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Coloring Mechanisms and Archaeometric Identification of Ancient Black Pottery: A Cross-Cultural Review

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Abstract

Black pottery is widely attested across Neolithic China and the Classical Mediterranean, yet the physicochemical origins of its black coloration differ substantially between these regions. This review classifies ancient black pottery firing techniques into four categories based on coloring mechanism: (1) reduction firing, where iron oxides are converted to magnetite or wüstite under oxygen-depleted conditions; (2) carbon infiltration, where free carbon from incomplete combustion deposits in the ceramic body; (3) three-stage oxidation–reduction–reoxidation firing, which produces black iron-based glass-ceramic coatings; and (4) burnishing, where directional alignment of platy minerals suppresses diffuse reflection. For each category, we review formation mechanisms, archaeological examples, and diagnostic microstructural features. A hierarchical analytical framework is then presented, ranging from non-destructive screening to micro-area quantitative analysis. Common pitfalls including post-depositional alterations and equifinality in technique attribution are discussed, alongside emerging techniques such as synchrotron micro-X-ray diffraction, X-ray absorption near-edge structure spectroscopy, and micro-computed tomography. Cross-cultural comparison reveals that Chinese and Mediterranean potters developed parallel yet distinct strategies for controlling kiln atmosphere and surface microstructure.

Keywords

Black Pottery; Firing Technology; Coloring Mechanism; Carbon Infiltration; Reduction Firing; Three-Stage Firing; Burnishing; Archaeometry.

1. Introduction

Black pottery is a broad category of ceramics with dark surface coloration, found in both the Middle to Late Neolithic of China and the Classical period of the Mediterranean. In China, the production of black-surfaced wares dates back at least six thousand years. In the Yellow River valley, fine black pottery emerged during the Early Dawenkou culture [1] and peaked during the Longshan period. The eggshell black pottery excavated at Chengziya, Zhangqiu, is the best-known example, noted for its jet-black color, sonorous quality, paper-thin walls, and mirror-like luster [2]. In the lower Yangtze region, charcoal-tempered black pottery appeared even earlier in the Kuahuqiao and Hemudu cultures, while the Liangzhu culture developed a distinctive tradition of applying dark slips enhanced by surface burnishing [1, 3]. In the Western Mediterranean, Athenian black-figure and black-gloss wares, produced from the sixth century BCE onward, are well known for their lustrous black surfaces. Their production relied on applying a fine, iron-rich clay slip to the vessel surface, followed by a three-stage oxidation–reduction–reoxidation firing sequence. During the reduction stage, both the slip and the body convert to magnetite; in the subsequent reoxidation stage, the finely grained, densely sintered slip resists oxygen re-entry and remains black, whereas the coarser body rapidly reoxidizes to red, producing the characteristic black-on-red contrast [4, 5].

Although Chinese and Mediterranean black pottery look similar, their coloration arises from different physicochemical processes. In Longshan eggshell black pottery, the dark color derives primarily from free carbon deposited through sealed-kiln carbon infiltration [6, 7]. In Liangzhu black-slip ware, the dark surface is attributed to organic matter from plant-ash admixtures and surface burnishing combined with carbon infiltration [3]. By contrast, the black surface of Greek black-gloss ware results from magnetite microcrystals within a vitrified coating [8]. Burnishing and polishing can independently produce a dark appearance by aligning platy minerals and thereby suppressing diffuse reflection [9]. These differences in coloring mechanism directly affect physical performance: carbon-infiltrated wares gain density as carbon particles fill open pores, three-stage fired wares develop a highly vitrified, wear-resistant surface, and burnished wares display improved impermeability.

Zhou et al. [6] employed thermogravimetric experiments and replication firings to reveal the carbon-infiltration nature of Longshan black pottery. Liu [7] conducted systematic experiments with Cangzhou clay and proposed a detailed carbon-infiltration model. More recently, Xiao and Cui [1] reviewed the existing literature on Neolithic Chinese black pottery, distinguishing between carbon-infiltration and slip-based coloring approaches. In Western archaeological science, Aloupi-Siotis [4] summarized characterization methods for iron-based glass-ceramic coatings on Greek black-gloss ware, and Solard et al. [10] applied micro-area two-dimensional X-ray diffraction (μ-XRD$_2$) and SEM-EDS to analyze the mineral phases and chemical composition of fourth-century BCE Atticising black-gloss ware from Asia Minor.

This review classifies ancient black pottery firing techniques into four categories based on coloring mechanism—reduction firing (iron-based), carbon infiltration (carbon-based), three-stage firing (crystalline-phase-based), and burnishing (structure-based)—and for each category reviews the formation mechanism, microstructural features, and archaeometric identification methods, while also discussing common analytical pitfalls and future technological prospects.

2. Classification and Scientific Identification of Ancient Black Pottery

Based on the physicochemical nature of the coloring agents, ancient black pottery firing techniques can be classified into four major categories (Fig. 1 and Table 1). Figure 1 presents a tree diagram organized by coloring mechanism, showing the four technique types and their representative archaeological examples. Two or even three techniques often overlap in actual archaeological finds; for instance, Longshan-period black pottery from the Taosi site exhibits both slip and carbon-infiltration features [11]. Nevertheless, classification by the dominant coloring agent remains a useful analytical framework.

2.1. Reduction Firing

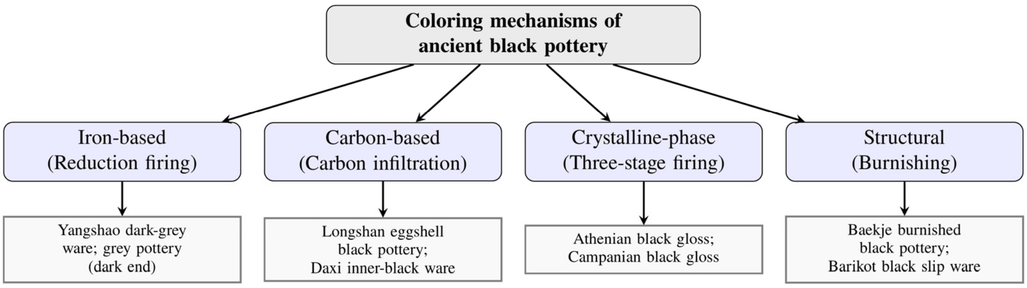

Fig 1. Classification of ancient black pottery by coloring mechanism.

Table 1. Summary of the four black pottery firing technique types

Type	Coloring agent	Typical examples	Diagnostic methods
Reduction firing	Fe_3O_4/FeO (magnetite/wüstite)	Dark-end grey ware; Yangshao dark-grey pottery	XRD magnetite peaks; refiring-reversion test
Carbon infiltration	Free carbon (soot)	Longshan eggshell black pottery; Daxi inner-black pottery	Raman D/G bands; EDS carbon gradient line scan
Three-stage firing	Magnetite/hercynite microcrystal coating	Athenian black gloss; Campanian black gloss	SEM-BSE coating/body interface; SR-μXRD
Burnishing	Directionally aligned minerals	Baekje burnished black pottery; Barikot black slip ware	PLM extinction; EBSD texture analysis

Reduction firing is the most basic black-coloring pathway. Under oxygen-depleted kiln conditions, hematite (Fe_2O_3) in the ceramic body is reduced to magnetite (Fe_3O_4) or wüstite (FeO), shifting the color from red through grey to near-black [12]. The depth of color depends on the degree of reduction and the iron content of the body; when the Fe_2O_3 content exceeds 5% and the oxygen partial pressure is sufficiently low, the body can reach a near-black deep grey [13]. An oxygen-free atmosphere must be maintained during cooling; otherwise, magnetite reoxidizes to hematite, causing the surface to revert to red [14].

Nodari et al. [14] examined Etruscan-Padan sandwich-structure pottery from the Po Valley, Italy, and identified a clear Fe^{2+}/Fe^{3+} gradient between the black exterior and red interior, confirming layered atmosphere control during firing. Maritan et al. [13] systematically investigated the influence of organic matter on the firing atmosphere through controlled experiments, demonstrating that organic constituents in the raw material consume oxygen during heating, creating localized reducing micro-environments that promote low-temperature body darkening. More recently, Lima et al. [15] used Mössbauer spectroscopy to quantify the relative abundances of Fe^{2+} and Fe^{3+} at different firing temperatures, but cautioned that the relationship between iron valence states and firing conditions is not straightforward and requires careful sample-specific interpretation. Xia et al. [16] confirmed through XRF and XRD analysis of Longshan culture pottery from the Yongcheng area that the presence of magnetite in deep-grey sherds is consistent with strongly reducing firing conditions.

The diagnostic criteria for reduction-fired black pottery include: (i) characteristic diffraction peaks of magnetite or wüstite in XRD patterns; (ii) color reversion to red upon refiring in an oxidizing atmosphere; and (iii) absence of carbon-combustion-related weight loss in thermogravimetric analysis. These three indicators effectively distinguish reduction-fired ware from carbon-infiltrated ware.

2.2. Carbon Infiltration

Carbon infiltration is the principal coloring technique of Neolithic Chinese black pottery. The underlying mechanism involves sealing the kiln during the later stages of firing and restricting air intake, causing the organic fuel to undergo incomplete combustion and generating abundant fine carbon-black particles [6]. Carbon deposition proceeds through two pathways: physical filling of surface-connected open pores by carbon-black particles, and chemical deposition through the Boudouard disproportionation reaction ($2CO \rightarrow CO_2 + C$), which precipitates solid carbon at lower temperatures [7]. Systematic experiments by Liu [7] demonstrated that carbon infiltration is most effective below 630°C, at which temperature the clay minerals retain their interlayer water and large specific surface area, conferring a strong chemical adsorption capacity for aromatic hydrocarbon volatiles. Above this threshold, illite loses its structural water, and adsorption capacity drops sharply, leading to a marked decline in infiltration efficiency.

The degree of carbon infiltration typically decreases from the surface inward. Li and Huang [17] performed detailed macroscopic observations and replication firings on Daxi culture black pottery, reconstructing four infiltration patterns—fully black, red exterior with black interior, red top with black bottom, and vertical black streaks—and proposed both in-kiln and post-kiln infiltration methods. Shen et al. [18] examined the microstructure and chemical composition of Longshan black pottery, finding abundant pores partially filled with carbonaceous material; although the body had a relatively high iron content, carbon infiltration proved to be the primary coloring mechanism. Zhu et al. [19] applied XRD, Raman spectroscopy, and SEM to black pottery from the Shuangdun site in the Huai River valley, confirming that the principal colorant was carbon black, and suggesting that plant residues in the body may have facilitated the infiltration process. In addition, Pan et al. [20] found that the surfaces of Western Han black pottery from the Shuanglong cemetery at Lu'an were coated with a mixture of carbon black and raw lacquer, demonstrating that carbon-based coloring techniques persisted in modified forms well beyond the Neolithic.

The diagnostic features of carbon-infiltrated black pottery include: (i) the D band (~1350 cm^{-1}) and G band (~1580 cm^{-1}) of carbon in Raman spectra; (ii) a pronounced decrease in carbon concentration from the surface inward, as revealed by EDS line scanning; and (iii) SEM observation of nanoscale carbon particles forming coral-like or dendritic aggregates filling pores [7].

2.3. Three-stage Firing and Black-gloss Ware

Unlike Chinese black pottery, which relies on carbon deposition, the black-figure and black-gloss wares of the Classical Mediterranean employed a different, coating-based coloring technique. Potters first applied a finely levigated, iron-rich clay slip with a particle size generally below 2 μm to the formed vessel, then subjected it to a three-stage oxidation–reduction–reoxidation firing sequence (Fig. 2) [4]. During the reduction stage, at approximately 900°C, hematite in both the slip and the body converts to magnetite. Upon entering the reoxidation stage, the fine-grained, densely sintered slip prevents oxygen from re-entering, preserving the magnetite and its black color, whereas the coarser, more porous body rapidly reoxidizes to red. This differential response produces the characteristic red body with a black coating [5].

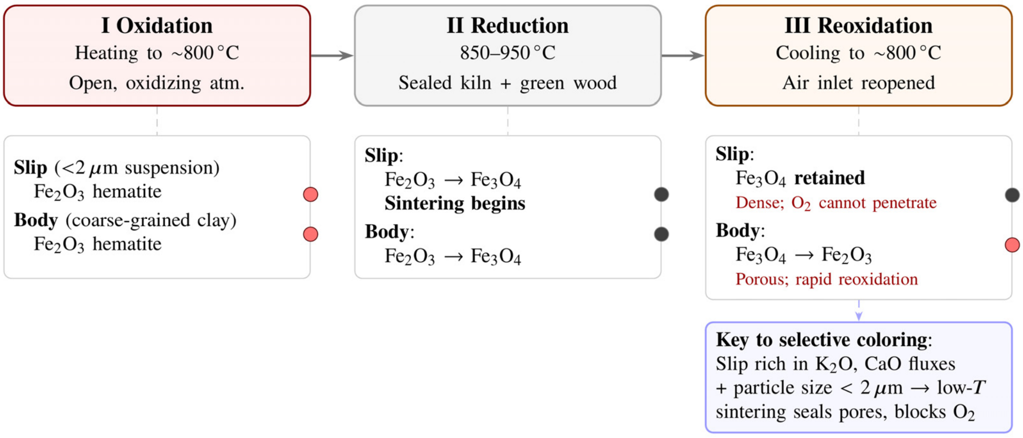

Fig 2. Three-stage firing process and selective coloring mechanism of Greek black-gloss ware [4, 5].

Cianchetta et al. [8] compared replicate and genuine Greek black-gloss sherds using micro-Raman spectroscopy and X-ray diffraction, confirming that the black phase in the coating consists primarily of magnetite and hercynite ($FeAl_2O_4$) microcrystals. Solard et al. [10] further applied micro-area two-dimensional X-ray diffraction (μ-XRD_2) and SEM-EDS to Atticising black-gloss ware from fourth-century BCE Asia Minor, showing that the coating is enriched in K_2O and CaO fluxes and that the coating–body interface is sharply defined in backscattered electron images. Łaciak et al. [21] demonstrated, through their study of Central European prehistoric black-coated pottery, that high iron content and fine particle size in the coating are common prerequisites for achieving analogous effects.

The diagnostic criteria for three-stage black-gloss ware include: (i) a sharp boundary in SEM-BSE images between coating and body with distinct compositional contrasts, the coating showing notably higher Fe and K contents; (ii) detection of magnetite or hercynite microcrystals in the coating by SR-μXRD; and (iii) resistance of the fully vitrified coating to color reversion upon refiring.

2.4. Burnishing

In some black pottery, the dark appearance relies neither on carbon deposition nor on iron-phase transformation but rather on fine surface polishing that aligns platy silicate minerals, suppressing visible-light diffuse reflection and producing a dark, lustrous surface [9]. This "structural coloring" mechanism has been documented in burnished black pottery from the Hanseong period of the Baekje kingdom on the Korean peninsula. Kim et al. [9] used SEM and mineral analysis to show that no additional carbon deposit or coating was detected on the black surface; the dark appearance resulted entirely from the physical alignment of surface mineral grains. Blackmore et al. [22] connected Baekje black pottery production to state-formation processes, arguing that burnishing, as a labor-intensive surface treatment, was a marker of social status. Uhm et al. [23] applied radioanalytical techniques and magnetic measurements to characterize the chemical composition and magnetic properties of Hanseong Baekje black pottery, providing supplementary data for identifying reducing firing atmospheres.

In South and Central Asia, Maritan et al. [24] analyzed the mineralogy and chemistry of black slip ware from Barikot in northwestern Pakistan, finding that the black slip had been fired under reducing conditions but showed only minor compositional differences from the body; platy minerals in the slip exhibited pronounced directional alignment. Choi et al. [25] combined XRD, SEM, and chemical analyses of Baekje pottery from the Sabi period, observing that burnishing significantly reduced surface roughness and enhanced glossiness. Moon et al. [26] used XRD to track structural changes in clay minerals within Baekje black pottery as indicators of firing parameters.

The diagnostic features of burnished black pottery include: (i) simultaneous extinction of surface minerals observed under cross-polarized light in polarized light microscopy (PLM); (ii) directional alignment of platy minerals quantified by electron backscatter diffraction (EBSD), a technique already applied in archaeological ceramic studies [27]; (iii) significantly lower surface roughness in burnished areas as measured by atomic force microscopy (AFM); and (iv) absence of free carbon or magnetite signals in EDS and Raman analyses.

3. Analytical Methods

Identifying the four black pottery types requires a hierarchical analytical framework, from macroscopic screening to micro-area quantification (Table 2). In practice, researchers typically begin with non-destructive or minimally destructive techniques for preliminary classification, then employ micro-area methods to obtain precise phase and elemental distribution data.

Table 2. Hierarchical analytical framework for identifying black pottery coloring mechanisms

Level	Representative methods	Information obtained	Applicable types
Non-destructive screening	Stereomicroscopy, portable XRF, colorimetry	Surface morphology, major elements, color parameters	All types
Micro-destructive qualitative	Raman spectroscopy, FTIR, PLM	Carbon/iron phases, mineral species, orientation	Carbon infiltration, three-stage, burnishing
Micro-area quantitative	SEM-EDS, Mössbauer spectroscopy, SR-μXRD, EBSD	Element distribution, Fe valence, microcrystal phases, crystallographic texture	All types

3.1. Firing Temperature Determination

Firing temperature determination forms the foundation of black pottery technological studies. The mineral-phase transition sequence recorded in XRD patterns provides reliable temperature indicators—for example, illite dehydroxylation is completed at 500–600°C, while mullite begins to form above 1000°C [7]. For carbon-infiltrated black pottery, the experiments of Liu [7] established that the effective carbon-infiltration window lies below 630°C, above which the adsorption capacity of the clay declines sharply. For reduction-fired black pottery, magnetite typically forms at 700–900°C [13].

3.2. Carbon Versus Iron Identification

Distinguishing between carbon-based and iron-based coloring is the critical first step in classifying black pottery. Raman spectroscopy is the most widely used technique: the D band ($\sim 1350\ \mathrm{cm}^{-1}$) and G band ($\sim 1580\ \mathrm{cm}^{-1}$) of carbon unambiguously indicate the presence of free carbon, whereas magnetite produces a characteristic Raman peak at $\sim 670\ \mathrm{cm}^{-1}$ [28]. van der Weerd et al. [29] combined infrared and Raman micro-spectroscopy to identify black pigments on prehistoric Southwestern American potsherds, successfully distinguishing carbon-based from iron-mineral-based black pigments. Tankova et al. [30] similarly confirmed through the study of red- and dark-decorated prehistoric pottery from Bulgaria that combined Raman spectroscopy and SEM-EDS can reliably differentiate iron-based from carbon-based black pigments. This combined analytical strategy is equally applicable to the preliminary classification of Chinese black pottery.

3.3. Iron Valence Quantification

Quantitative determination of iron valence states provides more precise diagnostic information for reduction-fired and three-stage black pottery. The application of Mössbauer spectroscopy to ancient ceramics dates back to the pioneering work of Cousins and Dharmawardena [31]. Ricciardi et al. [32] subsequently applied the technique to black-slipped pottery from Nepal, quantifying differences in the Fe^{2+}/Fe^{3+} ratio between coating and body. Most recently, Choi et al. [33] demonstrated that ceramic color alone is an unreliable proxy for firing conditions, and advocated the combined use of Mössbauer spectroscopy, XRD, and magnetic measurements to achieve more robust determinations.

3.4. Microstructural Characterization

Microstructural characterization is essential for precisely mapping the spatial distribution of coatings and carbon-infiltration layers. SEM-EDS line and area scans can clearly reveal either a carbon-enrichment gradient from the surface inward or an abrupt compositional discontinuity at the coating–body interface [10, 18]. Medeghini et al. [34] combined Raman spectroscopy, SEM-EDS, and XRD in a micro-area analysis of Pompeian black-gloss ware, showing that compositionally complex samples demand multi-technique analysis.

A comparison of the strengths and limitations of the principal analytical methods is presented in Table 3. These techniques, from sealed-kiln carbon infiltration in Neolithic China to iron-rich slip coatings in Classical Greece, reflect the range of solutions potters devised to control reducing atmospheres and surface microstructure [35].

Table 3. Comparison of principal analytical methods for black pottery studies

Method	Target	Advantages	Limitations
Raman spectroscopy	Carbon phases, iron oxides	Non-/micro-destructive; high spatial resolution; field-portable	Fluorescence interference; weak signal on dark samples
XRD	Mineral phases	Accurate phase identification; mature quantitative protocols	Requires powdered sample; insensitive to amorphous phases
Mössbauer spectroscopy	Fe valence states	Precise Fe^{2+}/Fe^{3+} quantification	Requires ~100 mg sample; limited equipment availability
SEM-EDS	Morphology, element distribution	Rich micro-area information; intuitive imaging	Requires vacuum; destructive sample preparation
FTIR	Organic matter, minerals	Small sample requirement; rapid analysis	Low spatial resolution
PLM	Mineral species/orientation	Simple equipment; non-destructive	Limited quantitative capability
SR-μXRD	Microcrystal phases	Extremely high spatial resolution	Requires synchrotron radiation source

4. Common Pitfalls and Limitations

4.1. Post-depositional Alterations

Burial environments frequently alter the surface of black pottery, complicating the identification of original coloring techniques. The most common issue is secondary manganese deposition: dissolved manganese ions in the soil can precipitate as black manganese-oxide films or patches on the ceramic surface under oxidizing conditions, closely mimicking the appearance of a carbon-infiltration layer [36]. De Vito et al. [36] found, in their study of black-gloss ware from Motya in western Sicily, that the black coloration on some sherds was actually manganese oxide deposited during burial rather than an original black-gloss coating. Such interference can be identified through anomalous Mn enrichment in EDS area scans.

Secondary adsorption of organic matter is another obstacle. Humic acids and other soil organic compounds can infiltrate surface pores, and their fluorescence emission frequently masks the carbon D/G bands in Raman analysis, leading to the misidentification of carbon-infiltrated ware as non-carbon-colored [37]. Scarpelli et al. [37] encountered severe fluorescence background interference in Raman analyses of black-coated pottery from Pompeii and ultimately achieved phase identification only by combining FTIR and SEM-EDS. Łaciak et al. [21] noted in their study of Central European prehistoric black-coated pottery that calcareous crusts overlying the ceramic surface interfere with surface chemical analysis and must be identified microscopically and carefully removed prior to measurement.

4.2. Equifinality in Technique Attribution

Even when post-depositional interference has been excluded, the identification of black pottery coloring techniques faces a fundamental challenge: the same mineral phase or the same analytical result may correspond to different formation processes. For example, magnetite can be either the product of reduction firing throughout the body or a component confined to the coating in three-stage black-gloss ware [4]. Detection of magnetite by XRD alone cannot determine whether it formed through bulk reduction of the body or localized reduction of a slip. Lu et al. [11] illustrated this ambiguity in their analysis of black pottery from the Taosi site, where the slip material itself had a sufficiently high iron content to produce a black, lustrous appearance without carbon infiltration. The situation at the Liangzhu ancient city site is even more complex: Lu et al. [3] found that the black surface was not a deliberately applied slip but rather a low-phosphorus clay layer formed when plant-ash-containing organic matter in the body migrated to the surface during burnishing.

To address equifinality, at least two independent analytical techniques should confirm the nature of the coloring agent, supplemented by spatial distribution data [34]. Amicone et al. [38] similarly emphasized, in their experimental archaeological study of Late Neolithic pottery in the Balkans, the importance of comparing experimentally replicated samples fired under known conditions with excavated sherds, which can substantially reduce ambiguity in technique attribution.

Destructive analysis and artifact conservation are inevitably in tension. Mössbauer spectroscopy requires approximately 100 mg of powdered sample, and SEM-EDS necessitates cross-sectioning and polishing. For thin-walled, high-value objects such as eggshell black pottery, any invasive sampling is difficult to justify. This tension is equally acute in the study of other precious black-glazed wares, such as Song-dynasty Jian bowls [39], and has driven growing interest in non-invasive, in-situ analytical technologies.

4.3. Emerging Analytical Techniques

Synchrotron micro-X-ray diffraction (SR-μXRD) and X-ray absorption near-edge structure spectroscopy (XANES) address several of the limitations noted above. SR-μXRD can acquire phase information at spatial scales of 10 μm or finer without requiring sample grinding [10]. XANES enables the direct, non-invasive determination of iron valence states and coordination environments; this makes in-situ identification of reduction-fired and three-stage black-gloss ware feasible [4]. Amicone et al. [40] systematically characterized firing products from different stages using XRD, SEM-EDS, and Raman spectroscopy in kiln experiments conducted at the Campus Galli open-air museum; these data serve as reference points for experimental–archaeological comparisons.

Micro-focus computed tomography (micro-CT) can non-invasively reconstruct the three-dimensional morphology and distribution of pores within the body, enabling indirect assessment of the depth and uniformity of carbon infiltration. Reedy and Reedy [41] combined micro-CT with 3D image analysis to characterize 42 parameters of the pore system in ceramics fired at different temperatures, 26 of which correlated significantly with firing temperature, confirming the technique's potential for pyrotechnological studies of archaeological ceramics. High-resolution transmission electron microscopy (HR-TEM) may further reveal the crystallographic characteristics of nanoscale magnetite or hercynite microcrystals in coatings—microstructural evidence that has not been accessible with other methods and that could help reconstruct three-stage firing processes in greater detail. Choi et al. [33] have already demonstrated that combining Mössbauer spectroscopy, XRD, and magnetic measurements can yield firing-atmosphere information that is unobtainable through conventional methods alone. Wider access to these instruments will allow more detailed reconstruction of ancient firing sequences.

5. Conclusion

This review has classified ancient black pottery firing techniques into four categories based on coloring mechanism: reduction firing (iron-based), carbon infiltration (carbon-based), three-stage firing (crystalline-phase-based), and burnishing (structure-based), and has reviewed the formation mechanism, representative archaeological examples, and archaeometric identification methods for each. The four categories differ in their coloring agents, microstructural features, and diagnostic indicators; however, overlap between techniques is common in actual archaeological finds and requires multi-method cross-validation for reliable attribution.

Cross-cultural comparison of Chinese and Mediterranean black pottery technologies reveals two parallel trajectories of ceramic technological evolution. Chinese potters relied principally on sealed-kiln carbon infiltration, achieving surface blackening through controlled carbon deposition, while Mediterranean artisans employed colloidal chemistry to prepare iron-rich slips and achieved selective coloring through three-stage firing. Despite these differences, both traditions required precise control over kiln atmosphere and surface microstructure. Synchrotron micro-area analysis, in-situ characterization, and experimental archaeology now make it possible to answer questions that older methods left open. Cross-cultural comparison of the resulting data can clarify where Chinese and Mediterranean potters converged on similar solutions and where they diverged.

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work, the author used Claude (Anthropic) for language translation and editing. After using this tool, the author reviewed and edited the content as needed and takes full responsibility for the content of the published article.

Declaration of Competing Interest

The author declares no competing interests.

Data Availability

No data were used for the research described in the article.

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