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APPLYING PORTABLE X-RAY FLUORESCENCE (pXRF) TO PROVENANCE OF COLONIAL CERAMICS: COMPARATIVE CASE STUDIES FROM NORTH AFRICA AND THE IBERIAN PENINSULA

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Abstract: This paper presents new chemical and mineralogical analyses of Early Modern Era pottery excavated from key archaeological sites at Ksar Seghir and Ceuta in North Africa, as well as Orduña in the Iberian Peninsula. Investigating these artifacts sheds light on provenance, trade dynamics, technological characteristics, and their broader socio-cultural implications. The diverse assemblage of glazed and unglazed ceramics – including kitchenware, storage vessels, transportation containers, and tripod stilts – offers not only evidence of cultural and economic exchanges during this period, but also valuable insights into daily life, illustrating the blending of Islamic, North African, and European influences. By employing chemical archaeometric techniques, this study benchmarks its findings against a comprehensive database of Medieval and Early Modern ceramics, providing a robust framework for ongoing and future investigations. Furthermore, the research makes a methodological contribution by applying Portable X-ray Fluorescence (pXRF), a technique renowned for its efficiency, speed, and *non-destructive* elemental composition analysis. This approach ensures the preservation and integrity of artifacts, offering a valuable tool for future comparative studies in archaeometry.

Keywords: Ceramics, North Africa, Portugal, Northern Iberian Peninsula, pXRF, Chemical analyses

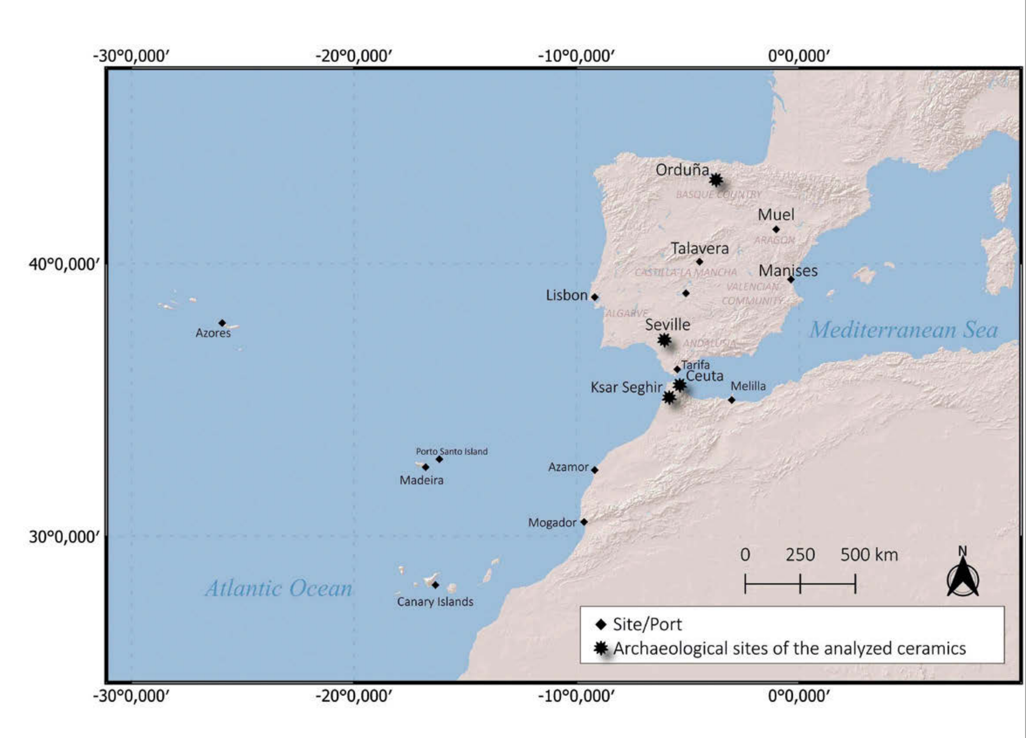


fig. 1. Location of the main archaeological sites and ports discussed.

1. Introduction

Maritime trade and navigation flourished remarkably during the 15th to 17th centuries, boosting the production and exchange of raw materials and manufactured goods across local, regional, and interregional levels. This period witnessed the establishment and expansion of port infrastructures in southern Spain, northern Africa, and along the Atlantic coastlines, which were instrumental in supporting these burgeoning commercial activities. The Portuguese expansion into Africa, often referred to as "*terra nullius*", alongside Africa alongside the Castilian annexation of the Canary Islands, marked the beginning of new commercial dynamics. These movements facilitated the supply and distribution of various goods, including ceramics, thereby intertwining the economic and cultural landscapes of these regions.

Utilizing advanced archaeometric techniques, this study reconstructs the extensive trade networks and distribution patterns of ceramics, providing a comprehensive view of the commercial practices prevalent during the Early Modern Age. Our research focuses on chemical and mineralogical analyses of colonial ceramic artifacts unearthed from key archaeological sites across North Africa and the Iberian Peninsula. These artifacts, dating from the 15th to the 17th centuries, reveal crucial information about the regional production origins, technological attributes, and socio-cultural implications embedded within these ceramic forms.

The diverse ceramic types examined in this study embody the confluence of cultural and commercial exchanges that were central to this geographical nexus. They offer a tangible representation of everyday life during the periods of Castilian and Portuguese expansion. Through meticulous analysis, this research highlights the integration of technological traits, and the broader socio-cultural ramifications encapsulated in these ceramics. For instance, the adoption of ceramic styles and techniques across regions reveals not only the diffusion of technology but also the assimilation of cultural practices and values (Skibo and Feiman, 1999; Skibo and Schiffer, 2008). This integration underscores the dynamic nature of identity formation during colonial encounters, where local traditions were both preserved and transformed in the context of imperial influence. Furthermore, the distribution of these ceramics across diverse sites suggests various degrees of access to trade networks and material culture, reflecting the social stratification and economic disparities within these societies.

Our investigation explores the synergistic interactions and cultural syncretism among the Islamic world, North Africa, and Europe. By examining both imported and locally produced ceramic artifacts – ranging from kitchenware to storage and transportation vessels – this study lights on the economic structures, cultural dynamics, and social practices of the populations involved.

This research highlights the commercial and cultural exchanges facilitated by maritime trade. It enhances our understanding of the technological advances and daily life during the early phases of European expansion into Africa and the Atlantic world (Johnson, 2021). The findings contribute significantly to the broader discourse on historical archaeology, offering new perspectives on the interconnectedness of past societies and the methodological implementation in the use of *non-destructive* techniques in the analysis of archaeological ceramics (fig. 1).

This study aims to present the outcomes of previous archaeometric investigations employing analytical techniques such as ICP-MS, XRD SEM-EDS, NAA, and Raman microscopy. The results of these studies have been systematically compared with the extensive database of medieval and early modern ceramics compiled by Iñañez and colleagues (Iñañez, 2007; Iñañez et al., 2007b; 2008; 2009; Buxeda et al., 2011), which effectively chemically categorizes ceramics and determines the provenance of these pieces from numerous production centers across the Iberian Peninsula, Canary Islands, Azores, and the American Continent.

A pivotal methodological advancement emphasized in this paper is the adoption of Portable X-ray Fluorescence (pXRF). This technique is known for its efficiency and rapid data acquisition, enabling swift display of elemental compositions. The versatility of pXRF facilitates its application in virtually any setting, though it requires specialized training for optimal operation. Its user-friendly setup and minimal maintenance requirements make pXRF an invaluable *non-destructive* tool for analyzing archaeological artifacts and historical heritage. In the context of ceramic analysis, pXRF is crucial for the initial classification and creation of geochemical reference groups for artifacts, establishing a robust foundation for subsequent detailed studies (Calparsoro et al., 2019; Speakman et al., 2011).

While previously mentioned analytical techniques have successfully identified major compositional groups and established the provenance of ceramics in regions distant from the Iberian Peninsula, this article aims to demonstrate the effectiveness of pXRF as a reliable tool for chemically classifying pottery production groups. Despite its limitations in precision and accuracy compared to established destructive laboratory techniques, pXRF demonstrates considerable potential for the rapid and non-destructive analysis of pottery, yielding results that are sufficiently precise according to current standards. This enables meaningful comparisons with chemical data obtained from more sensitive techniques, such as ICP-MS, XRD, SEM-EDS, or NAA, as it can also detect trace elements. However, it is essential to account for the inherent limitations of pXRF, as direct comparison with results from other techniques may introduce inaccuracies or misinterpretations. pXRF offers a practical solution in the field characterization of ceramics, facilitating non-destructive studies and expanding the possibilities for detailed analysis across several archaeological contexts. Its ability to provide both qualitative and semi-quantitative data (Moioli and Seccaroni, 2000; Bonizzoni et al., 2013) enables the estimation of the chemical concentration of each element through the application of various calibration methods. Portable XRF spectrometers include built-in calibration packages tailored for different substrates. Additionally, user-defined internal calibration methods can be fine-tuned through the measurement of certified reference materials (CRMs) or standards for clays in this case, enhancing the accuracy of reported concentrations within a specific dynamic range.

2. Ceramic Assemblages from North Africa and the Iberian Peninsula: Archaeological and Archaeometric Background

2.1 Portuguese and Spanish ceramics from Ceuta and Ksar Seghir

Ceuta is situated on a narrow strip of land connecting the smaller of the two Pillars of Hercules, the promontory known as Monte Hacho, to the African mainland. Its conquest in 1415 by the Portuguese monarchy marked the European expansion into the Atlantic, further enhancing its strategic importance in the maritime traffic through the Strait of Gibraltar, already well established by 1400 (Abulafia, 2021: 663-670). Recent archaeological excavations over the past decades have provided new insights into the supply networks and trade within the city, owing to its geostrategic position at the crossroads of the Mediterranean, the Atlantic, Africa, and Europe (Teixeira and Torres, 2015: 157-161). Ksar Seghir, located twenty kilometers from Ceuta, also experienced significant transformation in its material culture since its conquest in 1458. Recent studies have revealed shifts in ceramic production techniques and trade patterns, reflecting the site's integration into broader regional networks of exchange.

The archaeometric analysis of ceramics from Ceuta provides valuable insights into the supply networks during the early phases of the Iberian overseas expansion in both the Mediterranean and Atlantic regions. This research underscores the significance of Seville and Lisbon as major production hubs. Within this framework, Ksar Seghir and Ceuta testify how these commercial and military networks supported the Portuguese expansion in North Africa during the 15th and early 16th centuries (Iñañez et al., 2021).

However, these previous studies have focused on characterizing the technology and provenance of Iberian glazed ceramics, particularly lead-glazed earthenware, including tableware, cookware, storage and transport vessels, illumination devices, hygiene utensils, and bisque-fired pottery. Archaeologically examining these categories allows for a comprehensive analysis of their technological features, production methods, and usage contexts, providing deeper insights into the cultural and economic practices of the time.

Archaeometric analysis reveals distinct roles for Ceuta and Ksar Seghir in Portuguese colonial logistics in North Africa. Ceuta, occupied from 1415 to the seventeenth century, served as a central trade hub in the Strait of Gibraltar, integrating Iberian ceramics into local culture through steady commercial networks. In contrast, Ksar Seghir, captured in 1458, functioned as a strategic military outpost with intermittent ceramic supplies, primarily robust, lead-rich wares suited for storage and transport. Several chemical and mineralogical groupings have been identified, suggesting multiple centers of production, like Seville, Lisbon, and potentially other locations. The existence of distinctive chemical ceramic groups is established, with strong evidence of Sevillian influence in glazed ceramics and imports from Lisbon. Moreover, raw material use varied significantly, ranging from calcareous to non-calcareous ceramics, indicating differences in clay sources and firing methods regarding post-depositional contaminations, alterations in some samples were observed, such as the crystallization of minerals like wairakite or analcime, these secondary mineral formations provide critical information on the geochemical conditions that affected the ceramics after burial, offering insights into the post-depositional environment, including moisture levels and temperature variations. Such contaminations are invaluable in reconstructing not only the lifecycle of these artifacts but also the broader environmental and geological processes that influenced their preservation (Buxeda, 1999; Schwedt et al., 2006; Iñañez et al., 2021). This study thoroughly investigated ceramic production in the Iberian Peninsula by identifying the main production centers that disseminated ceramics across the Mediterranean Sea and the Atlantic Ocean during this period.

2.2 North Iberian Peninsula ceramics from Orduña Village

Orduña, situated in the central-northern region of the Iberian Peninsula, has a long-standing economic and commercial history deeply intertwined with its strategic location along key trade routes and its customs system. The village has served as a crucial exchange point since the 13th century, connecting the Spanish plateau with Basque coastal towns. Although the precise origins of pottery production in Orduña remain somewhat unclear, evidence suggests that pottery was integral to the village's development, paralleling trends of craft specialization across the Basque region dating back to the 9th century. Archaeological and archaeometric studies indicate that pottery trading in Orduña occurred as early as the 8th century, reflecting its long-standing role in regional commerce. Excavations on Zaharra and Tras-Santiago streets have provided the first definitive evidence of local pottery production, with kilns and ceramic fragments dating back to the 17th century, suggesting a continuous tradition of ceramic craftsmanship (Cajigas et al., 2004; Salazar and Llano, 2005; Solaun, 2005).

The pottery industry in Orduña underwent significant development in the late 18th and 19th centuries, particularly influenced by two key historical events: the opening of the access road to the Castilian plateau in 1774, which diverted commercial traffic from Balmaseda to Orduña, and the construction of a new customs office in 1792 to handle the increased flow of goods. Despite the historical importance of pottery in Orduña, studies have primarily focused on typological aspects, with limited archaeometric analyses prior to the establishment of Basque popular pottery. This popular ceramic typology, characterized by reddish earthenware with partial tin-lead glazes, became widespread before industrialization and persisted until the mid-20th century despite significant disruptions, such as the Spanish Civil War (Escribano-Ruiz, 2013; Iñañez et al., 2015).

Recent chemical analyses have identified two primary compositional groups of ceramics from Orduña, characterized by high calcareous content and varying levels of Fe2O3 and MgO. These findings suggest that some ceramics were potentially manufactured in Vitoria and Bilbao, 38 kilometers away, revealing complex regional and extra-regional pottery production and consumption patterns (Calparsoro et al., 2019). Prior studies, such as those by Iñañez et al. (2008) and Barrachina (2016), aimed to bridge the knowledge gap concerning Orduña's pottery production and distribution networks, offering a preliminary understanding of its production centers, technologies, and trade in the Basque region and northern Spain.

These investigations have expanded upon this foundational work, utilizing techniques such as ICP-MS, XRD, and SEM-EDS to delineate seven distinct compositional groups of ceramics. These groups reflect significant diachronic changes in production practices, from the earliest fragments identified in group ORD-B (1694-1750) to more diversified ceramic typologies and glazing technologies after 1788. The analysis of glazing recipes revealed traditional techniques, including the use of SnO_2 for white opaque glazes, CuO for green, MnO for black, and CoO for blue glazes, while honey-colored glazes were composed of PbO and Fe_2O_3. These variations in materials and techniques demonstrate the potters' intentional selection of raw materials to achieve specific finishes, employing firing temperatures between 850°C and 1050°C.

The archaeometric data also illuminate broader social and economic transformations. Ceramics from group ORD-A, which were once exclusive, gradually became more widespread, reflecting a shift in control from local oligarchies who commissioned pottery production primarily through artisans from the Alava region. This shift in production and distribution correlates with changes in the social and economic landscape of Orduña, as ceramics moved from elite-controlled goods to more accessible products for broader consumption.

This comprehensive archaeometric and typological study has thus provided a deeper understanding of the technological evolution of ceramic production in Orduña, from the 17th to the 19th centuries (Calparsoro et al., 2019; Calparsoro, Arana and Iñañez, 2019). It has highlighted the significant role that these ceramic products played in regional and extra-regional trade within the Iberian Peninsula and offered new insights into the technological features of ceramics used in the Basque Country during this period.

ANID	Site	Chemical Group	Type	Form	Chronology
CTA008	Ceuta	Lisboa 2	Unglazed red	Pot	1415-1550
CTA013	Ceuta	SEV-B	Honey lead-glazed	Plate	1415-1550
CTA020	Ceuta	SEV-B	Honey lead-glazed	Plate	1415-1550
CTA028	Ceuta	Lisboa 2	Unglazed red	Cup	1415-1550
CTA030	Ceuta	Lisboa 2	Unglazed red	Jar	1415-1550
CTA036	Ceuta	Lisboa 2	Unglazed red	Pot lid	1415-1550
CTA046	Ceuta	SEV-B	Tin-lead glazed	Bowl	1415-1550
CTA050	Ceuta	SEV-C	Green lead-glazed	Basin (lebrillo)	1415-1550
CTA052	Ceuta	SEV-C	Green lead-glazed	Basin (lebrillo)	1415-1550
CTA053	Ceuta	SEV-C	Green lead-glazed	Basin (lebrillo)	1415-1550
CTA055	Ceuta	SEV-C	Tin-lead glazed/green	Bowl	1415-1550
CTA057	Ceuta	SEV-C	Tin-lead glazed/green	Bowl	1415-1550
CTA063	Ceuta	SEV-C	Honey lead-glazed	Pichther	1415-1550
KSG001	Ksar Seghir	SEV-B	Green lead-glazed	Basin (lebrillo)	1458-1550
KSG004	Ksar Seghir	SEV-B	Honey lead-glazed	Basin (lebrillo)	1458-1550
KSG008	Ksar Seghir	Lisboa 2	Unglazed red	Basin (lebrillo)	1458-1550
KSG010	Ksar Seghir	Lisboa 1	Unglazed red	Pot	1458-1550
KSG015	Ksar Seghir	Lisboa 2	Unglazed red	Pot	1458-1550
MJ0118	Talavera	TAL	Tin-lead glazed	plate	1600-1700
MJ0341	Seville	SEV-B	Tin-lead glazed	plate	1550-1650
MJ0342	Seville	SEV-B	Tin-lead glazed	plate	1550-1650
MJ0346	Seville	SEV-B	Tin-lead glazed	plate	
MJ0361	Seville	SEV-B	Tin-lead glazed	plate	
ORD003	Tras Santiago	ORD-A	Tin-lead glazed	Bowl	1788-1850
ORD021	Tras Santiago	ORD-A	Tin-lead glazed	Jar	1788-1850
ORD022	Tras Santiago	ORD-A	Tin-lead glazed	Jar	1788-1850
ORD023	Tras Santiago	ORD-A	Tin-lead glazed	Vessel (potter-mistake)	1788-1850
ORD025	Tras Santiago	ORD-A	unglazed	Kiln-furniture	1788-1850
ORD027	Tras Santiago	ORD-A	unglazed	Kiln-furniture	1788-1850
ORD028	Tras Santiago	ORD-A	unglazed	Kiln-furniture	1788-1850
ORD029	Tras Santiago	ORD-C	honey glazed	Bowl	1788-1850
ORD030	Tras Santiago	ORD-A	Tin-lead glazed	Basin	1788-1850
ORD032	Tras Santiago	ORD-A	Tin-lead glazed	Basin	1788-1850
ORD033	Tras Santiago	ORD-A	unglazed	Kiln-furniture	1788-1850
ORD037	Tras Santiago	ORD-A	unglazed	Kiln-furniture	1788-1850
ORD068	Zahara 2-4	ORD-D	Tin-lead glazed	Home stoup	1790-1820
ORD075	Zahara 2-4	ORD-D	Tin-lead glazed	Jar	1735-1765
SEV001	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV002	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV003	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV004	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV005	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV006	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV007	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV008	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV009	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
SEV010	Catedral Sevilla	SEV-A	Olive jars	Botija	1500-1550
TAL006	Talavera	TAL	Tin-lead glazed	plate	1600-1700
TAL011	Talavera	TAL	Tin-lead glazed	plate	1600-1700
TRI007	Sevilla	SEV-B	Tin-lead glazed	tile	1600-1700
TRI008	Sevilla	SEV-B	Tin-lead glazed	tile	1600-1700

tab. 1. Archaeological ceramics analyzed by pXRF.

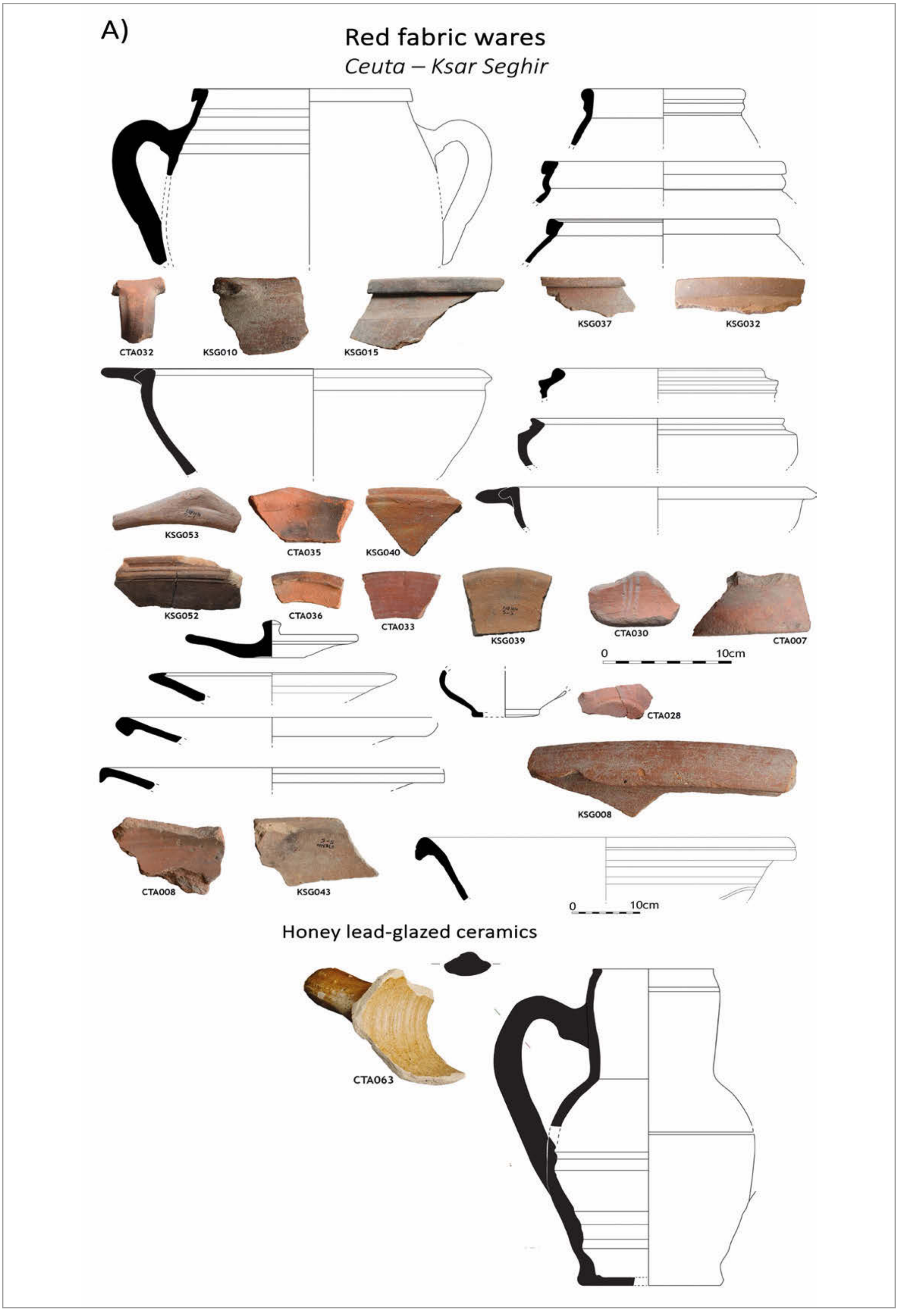


fig. 2a. Example of the main types of ceramics analyzed. A) Red fabric wares.

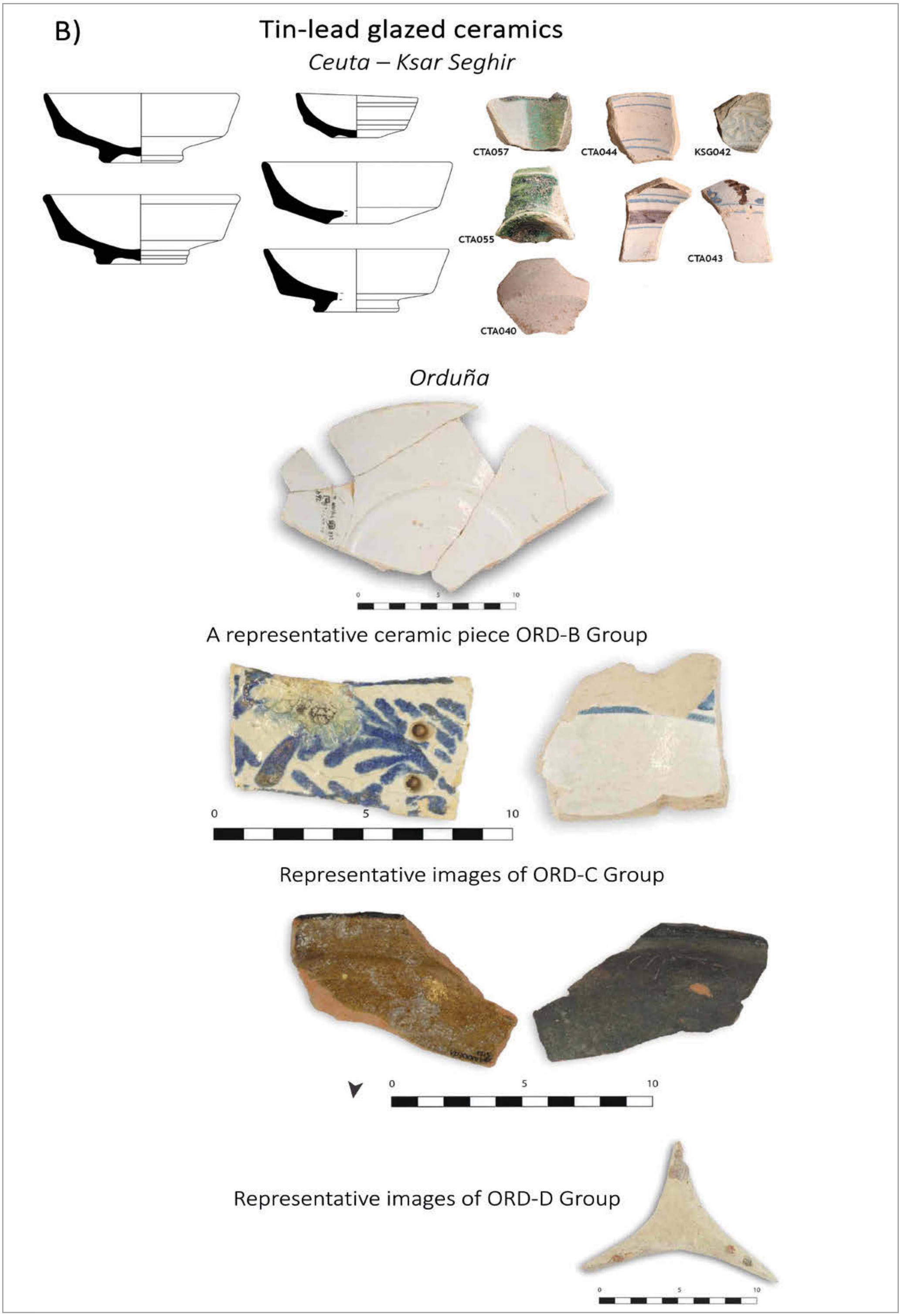


fig. 2b. Example of the main types of ceramics analyzed. B) Tin-lead glazed ceramics.

3. Materials and Methods

In the case of the pXRF technique, the analysis time is remarkably short, approximately 6 minutes per sample. This efficiency facilitates the execution of a substantial number of sample analyses within a single day, significantly enhancing the output of archaeological studies. Advancements in pXRF technology have further optimized its sensitivity and accuracy, making it a crucial tool in the field of archaeometry (Shackley, 2011; Speakman & Shackley, 2013). This method enables the collection of detailed information about major, minor, and trace elements present on the surfaces of ceramic pastes and finishes. By analyzing the average concentrations of these elements in all ceramic fragments, researchers can categorize artifacts based on their geochemical origin. The underlying assumption is, following the provenance postulate, that the ceramic material reflects the source of the raw materials used to manufacture the artifacts, allowing fragments made from the same ceramic paste to be grouped into chemically consistent zones (Craig et al., 2007; Weigand et al., 1977). This geochemical fingerprinting is instrumental in reconstructing ancient trade routes, production techniques, and the socio-economic interactions of past societies (Franke et al., 2017).

Archaeometric studies have demonstrated the efficacy of pXRF in distinguishing between local and imported ceramics, thereby providing insights into regional trade dynamics. For instance, it has been successfully applied to identify and differentiate ceramics from several production centers in the Mediterranean, revealing complex trade networks and cultural exchanges (Forster et al., 2011). Moreover, pXRF's non-destructive nature preserves the integrity of archaeological samples, which is particularly valuable when dealing with rare or fragile artifacts (Speakman & Neff, 2005). In addition to identifying the provenance of ceramics, pXRF can also contribute to understanding technological choices in ceramic production. By examining the elemental composition of glazes and slips, researchers can infer the technological capabilities and aesthetic preferences of ancient potters. Studies utilizing pXRF have uncovered variations in glaze recipes and firing techniques, shedding light on the evolution of ceramic technology over time (Sempowski et al., 2000). Furthermore, pXRF analysis can be integrated with other analytical techniques, such as petrography and X-ray diffraction (XRD), to provide a comprehensive understanding of ceramic artifacts. This multi-method approach allows for cross-validation of data and a more nuanced interpretation of the results (Albero Santacreu, 2014). The synergy between pXRF and these complementary techniques enhances the robustness of archaeological conclusions and broadens the scope of research possibilities (Grave et al., 2012).

In this research, the analyzed dataset comprises 51 archaeological ceramic specimens originating from North Africa and the Iberian Peninsula. For the North African assemblage, ceramics from Ceuta (CTA) (n = 13) and Ksar Seghir (KSG) (n = 5) were analyzed, with these specimens corresponding to the chemical groups previously identified as being associated with the production centers of Lisbon and Seville. In contrast, the Iberian Peninsula sample encompasses ceramics from, Orduña (ORD) (n = 14), and Talavera (TAL) (n = 2), as well as majolica wares from Triana workshops in Seville (TRI and MJ) (n = 6) and ceramic container fragments – specifically olive jars or *botijas* – from Seville (SEV) (n = 10). The selection criteria were primarily based on typological characteristics, including both glazed and unglazed wares. The selection includes several forms such as kitchenware, storage vessels, transportation vessels, and tripod stilts (kiln tools) (tab. 1).

Portable X-Ray Fluorescence (pXRF) and statistical routine

The application of analytical techniques using portable equipment such pXRF, is particularly well-suited for the elemental analysis of archaeological artifacts, providing a method widely recognized for its efficiency in the field (Frahm and Doonan, 2013). The key advantages of pXRF include its precision, speed, and ability to detect multiple elements, all while ensuring the integrity of the artifacts remains uncompromised. Unlike other analytical methods that may require complex sample preparation, potentially altering the physical or chemical properties of the object, pXRF demands minimal to no sample preparation. This allows for the safe characterization of artifacts without introducing chemical residues or causing irreversible modifications, thus preserving their archaeological and historical value.

Analyzing the elemental composition of archaeological ceramics offers critical insights into the production, distribution, and use of pottery across extensive regions. The technique has gained significant traction in global archaeology over the past decade, is favored for its ability to deliver consistent chemical data. While challenges persist in using pXRF to precisely source the raw materials of ceramics, particularly due to the complex geological diversity of some regions, advancements in multivariate statistical methods and machine learning have significantly enhanced the technique's ability to differentiate between ceramic samples from various origins. The success of provenance studies largely hinges on the chemical distinctiveness of the geographic source material. In many geological regions, accurate sourcing can be difficult, underscoring the importance of comprehensive reference databases, such as local clay deposits and standardized ceramic collections. In exceptional cases, when large amounts of securely attributed archaeological ceramics are available from well-documented contexts, these can serve as pseudo-reference materials, further refining our understanding of production technologies, trade routes, and intra-site distribution networks. By integrating pXRF data with other analytical techniques, such as petrography or ICP-MS, researchers are now able to construct a more detailed and nuanced picture of ceramic production and exchange networks in ancient societies (Glascock, 2016; Tykot, 2016; Buxeda & Fernandez, 2017; Hein & Kilikoglou, 2017; Liritzis et al., 2020; Drake & McDonald, 2022).

Recent technological advancements in pXRF instrumentation have significantly lowered the Limits of Detection (LOD) for light elements, such as sodium (Na) and magnesium (Mg), which were historically difficult to detect with earlier models. State-of-the-art devices now offer the capability to conduct measurements in a vacuum or under a helium atmosphere, optimizing the detection of these and other trace elements by mitigating interference from ambient gases. Moreover, integrating advanced calibration algorithms and multi-layer quantification techniques has further enhanced the precision and accuracy of elemental analysis in ceramics. These innovations have substantially broadened the scope of pXRF applications in ceramic provenance studies, contributing to refined geochemical fingerprinting of clay sources and manufacturing techniques. Although pXRF's utility in ceramic analysis has been previously debated (Hunt & Speakman, 2015; Speakman et al., 2017; Foster et al., 2011; Tykot, 2016; Drake & McDonald, 2022), recent studies demonstrate its increasing reliability when used alongside complementary techniques such as ICP-MS and NAA.

Furthermore, the effect of large amounts of lead in the clay matrix – the portion of the ceramic analyzed to determine its provenance – implies that strong lead (Pb) peaks can significantly affect the fluorescence emission of other lighter elements, masking signals from elements such as rubidium (Rb) or yttrium (Y), among others. This phenomenon can be observed in spectra where the lead-coated sample obscures some peaks that would otherwise be visible in an uncoated sample.

In this study, the analytical method employed was TRACER 5g (Bruker Nano GmbH) instrument, which, with a range of matrix-matched calibrations, can measure up to 48 elements. It uses a 50 kV, 4 W Rhodium (Rh) target as an excitation source, a 20 mm2 silicon derived detector (SDD), and a 1 μm graphene window using an 8 mm collimator to cover the largest area possible obtaining the highest representative data of the sample as possible. The elemental range spans from sodium to uranium in air and vacuum, and from fluorine to uranium when using a helium purge. In this study, ceramic pastes were removal of the top layer to eliminate surface contaminators and any surface slips/paints etc. prior to pXRF analysis. This step was undertaken to remove any surface contaminants, such as deposited salts, dust particles, and other residues that could potentially skew the chemical results. The removal of these contaminants is essential for ensuring the accuracy and reliability of compositional analyses, as their presence could interfere with the precise identification of the native chemical elements within the ceramic material. For the authors, these pre-treatment procedures are crucial, as they help minimize interference during analysis and ensure that the data accurately reflects the original characteristics of the archaeological material

Elemental analyses were carried out using the integrated GeoExploration calibration package and measurement mode from Bruker, which enables signal correction for analytes from Na to U. Spectral data was acquired during 120 s in 3 phases of 40 s each, and current and voltage adapted to analytical needs. For heavy elements, voltage was fixed to 45 kV and current to 15 μA using a Ti 25 μm-Al 300 μm filter, while for elements with $Z < 30$ a 30 kV voltage and current of 20 μm was applied. Instrumental parameters for light elements ($Z < 20$) consisted of a lower voltage (13 kV) and current of 40 μA. Repeatability was evaluated using a set of soil international CRMs and in-house standard C2-M2-Geosoil from Bruker™.

In the initial phase of data processing, raw counts of elemental concentrations were transformed into oxide percentages using a compositional data analysis approach, as outlined by Aitchison (1982) and Buxeda (2003). This step involved converting raw elemental counts to compositional data through closure to 100%, a necessary procedure to mitigate the issue of subcompositional incoherence in archaeometric datasets. This approach ensures that the data adheres to the principles of compositionality, where the parts of a whole must sum to a constant, thus avoiding spurious correlations. The conversion to oxide percentages allows for comparability between samples, which is essential before conducting multivariate analyses (Aitchison et al., 2000; Buxeda & Kilikoglou, 2003).

The following measured elements were the ones used in the final statistical treatment after removal of those showing values lower of the detection limit: Al2O3, Ba, Ca, Cu, Fe, K2O, MgO, Mn, Ni, P, Pb, Rb, SiO2, Sn, Sr, Ti, Y, Zn, and Zr. Logarithmic transformations were used to balance major and trace element scales. By dividing the chemical components by a selected component, potential biases were minimized. The additive log ratio (alr) transformation was used for Principal Component Analysis (PCA) by selecting the element with the lowest chemical variability as a divisor. For Hierarchical Clustering Analysis (HCA), the centered log ratio (clr) transformation was used, with the geometric mean as a divisor and the squared Euclidean distance displayed graphically using the centroid agglomerative algorithm. All statistical analyses and data visualization were conducted using R and the ArchFlow package, with routines available in the online repository GitHub (Calparsoro, 2018; Calparsoro et al., 2019; R Core Team 2022).

4. Results

The chemical analysis of ceramics from the North African and Iberian Peninsula sites analyzed in this study shows significant variations in the concentrations of Ca, MgO, SiO_2, and Pb. Samples from Lisboa1 and Lisboa2 exhibit low levels of Ca and MgO, whereas Ksar Seghir (ORD-A, ORD-B) displays intermediate levels of Ca and low to intermediate levels of MgO. Ceramics from Sevilla (SEV-A, SEV-B, SEV-C) show high variability in chemical composition, particularly in Ca and SiO_2. Talavera is characterized by high MgO and SiO_2 concentrations, indicative of specific refractory materials or specialized production techniques. Ceuta presents moderate levels of Ca, MgO, and SiO_2, with low Pb, implying consistent raw material properties likely linked to a specific source (fig. 3).

The variation matrix, which fully establishes the covariance structure of compositional data and yields the total variation (vt) of the examined ceramic assemblage, was computed as the initial analysis (Aitchison, 1986, Buxeda i Garrigós and Kilikoglou, 2003). The information entropy, also known as the Shannon index, evaluates how equally the chemical differences are connected to the retained components, whereas the total variation defines how diverse the chemical data are. For the entire data set, the total variation (vt) is equal to 9.82, indicating a polygenic group (fig. 4A). Moreover, the assessment of the compositional variation matrix identifies lead (Pb) as the most influential element affecting the variability in the ceramic samples, followed by calcium (Ca) and copper (Cu). Pb is the major contributor due to the presence of high-lead glazes commonly used in ceramics, where Pb content frequently exceeds 40-50% of the glaze composition, facilitating a smooth and glossy finish. These glazes were typical in the Iberian Peninsula. Copper (Cu) plays an important role as well, given that it was commonly added as a colorant to achieve green hues in the glaze. Furthermore, calcium (Ca) likely contributes to the glaze structure, acting as a stabilizing agent, especially in conjunction with lead to create durable surfaces (fig. 4A).

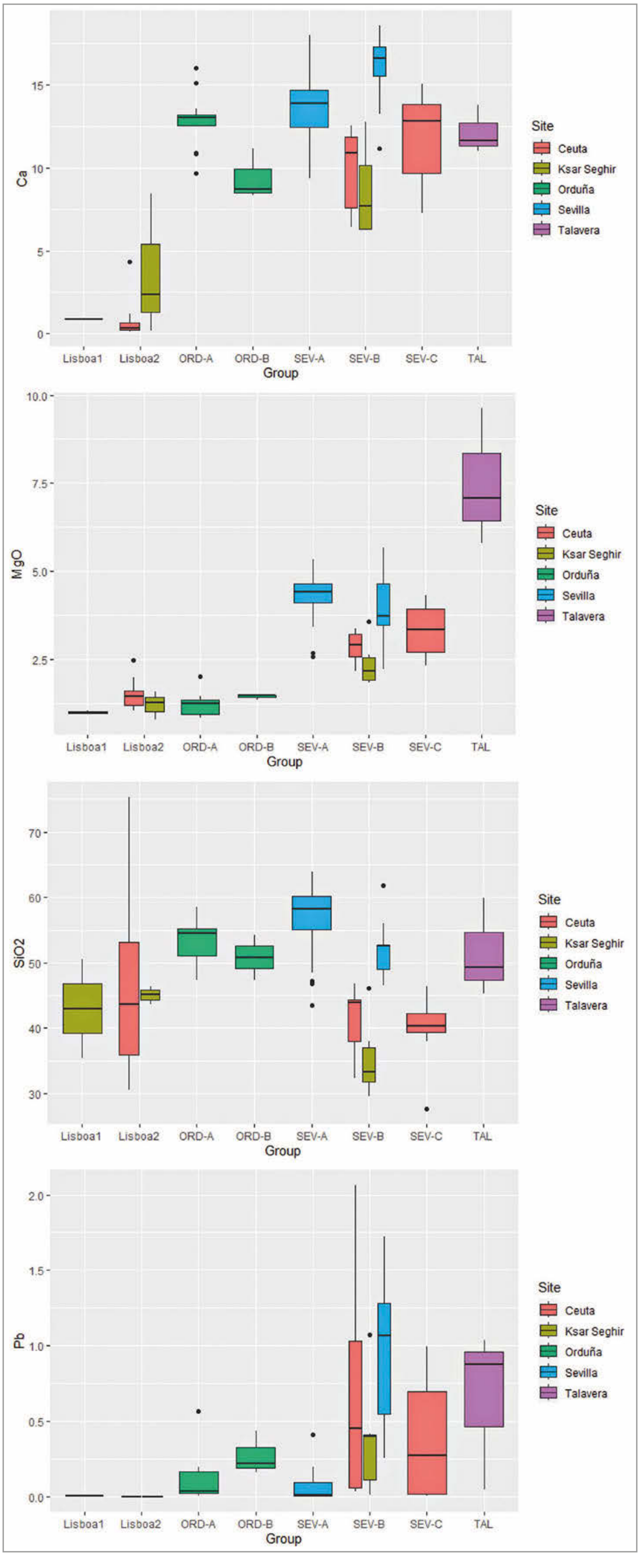


fig. 3. Box plots showing the concentrations of key chemical components (Ca, MgO, SiO2, Pb) in ceramic samples from the archaeological sites (coded in color) studied. Each group of ceramics (Lisboa1, Lisboa2, ORD-A, ORD-B, SEV-A, SEV-B, SEV-C, and TAL) displays distinct chemical signatures, reflecting variations in raw material sources.

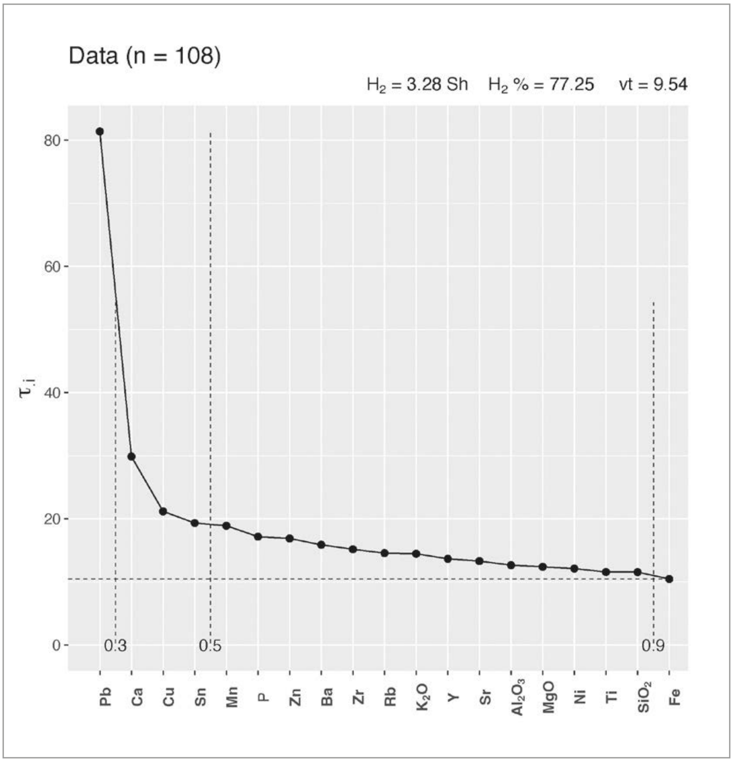
These elements highlight key technological choices in the use of glazes, pigments, and raw materials. Other elements such as tin (Sn), phosphorus (P), and barium (Ba) also contribute to differentiating the ceramic groups, indicating variations in raw material sources and production techniques. The presence of major components like SiO_2 and Al_2O_3 with consistent but lower variability underscores the fundamental composition of the ceramics. The provided plot (fig.4) illustrates the τ_1,j values for various chemical elements present in the ceramic samples (n=108). Key metrics such as H_2 = 3.28 Sh, H_2 % = 77.25, and vt = 9.54 indicate the dataset's complexity and the variance explained by the selected components.

Further analysis emphasizes calcium (Ca) as the next most significant element affecting the variability in the data set, followed by manganese (Mn), barium (Ba), and zirconium (Zr). The moderate contributions of MgO and K_2O further underscore the role of different clay sources and additives (temper). The second plot (fig. 4B), which includes 108 data points, presents key metrics H_2 = 3.32 Sh, H_2 % = 84.93, and vt = 3.86, still indicating a polygenic origin for the overall dataset. We recalculated the same metrics excluding the elements that are known to introduce variability due to potential contamination or post-depositional alteration, specifically Pb, Sn, Cu, P, and Cl. Ca exhibits the most noticeable change.

This shift is attributed to its technological role in the *chaine opératoire* of ceramic production. Calcareous and non-calcareous clays were intentionally selected by potters to achieve specific functional properties, particularly in terms of durability and firing behavior. The variability in Ca content reflects these deliberate choices, as different clay sources with varying lime concentrations were utilized depending on the desired characteristics of the finished product. This suggests diverse sources of clay, especially highlighting the choice of different calcareous materials with diverse lime content. Furthermore, it may show the existence of numerous raw materials origins, groups or provenances.

The dendrogram (fig. 5) provides a hierarchical clustering analysis of ceramic samples from several archaeological sites, excluding certain elements (Pb, Sn, Cu, P, Cl, Ca, Sr) to focus on other compositional differences. This clustering helps identify groups of ceramics with similar chemical compositions, offering insights into potential shared production techniques or raw material sources. The dendrogram reveals distinct clusters of ceramic samples, suggesting strong compositional similarities within each group. The Orduña (ORD) group forms a cohesive cluster, indicating consistent raw material sources or similar production techniques. Similarly, the Ksar Seghir (KSG) and Ceuta (CTA) clusters suggest that both sites drew from the same material sources. The Sevilla (SEV) cluster samples (SEV-A, SEV-B, SEV-C) form a distinct group, reflecting a cohesive compositional profile likely due to similar clay sources.

Inter-site comparisons show that Lisboa samples (Lisboa1 and Lisboa2) cluster together, indicating they might share similar clay sources or production methods. Within major clusters, subclusters can be observed, indicating slight variations within the broader compositional similarities. These could be due to different production batches, temporal changes, or slight variations in raw materials. For instance, the Orduña (ORD) subclusters suggest minor compositional variations, pointing to different production periods or sources.



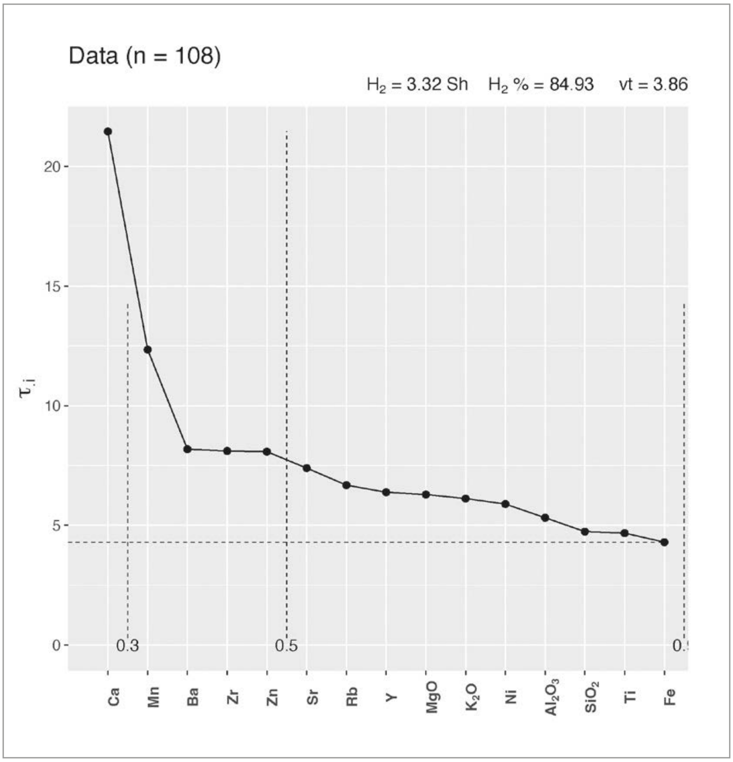


fig. 4. Graphical representation compositional variation matrix including quantified elements. The left plot (A) (n=108) highlights Lead (Pb) as the most significant contributor to dataset variability, followed by Calcium (Ca) and Copper (Cu). These elements indicate the use of lead-based glazes or pigments, calcareous clays, and copper-based decorations. The right plot (B) (n=108) shows Calcium (Ca) as the primary contributor to variability, followed by Manganese (Mn) and Barium (Ba).

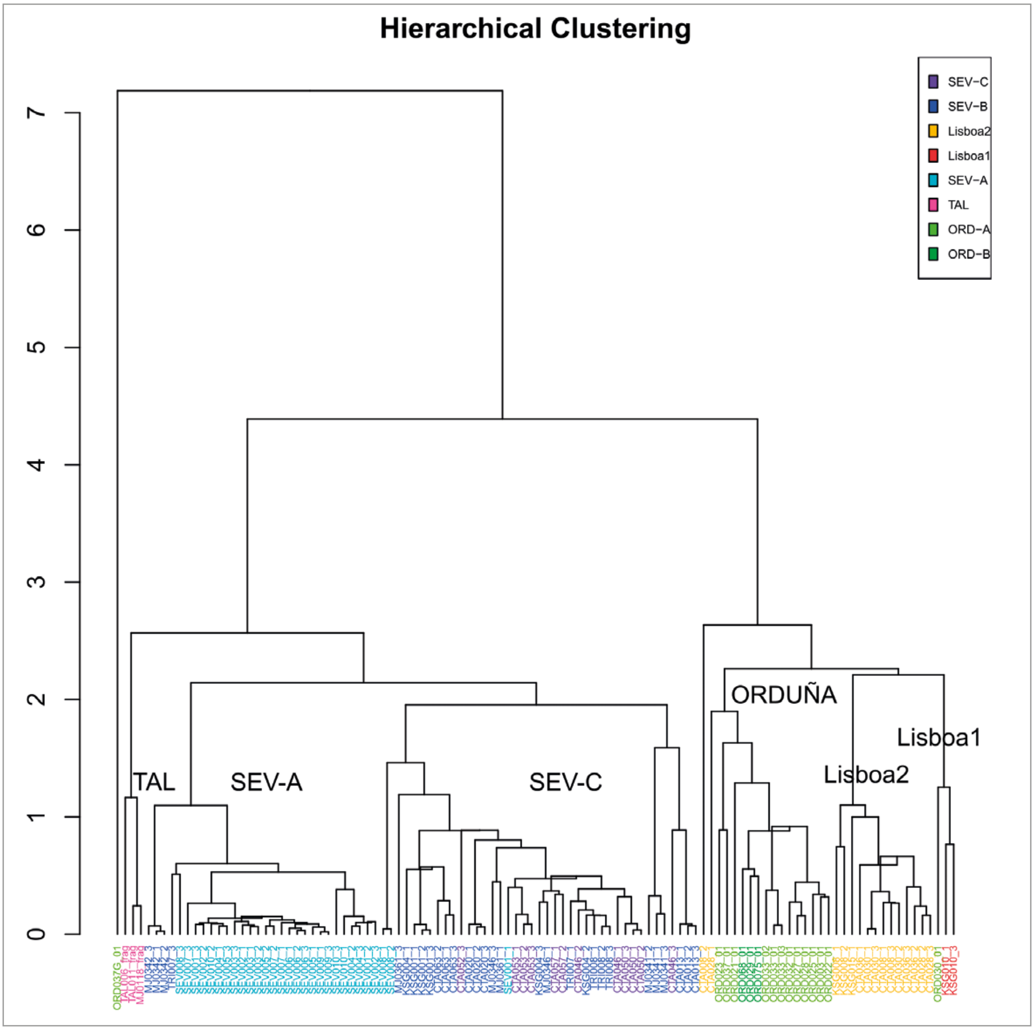


fig. 5. Hierarchical clustering dendrogram of ceramic samples from different archaeological sites, including Sevilla (SEV-A, SEV-B, SEV-C), Lisboa (Lisboa1, Lisboa2), Talavera (TAL), and Orduña (ORD-A, ORD-B).

The compositional analysis of archaeological ceramics, as depicted in the ternary diagrams (fig. 6), reveals significant chemical variations. For example, the CaO-Al_2O_3-SiO_2 system highlights that Lisboa1 and Lisboa2 ceramics cluster near the SiO_2 apex, indicating a high silica content, likely from silica-rich clays or quartz temper. Orduña (ORD-A and ORD-B) ceramics show a balanced composition between CaO and SiO_2, suggesting a mixture of calcareous and siliceous materials, this composition may point towards either an intentional mixture, crafted by artisans with specific material properties in mind, or a natural geological combination, where local raw materials with varying mineralogical content were utilized. Sevilla ceramics (SEV-A, SEV-B, SEV-C) scatter between SiO_2 and Al_2O_3, with SEV-C showing a notable lean towards CaO, suggesting lime additions or the use of more calcareous clays for

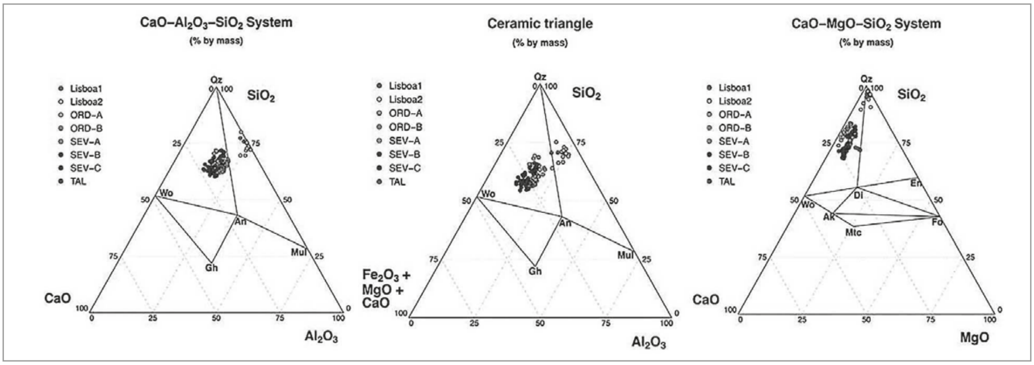


fig. 6. Ternary diagram showing the chemical compositions.

these productions. Talavera ceramics are positioned near the SiO_2 and Al_2O_3 line, indicating higher silica and alumina content.

In the Al_2O_3-SiO_2-(Fe_2O_3 + MgO + CaO) system (Heimann and Maggetti, 2019), Lisboa samples again cluster near the SiO_2 apex, reaffirming their high silica composition. Orduña ceramics show moderate fluxing agent presence, lowering melting points. Sevilla samples display significant variability, particularly SEV-C, which leans heavily towards the combined oxides, suggesting a flux-rich composition affecting sintering behavior and final hardness. Talavera samples show similar behavior than Sevilla ones, showing similarities in their major elemental composition, although in the high-end range of Mg composition. This composition suggests the intentional use of a specific temper, likely incorporating calcium- and magnesium-rich materials during the production process.

The CaO-MgO-SiO_2 system further strengthens the compositional relationships, with Lisboa ceramics consistently near the SiO_2 apex, emphasizing high silica content. Orduña ceramics show a balanced distribution between CaO and MgO, indicating the use of materials with mixed carbonate and silicate compositions. These ternary diagrams collectively provide a comprehensive understanding of compositional diversity, highlighting distinct technological practices and material selections. Lisboa ceramics' high silica content points to specific clay sources or additives, while Orduña ceramics exhibit balanced compositions. Sevilla ceramics, particularly SEV-C, show wider variability, suggesting diverse raw materials or technological practices. The ternary diagram analysis reveals significant compositional distinctions between the ceramic samples from Lisboa (Lisboa1 and Lisboa2) and those from ORD, SEV, and TAL. In the CaO-Al_2O_3-SiO_2 and CaO-MgO-SiO_2 systems, the Lisboa samples consistently show higher SiO_2 content, while the samples from ORD, SEV, and TAL cluster closely together, reflecting a more calcic composition with elevated levels of CaO and MgO. This compositional homogeneity among ORD, SEV, and TAL suggests shared similar sources of raw materials. In contrast, the separation of the Lisboa samples highlights the use of distinct raw materials.

The Principal Component Analysis (PCA) (fig. 7) conducted on the chemical compositions, including major oxides and trace elements (Al_2O_3, Ba, Ca, K_2O, MgO, Mn, Ni, Rb, SiO_2, Sr, Ti, Y, Zn, and Z), provides critical insights into the variability and interrelationships among the samples. The first principal component

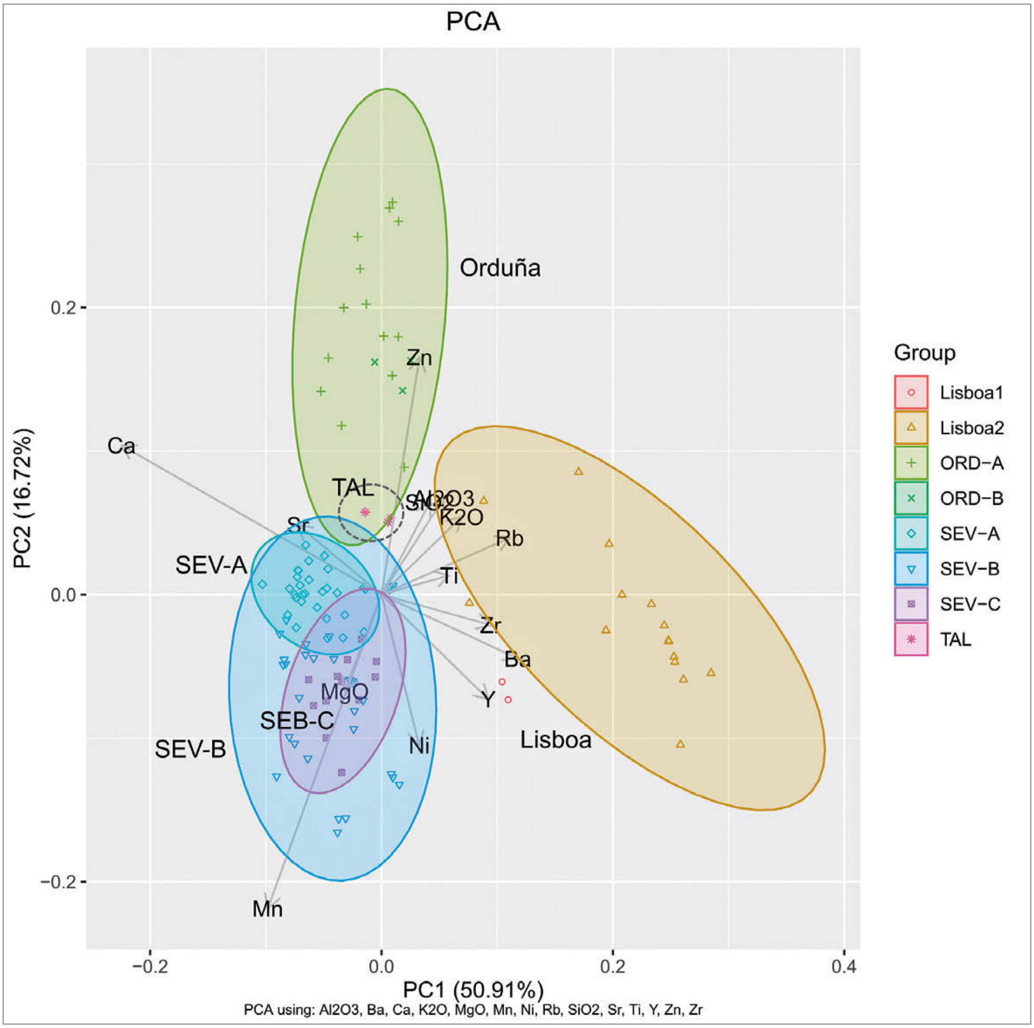


fig. 7. PCA illustrating the distribution of samples across PC1 (50.91%) and PC2 (16.72%). The ellipses represent 90% of confidence interval.

(PC1), which accounts for 50.91% of the total variance, predominantly differentiates the samples based on elements such as Al_2O_3, SiO_2, P, Cl, and K_2O, which exhibit positive loadings, and Mn, Fe, Cu, Zn, and Pb, which exhibit negative loadings. This differentiation implies that the ceramic samples can be distinguished according to their clay compositions and specific additives, thereby reflecting distinct sources of raw materials and/or technological practices. The second principal component (PC2), explaining an additional 16% of the variance, further differentiates the samples, particularly highlighting the intra-group variability within the Sevilla ceramics (SEV-A, SEV-B, SEV-C). The Lisboa samples (Lisboa1 and Lisboa2) are distinctly positioned, indicating unique chemical compositions characterized by high silica and alumina content. The spread of Sevilla samples suggests a broader range of compositional variability, likely due to varying raw material sources or production techniques. Orduña and Talavera samples, while not explicitly labeled in the plot, are implied to occupy distinct positions, emphasizing the diversity in their chemical compositions (fig. 7).

The PCA including elements such as Al_2O_3, Ba, Ca, K_2O, MgO, Mn, Ni, Rb, SiO_2, Sr, Ti, Y, Zn, and Zr, highlights the compositional diversity and relationships among the samples. The first principal component (PC1), accounting for 50.91% of the variance, highlights major differentiators such as SiO_2, Al_2O_3, and K_2O, indicative of specific clay compositions and tempering materials. In contrast, elements like Ca, MgO, and Mn, which load negatively on PC1, distinguish other ceramic groups, reflecting varied raw material sources and production techniques.

The PCA, explaining an additional 16.72% of the variance, provides further discrimination among the samples, particularly emphasizing the role of calcareous and magnesium-rich materials. Lisboa ceramics (Lisboa1 and Lisboa2) cluster together due to their high silica and alumina content, whereas Orduña samples (ORD-A and ORD-B) exhibit a balanced composition with significant contributions from calcium and magnesium. Sevilla samples (SEV-A, SEV-B, SEV-C) display considerable compositional spread, with SEV-C notably distinguished by higher calcium and magnesium content. Talavera samples (TAL) are uniquely positioned, reflecting distinctive raw material sources or production practices (fig. 7).

5. Discussion and conclusions

Currently, portable pXRF instruments have proven to be valuable research tools, though their widespread adoption has faced challenges. Many pXRF users have adopted a 'point-and-shoot' approach without critical assessment, often reporting data lacking archaeological and cultural significance. It is crucial to emphasize that handheld pXRF analyses are subject to the same limitations as any other pXRF spectrometer used for surface analysis. One of the most discussed issues in compositional analysis is material heterogeneity. These results from the non-homogeneous mixture of phases within a material, leading to a compositional analysis that is *not representative data* of its total chemical content or that varies across the sample area. The beam size plays a critical role regarding the material's degree of homogeneity, considering factors such as the number and type of inclusions (e.g., vitreous phases, silicates, organic residues), as well as their size and shape.

Furthermore, the effect of large amounts of lead in the clay matrix – the portion of the ceramic analyzed to determine its provenance – implies that strong lead (Pb) peaks can significantly affect the fluorescence emission of other lighter elements, masking signals from elements such as rubidium (Rb) or yttrium (Y), among others. This phenomenon can be observed in spectra where the lead-coated sample obscures some peaks that would otherwise be visible in an uncoated sample.

The application of Portable X-ray Fluorescence (pXRF) technology in the elemental analysis of archaeological ceramics represents a significant advancement in the field of archaeometry. Portable X-ray Fluorescence has a proven record for uncovering the technological choices and trade networks that shaped ancient societies. In this study, pXRF has been instrumental in revealing the elemental composition of ceramics from archaeological sites in North Africa and the Iberian Peninsula, providing critical insights into raw material sources and production practices. The findings contribute to a broader understanding of the complexity of ceramic production during the colonial period, highlighting the efficacy of pXRF as a key tool in archaeometric research.

The chemical analysis of ceramics from sites including Lisbon, Ksar Seghir, Seville, Talavera, and Ceuta show significant elemental variability, particularly in the concentrations of calcium (Ca), magnesium oxide (MgO), silicon dioxide (SiO_2), and lead (Pb).

The variability in ceramic composition highlights distinct choices in raw materials selection, likely shaped by local availability and technological traditions. For instance, lower levels of Ca and MgO in Lisbon samples point to a preference for non-calcareous clays, potentially chosen to achieve firing properties. In contrast, the Talavera ceramics, with elevated MgO and SiO_2 levels, indicate the deliberate use of magnesium-rich refractory materials, selected to enhance the thermal and mechanical performance of the ceramics. These choices reflect a sophisticated understanding of the geochemical properties of local clay sources and the technological requirements of production (Martínez and Pérez, 2020).

The observed chemical variability among the ceramic samples is indicative of diverse production techniques and raw material sources. The high compositional heterogeneity in the Seville ceramics, for instance, likely points to multiple workshops or production periods, echoing recent studies that emphasize the dynamic nature of ceramic production in urban centers (González et al., 2021). The elevated magnesium levels in the Talavera samples suggest a strategic selection of clays rich in MgO to enhance the ceramics' refractory properties, a practice aligned with the region's known geological resources.

Principal Component Analysis (PCA) reveals lead (Pb) as the most significant element contributing to the variability in the ceramic samples, a finding consistent with the use of high-lead glazes common in colonial ceramic production. Lead-based glazes, often in the range of 20-40% lead, were favored for their ability to produce smooth, glossy finishes and enhance the durability of ceramic surfaces. The presence of copper (Cu) in several samples further highlights its use as a chromophore, commonly employed to produce green hues in the glaze, reflecting long-standing glazing traditions in both the Iberian and North African ceramic industries. Calcium (Ca) emerges as another critical element, its variability linked to the use of calcareous clays, a choice driven by ceramicists' intentions to manipulate the firing behavior and mechanical properties of the ceramics.

Hierarchical clustering analysis complements the PCA findings, delineating distinct compositional groups that suggest strong similarities in raw material sources and production techniques across specific sites. Importantly, this study also emphasizes the need to exclude elements that may skew compositional data due to contamination or post-depositional alteration, such as Pb, Sn, Cu, P, and Cl, to achieve a more accurate interpretation of the original material compositions. By refining the focus on elements intrinsic to the production process, this approach enables more meaningful insights into technological choices and raw material procurement strategies, thus enhancing the interpretive power of pXRF data in archaeometry.

Furthermore, the effect of large amounts of lead in the clay matrix – the portion of the ceramic analyzed to determine its provenance – implies that strong lead (Pb) peaks can significantly affect the fluorescence emission of other lighter elements, masking signals from elements such as rubidium (Rb) or yttrium (Y), among others. This phenomenon can be observed in spectra where the lead-coated sample obscures some peaks that would otherwise be visible in an uncoated sample.

The pXRF technique has proven highly effective in differentiating Modern Era colonial ceramics based on their elemental compositions, offering nuanced insights into trade and production networks between North Africa and the Iberian Peninsula. While pXRF alone may not always allow for the precise determination of ceramic provenance, it excels in identifying compositional groups that suggest broader exchange patterns and potential trade routes. These findings contribute to the ongoing discourse on the economic and cultural connections between these regions, shedding light on the complex dynamics of colonial-era trade.

Furthermore, this study reinforces the broader utility of pXRF in archaeometric research, particularly in its ability to rapidly analyze large datasets without damaging valuable archaeological materials. The technique's capacity to cluster ceramics by elemental composition provides a first insight framework for understanding trade patterns and technological practices across different regions and time periods. However, to achieve more definitive provenance results, pXRF should be integrated with complementary analytical methods such as petrography, neutron activation analysis (NAA), inductively coupled plasma mass spectrometry (ICP-MS), and X-ray diffraction (XRD). The integration of these techniques allows for a more comprehensive understanding of production and distribution networks, thereby offering deeper insights into the socio-economic and cultural dynamics of historical societies.

Archaeometric studies conducted across North Africa and the Iberian Peninsula demonstrate the efficacy of these techniques in unraveling complex trade networks and cultural interactions, underscoring the critical value of pXRF in advancing archaeological knowledge. By facilitating a more precise classification and grouping of ceramics, pXRF not only enhances our understanding of ancient production systems but also reveals the broader socio-economic relationships that shaped these historical periods. This study's findings contribute to a growing body of archaeometric research that seeks to illuminate the technological sophistication and cultural interconnections, and commerce, positioning pXRF as a valuable tool for future investigations in the field of the post-medieval archaeology.

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