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The story of a soil that became a glaze: Chemical and microscopic fingerprints on the Attic vases

Artemi Chaviara *, Eleni Aloupi-Siotis

Thetis Authentics Ltd, 4 Diagora str, 11636, Athens, Greece

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ABSTRACT

In order to study the provenance of the clays used for the black-glaze (BG) decoration of Athenian pottery, we analysed in situ with the use of a Bruker handheld-PXRF system ~100 Geometric, Archaic and Classical decorated sherds from the 19th century excavations at the Acropolis of Athens (Graef and Langlotz, 1933), Boeotian ware from the Kavirion excavations and test pieces from the early excavations at the potter's quarter in Corinth. The sherds were also examined microscopically and documented by means of optical microscopy/digital photography. The results were compared with laboratory BG specimens produced by following the "iron reduction technique" at the THETIS workshop in Athens. The laboratory BG specimens used clay-colloids from 36 different ferruginous, illitic, low-calcium content, clay-sources in Attica. Trace element comparison between modern and ancient BG samples, with respect to the Zn content, points to the occasional use in antiquity of clay-deposits from Laurium. In addition, two phenomenological features of the ancient BG samples also present in prominent museum exhibits, i.e. the characteristic star-like micro-cracks and distinct brown-black colour shades, appear in the laboratory BG specimens produced from specific clay-deposits in the Panakton plateau and Mount-Parnes region.

1. Introduction

There is no single material of archaeological interest that has been studied as thoroughly from many different disciplines as the black-glaze (BG) that decorates the surface of the black and red figured Athenian vases. The material first attracted the interest of the French scholar Compte de Caylus and of the potter and entrepreneur Josiah Wedgwood in the mid 18th century, followed by John Davy and E. Durand -Greville in the second half of the 19th century. The historical survey by Binns and Fraser (1929) summarizes the research conducted until their times, while a less known article, by the chemist C.P.T. Naudé (1959) provides us with new insights in the story-line of the Attic BG. It is also worth mentioning the work by Tonks (1908, 1910) and by Foster (1908), which was decisive for the understanding of the nature of the material and the dissertation of Hussong (1928) that provided the basis for the replication experiments of Th. Schumann (1942). The parallel work done by the Dutch chemists, Rijken and Favejee in 1941 and Prins de Jong in 1944 (cf. Naudé, 1959) also deserve to be mentioned. The "*rich black with satiny surface and of astonishing durability*" as described by Richter (1923) had already reached a wider audience during the 1950's and this is evidenced by an article of general interest by L.J. Murray in 1954 on "Industrial Ceramics" (cf. Naudé, 1959).

A careful consideration of this bibliography shows that by the late 1950's the "established" knowledge on the Attic BG accessible to scholars, chemists and artisans described it very accurately as a partially vitrified material, a sinter, coloured by ferrous oxides, most probably magnetite, formed during a three-stage firing involving Oxidation, Reduction and Oxidation stages (ORO). The paint used for the decoration was described as based on clay-colloids, the fine particle size of the clay-paint being responsible for the surface sheen already apparent before firing. In the following decades, the advent of electron microscopy and electron probe microanalysis (EPMA, SEM-EDX) combined with petrographic and magnetic studies (XRD, Mossbauer) allowed the material characterization of the BG and the ceramic-body (Pavicevic, 1974; Longworth and Warren, 1975; Tite et al., 1982). R.E. Jones (1986) provides a detailed account on the Attic black-glaze and the physicochemical description of the ancient decoration technique, by then called "iron reduction technique". Maniatis et al. (1993) and Aloupi (1993) through the in-situ TEM examination of a BG specimen prepared with ion beam thinning, provided a new characterization of the BG in terms of its colourisation by polycrystalline magnetite nanoparticles (<200 nm), while the identification of a 1-2 μm thick glassy layer free of magnetite nanocrystals on the surface of the BG accounted for the surface sheen. This work has led to a faithful reproduction of the Attic BG based on the use of illitic clay-colloids in water, different from the clay used for the body, without any addition of dispersing or deflocculating agents. A successful application requires firing under ORO conditions to maximum temperatures in the range of 900–950 °C

* Corresponding author.
E-mail addresses: chaviaraa@gmail.com (A. Chaviara), aloupie@thetis.gr (E. Aloupi-Siotis).

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(900 °C < Tmax < 950 °C), involving a prolonged oxidizing stage followed by reduction with simultaneous decrease of temperature (Aloupi, 1993). The results of this research formed the basis of an Attic BG production unit, operating in Athens since 1999. Aloupi-Siotis (2008) has reported on the technical issues and understanding that become apparent through the routine full-scale reproduction and the ensuing contributions to archaeological research. Lühl et al. (2014) validated the optimal firing process, which now narrows to top temperatures in the range 890–910 °C, and verified the similarity of the modern BG relative to the ancient one. An important result obtained by confocal X-ray Absorption Near Edge Structure (XANES) in this study was that the best quality black-glaze of classical BG ware is characterized by the lower Fe(III)/Fe(tot) value (~20%) obtained by the finest clay fraction (ESD[1]<330 nm) and at intense reducing conditions. In modern terminology the Attic BG is a potassium-alumino-silicate glass coloured by magnetite nanocrystals, a ceramic glaze or glass-ceramic[2] with a high alumina content of order 30% wt responsible for its "astonishing durability". It is thus not surprising that Attic BG properties have attracted the interest of the space industry-NSF Award No 1,041,808 (NSF-National Scietific Foundation, 2010). Furthermore, due to the nature and chemical composition of the material we have re-adopted the use of the term "glaze", substituting the term "gloss" that only refers to its external appearance.

In spite of this impressive body of research on the nature of the Attic BG little attention has been paid to the raw materials, i.e. the ferruginous illitic clays that might have been used in antiquity for the production of the clay-paint resulting in the BG. This is partly due to the fact that the archaeological literature (for example see Oakley, 2009) is still constrained by the publication of J.V. Noble (1965) and his replication experiments which were based on the use of calgon, a sodium hexametaphosphate water softener developed in 1933 that in water would complex with calcium acting as deflocculant thus facilitating the preparation of the clay-colloid used for the BG. The relatively successful macroscopic results obtained by Noble with the use of calgon (or any other phosphate additives) led him to the erroneous conclusion that the clay used for the BG was the same as for the clay-body and hence not worthy of special attention. As shown by detailed experimentation with clay-colloids from Attica clays (Aloupi, 1993; Aloupi-Siotis, 2008) the absence of Ca-phosphate phases in the ancient BG layer combined with the low CaO content in the BG, leads to the conclusion that the clays used for body and surface decoration differ.

It was thus reasonable to embark on a search for clay-beds or clay-deposits in Attica suitable for BG production, focusing on ferruginous clays-soils, rich in illite, free of mica, with low $CaCO_3$ content (CaO < 1%).[3] Aloupi-Siotis (2008) had already suggested the presence of at least one such clay-bed located in the plateau between Attica and Boeotia (Panakton plateau/Skourta plain) which leads to excellent BG results while clay samples from Kalogreza and Pikermi tested in the past gave very poor results (Aloupi, 1993). This on-going work (Chaviara, 2014), involves the detailed comparative analysis of archaeological BG pottery samples and modern BG specimens produced in the laboratory, especially with respect to trace element composition. The μ-PIXE technique combined with a scanning ion microprobe allows analysis of the BG layer only (10–40 μm in depth). The analysis was performed at the ATOMKI Accelerator Centre (Institute of Nuclear Research of HAS, Debrecen, Hungary). The preliminary results reported so far (Aloupi-Siotis et al., 2012) refer to the analysis of thirty-five BG samples from recent excavations in Attica, dated to the 6th-4th centuries BCE, and 13 laboratory BG specimens and revealed a variation of the Zn content between ~300–2500 ppm in the archaeological samples. In view of the fact that similar measurements by LA-ICPMS have been recently reported on Attic BG pottery from the Getty Museum Collection (Walton et al., 2015) it is reasonable to attribute the elevated Zn content observed in some archaeological BG samples, either to the use of different clay-sources for the production of the BG or to a contamination mechanism, i.e. during firing.[4] In order to explore further the first hypothesis on the possible use of different clay-sources for the production of the BG in antiquity, the use of a handheld-PXRF system proved convenient for a rapid survey of zinc content in clay-source candidates and of decorated ancient samples bearing a BG in situ in museums.

2. Materials and methods

2.1. Archaeological samples

One hundred and two archaeological samples, dated between the 8th and the beginning of 4th centuries BCE were examined and analysed non-destructively. The archaeological sherds include 9 fragments of Geometric pottery (GE), 49 Archaic and 14 Classical Black Figured (BF), Red Figured (RF) and Black Glazed (BG), from the collection of the National Archaeological Museum in Athens (NAM), excavated in the 19th century and published by Graef and Langlotz (1933). Non-destructive, in-situ analysis in museums, allowed us to include a comparable sample of specimens consisting of 9 Classical pottery fragments (1 RF, 2 BF, 6 BG) from Kavirion near Thebes (Avronidaki, 2007) in the NAM, 10 decorated sherds (4 BF, 7BG) from a rectangular deposit at the foothills of the Acropolis, now held at the Acropolis Museum (Eleftheratou, 2009) and 11 fragments from the potter's quarter in ancient Corinth (7th -6th cent BCE) at the Corinth Archaeological Museum, 6 of which are test-pieces bearing brush-strokes (TP) (Stillwell and Benson, 1984). In order to achieve reliable XRF results, the archaeological fragments were carefully selected to have low curvature surfaces, thick and well-preserved BG layer as well as wide areas decorated or filled with BG of at least 1 cm × 1 cm (Fig. 1).

2.2. Laboratory samples

Before production of laboratory specimens, a study for the potential raw material resources was performed using geological and chemical characteristics of clay-source candidates in Attica (i.e. ferruginous, low calcium, illitic clay-soils). Raw material sampling took place in 2012–2013 and involved already known sources from earlier studies from the Panakton plateau (Aloupi-Siotis, 2008) and potential sources in the Mesogea region, Mount-Parnes, Mount-Hymettus, the Laurium region and in areas adjacent to the banks of the Ilissos River within the city of Athens (Chaviara, 2014) (Fig. 2).

The thirty-six clay-soil samples collected were processed to prepare a colloid clay-suspension in water following the refinement procedure for the separation of the finest fraction (ESD < 0.33 μm), without the use of any additives, as described by Aloupi (1993) and Chaviara (2014). The resulting clay-paints were then applied on flat clay briquettes with dimensions approximately 1 cm × 1 cm × 0.5 cm, in order to assess the resulting BG mechanical and optical properties such as crazing, adhesion and colour. In order to assess their adequacy

[1] Equivalent Spherical Diameter measured by particle size analysis (Dynamic Light Scattering_DLS).

[2] For example see McMillan (1964; 1974). Glass ceramics have many notable advantages. Some of those are thermal shock resistance, heat insulation, high strength, toughness, high temperature stability and isolation capabilities to name a few.

[3] The presence of organic matter that can reduce or even impede delamination in clays (Lagaly, 2006) and thus prohibits the production of the clay-colloids was also taken into account.

[4] The presence of a zinc containing material, i.e. brass objects or "cadmean earth" a zinc oxide which collects on the sides of furnaces where zinc is sublimed, in the ceramic kiln could lead to the formation of ZnO during the first oxidizing phase. In a carbothermic reaction, heating under reducing conditions with carbon, converts the zinc-oxide into zinc-vapour at around 950 °C ($ZnO + C \rightarrow Zn_{(Vapour)} + CO$), a temperature that is in the range of the 3stage ORO firing, i.e. 900–950 °C. In this case elemental Zn could be trapped in the alumino-silicate melt, evenly distributed within the BG layer.