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Zn in Athenian Black Gloss Ceramic Slips: A Trace Element Marker for Fabrication Technology

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The black-colored pottery slips produced in Athens from the 6th to 4th centuries B.C., had a consistent composition achieved through processing and refinement of raw clay. Little direct evidence has been established as to what were these refinement methods. To better understand how the slip material was prepared, the major and trace elemental compositions of 19 slips from different ceramic vessels and their corresponding bodies of Athenian red-figure and black-figure vases were determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Notably higher Zn concentrations were found in the slips (271–1959 ppm) than in their corresponding body ceramics (<361 ppm). The Zn concentrations in the slips were also found to be above the natural background for typical clay (between 10 and 300 ppm) suggesting an unintentional anthropogenic enrichment of this metal. Based on the abnormally high Zn content of the slip, it is speculated that the clay was treated using vitriol (concentrated acid mine runoff which is rich in Zn), to induce flocculation and remove carbonate mineral phases from the raw material that, if present, would prevent the slip from vitrifying. This same signature of elevated levels of Zn with a corresponding Ce anomaly is also observed for black glosses produced in Corinthian and Etrurian (Italy) workshops indicating that these trace element signatures were imparted to the material by means of shared methods of manufacturing instead of being indicative of a single unique source for this material.

I. Introduction

In the late Bronze Age (~1200 B.C.), the ancient Greeks started painting ceramics with dilute Fe-rich clay slips[1,2] that when fired created decorative glossy surfaces with a deep black color.[3] As exemplified by the vessel shown in Fig. 1, the art of vase painting reached its technical and aesthetic height during the archaic and classical periods (mid 6th–4th centuries B.C.) with vases produced in the black- and red-figure technique.[4] In the earlier black-figure technique (starting in the late 7th century B.C.), the figural shapes are blocked out as islands of slip into which decorative details are incised. The later red-figure technique (late 6th century B.C.) is the opposite of black figure wherein the figural shapes are outlined by slip and painted lines delineate details. Both techniques involve painting areas with Fe-rich illite clay slips—often called glosses due to their final appearance—which turn black upon firing in a reducing atmosphere, while areas not painted remain a buff reddish-orange color.[5]

Previous compositional analyses of Athenian fine ware pottery have successfully determined the geological provenance of the clay source of the body ceramic to be linked to the Amarousi region just outside modern Athens.[6–16] However, similar compositional studies aimed at understanding the geological origin of the slip materials have not provided such clear results[1,17,18] due to the fact that the clay-refining process alters many of the geologically relevant markers needed to determine provenance. In its most simplistic form, the refinement of a clay into a suitable slip material through a process known as levigation likely involved dispersing the clay into large vats of water and allowing the coarse grains to settle to the bottom of the tank, leaving the fine grains suspended in the solution.[5]

Kingery *et al.*[17] demonstrated that a black-colored slip could be made from a wide variety of illite clays with slightly different compositions. Despite the relative ease with which a black gloss could be made, Kingery also found that the composition of Athenian black gloss was sufficiently different from the body that clay levigation alone could not account for the gloss composition. Other studies similarly showed that there appears to have been a standard composition for the black slip material.[1,2,16,18–22] However, how this standard composition was achieved has not yet been fully determined. Two possibilities have been posited on how black gloss was produced:

1. The gloss is derived from the same clay as the body but has been chemically altered during levigation, or
2. A special glaze clay which had a unique composition was mined.

The study presented here was designed to test these two different scenarios. Comparing the composition of the black slip with the body clay on individual sherds should reveal whether materials were added to the levigation water vats to aid in the refining process, or added later to the refined clay slips to improve the sintering behavior.[15,17–19] Trace element composition of clay bodies reveals important information regarding the trade of ceramics, and, likewise, can be used to extract data on how artifacts are fabricated.[23,24] As shown in Table I, 19 sherds from the collection of the J. Paul Getty Museum (JPGM) were chosen to characterize the trace

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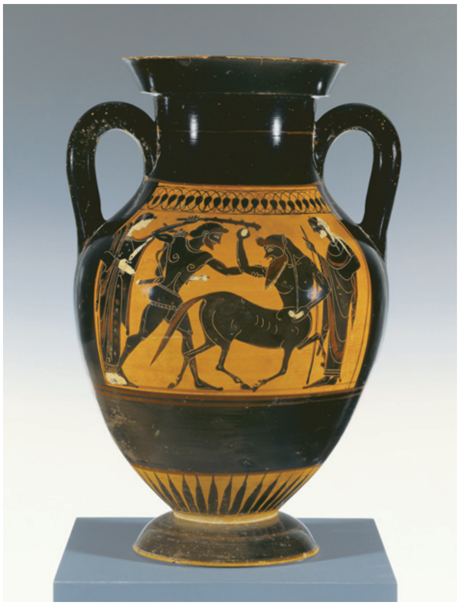

Fig. 1. An example of a 6th century BC black-figure vase (JPGM 88.AE.24, courtesy of J. Paul Getty Museum.).

element composition of Athenian black slips. Spanning the archaic through classical periods, the sherds were selected to represent the breadth of production from 6th to 5th centuries B.C. starting with black-figure vessels and spanning about 100 yr of production of red figure. The trace element data collected from these sherds allowed us to evaluate how the levigation of the clay was performed.

II. Experimental Procedure

(1) ICPMS

Both major and trace element compositions of the slips were determined using laser ablation inductively coupled plasma mass spectrometry. Only the broad washes of black slip material, known as background gloss,[25] were analyzed *in situ* for this study. Analysis was performed using a New Wave Laser Ablation system (ESI, San Jose, CA) coupled to an OptiMass 9500 ICPMS (GBC, Braeside, Australia). The laser was a frequency quintupled Nd–Yag (213 nm) unit operated at 1.8 mJ using a 10 Hz repetition rate and a 30-μm aperture. The laser was used to ablate material from a single hole in each sherd, starting from the surface, continuing through the gloss slip, and ending in the body ceramic. During the analysis, a full mass spectrum was collected at 30-ms intervals, thus oversampling each laser pulse by about three times. Since the ICPMS was not synched in time with the laser and not all materials were removed via ablation with the same efficiency, oversampling was utilized to ensure that the compositional changes through the entire gloss/ceramic cross section were captured. Figure 2 demonstrates how this sampling scheme works on a representative sherd (JPGM 87.Ae.82.5). The weight percent of several major oxides (Al_2O_3, CaO, K_2O, and Fe_2O_3) is plotted as a function of ablation time. Abundance changes in theses oxides indicate the transition between the gloss slip and the body: Al_2O_3, K_2O, and Fe_2O_3 start off relatively high and drop when the transition from the gloss to the body ceramic is crossed (at ~400 μS). Conversely, CaO starts off low in the gloss and rises to a plateau once the laser ablates into the body. The dashed line in Fig. 2 indicates the approximate transition point between the gloss and the body ceramic. The bulk composition for both the gloss and the body ceramic were determined by averaging the individual analyses from these regions. For the gloss, this typically amounted to ~10 spectra and corresponding to a 15–20 μm gloss thickness.

An external calibration was created by ablating NIST standard glasses 610–614 using the same laser fluence and repetition rate used to analyze the ceramic. The calibration was checked against Corning A and D archaeological reference glasses[26] for accuracy and precision. All data processing was performed in Igor (WaveMetrics, Portland, OR) using the Iolite add-in package.[27,28] Further details on the operating conditions of the ICP-TOFMS are found in Ref. [28].

(2) XANES

Micro X-ray absorption Near Edge Spectra (μ-XANES) were collected on beamline 2–3 at the Stanford Synchtron Radiation Light Source. Spectra were collected with spot sizes of 2 μm ×2 μm at the Zn K-edge. Specimens were introduced to the beam as thin sections with thicknesses less than 30 μm to allow for the collection of data in transmission to avoid self-adsorption. The edge region was scanned using step sizes of 0.35 eV and energy was calibrated with reference to a Zn metal foil by setting the edge inflection point to 9660.7 eV. All data were processed using Sixpack.[29] Zn mineral specimens supplied by the California Institute of Technology were used as references.[30]

Table I. Study Set of 19 Sherds

J. Paul Getty museum accession number	Description	Painter/potter	Approximate date (BC)
76.Ae.104.1.6	Attic Red-figure Oinochoe	Mannheim	Mid 5th Century
85.Ae.470	Attic Red-Figure Cup	Marlay	Mid 5th Century
83.Ae.434.25.3	Falsican (Italian) red figure krater	Del Chiaro	4th Century
86.Ae.54.7	Attic Red-Figure	Kleophrades	Early 5th Century
86.Ae.224.3	Attic Red-figure Skyphos	Kleophrades	Early 5th Century
95.Ae.31.2	Attic Red-Figure Skyphos	Kleophrades	Early 5th Century
87.Ae.82.5	Attic Red-figure Kantharos	Brygos	Early 5th Century
83.Ae.286.22	Attic Red-figure Kylix	Makron	Early 5th Century
90.Ae.36.43	Attic Red-figure Zone Cup	Douris	Early 5th Century
79.Ae.17.6	Attic Red-Figure Kylix	Onesimos	Early 5th Century
83.Ae.430	Attic Red-Figure	Oltos	Late 6th Century
77.Ae.94.1	Attic Red-Figure Kylix	Oltos	Late 6th Century
86.Ae.306.1	Attic Red-Figure	Epiketos	Late 6th Century
77.Ae.7	Attic Red-Figure Mastoid Cup	Andokides	Mid 6th Century
82.Ae.40.52	Attic Black_figure	Unknown	Mid 6th Century
90.Ae.15.2	Attic Black-Figure	BMN	Mid 6th Century
76.ae.92C	Corinthian Black Figure krater	Tydeus	Early 6th Century
80.Ae.5.1.D	Attic Black-Figure Siana Cup	Unknown	Early 6th Century
81.Ae.211.A18	Attic Red-Figure Stamnos	Kleophrades	Early 5th Century

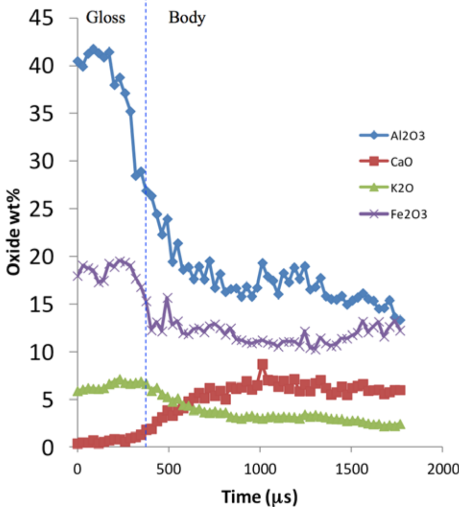

Fig. 2. Compositional depth profiles of oxides of major elements produced as the laser ablates material from a single pit in the gloss and body of JPGM 87.Ae.82.5.

III. Results

(1) Background Gloss Major Element Composition

The major oxide values for the black gloss from each of the 19 sherds—Al_2O_3 between ~22% and 37%, SiO_2 between ~40% and 49%, Fe_2O_3 between ~11% and 15%, variable K_2O from ~2% to 8%, and CaO ~1% by weight—show good correspondence with previous analyses and is consistent with a fine grained illite clay fraction that would have been produced clay levigation as described by previous researchers.[2,5,17,31] The full dataset may be seen in supplementary Table I.

(2) Compositional Comparison Between Gloss and the Ceramic

Enrichment–depletion diagrams illustrate how mineral phases fractionate during chemical weathering and the physical sorting of soils and sediments, similar to what would occur during levigation.[32] In Fig. 3 we use such a diagram to compare the average composition of the major oxide (Fig. 3a) and trace elements (Fig. 3b) in the black gloss and the body ceramic found for our study set. Al is uniquely associated with the clay mineralogy. Therefore, the only compositional changes expected between the body and gloss clay are the removal of large grain and heavy mineral fractions that quickly settle to the bottom of the levigation tanks. The fine-grained clay platelets remain in suspension. It is therefore assumed that all Al_2O_3 present in the raw unprocessed clay is transferred into the fine gloss fraction when levigation is used. To produce this diagram, each oxide and element measured in the gloss and body ceramic is normalized to Al_2O_3. The normalized gloss composition is then subtracted from the normalized body.

Figure 3 reveals that the body ceramic is enriched in SiO_2, MgO, and CaO, as well as Cr, Mn, Ni, Sr, and Ba relative to the black gloss. Notably, Zn is the only element enriched in the gloss material relative to the body ceramic. The remaining 22 oxides and elements plotted in Fig. 3, showed either no enrichment or an enrichment within the error of the calculated result.

The enrichment of SiO_2 in the body ceramic (Fig. 3) was expected since, in addition to its presence in the main clay minerals, this oxide also exists as large quartz inclusions that preferentially settle during levigation. Likewise, the enrichment of MgO, CaO, Mn, Sr, and Ba in the body may be explained by the fact these oxide/elements are typically hosted in carbonate phases such as calcite $CaCO_3$.[33] The Cr and Ni enrichment in the body may be markers of chlorite clays that are often found in interlayered with illite throughout the Mediterranean world[34,35] but they can also be incorporated into pedogenic carbonates at trace levels.[36] The overall levels of Cr and Ni in both the body and gloss are indeed high when compared to many natural clay materials and is suggestive that both of these materials may come from a single local.

However, the enrichment of Zn observed in the gloss was unexpected. Thus, further investigation was undertaken to assess if these data indicated whether the gloss was derived from a separate clay source than the body ceramic. Figure 4(a) shows the concentration of Zn in glosses compared to the body ceramics for all 19 sherds examined. Zn concentrations in the glosses are broadly distributed between 271 and 1959 ppm. The ceramic bodies are much more tightly clustered with values ranging between 163 and 361 ppm with a single outlier at 535 ppm. Since the average concentration of Zn in the earth's sediments ranges between 10 and 300 ppm,[37,38] the range of Zn in the bodies corresponds to what would be expected from a clay derived from a natural and uncontaminated environment. The Zn in the glosses, however, is on average elevated above the natural background levels (up to levels 10 times higher) suggesting an unintentional anthropogenic input of Zn into the gloss raw material.[39–44]

To evaluate the origin of the Zn enrichment in the glosses, the chemical state of Zn was investigated using X-ray absorption near edge spectroscopy (XANES). Figure 4(b) shows a representative Zn K-edge XANES spectrum from black gloss compared to a Zn-aluminate spinel reference,

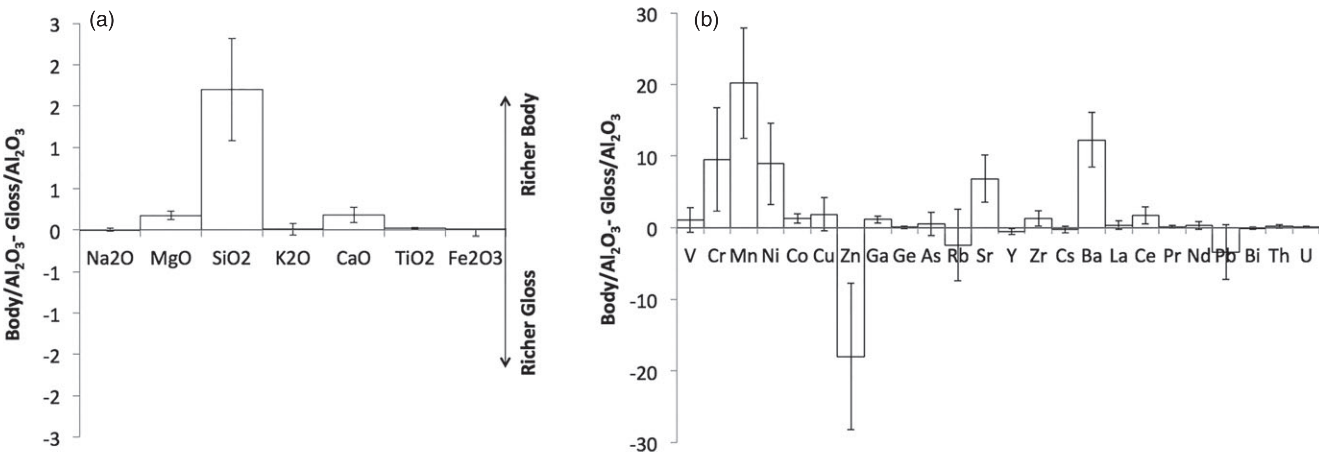

Fig. 3. Enrichment/Depletion plots. (a) Major Oxide elements. (b) Trace elements.

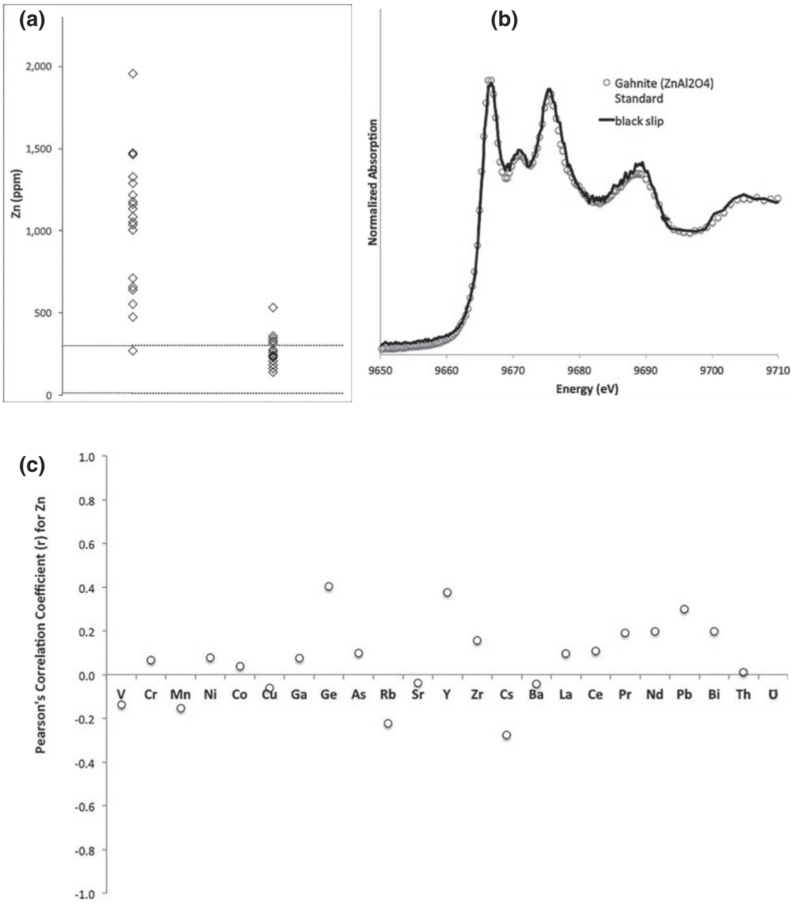

Fig. 4. (a) Range of Zn present in glosses and their corresponding bodies. The dashed line demarcates range of values associated with natural abundance of Zn in the environment (b) X-ray absorption near edge spectra (XANES) at the Zn K-edge. (c) Correlation coefficients between Zn and trace element suite.

gahnite $ZnAl_2O_4$.[30] Based on this comparison, it is found that the Zn is hosted in a spinel environment (analogous to the gahnite mineral structure) formed through the interaction of Zn with the surrounding aluminum-rich clay. Since the Zn spinel can only form under high temperatures (~1000°C) such as those reached in a ceramic kiln,[45] this indicates that the Zn was present in the raw clay material prior to firing rather than it being introduced as a ground water contaminant during burial.

Figure 4(c) shows the Pearson correlation coefficients (r) for Zn and the measured suite of trace elements. Coefficients near zero on this plot would indicate that there is no linear relationship between Zn and any other trace elements in the suite. Respectively, coefficients near 1 or -1 would demonstrate a high positive or negative linear correlation between Zn and a respective element. In practice, for a homogenous group, r values above 0.8 are required to demonstrate a strong linear relationship.[46] Since the r values in Fig. 4(c) range between 0.4 and -2.8, this indicates that Zn is not strongly correlated with any of the gloss trace elements and is therefore not hosted with the intrinsic mineralogy of the clay. These data suggest Zn could not have been incorporated into the clay during a sedimentary process in which it would be associated with specific mineralogy.

(3) Negative Ce Anomaly in Gloss

To further explore the compositional relationship between the body ceramic and gloss slip materials, rare-earth element (REE) distributions were measured. Normalized REE distributions are useful for determining whether the clay of the body and gloss are derived from the same geological source since this suite of elements is resistance to chemical mobilization and thus displaying coherent behavior during weathering.[47,48] In Fig. 5, the REE distribution plots normalized to chondritic meteorite[32,49] are shown for the average of all 19 glosses and their associated body ceramics. The overall patterns for both the body and gloss are similar, but not identical. The body exhibits a pattern, where light REEs (La and Ce) are elevated and decrease toward heavier REEs (>Eu) that then flatten out from Gd to Lu. This pattern with strongly depleted heavy REE content relative to chondrite is typical for clays and other weathered sediments.[50] The gloss follows the same trend as the body with the sole exception of Ce that is significantly depressed relative to La and Pr. This feature is called a negative Ce anomaly.[32] REE elements typically exist in a trivalent state, but due to the unique configuration of their 4*f* electron shell only Eu and Ce can change oxidation state (e.g., Ce^{+3} can oxidize to Ce^{+4}) in conditions of alkaline pH or in anoxic environments.[51] Oxidation of Ce can therefore lead to depletion of this element relative to the other REEs via preferential complexation and precipitation reactions.[52] Therefore, the Ce anomaly in the glosses indicates that the Ce was lost from the REE suite either during an anoxic weathering environment[53,54]or through chemical treatment of the clay during its refinement.

(3) Zn and Ce in Black Glosses from Various Manufacturing Centers

The heavy REE profiles and Zn concentrations were examined for black gloss ceramics and their corresponding bodies manufactured in Athens as well as in Corinth, Greece, and in Etruria (ancient Italy). These data are shown Fig. 6. The

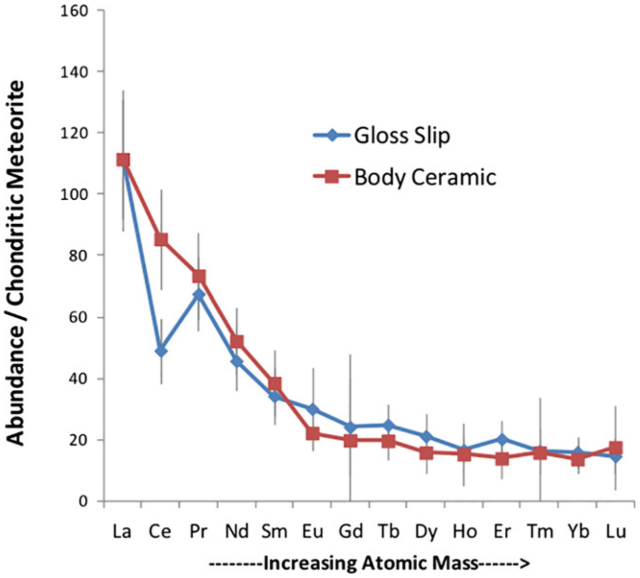

Fig. 5. REE profiles showing the differences between body and gloss. The Ce anomaly in the gloss pattern points to different source of clay for this material.

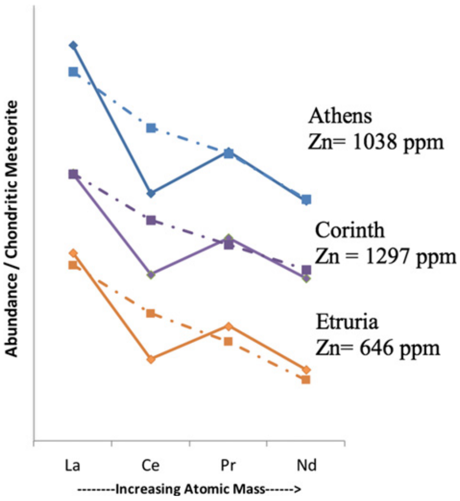

Fig 6. Heavy REE profiles showing similar pattern for the major centers of black gloss production.

REE profiles for all three of these manufacturing areas are almost identical, showing a distinct Ce anomaly and Zn values above the background level of 200 ppm.

IV. Discussion

Levigation alone does not alter the relative amount of calcite in the increasingly finer fractions of clay collected[17,18] and therefore no depletion in the elements/oxides associated with the calcite phases should be observed if levigation alone was used to produce both the body ceramic and gloss. Our data, which show a distinct depletion of calcite-related elements/oxides in the gloss with respect to the body clay, instead suggests that the Athenian black glosses were made either from clay specifically mined for its low calcite content or that the raw material was treated in some manner to preferentially remove the calcite phases. If calcite is present, this mineral evolves CO_2 at high temperatures creating pore structures that would allow oxygen back into the gloss material, thus oxidizing the Fe color centers from Fe^{+2} to Fe^{+3}, thereby producing a red instead of the desired black gloss.[22,24,25] One possible way to remove calcite from clay is to treat the material with a mild acid. As will be discussed in detail below, the use of acid in the fabrication of the glosses is supported by our finding of elevated levels of Zn in the black gloss (Fig. 4).

In today's environment, Zn is ubiquitous, with variable concentrations in soil ranging from a few ppm to a few thousand ppms, due to input from many anthropogenic sources:[41] from sewage, automobile emissions, burning of fossil fuels, agrochemicals, and mining activities. In antiquity, sources of enrichment of Zn in soil are limited to metallurgical activities[55] and, to a minor extent, the weathering of Zn-rich rocks. As shown in Fig. 4(c), Zn is not correlated with any other elements in the glosses, and thus the weathering of Zn-rich rocks can be eliminated as the source of Zn. Metallurgical activity therefore remains as the most likely source for the Zn enrichment in these glosses.

The sorption of Zn into phyllosilicate clays from ground water is common and is often associated with acid mine drainage (AMD) where low pH as well as the presence of hydrated iron oxide species contributes to the formation of hydroxide–Zn complexes.[56,57] AMD, in this case, is sulfuric acid generated from the oxidation of sulfide minerals, mostly pyrite, but also associated with ZnS, which then produces Zn hydroxides. Based on our observation of elevated Zn levels in the black glosses, we explored the possibility that the clay may have an association with mine activity and AMD. In ancient Greece, the most notable source of acid mine runoff near Athens with a significant Zn sulfide mineralogy would have been the ancient mining sites of Lavrion on the Sounion peninsula of Greece.[58] These mines are rich in ancient Zn carbonate and sulfide tailings even to this day.[59,60]

There are two possible explanations for the observed elevated Zn in the glosses together with the Ce anomaly (as shown in Fig. 5). These data could be a very specific signature for a single and unique source of this clay; namely, an environment heavily contaminated with Zn (like Lavrion) and with clay that had been subjected to an anoxic weathering environment as denoted by the Ce anomaly.[61,62] There are numerous horizons of Fe-rich dark colored clay around the Mediterranean that are associated with anoxic formation processes. The horizons could provide the specific clay mined to make black gloss. However, the overall shape similarities in the REE profiles of the body and gloss, including the almost identical total REE concentrations (with the exception of Ce) argue against dissimilar geological formation for these clays. Even more surprisingly, and difficult to explain by natural geochemical processes, is the fact that almost identical Zn and Ce signatures are found not only for black glosses produced in Athens but also in Corinth, and, from across the Adriatic sea, in Etruria (Fig. 6). Since there are many local clays suitable for producing black gloss available in each of these areas and due to the impracticalities of moving large amounts of a soil material, it is unlikely that Athenian clay would be transported such long distances. This idea is supported by anthropological and archaeological studies that indicate, in the vast majority of contexts, the distance of a clay source to a workshop is typically less than 3 km.[63]

A second possible explanation of our data is that the Zn signatures could be evidence for shared fabrication methods at each locality and not indicative of the provenance of the raw material. We suggest that the method of processing the gloss clay was to soak the material with a commonly used acid in antiquity called vitriol. As described by Pliny the Elder (Natural History, book XXXIV, section XXXII) and reiterated later by Dioscorides and in Agricola's De Natural Fossilium, vitriol was the first acid employed in ancient industry.[64] The starting material for vitriol was sulfuric acid rich AMD.

The AMD produced at Laurion would have been formed from the crushing and washing of argentiferous lead ores with the aim of extracting silver metal. The ore consist of sphalerite (ZnS) which is interlayered with the silver-rich galena (PbS). During the beneficiation process, the sphalerite and galena would be continually washed in the ore washeries (these structures still exist to this day) to remove unwanted mineralogical phases,[60] such as the ZnS. Since ZnS is more soluble than the desired PbS, especially in the increasingly acidic conditions of wash waters as more sulfides are dissolved, Zn becomes preferentially enriched in the wash waters.

These wash waters would be concentrated through evaporation, thus creating white $ZnSO_4$ crystals. This crystallized material was a widely traded commodity readily available to the ancient Athenian craftsman who used the material in a broad variety of ancient industrial processes such as in leather tanning, medicine, and as a assay for metal.[65] One reason to use vitriol for the processing of clay would have been to induce flocculation or aggregation of the clay particles as a last step in the refinement process after all the coarse grains had been separated from the clay mass. In contemporary pottery practices, mild sulfuric acid is a common clay flocculant used to rapidly settle levigated clay.[66] The second, and more important, benefit of a vitriol treatment could be the removal of calcite inclusions remaining in the fine fractions of the clay that would otherwise prevent vitrification in the gloss and its conversion to a characteristic black color.[25]

We propose a two-step process. First, the fine-grained fraction from the raw clay would be harvested by dispersing the clay in water and allowing the coarse grains to settle to the bottom of the levigation tank. In the second step, the fine-grained fraction would be channeled into a second tank and treated with the vitriol to cause the fine-grained clay to be removed from suspension. This step is necessary to siphon off excess water and to control the rheology of the mixture to create a suitable gloss application. During this second step fine calcite crystals would readily dissolve into solution.

V. Conclusions

Through these data, we have established that an element typically associated with contaminants in the environment could be a marker of a specific provenance or fabrication technology for black gloss. In the case here, anomalous Zn levels in the gloss could not be associated with natural geological processes such as sedimentation. Instead, we find that the observed high levels of Zn were due to anthropogenic enrichment in the raw clay.

One explanation for the observed high levels of Zn is that the black gloss clay is derived from a single source located near a mine, such as Lavrion in Greece, where extractive metallurgy of silver from zinc sulfide deposits has contaminated the clay. However, given that black gloss produced in workshops in Corinth and Ancient Italy also have this same trace element signature, a single unique source for the gloss material seems unlikely given the extreme expense and trade impediments to transport local Athenian clay long distances.

Instead, we hypothesize that ceramic workshops around the Mediterranean were sharing clay refinement methods that would imprint the gloss material with the observed trace element characteristics. The elevated Zn values are therefore attributed to the acid treatment of the clay with Pliny's vitriol, which would serve to induce flocculation and remove remaining $CaCO_3$ that, if present, would prevent the gloss from turning black in color during firing.

Acknowledgment

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. LA-ICPMS Data, Athenian Black Glosses and Body Ceramics.

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