PIXE analysis of decoration pixels in Classical Attic Pottery

Aloupi-Siotis E. [1], Chaviara A. [1], Kertész Z. [3], Huszánk R. [2,3], Lagoyannis T. [2], Csedreki L.[3], Furu E.[3], Kiss Á.[3], Simon A.[3], Török Z.[3], Uzonyi I.[3] & Szikszai Z.[3]

[1]Thetis Authentics LTD, 4 Diagoras str., GR-11636, Athens, Greece
[2]Tandem Accelerator Laboratory, Institute of Nuclear Physics, NCSR "Demokritos" POB 60228, GR-153.10 Aghia Paraskevi, Athens, Greece
[3]Institute of Nuclear Research of the Hungarian Academy of Sciences, Bem tér 18/c, H-4026 Debrecen, Hungary

Introduction

The work focuses on the study of special techniques of the Athenian vase-painters, applying the non destructive proton induced X – ray emission technique combined with a scanning ion microprobe (micro-PIXE). The aim is to make a direct comparison of archaeological black-glazed (BG) ceramic sherds with black-glazed (BG) specimens produced in the laboratory so as to address, for the first time, the long standing archaeological question of the source locality, and geology, of the clays used for attic pottery decoration.

Analytical work on archaeological sherds and on laboratory produced samples was performed at the ATOMKI Accelerator Centre (Institute of Nuclear Research of HAS, Debrecen) in Hungary. Part of this work was carried out within the framework of CHARISMA (Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/ Restoration), an EU-funded integrated activity in FP7/ Capacities Specific Programme, and part supported by NARNIA Marie Curie Initial Training Network.

Samples

Forty-eight samples bearing BG decoration (35 archaeological ceramic fragments and 13 laboratory specimens (Figs 1,2,11) have been analysed so far. An important prerequisite for the selection of archaeological sherds for the non-destructive surface analysis was that the BG layer a) has a thickness of at least 20-23 μm and b) is free of visible weathering features (i.e. discoloration, pits, crackles).

Archaeological Samples : The samples dated from 7th century B.C. to the 3rd century B.C. were collected from the historic area of the Acropolis and the area of Keramikos where the potters' quarter was located in Classical antiquity. Other samples had been excavated in the previous decade during the construction of the Metro (tube) of Athens, the Attica highway and several building projects in 2004 for the Olympic Games i.e. Pallene, Raphina (Fig. 3). Some of the archaeological sherds are decorated with very fine relief lines of black glaze (red figure style) of the order of 0,2-1mm wide with occasional presence of added colours (white, purple, coral red) (Figs. 1 & 2) . Archaeological samples of similar technology i.e. 2 terra sigillata and 2 black glazed ware (Campanian or Attic imports) from Badalona (Spain) were also included, the first 2 sherds being *de facto* outliers.

Laboratory samples: For the production of the laboratory specimens a geological survey was carried out on iron rich illitic clays covering a plateau at the NW part of Attica (Panakton area), near the borders with Boeotia and Attica (Figs 3 & 4) and from two sites in the east of Attica (Figs 3,5). The samples collected were processed at the THETIS laboratory for the preparation of clay slips, i.e. colloidal suspensions of the clays in water (Fig 6). Each concentrated clay slip was applied to flat clay briquettes and to curved clay surfaces. These shaped surfaces allowed the mechanical properties to be studied at all the stages of the ceramic production (Figs. 7, 8, 9 & 10). The samples were fired under a 3-stage ORO cycle at Tmax 920^0 imitating the ancient iron reduction technique.

Figure 1: Red – figured archaeological attic sherds bearing a relief line from the Akropolis .

Figure 2: Black- glazed archaeological samples. The Attic black glaze (gloss) is a potassium / aluminosilicate glass that contains nanocrystals of Fe_3O_4

Figure 3: Map of Attica . The blue and red flags represent the areas of the archaeological and geological sample collection respectively.

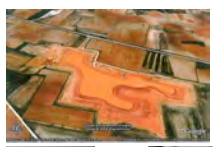

Figure 4: Spontaneous clay dispersion in water as observed in a clay –bed at the Panakton plateau

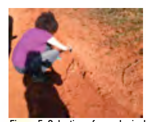

Figure 5: Selection of a geological sample.

Figure 6: Preparation of the clay water suspensions.

Figure 7: Painting a flat clay surface.

Figure 8: Painted clay surfaces of different curvature, before firing.

Figure 9: Laboratory specimens in the kiln.

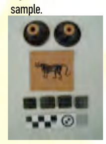

Figure 10: Black glazed ceramics after firing.

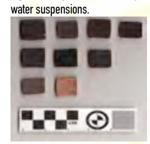

Figure 11: Laboratory specimens with variation in black- glaze quality.

Figure 12: Full scale black glazed reproductions.

Analytical results

April 2010 : Trace element analysis, especially with respect to the Zn content, of the relief line on some of the black-glazed sherds, points to the use of at least two different clay sources for the preparation of the slip that eventually becomes black (Fig. 14). ***January 2011:*** Analysis was carried out on a second group of 25 archaeological sherds, focused on the detailed mapping with a submicron spatial resolution of the black glaze trace element content. ***January 2012 :*** Differentiation patterns with respect to trace element composition (Ti, Mn, Ni, Co, Cu, Zn, As, Pb) were observed with local concentration of certain elements extending over areas of 5-10μm.

The analysis of the laboratory samples was also focused on differentiation patterns in the black glaze with respect to trace element composition (Mn, Cr, Ni, Zn, Mg, Rb, V, Pb, As (Fig 15). Except for the 2 Terra Sigillata sherds from Bandalona and 2 outliers that present the higher Zn and Pb respectively values the rest of archaeological samples group well with 4 out of 13 modern BG samples coming from the NW and Eastern Attica. Further separation is obtained when introducing 2 major (Fe, K) and 2 minor (Ca, Mg) elements to the above data set that constitute key elements for the clay slip preparation and glaze formation (Fig 16) and there it reflects a qualititative feature since the best quality modern glazes group with some archaeological BG samples from the centre of Athens.

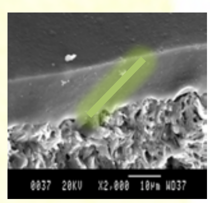

Figure 13: SEM micrograph of an ancient sample (fresh – fraction surface).

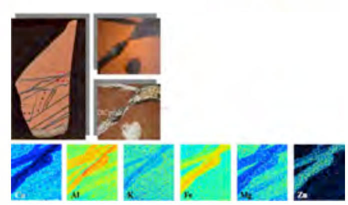

Figure 14: Elemental mapping of the relief line decoration on RL_ACROP-4 sherd with increased Zn content (1520 ppm).

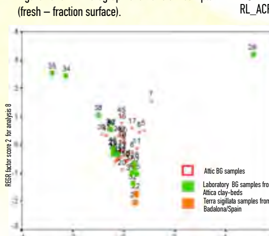

Figure 15 : PCA plot of trace elements Mn, Cr, Ni, Zn, Mg, Rb, V, Pb (missing Pb:22 ppm), As (missing As: min-1 = 10 ppm.).

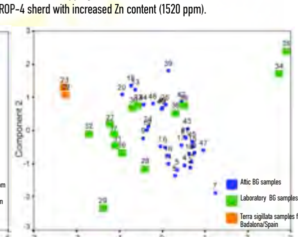

Figure 16 : PCA plot of K, Ca, Mn, Cr, Fe, Ni, Zn, Mg, Rb, V, Pb (missing Pb: min -1 = 22 ppm), As (missing As: min-1 = 10 ppm) .

Conclusions

The analytical comparison of Black Glazes bearing geological and archaeological information has both innovations and constraints:

a) This is the first time that the trace element analysis compares ancient and modern black glazes produced by the same process.

b) Archaeological BGs group well with 4 modern BGs from NW and Eastern Attica: The outliers are explained either by a *defacto* different origin or by secondary characteristics (i.e. contamination during firing).

c) Since the clay-paint material used for the BG is almost free of accessory minerals, which might be indicative of the parent clay-bed, the trace element finger print of the BG rather reflects characteristic features of the clay mineral component of the paint (i.e. ionic substitution for Al and Si in illites).

d) The increased Zn content in 7 out of 35 archaeological samples provides us with a strong discriminating tool that requires further examination before proceeding to dichotomic explanations.

e) It is therefore necessary to continue with the analysis of well documented and selected archaeological samples from the Acropolis and Keramikos areas in order to establish reliable reference groups.

Acknowledgements : The work was made possible due to the enthusiastic collaboration and support of archaeologists from the Greek Archaeological Service (Ministry of Culture) and especially Mrs St. Eleftheratou (Curator of Vase Collection at The Acropolis Museum , A'EPKA Athens.