THE NON-DESTRUCTIVE STUDY OF ANCIENT GREEK POTTERY OF CORINTHIAN STYLE EXCAVATED IN KARABOURNAKI. DESCRIPTION, QUANTITATION, PROVENANCE

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INTRODUCTION

The systematic study regarding the recognition and identification of ancient Greek pottery is traditionally based on the observation of clay through naked eye and the stylistic approach with the analysis of decoration styles. However, modern archaeometric studies include a more objective approach through the study of pottery with a suitable instrumental method of analysis.

Micro x-ray fluorescence spectroscopy (μ-XRF) is a relatively new technique that allows the reliable qualitative and quantitative analysis of numerous chemical elements (major and minor mainly). Most importantly, μ-XRF enables the non-destructive, multi-elemental analysis of pottery since it does not require elaborate and time consuming sample preparation procedures (e.g. digestion).

The samples studied fall into three categories (Figure 1) :

- Group A: includes 12 samples, imported from Corinth
- Group B: includes 5 samples that follow precisely Corinthian style of decoration, but with problematic provenance (Corinthian or imitations)
- Group C: includes 12 samples, manufactured perhaps in the vicinity of Thermaic Gulf that also follow the Corinthian style of decoration.

This study presents the analysis of three groups of Corinthian style pottery with the aim:

- To identify if there is any compositional differences between the three groups that implies the different origin of the clay.
- To determine if the stylistic similarities in group A and group B also reflects a similar chemical composition
- To investigate the provenance of samples in group C and group B.
- To confirm the archaeological categorization and identification based on chemical elemental analysis

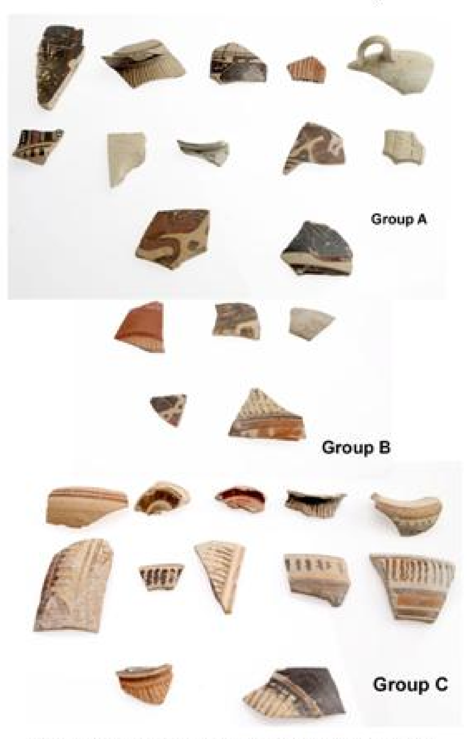

Figure 1: The studied samples

EXPERIMENTAL

Micro-XRF measurements were performed directly on the inner clay of the profiles of the ceramics, after simple cleaning and careful removal of 1-2mm of 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 μm.

RESULTS AND DISCUSSION

Nine chemical elements (Si, K, Ca, Ti, Cr, Mn, Fe, Rb and Sr) were detected in the pottery fragments. These include three major (Si, Ca, Fe), four minor (Ti, Cr, Mn, K) and two trace elements (Rb, Sr). Six of the above elements are quantified using a suitable ceramic standard reference material (SARM69, MINTEK, South Africa)

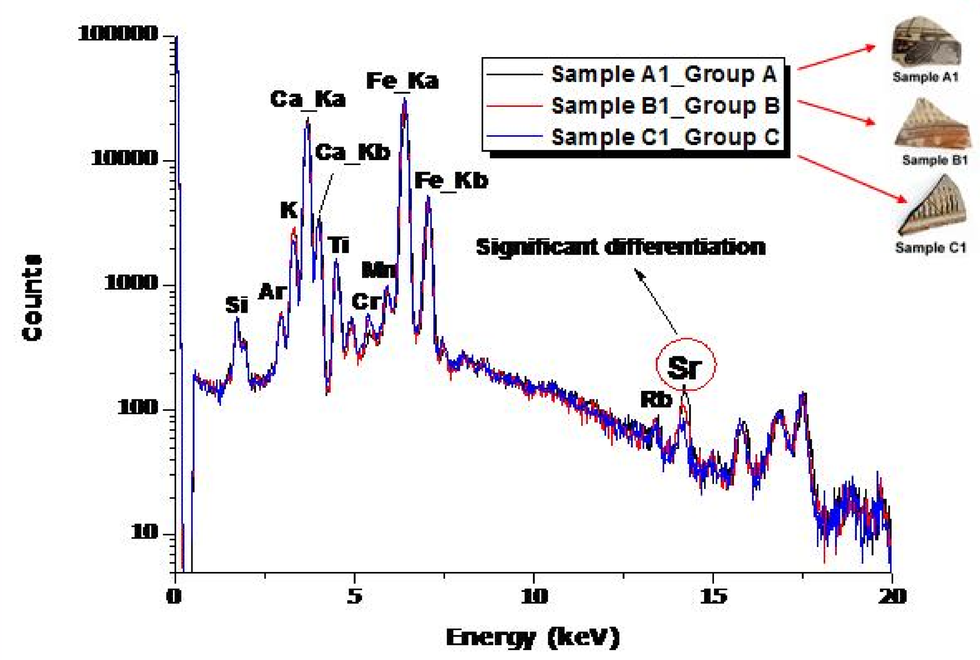

Figure 2: Comparison of x-ray spectra of three samples, one of each group

Table 1: Elemental concentration ranges for the three studied groups (% w/w as oxides)

	Group A	Group B	Group C
K	0.97 ± 0.12 - 3.73 ± 0.10	1.88 ± 0.18 - 3.78 ± 0.11	1.39 ± 0.14 - 4.14 ± 0.44
Ca	14.33 ± 2.52 - 22.33 ± 2.08	12.57 ± 1.25 - 19 ± 0.01	7.07 ± 0.50 - 20.32 ± 0.58
Ti	0.73 ± 0.04 - 1.23 ± 0.06	0.80 ± 0.05 - 1.03 ± 1.06	0.48 ± 0.04 - 1.43 ± 0.06
Mn	0.12 ± 0.01 - 0.20 ± 0.01	0.13 ± 0.01 - 0.21 ± 0.02	0.14 ± 0.04 - 0.22 ± 0.08
Fe	7.25 ± 0.49 - 12.17 ± 0.38	8.77 ± 0.55 - 12.20 ± 0.01	6.70 ± 0.40 - 13.27 ± 0.61
Si	39.5 ± 3.5 - 62.0 ± 2.6	41.0 ± 5.3 - 54.7 ± 1.5	26.3 ± 2.9 - 64.7 ± 5.1

* Mean values from three replicate measurements

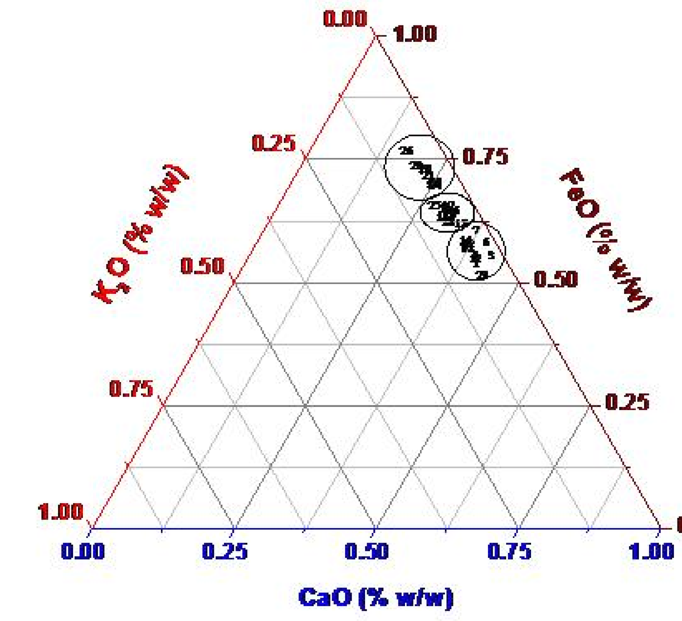

Figure 3: Ternary diagram based on K_2O, FeO and CaO concentration

Preliminary discrimination of the studied samples into three relatively distinctive groups, based on the concentration of K_2O, FeO and CaO

Cluster analysis of the analytical data reveals the presence of three groups. However, these groups do not correspond to the archaeological classification, since the samples are scattered throughout all groups. This observation indicates that either more samples should be analyzed, or that the archaeological categorization should be re-examined

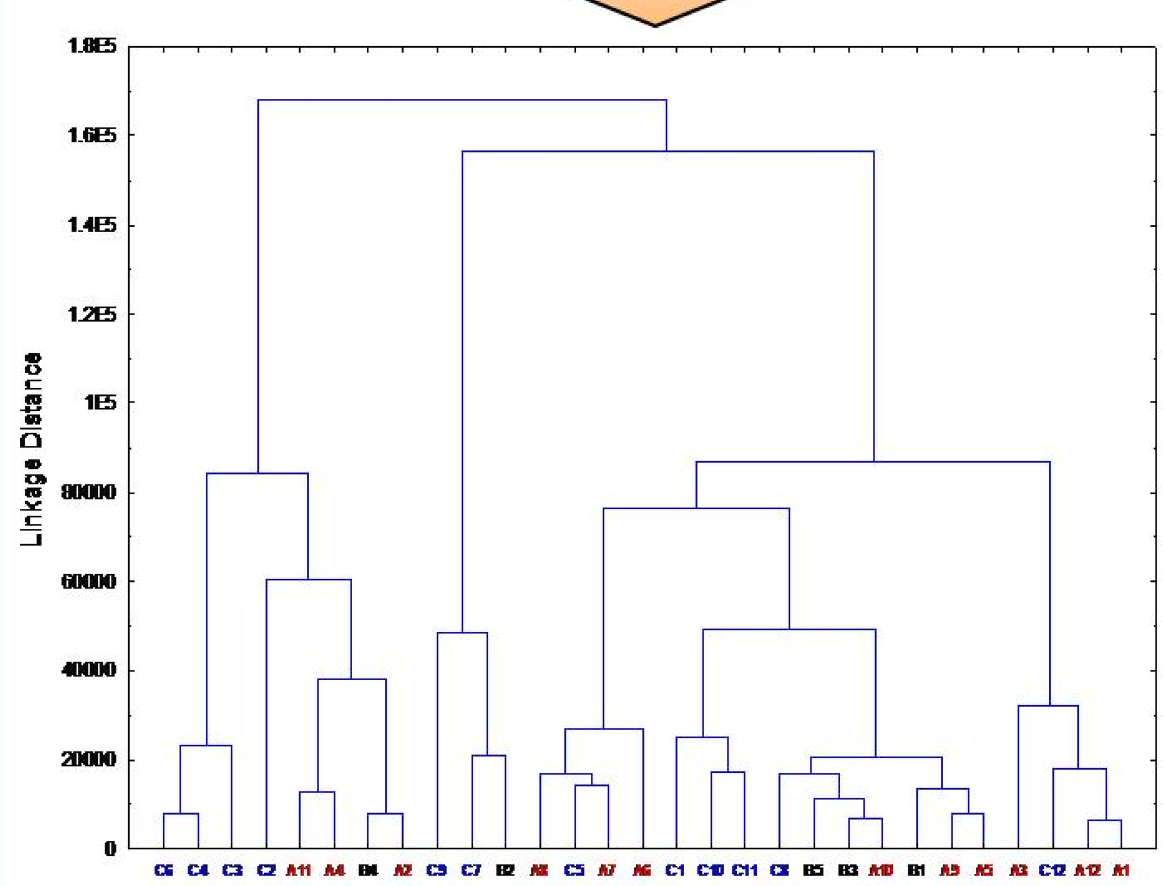

Figure 4: Tree diagram for 29 samples (Single Linkage, Euclidean Distances)

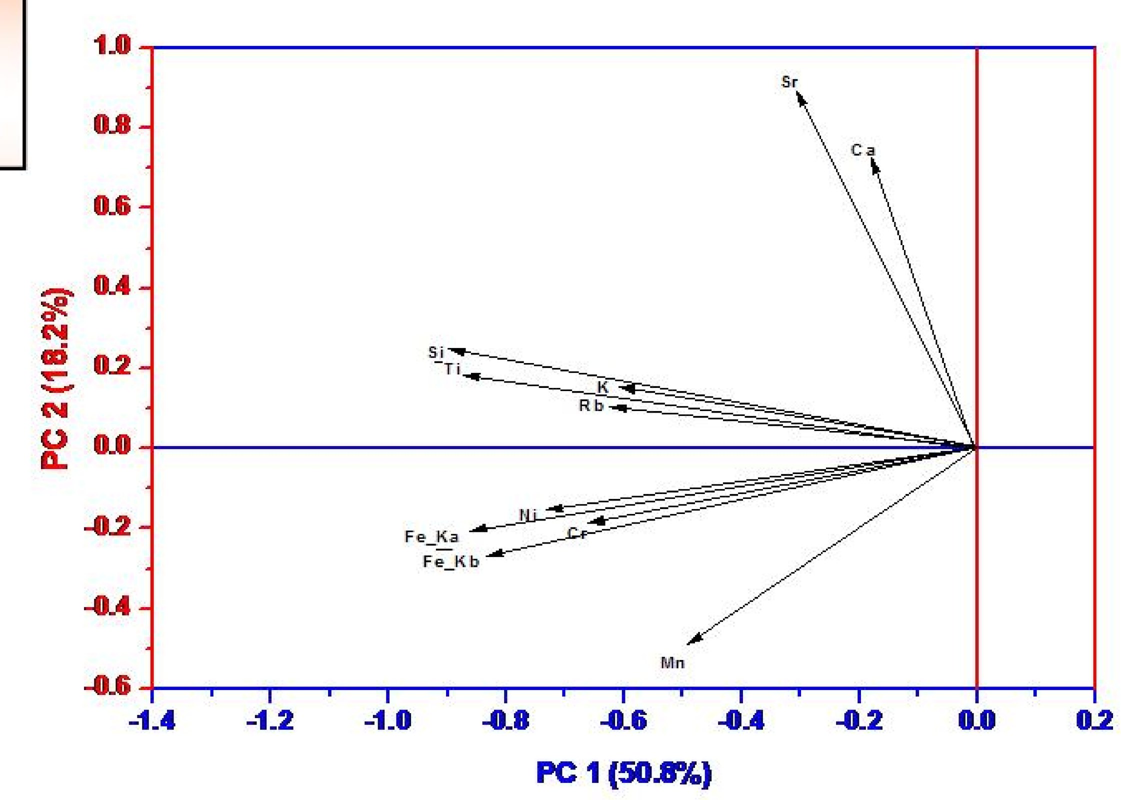

Figure 5: A PCA loadings plot showing the effect of elemental variables on PC1 and PC2 axes

Principal Component Analysis, shows that the first two principal components account for 50.8% and 18.2% respectively of the total variance in the data set. Negative PC1 is dominated mainly by Si, Fe and Ti. Concerning PC2, a strong effect towards positive direction is caused primarily by Sr and Ca, while negative PC2 values are related to high Mn content.

It is observed that samples are randomly scattered, revealing that some samples may belong to different archaeological groups, in contrast to the initial classification. However, samples of Group A show a relatively stronger group membership, providing significant evidence of their Corinthian provenance. It is noticeable that sample A9, is isolated from Group A

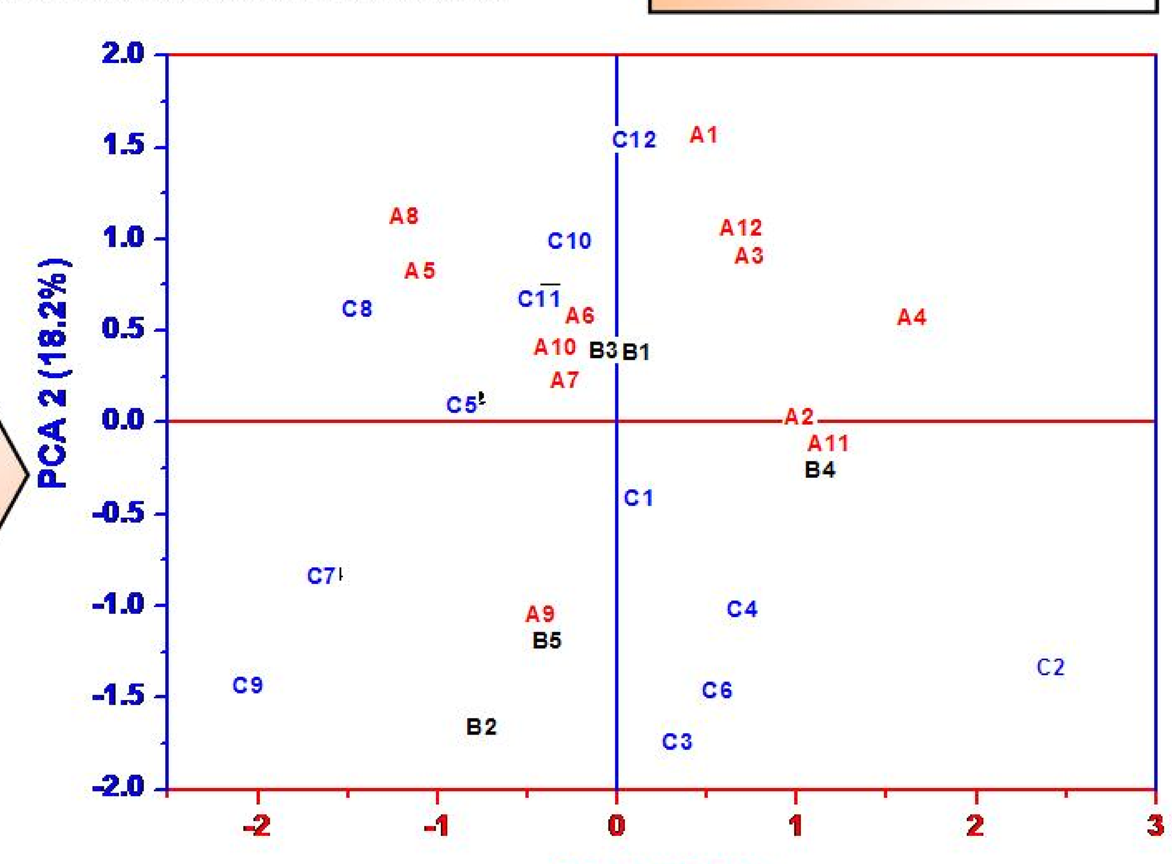

Figure 6: Plots of the first two Principal Components, showing the discrimination of the samples

Table 2: Discriminant Analysis classification matrix. Rows: Observed classifications. Columns: Predicted classifications

group	percent correct	A p=0.3333	B p=0.3333	C p=0.3333
A	83.33	10	0	2
B	80.00	0	4	1
C	66.67	1	3	8
Total	75.86	11	7	11

Table 3: Discriminant Analysis posterior probabilities. Incorrect classifications are marked with red color

Sample	observed classification	A p=0.3333	B p=0.3333	C p=0.3333
A1	A	0.747761	0.136106	0.116133
A2	A	0.254332	0.353628	0.392040
A3	A	0.947213	0.016672	0.036115
A4	A	0.655259	0.101688	0.243054
A5	A	0.532542	0.019216	0.448242
A6	A	0.955437	0.005225	0.039338
A7	A	0.911873	0.053405	0.034722
A8	A	0.402066	0.289925	0.308009
A9	A	0.043692	0.226132	0.730176
A10	A	0.506171	0.373199	0.120630
A11	A	0.542940	0.124729	0.332331
A12	A	0.852108	0.038198	0.109695
B1	B	0.372804	0.400908	0.226288
B2	B	0.018587	0.920414	0.060999
B3	B	0.296839	0.476008	0.227153
B4	B	0.237428	0.227030	0.535542
B5	B	0.007283	0.931357	0.061360
C1	C	0.225127	0.115280	0.659592
C2	C	0.109597	0.429981	0.460422
C3	C	0.100489	0.467385	0.432126
C4	C	0.262143	0.023589	0.714269
C5	C	0.190086	0.376987	0.432927
C6	C	0.089102	0.452247	0.458651
C7	C	0.137772	0.466646	0.395582
C8	C	0.084566	0.066676	0.848758
C9	C	0.016173	0.007096	0.976731
C10	C	0.329109	0.516194	0.154698
C11	C	0.184752	0.396685	0.418563
C12	C	0.759031	0.015455	0.225514

Discriminant Analysis, reveals that group A is the most homogenous in agreement with PC Analysis (Figure 6). This observation is enhanced by the posterior probabilities, which are generally higher for Group A, compared with group B and C. In total, the archaeological classification is 75% correct. 2 out of 12 samples of group A seems to belong in group C, 1 out 5 samples of group B seems to belong also in group C, while 3 samples out of 12 samples of group C seems to belong in group B and 1 in group A.

CONCLUSIONS

- Micro XRF elemental analysis, seems to be rather suitable to characterize ceramic pottery of archaeological importance, by non destructive means
- Statistical interpretation of the data obtained from elemental analysis, derive useful information concerning description, discrimination and provenance of the studied material
- Preliminary discrimination of the material into the three archaeological groups is observed
- The most significant elements causing the discrimination of the samples are Si, Ti, Fe, Sr, Ca and Mn
- Group C seems to be the most homogenous as expected, since the origin of its samples is possibly from Corinth
- More samples are necessary to be analyzed in order to evaluate the studied material with greater validity and to observe clearer discrimination between the three groups

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REFERENCES

[1] J.B. Lambert, in: *Traces of the past—Unraveling the secrets of Archaeology through chemistry*, Perseus Books, Massachusetts, 1997, p. 48., [2] E. H. Bakraji, X-Ray Spectrom. 35 (2006) 190., [3] F. P. Romano, et al., X-Ray Spectrom. 35 (2006) 1.[4] C. Papachristodoulou, et al., Anal. Chim. Acta 573–574 (2006) 347, [5] R. Padilla, et al., Anal. Chim. Acta 558 (2006) 283.