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INTRODUCTION

Technological methods are exceedingly used in typological and comparative archaeological studies to provide more objective scientific criteria. Non-destructive methods are preferred since they offer the advantage of leaving the sample intact for additional measurements and future re-examination. The present work describes the application of such methods in the study of black-glazed sherds from the archaeological site of Karabournaki in northern Greece in order to clarify their provenance. Optical stereo-microscopy was used to study the clay body and surface glaze. A digital spectrophotometer was used for color definition, and the composition of both clay and glaze was determined by micro X-ray fluorescence (μ -XRF) analysis. The results were compared by multivariate statistical treatment. From the combined results, a detailed characterization of the samples is derived regarding their color, texture and composition.

Description of samples

The archaeological material under study consists of 52 ceramic sherds (six red figured, one black figured and forty five black glazed) collected from the area around the ancient settlement of Karabournaki in Thessaloniki, Greece and dated from the late 6th till the early 4th century B.C.

Optical observation divides the samples into 3 groups according to their provenance:

- Group A: Attic. It includes 31 samples. They are subdivided into 5 smaller groups according to their dating.

- Group B: Problematic. It includes 12 samples with uncertain provenance. They recall the Attic manufacture but they bear special characteristics which slightly differentiate them from the Attic workshops. They are subdivided into 4 smaller groups according to their dating.

- Group C: Non Attic. It includes 9 samples which seem to be imitations of the Attic products, manufactured in other areas. They are dated to 4th century B.C.

Archaeological questions

The aim of this study is specified by the archaeological research and is shortly described as follows:

- The clarification of the provenance of the samples of group B.
- The confirmation of the archaeological categorization of Group A and C through the elemental analysis.
- The comparison of the clays and the glazes of the samples and the identification of the elements which cause the major visual and compositional differences.



Group A



Group B



Group C

Micro-XRF spectroscopy was used to obtain compositional data and the results were treated by suitable multivariate statistical exploratory tools such as Principal Component Analysis (PCA) and Discriminant analysis (DA) for comparison purposes.

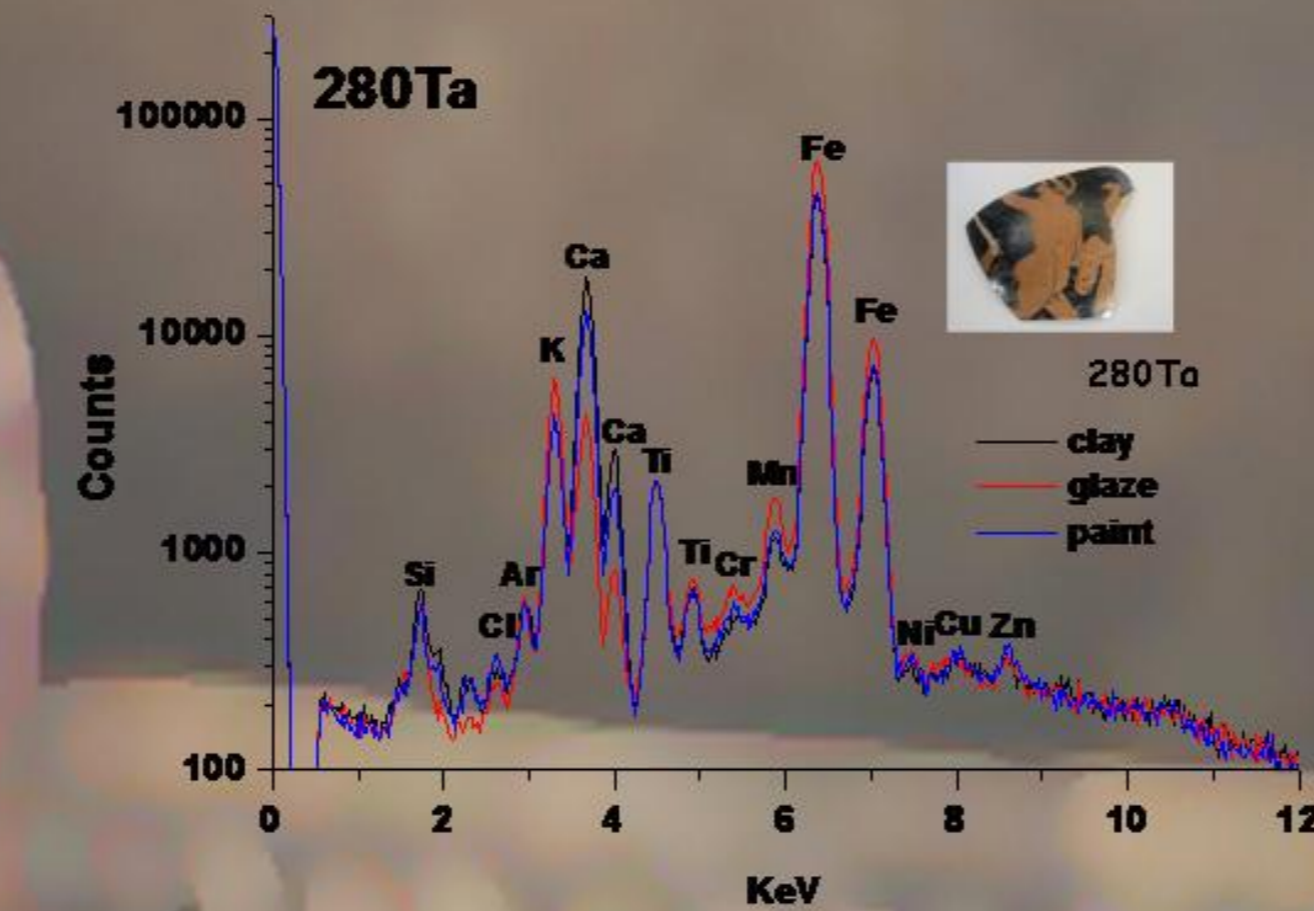
EXPERIMENTAL

Micro-XRF measurements were performed on the clay of the profiles of the ceramics, after simple cleaning and careful removal of approximately 1mm of the upper clay layer.

A compact portable instrument with a side-window x-ray tube with Mo anode (Series 5011, Oxford Instruments) and a maximum tube voltage/current of 50 kV/1mA respectively was used. The x-ray optics include a straight mono capillary. The detection of the fluorescence x-rays is performed by a solid state Si(Li), Peltier-cooled detector, oriented at 90° relative to the micro beam. The nominal beam size is <150 μ m.

For the optical study of the material, a Leica MZ APO optical stereo- microscopy was used, while for the color definition of the clay and the glaze of the samples a Minolta CM2600d digital spectrophotometer.

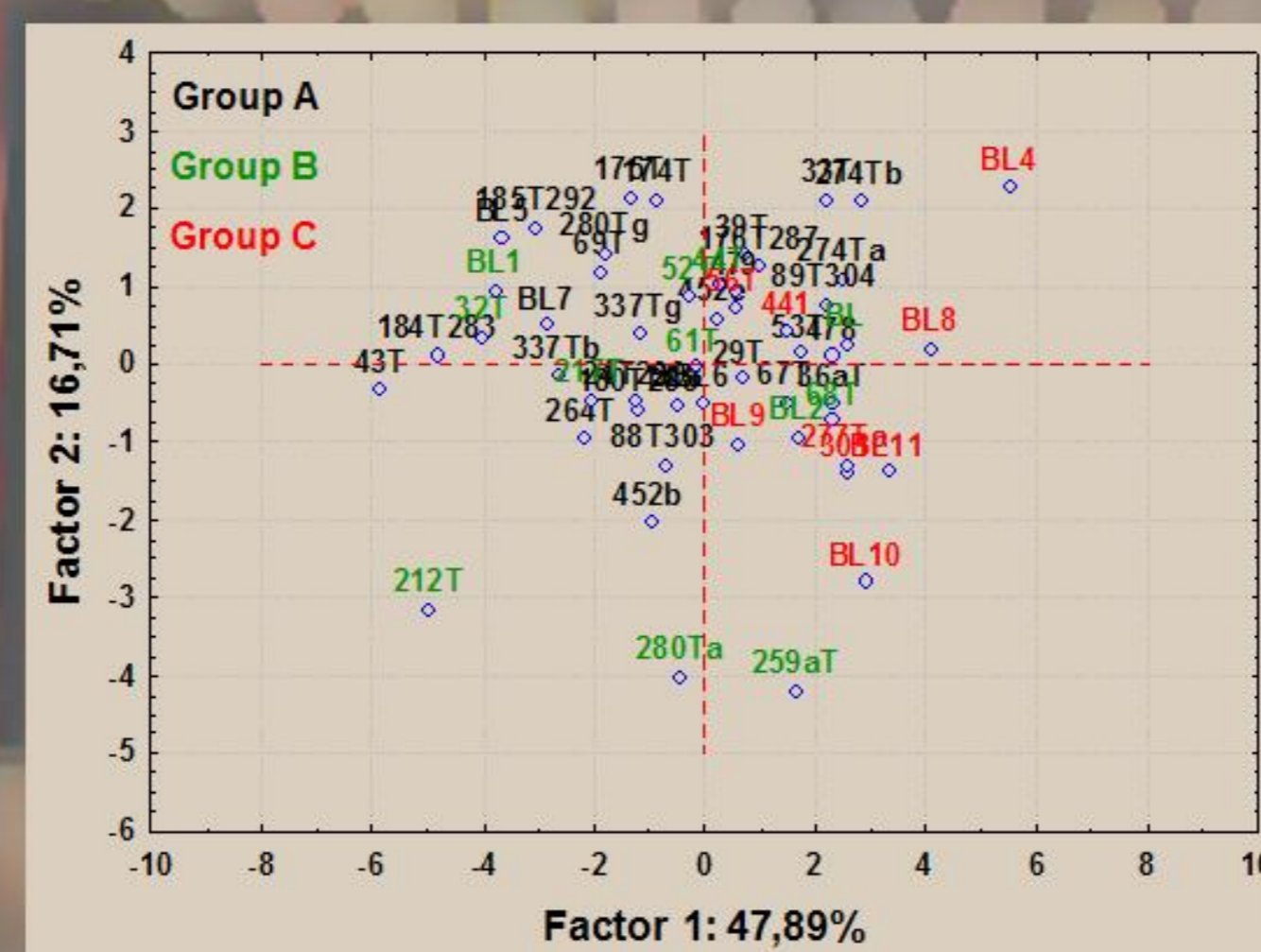
RESULTS AND DISCUSSION



Optical stereo-microscopy allows the detailed observation of the texture of the samples and reveals differences in the composition of their clays which sometimes are not visible with naked eye. In general it is observed that:

- Samples of Group A have less porous clay with fine grains and not many inclusions.
- Samples of Group B present a big variety in the composition of their clays, as expected.
- Most of the samples of Group C have clay of lesser quality, porous with many inclusions.

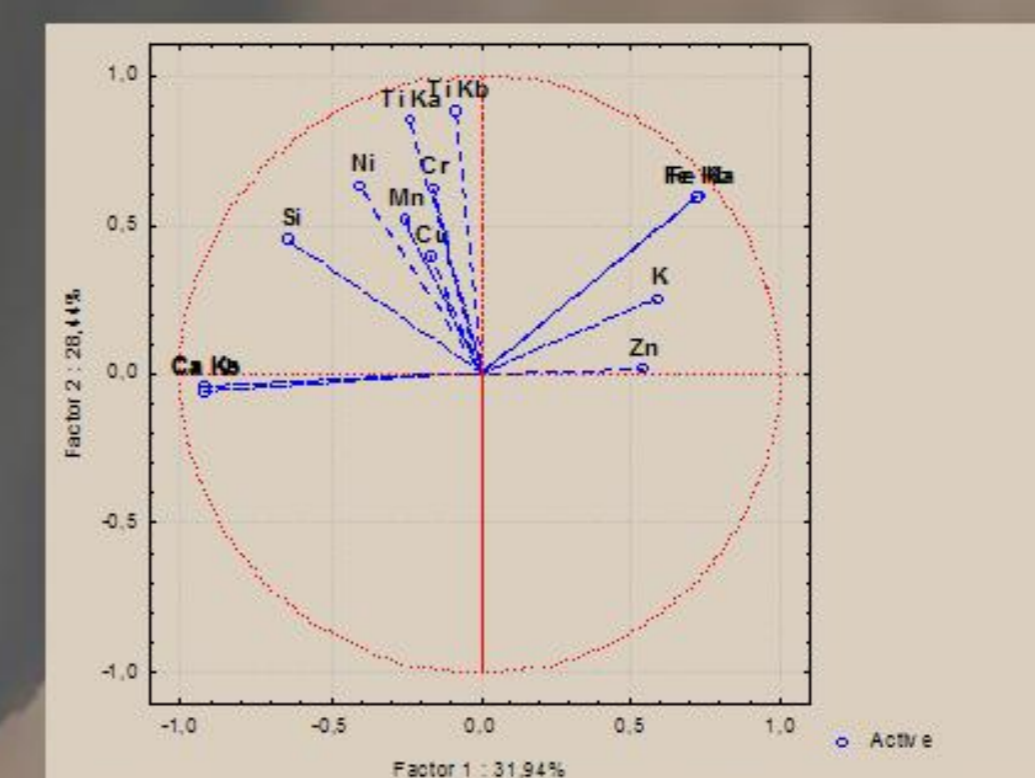
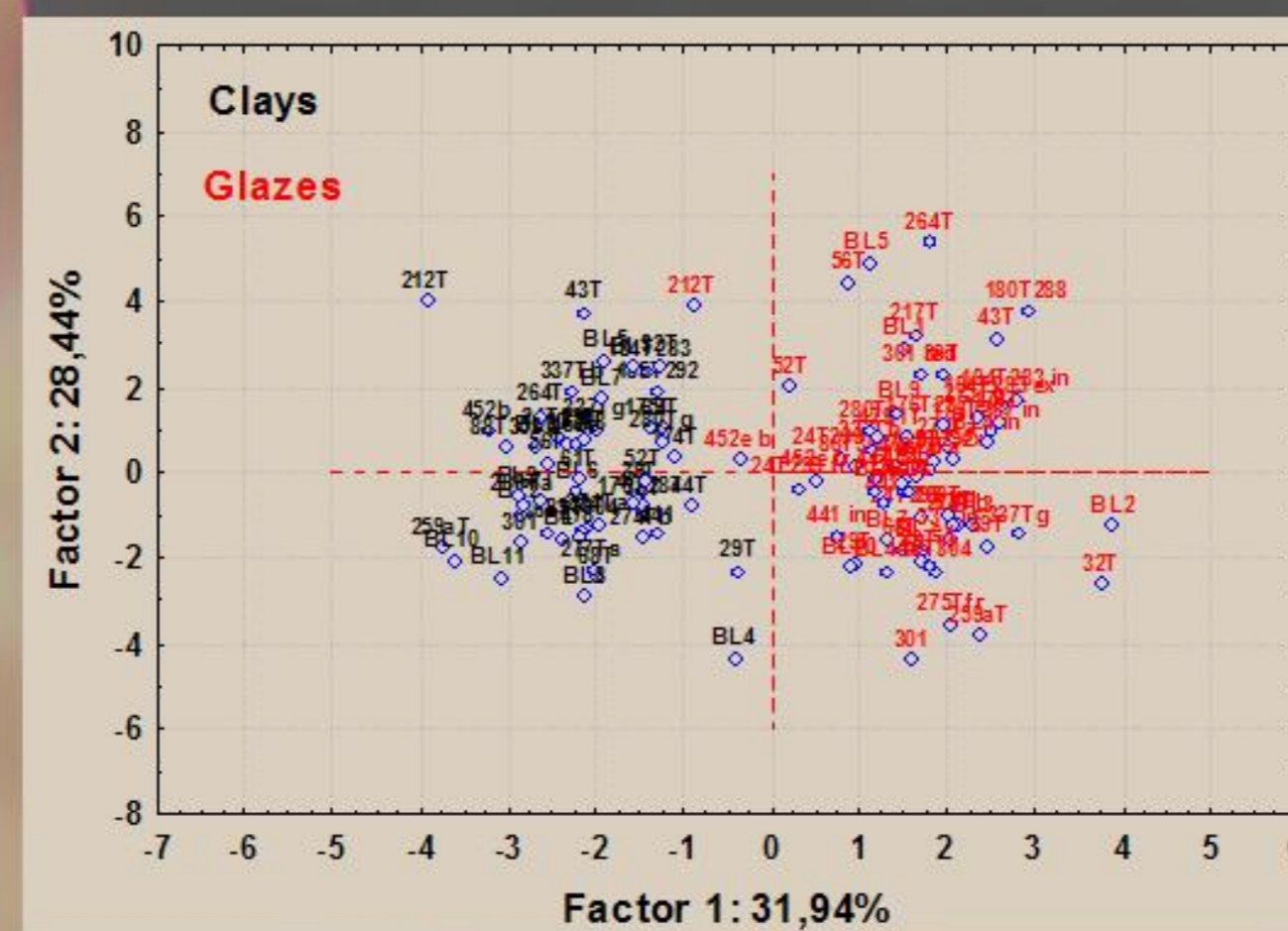
XRF spectra show that the white paint and the clay are rich in calcium (Ca) where the glaze is rich in iron (Fe)



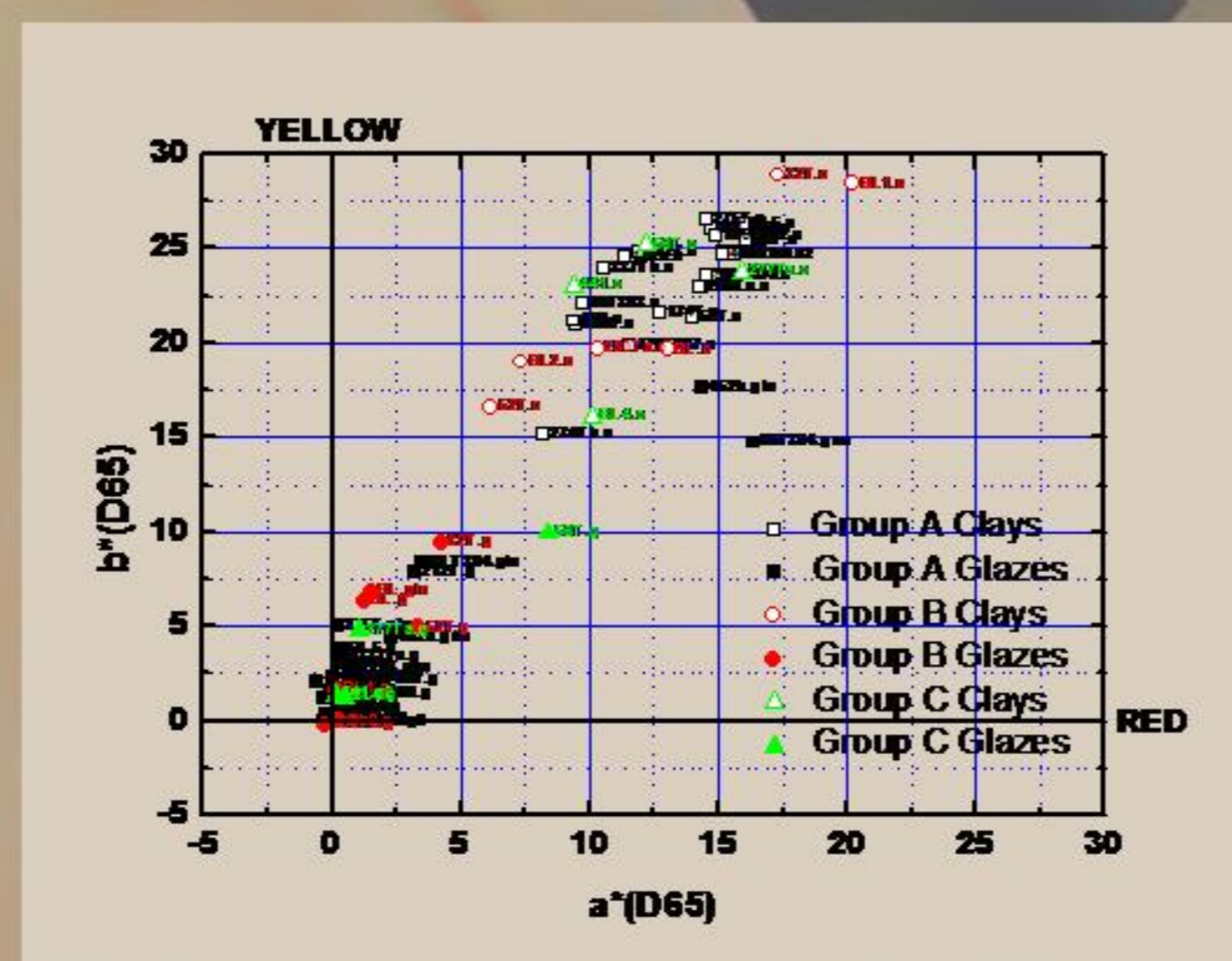
Group	percent correct	A p=0.3333	B p=0.3333	C p=0.3333
A	80.64	25	4	2
B	50.00	4	6	2
C	88.88	0	1	8
Total	75.00	29	11	12

- A clear distinction is noticed between the Attic (group A) and the non Attic sherds (group C), confirming in general the archaeological classification. Samples 56T and 441 of Group C seem to be mixed with Group A. This indicates either that they are second class Attic products, or that they are products of a local manufacture (north Greece), which imitate successfully the Attic clay.
- Most of the samples of group B are closer to group A implying an Attic origin. Exception are samples 280Ta, 259aT, 212T and possibly 68T and BL2, suggesting that they are non Attic.

- Discriminant analysis reveals high degree of homogeneity for Group C and Group A. In contrast, Group B presents high heterogeneity indicating apparently different origins.
- Additionally, DA supports the archaeological assumption that samples 56T and 441 are possibly non Attic.



A clear distinction is observed between the composition of the clay and the glaze of the ceramic sherds. The most significant elements causing this discrimination are iron (Fe) and calcium (Ca). Clays are richer in calcium (Ca) and glazes in iron (Fe).



- The study of the color of the samples with the digital spectrophotometer according to the LAB color space, does not appear any notable variation between the groups neither to the clay nor to the glaze of the sherds, confirming the visual observation.
- On the contrary, a clear distinction is noticed between the color of the clay and the glaze of each group, as expected.

CONCLUSIONS

- The results from the elemental analysis in most of the cases confirm the visual observations and the archaeological classification.
- A clear distinction between Groups A and C is noticed, indicating the different provenance and manufacturing workshops of the two groups.
- The samples associated to the Attic workshop are characterized by homogeneity in the composition of their clays, suggesting the use of similar resources through the centuries. The non Attic samples reveal a bigger dispersion, as expected since they are not of the same origin.
- The differences between the composition of the clay and the glaze of the samples is indicative of different manufacturing methods used in their production.
- Statistical interpretations of the data obtained from elemental analysis derive useful information concerning description, discrimination and provenance of the studied material, however relatively a large number of samples is necessary for more reliable results.
- The study of the samples with the stereoscope allows the detailed observation of both clay and glaze of the sherds and is useful for the classification of the material and for the study of the techniques of decoration that were used for the ancient Greek pottery. It is revealed that the Attic samples in comparison to the non Attic, have generally clay of better quality, less porous and without many inclusions.

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