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# Reverse Engineering Ancient Greek Ceramics: Morphological and Spectral Characterization of Replicates

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Athenian pottery, the ceramics produced in the Attica region of Greece between the 6th and 4th centuries B.C., is considered a benchmark technological achievement of the preindustrial world. This work advances our understanding of the firing protocols employed by the ancient Greeks to produce their blackon-red designs by characterizing replicates painted with a refined illite clay and fired under oxidizing/reducing/reoxidizing conditions (three-stage firing). Systematically varying the temperature, atmosphere, and duration of each firing stage within the three-stage firing scheme allowed the conditions necessary to obtain black and red gloss, both of which are observed on ancient vessels, to be determined. The morphology and elemental distribution of particles formed within the gloss thus formed were characterized using transmission electron microscopy and spectrocolorimetric measurements. Comparison of the results obtained from ancient sherds with those obtained from the replicate samples provides a means of estimating the firing conditions used to create the ancient vessels.

# I. Introduction

A THENIAN figure-decorated pottery, produced between the 6th and 4th centuries B.C., provides a rich body of material with which to understand and explore the culture and society of ancient Greece. The vessels were decorated by two techniques: black figure (dating from the late 7th century, with the black figures painted on the red clay back-ground), or red figure (introduced in the late 6th century, with figures left in reserve and the background painted black). In both techniques, the creation of the imagery relied on the ability to produce smooth, glossy, black surfaces—termed black gloss—that contrasted sharply with the red clay body of the vessel. For decades, materials scientists and archeologists have studied black gloss to gain insight into technological development and craft organization in the ancient world.<sup>1–11</sup>

In most cases, Fe-rich illite clays were used for both the body and the gloss.<sup>4,9,12,13</sup> Decorations and background washes were painted using a refined clay slip (depleted of carbonates and larger particles) that vitrified during firing. The

final color was achieved by controlling the kiln atmosphere, which in turn controlled the Fe redox chemistry at a very local scale: red was produced by oxidized Fe<sup>3+</sup>, formed as the minerals hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), and black was produced by reduced Fe<sup>2+</sup>, formed in the minerals magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hercynite (FeAl<sub>2</sub>O<sub>4</sub>). Recent material characterization studies suggest that by alternating the atmospheric conditions in the firing kiln, Athenian, and later Roman, potters achieved the desired local redox chemistry by controlling oxygen transport/diffusion through manipulation of the porosity/densification of the matrix, such that the highly contrasting red and black designs could be produced.<sup>14,15</sup>

Studies by our group of sherds of both red- and blackfigure vessels ranging from the 6th to the 5th century B.C. have yielded examples evidencing the use of more than one firing/application of refined clay, on the same vessel, in order to achieve complex architectures and designs.<sup>4,5,14,15</sup> These new findings challenge the long held belief that a singular, commonly shared technology consisting of a single, threestage (oxidation/reduction/oxidation) firing was universally employed.

Here, we present our work on the characterization of replicates produced using a refined commercial illite clay, determined to be a reasonable surrogate for the type of clay used for the production of Greek ceramics.<sup>1,16–19</sup> Systematically varying the temperature, atmosphere, and duration of each firing stage within the three-stage firing scheme allowed us to determine the conditions necessary to successfully produce black gloss. This study also shed light onto those conditions that may have been employed, either intentionally or unintentionally, to produce other types of gloss, in particular red gloss<sup>4,20</sup> or misfired areas.

The thermal transformation of the clay was studied using transmission electron microscopy (TEM) to characterize the particle morphology and map the distribution of key elements within the glossy slips. The results are used to build a mineral phase/time-temperature matrix that describes the kiln conditions necessary for the production of different glosses and, in particular, the black-on-red design characteristic of ancient Greek vessels. By comparing results obtained from ancient sherds with those obtained from replicate samples prepared under known conditions, an estimate of the firing conditions for the ancient sherds may be deduced.<sup>14,15</sup> However, the removal of samples from ancient artifacts and the ability to perform high-resolution TEM analyses is not an approach typically available to many cultural heritage institutions. Therefore, we also evaluated the use of

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spectrocolorimetric measurements, which require only a simple, inexpensive, and noninvasive tool often available in conservation laboratories, as a means to characterize ceramic materials and assess the firing conditions used to create the ancient vessels.

## **II. Experimental Procedure**

#### (1) Tile preparation and firing

A commercial illite clay (Redart clay, Resco Products Inc., Pittsburgh, PA), was used to prepare the replicates. Unrefined clay was used to make tiles measuring approximately  $2 \times 2 \text{ cm}^2$ . A refined clay mixture for painting the tiles (described previously<sup>14</sup>) was prepared by mixing the clay with  $0.25\%_{wt}$  Na<sub>2</sub>(SiO<sub>2</sub>)<sub>n</sub>O and NaCO<sub>3</sub>, then diluting with water until a specific gravity of 1.2 was reached. The supernatant was collected after 14 h and dried. A water dispersion of the refined clay, 2 mg/0.5 mL, was used to paint the tiles to a thickness of between 30 and 100 µm, comparable with that observed in samples of ancient Greek gloss.<sup>5,18,19</sup>

The replicate sherds were fired in a quartz tube electric furnace (GSL-1600X, MTI Corporation, Richmond, CA) equipped with PID temperature control via SCR power control, and an oxygen sensor (DS oxygen probe, Australian Oxytrol Systems Pty. Ltd, Eaglehawk, Australia). Reducing conditions were obtained with a continuous flow of 100 mL/min (set with a mass flow controller, Aalborg DFC26 Orangeburg, NY) of CO (compressed carbon monoxide tank, Advanced Specialty Gases, Reno, NV) in the firing chamber.

The replicates were fired using a three-stage (oxidation/reduction/oxidation) firing scheme. To separately evaluate the effect of the temperature and duration of the two oxidizing stages, the firing process was conducted in two steps. First, the painted tiles were placed in the furnace and the temperature raised at a rate of 12°C/min until T1, the temperature of the first (oxidizing) stage, was achieved; the furnace was held constant at T1 for time = t1. A series of four replicates labeled A, B, C, and D were fired at T1 = 700°C, 800°C, 900°C, 950°C for t1 = 10 h, and a second series of three replicates, labeled b, c, and e, were fired at  $T1 = 800^{\circ}C$ , 900°C, 1000°C for t1 = 30 min, respectively (note that replicates subjected to different firing durations are labeled using the same letter if T1 is the same). An "E" series  $(T1 = 1000^{\circ}C \text{ for } t1 = 10 \text{ h})$  was not produced as this was out of the specified safety range of the furnace's quartz tube. The "A" series showed so little change in 10 h, an "a" series was not produced as no determinable results would be produced in 30 min. Similarly, a separate "d" series  $(T1 = 950^{\circ}C)$ for t1 = 30 min) was not produced because, again, given the short duration of the firing stage the thermodynamic aspect of the formation of different minerals in the slip would have dominated over the kinetic aspect, and thus no significant difference from the "e" series (T1 =  $1000^{\circ}$ C for t1 = 30 min) was expected. In order to facilitate comparison between the replicates, we have labeled the series fired at  $T1 = 1000^{\circ}C$  for t1 = 30 min as d/e.

For all replicates, the temperature was then increased/decreased at a rate of  $12^{\circ}$ C/min until the temperature in the second (reducing) stage, T2 = 850°C, was reached, which was kept constant for t2 = 30 min. The replicate tiles were cooled to room temperature and characterized (see below) before the second reoxidative firing was performed: each series of replicates were fired at T3 = 800°C, 900°C, 1000°C for t3 = 30 min.

The range of temperatures employed was chosen to (1) induce a thermal transformation in the illite clay and produce glass formation,<sup>21-23</sup> and (2) reproduce temperatures realistically achievable in ancient kilns.<sup>3,11,24</sup> In a wood kiln, the temperature is known to decrease upon changing from oxidizing to reducing conditions.<sup>13</sup> However, for the purposes of these experiments, a single temperature for the reducing stage, selected to be midway in the range of temperatures of the two oxidizing stages, was used (T2 = 850°C).

## (2) Cross Section preparation

Samples measuring  $5 \times 5 \times 2 \text{ mm}^3$  were cut from the replicates with a diamond saw (Buehler, Lake Bluff, IL). The samples were embedded in resin (SpeciFix epoxy resin mixed with SpeciFix-20 curing agent, 5:1 ratio, Struers Inc., Cleveland, OH) and cured for 24 h at room temperature. After drying, the embedded samples were polished with SiC paper (Buehler grinding paper P400, P600, P1200, P4000) to expose cross sections of the gloss layers and ceramic body.

## (3) Spectrocolorimetry

Spectrocolorimetric analysis, consisting of both reflectance spectra and CIE L\*a\*b\* colorimetric measurements,<sup>25</sup> were acquired with a spectrophotometer (Agilent Cary 50 UV-Vis Bio (Santa Clara, CA), wavelength range 360–830 nm, 1 nm interval, standard illumination D65, observer angle 2°); each measurement was referenced to the standard white calibration certified reflectance standard (Labsphere, North Sutton, NH).

## (4) TEM and EDX characterization

Sample preparation for TEM used focused ion beam (FIB) milling procedures developed and well documented<sup>26</sup> for analysis of microelectronic device cross sections for the semiconductor industry. Care was taken to minimize beaminduced modification of the phases and structures comprising the analyzed black gloss samples.

FIB sample preparation was conducted in an FEI Co. (Hillsboro, OR) Strata 400 Dual-Beam (SEM-FIB) instrument with an Omniprobe 200 manipulator to facilitate in situ transfer of a FIB extracted sample to a copper Omnigrid type sample holder. Before FIB milling, a protective layer of carbon was deposited on the sample by evaporation of carbon rods; pulse-mode rod evaporation was done to prevent temperature rise in the sample on which carbon was deposited. Initial FIB milling employed beam currents in the range of 3-10 nA, although reduced beam currents were employed as the sample was thinned to prevent significant beam-induced sample heating. After most of the thinning was completed with 30 keV Ga+ ions, a standard "low-keV clean"<sup>27,28</sup> was performed with 2 keV Ga+ ions to reduce the final damage layer thickness to that expected to be generally insignificant. Ion beam currents were reduced as the TEM sample was thinned to avoid energytransfer rates that could raise temperatures within the remaining thickness of material.<sup>29,30</sup>

TEM analyses were conducted in a JEOL 3100F UHR instrument (JEOL USA, Peabody, MA) using both conventional and high-resolution parallel beam modes as well as focused beam scanning mode (STEM) employing 300 keV primary beam energy. FWHM of the STEM probe used for high-resolution imaging was 0.14 nm, while for chemical analyses a probe diameter of ~0.24 nm was used. The STEM probe convergence semiangle was 11 milliradians. High-angle annular dark field (HAADF) images were recorded by collection of electrons scattered to semiangles ranging from approximately 50 to 150 milliradians on a Gatan 806 annular detector (Gatan, Pleasanton, CA) mounted below the microscope's viewing chamber with custom camera lengths defined in free-lens mode on the 3100F. Energy-dispersive X-ray spectra (EDXS) were collected using a 30 mm<sup>2</sup> SiLi detector from Oxford Instruments (Abingdon, UK); IncaTEM software was used for data analysis including quantification using Oxford's "remote standards" methods following the Cliff-Lorimer k-factor method.

#### III. Results and Discussion

## (1) Painted Tiles: Visual Appearance of Surfaces

In Fig. 1 the top surfaces of the replicate tiles fired under different temperatures are shown: Figure 1(a) shows the replicates fired for t1 = 30 min (we will refer to this as 30MS -

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Fig. 1. Top view of replicates fired for (a) t1 = 30 min and (b) t1 = 10 h. Column 0 of each series shows samples that have undergone an incomplete firing cycle of only oxidation/reduction (no reoxidation applied).

30 min series) while Fig. 1(b) shows the replicates fired for t1 = 10 h (we will refer to this as 10HS - 10 h series). In each matrix of images, each row corresponds to a different series (corresponding to a different T1, increasing from bottom to top). The first column of images (column 0) shows the replicates after the reduction stage (T1 and T2 only); note that black gloss over a gray body is observed at any time–temperature combination. The next three columns (1, 2, and 3) show the replicates after reoxidation at T3 = 800°C, 900°C, 1000°C, respectively; these three columns of images comprise a T1/T3 temperature matrix—with T1 increasing along the *y*-axis and T3 along the *x*-axis. (Hereafter, the replicates will be referred to by their series and matrix coordinates, e.g., 30MS\_b3, 10HS D1, etc.).

After reoxidation, from visual examination it appears that a successful firing—the production of black gloss over a red body—falls within a small region of the T1/T3 matrix (outlined in black). For the replicates subjected to short initial oxidative firing [i.e., 30MS, Fig. 1(a)], black gloss is obtained in the lower left portion of the T1/T3 matrix: all three replicates in column 1 (30MS\_b1, 30MS\_c1, 30MS\_d/e1), and the lowest T1 in column 2 (replicate 30MS\_b2). By contrast, when the first oxidative firing is held for a longer time [10HS, Fig. 1(b)], only replicate 10HS\_B1 produced black gloss.

The conditions to form red gloss are also found (outlined in red), and for both short and long initial firing times are those replicates in the upper right portion (higher temperatures) of each T1/T3 matrix. Interestingly, replicates which might be classified as "misfires"—that is, having co-presence of both black and red iron oxides in the gloss—are also seen (outlined by dashed gray line, falling between the black and red gloss in the T1/T3 matrices). For the short (30MS) firing, there is a very narrow range for co-existence of both red and black, and only one replicate (30MS\_c2) falls into this category. By contrast, for the longer (10HS) firing time multiple, the range is larger, consisting of replicates 10HS\_A1, 10HS\_A2, 10HS\_B2, and 10HS\_C1.

## (2) Painted Tiles: Visual Appearance of Cross Sections

While the visible surface appearance of the final product is arguably the primary criterion, and the one which ancient potters undoubtedly relied on, to judge the success or failure of gloss production, examination of cross sections can help us characterize the physiochemical transformations taking place at the different temperatures, and their effect on the development of the final color. Figure 2(a) and (b) contain cross-section images of the replicates shown in Figs. 1(a) and (b), presented in the same temperature matrix.

The surface appearance of all the replicate samples after the reduction firing [Figs. 1(a) and (b), column 0] showed a black gloss layer over a black body. However, as can be seen in Figs. 2(a) and (b), when viewed in cross section, it is immediately apparent that the gloss layer in the samples subjected to the highest oxidation firing temperatures—30MS d/ e0 and 10HS D0 at T1 = 1000°C and 950°C, respectively—is not black all the way through, but rather consists of a thin (few µm thick) film of black over a red gloss layer [see Fig. 2(c)]. Replicate 10HS C0 (fired at  $T1 = 900^{\circ}C$  for 10 h), also is not homogeneously black, but rather shows the formation of black gloss with localized red spots. A truly successful firing-deep black gloss over a vibrant red bodyonly occurs in replicates 30MS\_b1, 30MS\_c1, and 10HS\_B1, indicating that very precise control of firing temperatures is required to produce high-quality black gloss.

These observations are consistent with a mechanism in which the degree of vitrification controls the extent to which hematite formed during the first stage can be reduced to black in the second stage.<sup>21,22</sup> For the highest T1, the degree of vitrification is high, so only the very top surface is reduced [such as in replicates 30MS\_d/e0 and 10HS\_D0, shown in Fig. 2(c)]. As T1 is reduced, both red and black phases are produced within the gloss layer (replicate 10HS\_C0), and below a threshold the permeability is sufficient to allow full reduction of the layer to black (replicates 10HS\_A0, 10HS\_B0 and 30MS\_b0, 30MS\_c0). The total thermal exposure, a combination of temperature and time, determines the



**Fig. 2.** Photomicrographs of cross sections of replicates fired for (a) t1 = 30 min, and (b) t1 = 10 h. Width of each image in (a) and (b) is 100  $\mu$ m. (c) Photomicrograph of cross section 10HS\_D0 showing the formation of a reduced layer, 3  $\mu$ m thick, on top of the red gloss. (d) Photomicrograph of cross section 10HS\_B2 showing the reoxidation of the black gloss from the top of the slip.

extent of the clay decomposition, and glass and hematite formation. Thus, the value of the threshold for the complete reduction of the slip changes between 800°C and 900°C, depending on the firing duration.<sup>31,32</sup>

After the reoxidation stage (T3) in all the replicates, the body turns red, since the high porosity of the unrefined clay allows reoxidation of the iron. Notably, in contrast to what was observed from surface appearance alone, in cross section, the production of a successful firing is observed in an even smaller range of the T1/T3 matrix: samples 30MS b1, 30MS c1, and 10HS B1 (outlined in black in Fig. 2). Replicate sample 30MS d/e1, which on the surface appears black, in fact consists of a layer of red gloss of which only the top few µm are black, consistent with the observation of it not having been completely reduced in the second stage (see above). The results shown in Fig. 2 indicate that in order to obtain a homogeneous layer of black gloss over a red body at the end of the three-stage firing, the final oxidative stage has to be carried out at a temperature equal to or lower than the temperature of the first two stages:  $T3 \le T1$ , T2. If T3 > T1, T2, reoxidation of the slip occurs from both the top of the slip and at the interface with the body, as shown in Fig. 2(d) for replicate 10HS B2, fired at  $T1 = 800^{\circ}C$  and T3 = 900°C; this condition leads to the formation of misfires (replicates 30MS: b2, b3, c2, d/e1, 10HS: A1, A2, B2, C1, C2) and as T3 is increased, eventually leads to the formation of red gloss (samples 30MS: c3, d/e2, d/e3, 10HS: A3, B3, C3, D1, D2, D3).

(A) Effect of Oxidative Stages on the Production of Black Gloss: T1/T3 Diagrams: Figure 3 shows schematic T1/T3 diagrams derived from the observation of the cross sections as discussed above. In each diagram, the black area corresponds to the conditions under which black gloss is produced, the red area to conditions favorable to obtaining red gloss, and the gray area to conditions that lead to misfires. These diagrams help us extend the observations generated by the individual replicates to the broader T1/T3 space and also facilitate understanding the effect of the duration of the first firing stage. Comparison between the T1/T3 diagrams for short (30MS) and long (10HS) t1 reveals that the temperature space under which black gloss is successfully produced becomes more limited with longer firing, and the conditions under which misfires and red gloss result become correspondingly broader. It is also notable that the temperature for black gloss (and misfires) formation shifts to lower temperatures with longer firing times. The observation that red hematite precipitates in the slip at lower temperatures in the long (10HS) compared to the short (30MS) firing series (cf.

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Fig. 3. T1/T3 diagrams for replicates, as they appear in cross sections, fired for (a) t1 = 30 min and (b) t1 = 10 h.



Fig. 4. (a) TEM image of sample 10HS\_A1 (T1 = 700°C, T2 = 850°C, T3 = 800°C), red square indicates area over which elemental maps were acquired; scale bar 0.5  $\mu$ m. Maps of (b) Al, (c) Si, (d) K, (e) Mg, (f) Fe, and (g) Ti; elemental map scale bars 300 nm.

replicates 30MS\_c0 and 10HS\_C0) suggests the process changes from a thermodynamically driven process to a kinetically driven process with increasing firing duration.<sup>21,33</sup> Thus, the conditions favorable to the production of black gloss are dependent not only on the temperature, but also on the duration of the firing. Therefore, although for the purposes of discussion we refer to the temperature of each of the stages as the defining parameter, is it important to keep in mind that it is the total thermal exposure that is important.

(B) TEM Characterization and EDX Maps: Effect of TI: Morphological characterization of the slips was performed in order to assess, at the microscopic and nanoscopic level, the transformations induced in the clay by the different thermal treatments and identify the boundary conditions for the different phases formed during the firing. To evaluate the effect of the initial firing temperature, three replicates fired at T1 for 10 h and reoxidized at T3 = 800°C were selected for study: 10HS\_A1 (fired at low T1, showing mixed black and red gloss (misfire)); 10HS\_B1 (successful production of black gloss), and 10HS\_D1 (fired at high T1, red gloss). TEM images of samples taken from replicates 10HS\_A1, 10HS\_B1, and 10HS\_D1 together with EDX maps are presented in Figs. 4, 5, and 6, respectively.

The TEM image of the "misfire" sample (10HS\_A1) presented in Fig. 4(a) shows an extremely high porosity and the presence of elongated layered structures typically observed in unfired clays.<sup>34–36</sup> EDX maps indicate that the stratified structures observed in the TEM images are mainly composed of Al, Si, and K [Figs. 4(b)–(d)]. Due to the low firing temperature (T1 = 700°C), the clay does not undergo significant melting, leaving residual iron oxide particles from the raw clay (7.04%<sub>wt</sub> of Fe<sub>2</sub>O<sub>3</sub>). Nanometric (on the order of 30 nm) crystals of Fe-oxides, homogeneously dispersed in the gloss, are also observed [Fig. 4(f)], together with some isolated Fe–Ti–Mg compounds [Figs. 4(e)–(g)].

The TEM image of the successfully reproduced black gloss (sample 10HS\_B1), is shown in Fig. 5(a); elongated well-faceted crystals (approximately 20 nm in width) dispersed in a glassy matrix are observed. EDX maps indicate the glass matrix is mainly formed by oxides of Si and K [Figs. 5(c), (d)] while the elongated crystals are composed of Al, Fe, and Mg [Figs. 5(b), 5(e), 5(f)]; isolated Fe–Ti–Mg compounds are also present [Figs. 5(e)–(g)]. Similar elongated crystal structures have previously been observed in other studies on ancient black gloss and have been identified as hercynite; substituted-magnetite, magnetite in which the Fe atoms are



Fig. 5. (a) TEM image of sample 10HS\_B1 (T1 =  $800^{\circ}$ C, T2 =  $850^{\circ}$ C, T3 =  $800^{\circ}$ C). Maps of (b) Al, (c) Si, (d) K, (e) Mg, (f) Fe, and (g) Ti. All scale bars 900 nm.



Fig. 6. (a) TEM image of sample 10HS\_D1 (T1 = 950°C, T2 = 850°C, T3 = 800°C). Maps of (b) Al, (c) Si, (d) K, (e) Mg, (f) Fe, and (g) Ti. All scale bars 900 nm.

substituted with Al, Mg, and Ti, have also been observed.<sup>3,5,37–41</sup> Hercynite was identified in this gloss sample by XANES spectroscopy<sup>42</sup> and the presence of substituted-magnetite was inferred from the EDX maps and confirmed by Raman spectroscopy<sup>15</sup> through observation of a shift in the  $A_{1g}$  mode at 670 cm<sup>-1</sup> (data not shown). These mineralogical studies, together with the morphological and chemical characterization obtained by TEM reported here, confirm, at both the macro- and nanoscale, that the replicates in fact successfully reproduce ancient black gloss under temperature conditions compatible with what was realistically achievable in ancient times.

A TEM image of the red gloss slip formed at T1 = 950°C (sample 10HS\_D1) is shown in Fig. 6(a). Much larger crystals (of about 100 nm width) than those obtained at lower temperatures are observed. No elongated clay structures are evident, suggesting the clay has undergone complete decomposition, resulting in the formation of glass. Indeed, EDX maps show that the glassy matrix has an even distribution of Al, Si, and K [Figs. 6(b)–(d)], while the crystals embedded within are composed of Fe, Mg, and Ti [Figs. 6(e)–(g)], compatible with hematite and substituted-hematite.<sup>21</sup>

The microstructures observed in these samples are similar to those observed in archeological sherds. For example, sample 10HS A1 resembles the type of Coral red obtained with a high Ca-containing clay;<sup>4</sup> the presence of carbonates denotes a lower refinement of the clay, which leads to a higher melting point and thus an underfired microstructure with large porosity and features typical of unfired clay. Likewise, sample 10HS\_B1 presents well-faceted spinel crystals embedded in a glassy matrix similar to those found in samples of ancient black gloss.<sup>5</sup>

These data clearly demonstrate that the temperature of the initial oxidative firing stage impacts the final color of the gloss slip through competing mechanisms (glass versus hematite formation), a balance of which is necessary to achieve a successful black gloss. T1 temperatures that are too low result in a gloss layer that is insufficiently vitrified, allowing reintroduction of oxygen in the final stage, producing areas consisting of a mixture of black and red—a misfire. T1 temperatures that are too high (or held too long) result in the precipitation of hematite in a solid, glassy matrix, which cannot be reduced to black in the following reductive firing stage, thus producing red gloss. In-between is a range of T1 temperatures that are low enough to prevent precipitation of hematite but high enough to produce a sufficiently glassy matrix to prevent reoxidation of the black slip.

(C) Spectrocolorimetry: Combined Effect of the Oxidative Stages (T1 and T3): In previous studies<sup>15,42</sup> we demonstrated the relevance of XANES and Raman spec-



**Fig. 7.** (a) Reflectance spectra of replicate samples 10HS\_A1 (black trace), 10HS\_B1 (red trace) and 10HS\_D1 (green trace) (red and green traces offset for clarity); (b) reflectance spectra of replicate samples 30HS\_b1 (red trace) and 10HS\_d/e1 (green trace) (green trace offset for clarity); (c) reflectance spectra of replicate samples 10HS\_B1 (red trace), 10HS\_B2 (blue trace) and 10HS\_B3 (gray trace) (blue and gray traces offset for clarity); (d) reflectance spectra of replicate samples 30HS\_b1 (red trace), 30HS\_b2 (blue trace) and 10HS\_B3 (gray trace) (blue and gray traces offset for clarity).

troscopy to describe the mineralogical content of the replicates. In particular, these techniques provided identification of the three iron spinels—maghemite, hercynite, and magnetite—which serve as diagnostic markers to determine the firing conditions necessary to obtain a successful firing. In this study, TEM images and EDX maps provide an excellent picture of the temperature history within a gloss layer. However, all these techniques require the removal of samples for analysis, which is not always possible for ancient vessels. Therefore, to correlate the spectral features of the slips with the chemical, morphological, and mineralogical analyses already performed, the reflectance spectrum and the CIE L\*a\*b\* coordinates of the replicate sample sets were measured.

To better understand the effect of the temperature of the first oxidative stage, T1, reflectance spectra corresponding to the three replicate samples fired for 10 h and characterized by TEM and EDX (moving along the *y*-axis of the T1/T3 diagram of Fig. 3(b) [T3 fixed at  $800^{\circ}$ C)] are shown in Fig. 7(a). Similarly, the reflectance spectra of replicates fired for 30 min are shown in Fig. 7(b). To investigate the contribution of the last reoxidation step, T3, on the color of the gloss produced, the reflectance spectra of replicate samples moving along the *x*-axis of the same T1/T3 diagram (T1 fixed at  $800^{\circ}$ C) are shown in Figs. 7(c) and (d), for 10 h and 30 min, respectively.

In general, reflectance spectra of clays and ochres are dominated by hematite (which shows two bands, peaked around 600 and 750 nm) due to its high coloring power compared to the other components (e.g., silicates, quartz, calcite, anhydrite, gypsum) present.<sup>43–45</sup> Therefore, for this discussion, we will focus only on the hematite content using colorimetry; the full mineralogy has been characterized using XANES and Raman.<sup>14,15</sup>

The spectrum for replicate 10HS\_B1 [Fig. 7(a), red trace] shows no contribution from hematite, consistent with its black color. The reflectance spectra for replicates 10HS\_A1 (black trace, fired at lower T1, exhibiting large porosity which permits reoxidation) and 10HS\_D1 and 30MS\_d/e1 (green traces, fired at higher T1, exhibiting precipitation of hematite in a glassy matrix) all show an increase in the range 600–800 nm, consistent with the presence of hematite in the gloss layers.

As shown above, the formation of hematite can occur in the first stage if the temperature is sufficiently high, but it can also be produced during the reoxidation stage if the gloss layer has sufficient permeability. Therefore, in order to examine the effect of the reoxidation stage on the formation of hematite, spectra collected from replicates fired at T1 = 800°C (below the hematite precipitation threshold) and at different T3 are presented in Figs. 7(c) and (d): for both long and short firing times, an increase in the area of the broad band peaked at 600 nm is observed for increasing T3 values. (Note that no contribution was observed for the black gloss samples, 10HS\_B1 [Fig. 7(c)] and 30MS\_b1 [Fig. 7(d)], red traces, fired at T1 = 800°C and reoxidized at T3 = 800°C).

The CIE L\*a\*b\* coordinates collected from the surface of the gloss and body sides of both the 10HS and 30MS replicates are plotted in Figs. 8(a)-(d). The different symbols correspond to different temperatures of the first stage, T1, while different colors correspond to different reoxidation temperatures, T3.

After the reducing stage (T3 = NA, black symbols in Figs. 8(a) and (b) for the gloss, Figs. 8(c) and (d) for the body), both the body and the gloss have a\* and b\* values close to zero, consistent with the production of a black gloss over a gray body. It is worth mentioning that the gloss of



**Fig. 8.** a\*b\* plot of 10HS and 30MS replicates fired at different temperatures (T1 = 700°C, triangles; T1 = 800°C, dots; T1 = 900°C, squares; T1 = 950/1000°C, diamonds) and reoxidized for 30 min at T3 = NA (black), T3 = 800°C (red), T3 = 900°C (green) and T3 = 1000°C (blue) for (a) 10HS gloss, (b) 30MS gloss, (c) 10HS body, (d) 30MS body.



**Fig. 9.** Mineral phase/time-temperature diagram combining Raman and XANES analyses with the TEM and colorimetric data of this study. See text for explanation of diagram components.

sample 10HS\_D1 and 30MS\_d/e1 (black diamond in Figs. 8(a) and (b), respectively) have a larger a\* value than the rest of the non-re-oxidized samples. Although from an external inspection these glosses look black, the color mea-

surement is able to discern the red gloss underneath the reduced layer [see Fig. 2(c)].

Consistent with the increased production of hematite produced by longer firing times as discussed above, the replicates fired for 10 h have greater values of a\* than those fired for 30 min (for the same T1/T3). For all the replicate glosses produced, an overall increase in both a\* and b\* with increasing T3 is observed [Figs. 8(a) and (b)], but there is no clear correlation between color and either T1 or T3. However, a positive correlation between a\* and T3 is observed for the body [Figs. 8(c) and (d)], suggesting that the last stage of the firing alone determines the color of the body.

This last result is intriguing in that it implies that color might be used to infer information about the reoxidation stage. However, the final color is a measure of the total amount of hematite formed, which is a function of the total iron content of the clay. While all the replicates were prepared using a single clay source, with a uniform iron content, the iron content of the clays used to make ancient vessels may have varied. The iron content of the body ceramics of ancient Attic pottery have been found to vary between  $8\%_{wt}$  and  $11\%_{wt}$ .<sup>1,3,8,18</sup> Therefore, if the iron content can be determined, the use of calibration curves for different iron concentrations would allow us to infer T3 through a measurement of the redness coordinate, a\*.

(D) Mineral Phase/Time-Temperature Diagram: Combined Effect of Temperature and Duration of Oxidative Stages: The combination of the TEM and spectrocolorimetric analyses performed in this study, together with the mineralogical studies previously conducted with Raman and XANES spectroscopy,<sup>14,15</sup> allow us to summarize the minerals and phases produced in the three-stage firing in a mineral phase/time-temperature diagram (Fig. 9). The temperature at which minerals are formed during the first oxidizing stage, T1, is plotted along the y-axis; the temperature at which minerals are formed during the third reoxidative stage, T3, is plotted along the x-axis; the minerals formed during the second reducing stage,  $T2 = 850^{\circ}C$ , are shown in the midsection of the diagram. In each section, the area enclosed by dashed lines describes those results specific to the short firing (t1 = 30 min); all other results are for t1 = 10 h.

Looking first at those processes taking place during different temperatures of the first stage of firing (the left part of the diagram, t1 = 10 h), it can be seen that for T1 > 800°C the decomposition of the matrix occurs together with glass formation, and at temperatures higher than 900°C, hematite precipitation starts. In the middle part of the diagram, the mineralogical phases observed during the reduction stage, performed at fixed temperature T2 = 850°C, are reported relative to the temperature of the first firing stage. At  $T1 < 900^{\circ}C$  (T2 = 850°C), only ferrous compounds (magnetite, Fe<sub>3</sub>O<sub>4</sub>, and hercynite, FeAl<sub>2</sub>O<sub>4</sub>) are observed. At  $900^{\circ}C \le T1 \le 1000^{\circ}C$  (T2 = 850°C), mixed phases (magnetite, hercynite, and hematite) are detected.

The phases found after the application of the reoxidation stage are reported on the right part of the diagram, relative to both T1 and T3. At T3 = 800°C, four different regions are observed corresponding to different T1: T1 < 800°C  $(T3 = 800^{\circ}C)$  mixed phases of ferrous (magnetite, hercynite) and ferric (hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and maghemite,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) oxides are formed;  $800^{\circ}C \le T1 < 900^{\circ}C$  (T3 =  $800^{\circ}C$ ) only ferrous compounds, hercynite and magnetite, are produced;  $900^{\circ}C \le T1 < 950^{\circ}C$  mixed phases are observed;  $T1 \ge 950^{\circ}C$  $(T3 = 800^{\circ}C)$  only hematite is produced for long firing while mixed phases are produced for short firing (reported in the dashed square). At T3 = 900°C, mixed phases of ferrous and ferric compounds are observed when  $700^{\circ}C \le T1 < 950^{\circ}C$ , and only hematite is formed when  $T1 \ge 950^{\circ}C$ . At T3 = 1000 °C only hematite is produced, for any initial temperature T1.

Interestingly, comparison of this mineral phase/time-temperature diagram with the T1/T3 diagrams presented in Fig. 3 shows that the black gloss regions correspond to the production of ferrous compounds (magnetite and hercynite); the misfire regions correspond to the presence of both ferric (hematite and maghemite) and ferrous (magnetite and hercynite) compounds; and that hematite is the only mineral observed in red gloss. Furthermore, it is worth noting that hematite is the only ferric mineral produced during the first oxidative stage but, during the re-oxidation, both the  $\alpha$ - and the  $\gamma$ -phase of Fe<sub>2</sub>O<sub>3</sub> are produced at temperatures lower than T3 < 1000°C. The presence of the  $\gamma$ -phase has been extensively discussed in our previous paper,<sup>14</sup> and it is due to the topotactic transition of iron spinels (magnetite and hercynite) into maghemite at low temperature in oxidative environment.

#### **IV.** Summary/Conclusions

The successful formation of black and red gloss over a red body is a complex process in which every component plays a crucial role for the final appearance of the object. Many parameters are involved in the production of the black gloss: the material (chemistry of the raw clay, refinement of the clay, density of the dispersion used to paint the images, and thickness of the painted slip) and the firing conditions (temperature of the stages, atmosphere of the kiln, duration of the firing stages). However, only a small combination of parameters leads to success, a testament to the incredible refined mastery of the ancient Greek potters. This study probed the effect of two of these parameters-temperature and duration of the oxidizing stages-yielding the following conclusions:

1. During the first, oxidizing, firing stage, the decomposition of the clay matrix leads to the formation of a glassy phase and the growth of hematite crystals. The balance between these two processes determines the production of black gloss or red gloss at the end of the second, reducing, stage.

- 2. The temperature at which hematite precipitation occurs is dependent on the duration of the first firing stage, since the formation of this mineral is both a thermodynamic and a kinetic process: a long duration of the first stage favors the growth of hematite crystals at lower temperatures (900°C) than needed for short firings.
- The third, reoxidizing, firing stage controls the reoxidation of the Fe<sup>2+</sup> formed during the second stage. The temperature of this stage has to satisfy the relation T3 < T1, T2 to avoid reoxidation of the slip and the production of misfires.

The identification of the minerals and the regions of their stability, within the range of temperature used to produce the replicates, has been a valuable tool to infer the conditions employed for the production of the ancient pottery and to determine the sequence of steps for the making of complicated design and architectures observed in the study of ancient sherds.

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