DOI: 10.53469/jssh.2024.6(10).18

Approaches to Ceramic Provenance Interpretation

Yao Luo[1], Yue Zhang[2]

[1]Sichuan University of Culture and Arts, Sichuan 621000, China
[2]Shaanxi History Museum, 710069, China

Abstract: ***The investigation of ceramic provenance is a crucial aspect of ceramic archaeology and artifact identification. As modern analytical techniques have advanced, a range of methods has been increasingly utilized to trace and interpret the origins of ceramic materials. This study provides a comprehensive overview of the foundational principles underlying commonly employed techniques for ceramic provenance research. It further explores the comparative applications of these analytical methods, highlighting their respective strengths and limitations.***

Keywords: Ceramic provenance, Thin-section petrography, Chemical analysis, Archaeological ceramics**.**

1. Introduction

Ceramics have played a pivotal role in human society since their inception, serving as fundamental artifacts of both daily life and cultural expression. With a rich history spanning diverse geographical regions and production techniques, ceramics exhibit a remarkable variety in form and function. Beyond the numerous artifacts passed down through generations, significant quantities continue to be unearthed through archaeological excavations and recovered from marine environments. Understanding the provenance of ceramics is essential, as it provides critical insights into the development and transformation of ancient kiln sites and their associated production practices. Additional, provenance studies offer an important framework for the accurate identification and classification of ceramic artifacts.

The conventional approach involves identifying specific types of search points based on ceramic artifacts. By utilizing these search points and accumulating historical data and provenance related to various ceramic types, it is possible to gradually establish and create a ceramic distribution map [1]. However, this method is inherently subjective and lacks authenticity. Furthermore, the increasing prevalence of counterfeiting techniques in ceramics indicates that traditional methods are insufficient to meet the demands for accurate and effective traceability.

With the development of science and technology, contemporary analytical techniques have evolved rapidly and have been extensively utilized in the analysis of ancient ceramic body glazes. This encompasses a range of compositional, structural, and microscopic analysis techniques. This study aims to summarize the commonly employed analytical methods, elucidate their fundamental principles, and examine their applications in determining the provenance of ceramics. Additionally, it will address pertinent issues related to specific detection and analysis. It is anticipated that this discussion will assist practitioners in selecting the most appropriate analytical methods based on their specific needs, thereby facilitating a scientifically rigorous approach to ceramics traceability.

2. Provenance

The provenance of ceramics pertains to the geographic origin of ceramic production, which often differs from the locations where these ceramics are discovered. The investigation into the provenance of ancient ceramics is predicated on the premise that ceramics derived from identical raw materials will display comparable chemical compositions, thereby allowing for differentiation from ceramics produced in different temporal contexts [2]. Therefore, the origin of ceramics is typically elucidated through an analysis of the raw materials employed in their manufacture.

In most cases, natural clay is not inherently suitable for ceramic production, as it requires sufficient plasticity for molding and must exhibit a controlled shrinkage rate during drying to prevent cracking. To achieve these properties, raw clay is typically refined to remove non-plastic inclusions or supplemented with tempering agents. Common tempering materials include sand, crushed minerals, clinker, organic matter, shells, and slag. These additions not only improve the workability and durability of the clay but also provide valuable information for provenance studies, as they reflect the material selection and technological practices of the producers.

3. Analysis Methods

Ancient ceramics were selected and produced on-site, with the production location and the origin of raw materials being largely consistent. However, due to variations in diagenetic processes and soil formation conditions, the rocks, minerals, and clays sourced from different regions or from different geological layers within the same region exhibit significant differences in their chemical element compositions. This is particularly evident in certain trace elements, where the disparities between different regions are considerably greater than those observed within various sections of the same clay source. Consequently, ceramic products derived from these natural resources inherently possess distinctive characteristics that reflect their raw material origins, often referred to as "fingerprint information". By analyzing the composition, concentration, and ratios of chemical elements in ancient ceramics, and by employing statistical data analysis to identify similarities and differences, researchers can trace the origins of these ceramics and uncover clues regarding their provenance. This approach provides a crucial theoretical foundation for the study of the origins of ancient ceramics.

3.1Thin-section Petrography

Ancient ceramics are classified as either single-phase or multi-phase polycrystalline materials, which are produced from natural clay, feldspar, quartz, and other raw materials through processes of molding and high-temperature firing. These ceramic crystals exhibit similarities to rock crystals found in the Earth's crust, predominantly comprising silicon (Si) and aluminosilicate minerals, as well as other rock-forming mineral crystals. Given the surface geology of various regions, along with the resultant diversity in clay sources and rock types, the classification of the geological characteristics of ceramics through macroscopic structural analysis (particularly petrology) serves as a valuable method for determining the provenance of ceramics [3]. Furthermore, the presence of inclusions, whether inherent in the clay or intentionally added as tempering agents, provides insights into the geological conditions of the area from which the clay is sourced or modified [4].

Thin-section petrography is a highly effective technique for investigating the compositional properties of archaeological ceramics. In practical applications, specimens are meticulously sliced and examined under a polarized light microscope to observe the characteristics of various inclusions within the thin section. This includes analyzing properties such as size, shape, distribution, and the relative proportions of particles. Both qualitative and quantitative analytical methods are employed to identify, document, and quantify the petrographic data pertaining to the structure of the specimen.

Thin-section petrography is primarily employed to examine the clay matrix, inclusions (which encompass tempering materials and mineral particles within the clay), and pores. These three components yield detailed and precise information regarding the composition of mineral admixtures, which is affected by local geological conditions as well as the practices and expertise of artisans involved in ceramic production. Consequently, this composition exhibits significant variability across different regions.

It is feasible to accurately ascertain the percentage of clay within ceramics, as well as the size and particle size distribution of clay and clay particles exhibiting specific properties. These data provide insights into the level of raw material processing and the molding techniques employed by ceramic artisans. Furthermore, such information can assist researchers in estimating the firing temperature through visual observation, as minerals undergo various phase changes at elevated temperatures; for instance, calcite transforms into calcium silicate, while quartz may convert into quartzite or form glassy compounds. Porat et al. [5] conducted a rigorous petrological analysis to differentiate between Nile alluvial deposits, marl sediments from Egypt, and artificial products found in loess. Their research indicates that different types of loess are utilized in the production of local Enbesor and Elani ceramics. Additionally, the results reveal that certain flower pots were imported from Egypt, whereas other artifacts, particularly household items, were produced locally. En Besor and Tel Erani are part of a series of sites where Egyptian pottery is manufactured domestically.

The presence of microfossils in ceramics allows for the determination of the raw materials and manufacturing processes utilized in their production through thin-section analysis. For instance, calcareous microfossils have been identified across various regions and time periods in Aegean and Mediterranean Seas, notably during Bronze Age in Crete. The calcareous skeletons, which encompass a range of microorganisms such as foraminifera and ostracods, constitute a significant component of archaeological ceramics from this area and era. By isolating and microscopically examining calcareous microfossils found in Bronze Age ceramics from Aegean Sea, researchers have traced the origins of pyxides from mid-Bronze Age dark cut pottery in Knossos to early Pliocene calcareous marine sediments located in northern Crete. These microfossils serve as indicators of both geological age and the environmental conditions in which they existed.

The use and disposal stages of ceramics can significantly impact the compositional characteristics of ceramic slices due to external environmental factors. For instance, in specialized usage contexts, the physical structure of the clay matrix and the individual mineral component particles may undergo alterations. During the burial process, groundwater can affect the concentration of soluble component particles. Additionally, the outer layer of the ceramic slice may provide insights into the geological sediments present in the burial environment of the sample. Consequently, data extraction in this context is heavily reliant on the specific archaeological background associated with the sample. Furthermore, thin section analysis necessitates a robust foundation in geological practices and archaeological knowledge, which imposes certain limitations on its application.

3.2 Chemical Analysis

As early as 1864, Dr. A. Damour, a French mineralogist, conducted an analysis of the mineral and elemental composition of a collection of hard stone axes utilized by Celts. He identified their mineral sources and proposed the concept of tracing their provenance through the chemical elemental composition of cultural artifacts. Numerous scientific methodologies are employed to analyze and assess the chemical elemental composition of ancient ceramics. These methods include various chemical techniques, neutron activation analysis (NAA), X-ray fluorescence spectroscopy (XRF), proton-induced X-ray emission spectroscopy (PIXE), synchrotron radiation X-ray fluorescence (SRXRF) analysis, inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.2.1 XRF

XRF has been utilized since the mid-1950s as a non-destructive analytical technique that imposes no specific requirements regarding the shape, size, or material of the sample under examination. The integrity of the sample remains unchanged before and after measurement. This method is characterized by a rapid analysis speed, typically requiring only a few minutes to detect a sample. Furthermore, XRF demonstrates high precision and accuracy, and it can be operated automatically, enhancing both convenience and efficiency. Its application in the analysis of ancient ceramics has gained prominence, establishing it as a prevalent method in ceramics analysis. XFR spectrometers are generally categorized into two fundamental types: wavelength dispersive X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF).

One of the most significant advantages of EDXRF is the ability to conduct qualitative and quantitative analyses without the need for sample preparation. This technique imposes no specific requirements regarding the shape, size, or material of the analyzed object. Consequently, it can directly analyze a variety of archaeological artifacts, thereby minimizing the risk of damage to larger, valuable ancient ceramics and other cultural relics during scientific examination and research. EDXRF boasts a broad elemental detection range, encompassing elements from sodium (11Na) to uranium (92U). Additionally, it is characterized by rapid analysis speed, high accuracy, and excellent precision, with an absolute detection limit ranging from 1.0 ng to 0.1 ng. Furthermore, EDXRF can be automated, facilitating convenient operation.

WDXRF is a widely utilized analytical technique. In comparison to EDXRF, the WDXRF method offers a broader range of detectable elements and demonstrates enhanced accuracy, particularly for lighter elements. This technique is capable of analyzing elements from sodium (11Na)to beryllium (4Be), effectively encompassing nearly all major and trace elements present in ancient ceramics. Additionally, WDXRF is characterized by its rapid analysis speed. However, WDXRF spectrometers typically employ high-power X-ray tubes, which can result in significant color damage to the surface of certain ancient ceramics during testing and analysis. Despite this limitation, WDXRF remains a valuable tool in practical applications and has yielded significant research results regarding the provenance and dating of ceramic artifacts.

3.2.2 ICP-MS

The advantages of ICP-MS in trace element analysis are particularly significant [6]. This technique employs ICP as the excitation light source to energize the atoms of each component within the sample under investigation, resulting in the emission of characteristic spectral lines. The identification of chemical elements and their concentrations in the sample is subsequently determined based on the wavelength and intensity of these spectral lines. A notable feature of ICP-MS is its capability to conduct trace and ultra-trace analysis of multiple elements, as well as isotope ratio analysis. Given that the trace elements in ceramic raw materials often exhibit more pronounced variations compared to major elements, ICP-MS can yield extensive information pertinent to the study of ancient ceramics.

ICP-MS is a highly advantageous analytical technology characterized by its low detection limits, which can reach levels as low as one billionth. This method offers high precision and allows for the simultaneous determination of multiple elements. Additionally, ICP-MS is noted for its rapid analysis speed and the capability to analyze a diverse array of elements, encompassing both major and trace elements, with the potential to assess up to 70 different types. Furthermore, it enables the measurement of isotopic compositions of elements such as strontium (Sr) and lead (Pb) in ceramic materials. Given these attributes, ICP-MS has found extensive applications in the field of archaeology, establishing itself as a crucial method for analyzing the provenance of cultural artifacts [7].

However, ICP-MS presents several limitations, including the high cost of analytical instruments, vulnerability to sample contamination, significant technical and experiential demands on operators, and the complexity of sample preparation. Despite the small sample volume required, this method can still inflict certain degree of damage to the sample. Furthermore, ICP-MS poses challenges in the analysis of two prevalent elements found in ancient ceramics, namely Si and calcium (Ca), thereby imposing certain constraints on its applicability [8].

3.2.3 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

SEM-EDS integrates morphological observation with the analysis of chemical element composition in samples, facilitating both micro-area analysis and compositional assessment. Its primary advantage in the analysis of cultural relics is the minimal sample size required, provided that the dimensions of the sample chamber are appropriate. However, this technique is classified as a micro-damage testing method and necessitates specific sampling and sample preparation protocols, which impose certain limitations on the examination of intact objects.

3.2.4 NAA

NAA technology has been utilized in archaeological research since the 1950s, primarily within the domains of archaeology, materials science, and environmental science. This analytical method facilitates the determination of elemental composition and concentrations in materials by detecting the characteristic radiation emitted by radioactive nuclides generated through neutron nuclear reactions.

NAA offers numerous advantages, including the ability to conduct synchronous analysis of multiple elements and a rapid analysis speed. This technique eliminates the need for quantitative separation, is not affected by blank samples, and circumvents the challenges associated with quantitative separation operations in trace element analysis, thereby preventing sample contamination. NAA is capable of analyzing over 80 elements from the periodic table and is currently one of the most widely employed methods for obtaining a comprehensive range of elements in elemental composition analysis.

However, NAA presents several limitations, including interference reactions that may occur during the analytical process. Certain elements, such as Si, are unmeasurable, while Ca exhibits a significant measurement error. Additionally, when the duration of testing exceeds a few minutes, the quantification of critical trace elements in ancient ceramics, including aluminum (Al), titanium (Ti), magnesium (Mg), manganese (Mn), and potassium (K), becomes unfeasible.

The analytical procedure is complex and necessitates the transportation of samples to a specialized NAA laboratory, resulting in an extended testing cycle. Although the analysis typically requires milligram-level samples, for specific types of samples, the collection of additional material to mitigate the effects of non-uniformity may lead to potential damage to the specimens.

3.3 Comprehensive Method

The two aforementioned methods are highly effective. Given their complementarity in the field of archaeology, various techniques, including typology, petrology, and chemical analysis, can be integrated to ascertain the provenance of ceramics more efficiently and effectively.

Firstly, the classification of ceramics can be utilized to ascertain whether a particular ceramic piece is representative of local production. Generally, ceramics that exhibit strong representativeness are indicative of local production, whereas a limited quantity of pottery may not originate from the local area. Petrographic and elemental analyses can be employed to compare the geochemical properties of clay from the ceramics with those from local or other regions. This comparison aids in determining the provenance of the ceramic and in identifying areas with similar geochemical compositions.

For instance, Llobera et al. [9] conducted a comparative analysis of various groups of early-Bronze Age ceramics from Crete utilizing NAA and thin layer petrology (PE). Through a series of case studies, the strengths and limitations of these two analytical techniques in the examination of ceramic materials have been elucidated. The results advocate for the incorporation of a research design in ceramic studies that integrates mineralogical and chemical methodologies with stylistic information.

4. Conclusion

As technology continues to advance, an increasing number of analytical methods are being applied to interpret the provenance of ceramics. However, it is important to recognize that all technologies have inherent limitations, and techniques such as thin-section petrography and elemental analysis are no exception. In the study of ancient ceramic provenance, relying only on the chemical composition of elements is insufficient. Even with advanced analytical tools, the results may not always accurately reflect the true origins of ceramic artifacts. For instance, the sedimentation method used to remove impurities from clay during pottery production may eliminate certain trace elements, while the interaction of clay with water may introduce insoluble minerals, altering the trace element profile. Additionally, volatile elements may escape during the sintering process, further contributing to inconsistencies between the trace element composition of the final product and the original clay. To mitigate these issues and improve the accuracy of provenance determinations, it is essential not only to enhance the reliability of analytical technologies but also to develop a comprehensive understanding of the historical production processes and techniques used in ancient ceramic manufacturing.

References

[1] Orton, C., Hughes, M. and Hughes, M., 2013. Pottery in archaeology. Cambridge University Press.
[2] Hein, A. et al., 2004. Red clays from Central and Eastern Crete: geochemical and mineralogical properties in view of provenance studies on ancient ceramics. Applied Clay Science, 24(3), pp.245–255.
[3] Quinn, P.S., 2013. Ceramic petrography. The interpretation of archaeological pottery and related artefacts in thin section: Oxford, Archaeopress.
[4] Tite, M.S., 1999. Pottery production, distribution, and consumption—the contribution of the physical sciences. Journal of archaeological method and theory, 6(3), pp.181-233.
[5] Porat, N., Yellin, J., Heller-Kallai, L. and Halicz, L., 1991. Correlation between petrography, NAA, and ICP analyses: application to Early Bronze Egyptian pottery from Canaan. Geoarchaeology, 6(2), pp.133-149.
[6] Eggins SM, Woodhead J D, KinsIey LPJ, et a1. A simpIe method for the precise determination of≥40 trace eIements ingeoIogical sampIes by ICPMS using enriched isotope internaI standardisation. Chemica1 Geo1ogy, 1997, 134(4):311-326
[7] Jianzhu (2006). Research on the Origin of Primitive Porcelain from the Shang and Zhou Dynasties. Ph. D. Thesis, University of Science and Technology of China, Hefei.
[8] Junwu. Research and Identification of Ancient Ceramic Technology. Beijing: Science Publishing, 2009.
[9] Llobera, M., 1996. Exploring the topography of mind: GIS, social space and archaeology. Antiquity, 70(269), pp.612-622.