minimum. Ultrapure water was used throughout and all reagents used were of analytical grade. In all flame and emission spectroscopy determinations, blanks of reactive were analyzed giving signals under the detection limits.

Light and heavy mineralogical fractions were separated by using bromoform (2.89 of specific gravity) [20]. The lighter fraction remains floating in the surface while the heavier one is deposited at bottom. Grains were identified through optical microscopy [21]. The mineral composition of the original samples and of heavy and light fractions was determined by X-ray diffraction spectrometry (XRD), with the powder method [22–24] by using a Siemens D-5000 diffractometer and working with Cu Kα radiation and Ni filter. Applied voltage and anodic current were 40 kV and 20 mA, respectively.

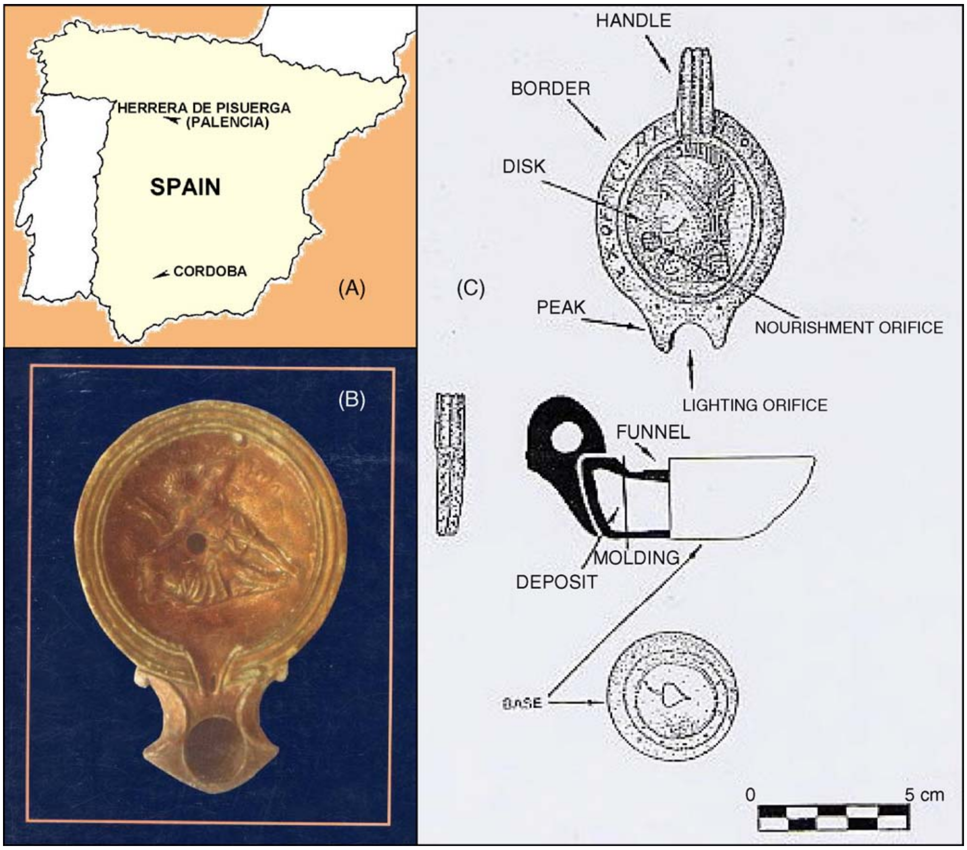

Fig. 1. (A) Location map of the archaeological sites. (B) Oil lamp photograph. (C) Oil lamp elements.

Transversal thin sections of the samples (20–25 μm) were cut off. When it was impossible to obtain thin sections of samples, they were consolidated with resin and cut off after drying as described. Mineral components and ceramic paste texture were observed using a Petrographic Polarisation Orto Plan Pol Leitz Microscope. In addition, observations of 1 μm layers corresponding to some ceramic samples, polished with diamond, were made by scanning electron microscopy (SEM) using a Carl Zeiss 500E microscope and quantified with an energy dispersive X-ray (EDX) analyzer.

Thermal behaviour of samples was studied using a Adamel-Lhomargy dilatometer in the following conditions: a 7 mm of length cylinder was used in an air stream in a range of temperatures from 25 °C to 1000 °C, with a heating rate of 5 °C min^{-1}, using an alumina standard.

2.3. Statistical study of some chemical and mineralogical parameters

A statistical processing of the data was carried out using the SPSS program, version 11.5 for Windows®. Correlation and multivariate statistical analyses were performed by using chemical and mineralogical data of the 54 studied samples. The variables were grouped in three different studies: (i) 14 corresponding to chemical data (SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, TiO_2, Cu, Cr, Ni, Pb and Zn), (ii) 9 variables corresponding to data of total mineralogical composition (calcite, quartz, dolomite, gehlenite, anorthite, feldspars, phyllosilicates, piroxene and wollastonite) and (iii) those 12 for heavy mineralogical fraction (tourmaline, zircon, rutile, garnet, andalousite, distene, epidote, diopside, apatite, hornblende, sillimanite and staurolite). Supervised Pattern Recognition was applied in this study. Linear discriminant analysis was used for hard classification purposes, trying to establish possible connections among groups of samples and variables [4,25]. This procedure is useful for classifying the oil lamp dataset into groups according to the places where the samples were found. It generates a small number of functions of quantitative measurements which are linear combinations of the standardized pattern variables with weight coefficients. These functions are called canonical discriminant functions and help to discriminate among groups of oil lamp samples with different origin. The procedure assumes that the variables are drawn from population with multivariate normal distributions and that variables have equal variances.

3. Results and discussion

3.1. Chemical analysis

Major constituents, such as Si, Al, Ca, Fe, K, Mg, Mn, Na and Ti, were determined in the samples and the results calculated as percentage of their respective oxides. The content

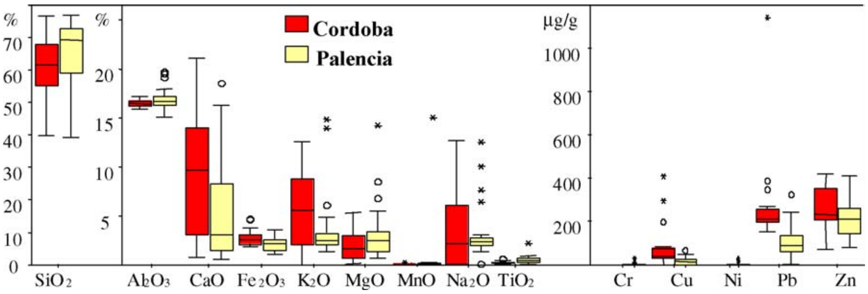

Fig. 2. Box & Whisker Plot of the chemical components.

of some minor elements (Cu, Cr, Ni, Pb and Zn) were also obtained. The results deduced for each compound are represented in Box & Whisker Plot (Fig. 2). In this plot, each box encloses the middle 50%, where the median is represented as a horizontal line inside the box. Vertical lines extended from each end of the box (called whiskers) enclose data within 1.5 interquartile ranges. Values falling beyond whiskers, but within three interquartile ranges (*suspect outliers*), are plotted as individuals points (○). Far outside points (*outliers*) are distinguished by asterisks. This plot has been divided into three different scale zones. SiO_2 content is represented in the left part of the diagram, where samples found in both workshops, *Cordoba* and *Palencia*, show similar dispersion with negative asymmetry.

Major chemical elements are represented in the central part of the plot. A great variability in CaO content is observed, mainly caused by lime milk treatments. Dispersion and mean value are higher in samples found in *Cordoba* than in *Palencia* ones and both show a positive asymmetry. K_2O and Na_2O have more dispersed values in samples found in *Cordoba*, although the averages are similar for Na_2O and higher for K_2O in *Cordoba* samples. There are more outliers and extreme values in those from *Palencia* corresponding to samples probably of *Italian* origin.

Minor chemical elements, selected as indicators of the raw materials as well as of the deliberated addition of certain substances to improve the properties of the ceramic pastes are represented in the right part of the plot. In this sense, concentrations of Cu, Pb and Zn are higher in samples from *Cordoba* than those from *Palencia*. Cr and Ni are non-detected elements in all cases except in four isolated samples from *Palencia* supposedly of *Italian* origin.

A Supervised Patterns Recognition Study was applied to all chemical results obtained for the 54 samples. Linear discriminant analysis was designed to develop a set of discriminating functions which can help to classify samples and to extract all those lamps with significant differences in chemical composition. 54 cases were applied to this study and 14 predictor variables were entered: 9 major constituents (SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O and TiO_2) and 5 minor or trace elements (Cu, Cr, Ni, Pb and Zn).

Fig. 3 is a graphical representation of the samples as a function of the two canonical discriminant functions. F1 represents 90.1% of the variance and F2 9.9%. These functions with *P*-values less than 0.05 are statistically significant at 95% confidence level. The projection of each variable is also represented in the figure. MnO variable was not considered in this study since the analysis did not overcome the tolerance

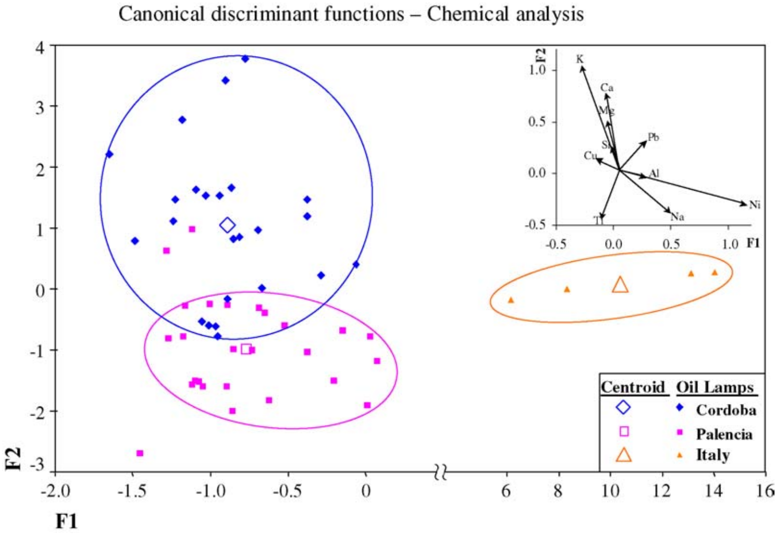

Fig. 3. Linear discriminant analysis of the chemical components.

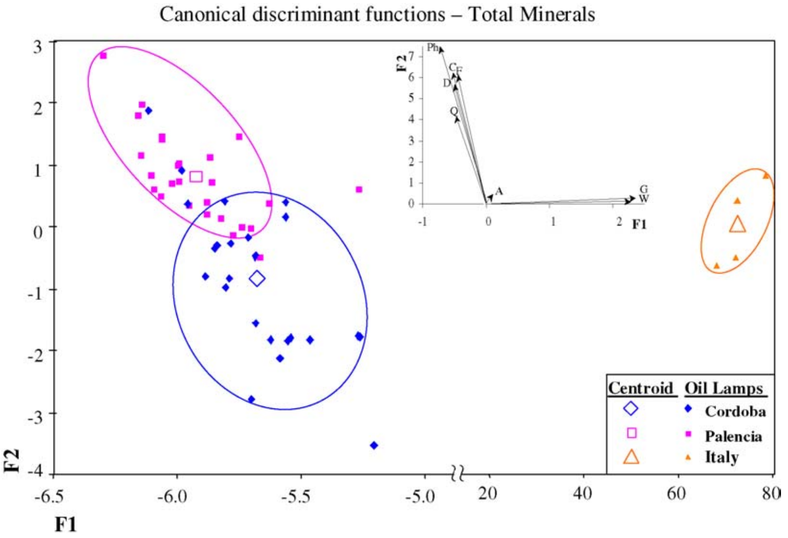

Fig. 4. Linear discriminant analysis of the total mineral components.

test (0.001). Three different categories were selected according to the origin places (*Cordoba*, *Palencia* and *Italy*). Each category is well represented in Fig. 3 and it is characterized by a centroid (marked as a big point without filling) which is the average for each group (unique value in the classification factor field). The oil lamp samples belonging to each category are group inside an enclosure. Only three points were estimated as aberrant patterns (or outliers) and they were not included in the group of *Palencia*.

Suspected samples from *Italy* are located really far away at high values of F1, mainly due to the elevated concentrations of Ni and Na_2O, while samples from *Cordoba* and *Palencia* have negative values of this function or very close to zero. On the other hand, samples found in *Cordoba* showed more dispersive values than those in *Palencia*, as a consequence of higher dispersion in the concentrations of K_2O and Na_2O already mentioned above. Some additional samples were also analyzed. They were taken from clays found in the surroundings of the *Palencia* and *Cordoba* settlements. The analytical results were introduced in this statistical study and they are according with their corresponding sherds of oil lamps results. This is an evidence that these specimens were likely local products, and compositional differences between local oil lamps might account for the use of different clays, for clay mixing or for addition of different tempers or additives; besides, compositional variability with a single clay bed might also be taken into account, particularly if the exploitation went on for a relatively long period of time. Only the four samples highly displaced in Fig. 3 seem to be imported products owing to their really different composition.

3.2. *Mineralogical analysis*

The mineralogical characterization of the original samples was deduced by XRD. Quartz, phyllosilicates, feldspars, calcite and dolomite were the major mineral constituents. In general, samples found in *Cordoba* showed a lower proportion of feldspars and quartz and they were enriched in calcite. A statistical study similar to the one carried out with the chemical results was made with the nine crystalline phases found by XRD as predictor variables in the 54 cases (Fig. 4). Canonical discriminant functions were deduced from the mineral composition (quartz (Q), calcite (C), dolomite (D), feldspars (F), phyllosilicates (P), anorthite (A), wollastonite (W), gehlenite (G) and pyroxene (P)). F1 represents 99.8% of the total variance and it is affected mainly by the presence of gehlenite and wollastonite. As it can be seen, there is also an association of phyllosilicates, calcite, dolomite, felspars and quartz. These minerals behave in different way to gehlenite and wollastonite, whereas anorthite and pyroxene appear more dispersed, with a more individualized behaviour and with a scarcely influence in the score. F1 allows us again to distinguish a group formed by four samples found in *Palencia* settlement with a mineralogical composition clearly different from the other samples. These samples are the same ones that showed a noticeable difference in the chemical analysis. They showed the strongest peaks for quartz and clay mineral relics. Peaks of the diffractogram at 3.30 Å and 2.85 Å correspond to calcite and gehlenite, respectively. In these samples a displacement was observed in the peaks of calcium aluminiumsilicate due to the solid solution of iron and magnesium on the gehlenite similar to those observed by Peters and Iberg [26]. Similar effects were observed in the pseudowollastonite (peaks at 2.98 Å and 2.94 Å). Peaks at 3.27 Å, 3.22 Å and 3.18 Å show the formation of anorthite, with small size and low crystallisation degree. The presence of gehlenite, wollastonite and, in a lower extent, anorthite and diopside in the supposed *Italian* samples are found is a consequence of the reactions occurring when Ca-rich clays are fired [11]. These samples will be considered of *Italian* origin from now on and they are displaced in Fig. 4 due mainly to the presence of gehlenite and wollastonite, both undetected in the oil lamp samples from *Palencia* and *Cordoba*. Samples from *Cordoba* and *Palencia* are also scattered in two zones with a small communal area due to their differences in quartz, calcite, dolomite and felspars contents. This grouping provides the proper classification of 85.2% of the original cases.

In additional studies, it has been proved that the bulk of *Palencia* samples showed a mineralogical composition (silicates, phyllosilicates and carbonates) in agreement with local muddy lodes sited in the *Pisuerga Valley* [27].

On the other hand, samples were subjected to a treatment with bromoform to isolate the heavy minerals from the light ones. This separation drives to the characterization of the heavy minerals that otherwise could not be detected due to their low-level contents. Both fractions (heavy and light minerals) were analyzed by XRD. The light fraction was the most abundant (84% in the *Palencia* samples and 94% in the *Cordoba* samples). The diffractograms were very similar in all cases to those obtained from the original sample. This fraction was mainly constituted by phyllosilicates, quartz and calcite, with important amounts of dolomite and feldspars in most samples. It can be observed the presence of other crystalline phases, such as wollastonite and gehlenite, only detected in the four *Italian* samples and the presence of much higher amounts of anorthite in these samples. The distributions of the average values of minerals found in each fraction classified by their origin are shown in the histograms of Fig. 5. Samples were grouped in samples from *Cordoba*, *Palencia* and *Italy*. The latter correspond to those samples found in *Palencia* with a remarkable different composition and presumably with different origin. It was very interesting to detect the presence of pyroxene, a mineral associated to volcanic rocks, in samples from *Cordoba* and *Italy*. The inclusion of these volcanic materials has always been one of the main characteristics of the ceramic productions from the *campano-lacial area*, a very famous *Italian* zone due to its remarkable volcanism. In the same way, the presence of volcanic areas is nowadays well documented in different zones of the south of the Iberian Peninsula (*Alboran Sea* and *Baetic Mountains*) [28]. These volcanic materials were frequently added to ceramic pastes in order to decrease the plasticity of the pastes during the firing process avoiding cracks [7] and they are evidences of the presumable local manufacture of ceramic pieces from *Cordoba* and of *Italian* origin of those four anomalous samples found in *Palencia*.

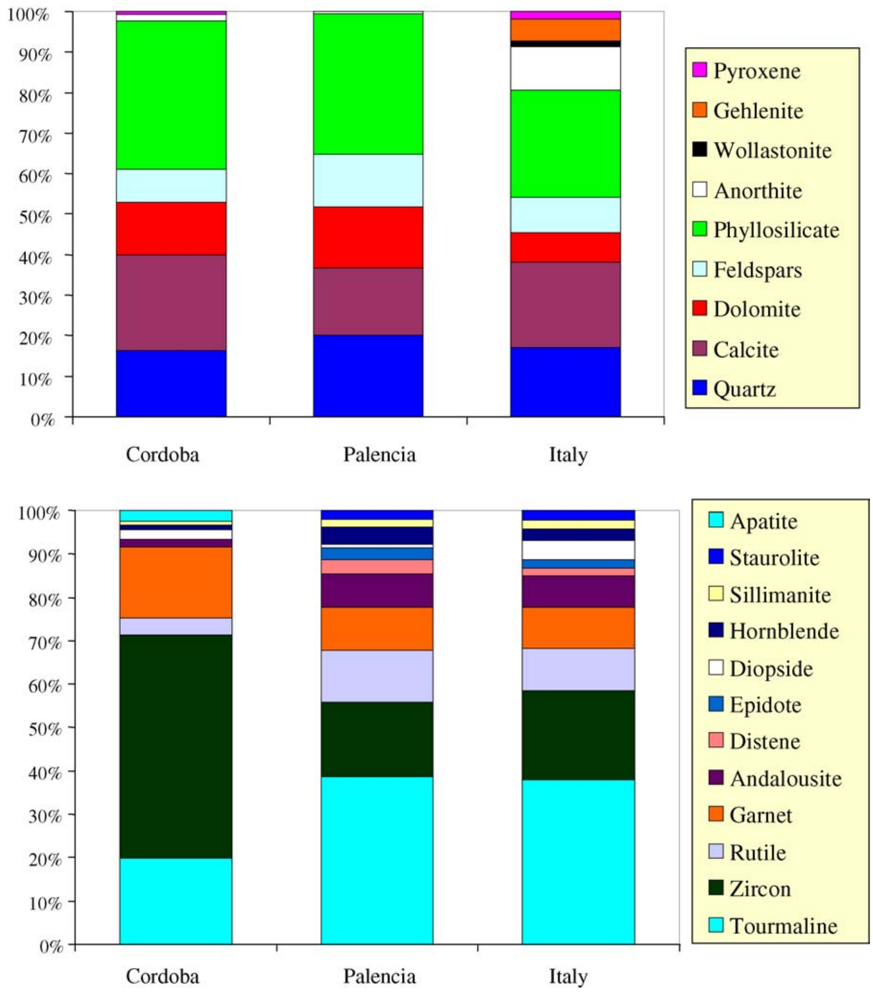

Fig. 5. Histograms of the average proportion of minerals in the studied oil lamps (top: total minerals; bottom: heavy mineral fractions).

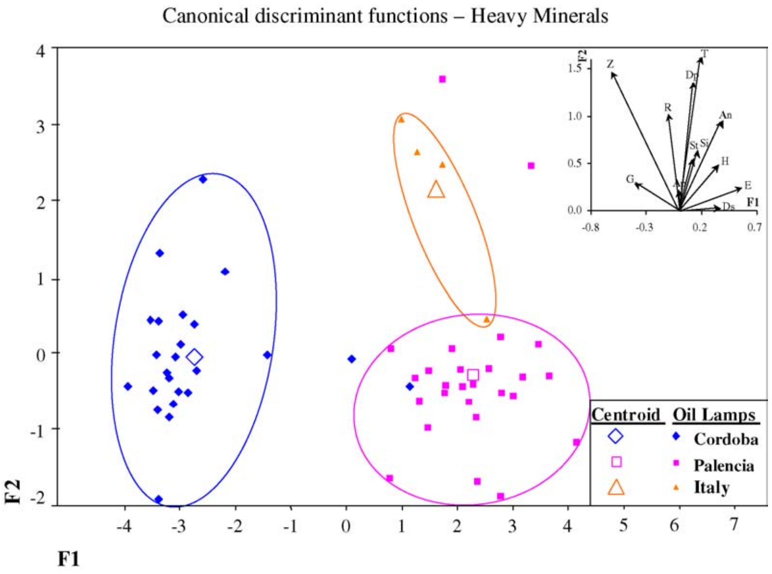

Fig. 6. Linear discriminant analysis of the heavy mineral components.

Heavy minerals are characteristic of the origin of the raw materials employed in the manufacture of oil lamps. This fraction was formed in a large extent by tourmaline and zircon. A noticeable difference in this fraction was the important amount of garnet in the *Cordoba* oil lamps, and rutile and andalousite in the *Palencia* ones and it is also remarkable the important amount of diopside in the four *Italian* samples. Minor minerals, such as distene, epidote, diopside, hornblende, sillimanite, staurolite and apatite, are present in some samples.

Another lineal discriminant analysis was carried out with the heavy mineral results (tourmaline (T), zircon (Z), rutile (R), garnet (G), andalousite (An), distene (Ds), epidote (E), diopside (Dp), hornblende (H), sillimanite (Si), staurolite (St) and apatite (Ap)). The score plots for the two canonical discriminant functions, F1 and F2, are represented in Fig. 6. They represent, respectively, 94.6% and 5.4% of the variance. Each mineral projection is also detailed in this figure. The oil lamp samples from *Cordoba* are distributed in the left area (negative values of F1) due to their high content of zircon and garnet whereas samples from *Italy* and *Palencia* and located in the right one (positive values of F1). Major differences between *Italy* and *Palencia* results are found in the higher zircon and diopside contents in *Italian* samples.

3.3. Morphological and microscopical analysis

A great number of *Palencia* oil lamp samples showed a careless manufacture process. Generally, the engobium (colloidal solution used as external coating for the final appearance enhancement) has not similar colour than the ceramic paste as it is common in this type of ceramic pieces [4,7]. Most samples showed unclear ornamental pictures and more and more reduced dimensions. It is a consequence of the repetitive use of a reduced number of moulds that became to get worn out (“overmolding” technique) [29,30]. The principal objective of this local workshop was covering the basic necessities of the military troops. Therefore, ceramic oil lamps were manufactured to be employed by not very demanding users with mainly a functional use. However, the considered *Italian* oil lamps showed a more careful aspect, such as the same colour of the ceramic paste and the engobium, and clearer ornamental pictures, representing a more decorative use.

Observations made by polarization microscopy, using thin sections of the samples, allow us to distinguish different material types in relation to their texture and mineral composition and the classification of the ceramic pastes as artificial micro-conglomerates. In all cases they were formed by clayish–carbonaceous tempers and cement. Some microphotographs representative of local and imported oil lamps are shown in Fig. 7. In local samples from *Palencia* (Fig. 7A), fine grains of quartz and feldspars, andalousite and distene can be seen. In those from *Cordoba* (Fig. 7B), garnet, zircon, diopside and apatite clearly appear, as well as certain fossils corresponding to sedimentary rocks. Fig. 7C shows an image of a sample found in *Palencia* considered of *Italian* origin, where an association of zircon, garnet, rutile, sillimanite and tourmaline was identified, as well as quartz crystals, fragments of metamorphic rocks and a fossil foreign to *Pisuerga Valley*, corroborating the external provenance of this oil lamp.

Some representative samples were analyzed by SEM–EDX demonstrating that all of them are characterized by their great porosity, due to decarbonatation processes followed by CO_2 elimination, and by an irregular distribution of porous size (many of them of big size). They showed the presence of micaceous forms and long particles with vitrified structures from illite, as well as contents of K_2O between 12% and 15%. The presence of pseudowollastonite and a small amount of anorthite, with secondary origin, could be observed in these samples as well as grains of calcium carbonate that

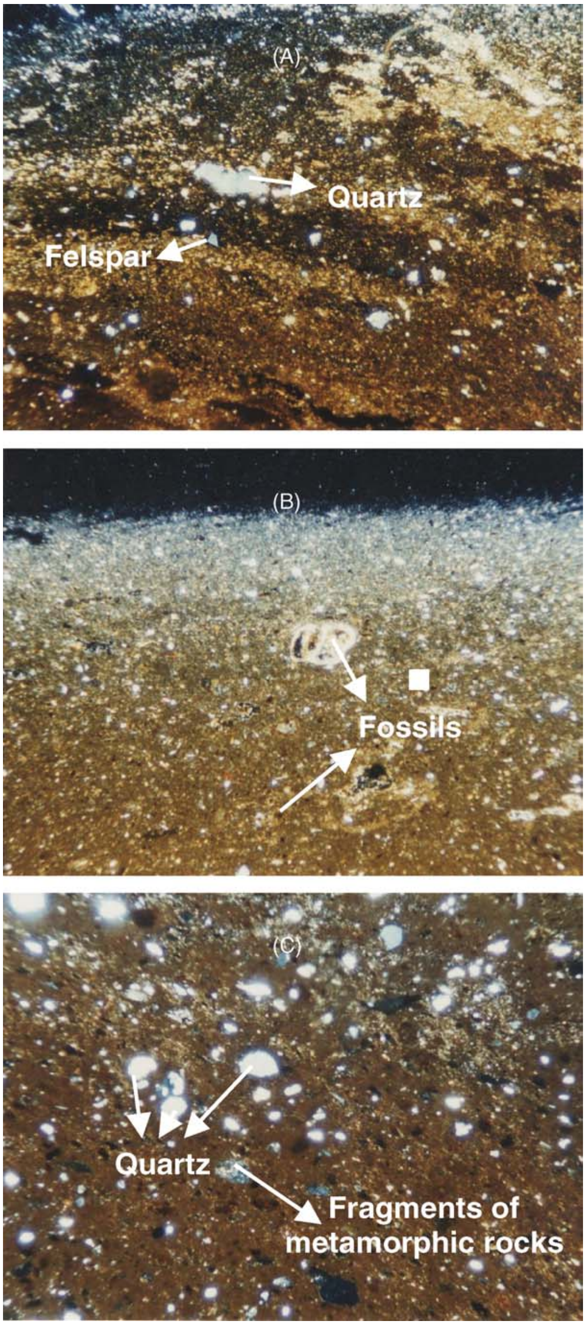

Fig. 7. Microphotographs of oil lamp samples from (A) *Palencia*, (B) *Cordoba* and (C) *Italy*.

have produced bulks of CaO which break off during the original thermal treatment.

Micaceous layers with different degrees of alteration as well as feldspars and even big grains of rutile could be also identified in these samples. Big masses can be attributed to calcium carbonated destroyed in the original firing process (in spite of a posterior partial recarbonatation). Whereas the supposed *Italian* samples present a large proportion of gehlenite, only small dark grains of gehlenite were observed in the rest of the samples (not detected by XRD). A similar behaviour was observed for wollastonite and anorthite. It could also be observed that the iron minerals maintain their acicular shape with contents of Fe_2O_3 higher than 18%. The observed dark zones are rich in CaO (22%) and Fe_2O_3 (5%), whereas the light ones are rich in CaO, Fe_2O_3 and MgO with a decarbonatation grade lower than 7%.

Fig. 8 shows a SEM microphotograph corresponding to one of the samples collected in *Herrera de Pisuerga* (*Palencia*) and considered of *Italian* origin. This figure has been chosen because it shows some differences with respect to the Spanish oil lamps. It is remarkable the presence of important amounts of gehlenite detected by XRD only in the four samples from *Italy* and it is corroborated by SEM–EDX. In the same way, the presence of glass filaments and some minerals, such as anorthite and wollastonite, is observed in a large proportion. It is a specific characteristic of this *Italian* samples and it is an evidence of an incipient vitrification process in which large glass filaments are generated as consequence of a higher firing temperature (about 900 °C). Higher temperatures would drive to the transformation of gehlenite in mullite [31,32] and the latter has not been detected. In contrast, the proportion of these minerals in the Spanish samples is considerably lower and it is difficult to detect them by SEM and the glass filaments have been scarcely developed. These *Italian* samples exhibit a defective synterization with the presence of heterogeneous zones, since temperatures and times used in the firing treatment probably were not homogeneous and high enough, respectively. The internal zone is smooth and composed by long filaments of glass with porous structure. The stability of gehlenite depends on Ca(II) diffusion in these glass filaments. According to Peters and Iberg [26] when temperature increases, diffusion of Si(IV) and Al(III) leads to the formation of wollastonite, diopside and anorthite. Big quartz grains are also observed, with diameters about 100 μm that do not seem to have been attacked in the centre. CaO, Al_2O_3 and Fe_2O_3 were present in concentrations up to 20% in the edges. The intermediate zone, with a thickness higher than 5 μm, is more porous. The external zone is denser and it is composed by a vitrified area covered by filaments, which are in contact developing a continuous layer.

3.4. Thermal analysis

The total dilation observed in the temperature range from 25 °C to 1000 °C was lower than 1%, which represents minimum contraction–expansion effects and comparable to those previously obtained in similar Roman materials [33]. A more detailed study of these typical dilation–contraction curves versus temperature obtained for a large number of these samples showed two variations in the ranges of 550–650 °C and 650–700 °C. The expansive effect of about 600 °C can be attributed to the quartz transformation (α–β transformation). The material contracts slightly until a temperature of 750 °C is reached, in this moment the synterization step starts. The presence of calcium carbonate causes a second expansive effect about 700 °C due to the formation of CO_2. In the same way, the thermal effect observed around 800 °C is probably

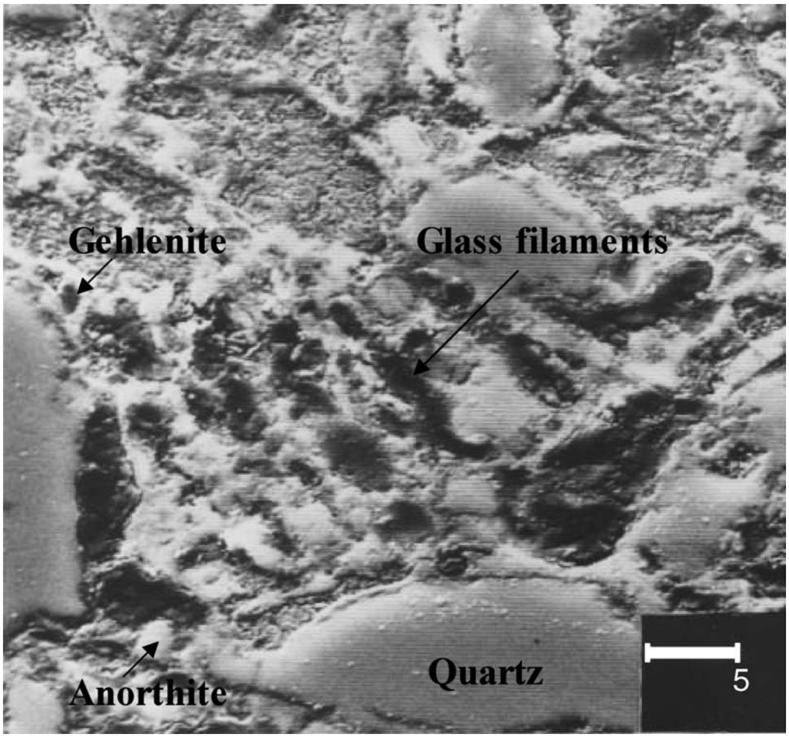

Fig. 8. SEM image of an oil lamp from *Italy* with a very heterogeneous microstructure. Among others, quartz grains, gehlenite and various aluminiumsilicates can be observed.

due to the transformation of calcite in gehlenite. In these materials with high contents of calcium carbonate, up to 15%, an additional expansible effect is observed, at around 900 °C, attributed to the formation of crystalline calcium silicate (wollastonite type) from breakdown of the previous amorphous materials. At temperatures greater than 1050 °C, at which the fusion begins, a new contraction appears, probably due to the transformation of gehlenite in mullite [31,32].

Some authors have found gehlenite at temperatures lower than 800 °C [34]. In the kaolinitic clays with calcium carbonate, the formation of gehlenite at 850 °C from the lime has been recognised by Maniatis et al. [35], who also references the carbonate destruction between 850 °C and 1050 °C [36] with the incorporation of calcium causing a vitrification process. A quick diffusion of calcium ions toward quartz grains, feldspar and clay minerals was observed and melilite type, gehlenite and iron-gehlenite had to be formed from CaO around 850 °C. According to Schüller [37], the growth is controlled by the interface, and the range of diffusion is higher when the concentration of silica and alumina is not similar than calcium concentration.

Thermal analysis is often a very useful tool to discern among different ceramic pastes since their thermal behaviour depends on the raw materials employed. But in this particular case, the thermal study carried out does not allow us to distinguish samples according to their origin. Since the mineralogical composition of the elements with a critical thermal behaviour is similar in all analyzed samples, there are not significant differences in the dilatometric study.

From the morphological and mineralogical studies, we could conclude that the presence of large quantities of SiO_2 indicates that the reached temperature was not high enough for silicates formations. Samples also exhibited a defective syntherization, high porosity and irregular distribution of porous size with a higher density in the outside area, easily detected by microscopy. These effects were a consequence of a short and heterogeneous heating process that provides decarbonatation processes followed by the elimination of CO_2, as well as the cracking of the ceramic material caused by the quick transformation of calcite in CaO [35,38,39]. On the other hand, *Italian* lamps were manufactured at higher firing temperatures than the local *Spanish* ones. The presence of mineral geothermometers [14] in the *Italian* ones, such as gehlenite ($SiO_2 \cdot Al_2O_3 \cdot 2CaO$), a compound formed at the same time as $CaCO_3$ decomposition (about 800 °C), and wollastonite ($SiO_2 \cdot CaO$), a compound formed after gehlenite at higher temperature, is a consequence of a treatment at temperatures close to 900 °C or higher.

4. Conclusions

A suitable combination of the physicochemical and chemometric analytical techniques used for studying ceramic oil lamps provides useful information about texture, inclusions, and chemical and mineralogical composition. It helps to shed more light on the nature of the raw materials used in the manufacture of the pieces, possible origin, production and firing technology, providing arguments to predict and to confirm archaeological hypothesis.

Morphological, physicochemical and chemometric analyses showed a clear difference among samples corresponding to different locations. In this sense, a difference in CaO, K_2O and Na_2O content was observed between *Cordoba* and *Palencia* samples and there were more outliers and extreme values in samples from *Palencia* corresponding to samples of *Italian* origin. Among minor chemical elements, concentrations of Cu, Pb and Zn were higher in samples from *Cordoba* than those from *Palencia* and Cr and Ni were non-detected elements in all cases except in four isolated samples from *Palencia* supposedly of *Italian* origin. In the same way, these *Italian* oil lamp samples showed a more careful aspect, such as same colour of ceramic paste and engobium and clearer ornamental pictures, than *Palencia* ones, establishing differences in the technology used in each production centre during the manufacturing process. Minerals, such as gehlenite and wollastonite, undetected in the oil lamp samples from *Palencia* and *Cordoba*, were presented in samples from *Italy* and lead us to the conclusion that *Italian* lamps were manufactured at higher firing temperatures than the *Spanish* ones. It was also very interesting to detect the presence of pyroxene, a mineral associated to volcanic rocks, in samples from *Cordoba* and *Italy* being another evidence of the presumable local manufacture of these ceramic pieces. Some additional clay samples found in the surroundings of the *Palencia* and *Cordoba* settlements were also analyzed and analytical results are according with their corresponding sherds of oil lamps results. This was a proof that these specimens were likely local products, and compositional differences between local oil lamps might account for the use of different clays, for clay mixing, for addition of different tempers or additives and for a relatively long period that the exploitation went on. Only the four isolated samples from *Palencia* seemed to be imported products due to their clearly different composition. All these results supported archaeological hypothesis previously established about locations of production centres in *Cordoba* and *Palencia* and the *Italian* origin of some isolated samples found in *Palencia*.

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