AN X-RAY MICROANALYTICAL STUDY OF RED GLOSS FINE WARE PRODUCED IN ANCIENT CASSOPE

C. Papachristodoulou [1], K. Gravani [2, 3], A. Oikonomou [4], K. Ioannides [1, 3]

[1] *Department of Physics,* [2] *Department of History-Archaeology,* [3] *Archaeometry Center,* [4] *Department of Materials' Science & Engineering*

University of Ioannina, 451 10 Ioannina, Greece

University of Ioannina

INTRODUCTION

Methods of X-ray microanalysis are well-suited for studying the provenance and technology of ancient pottery. Provenance may be assessed on the basis of compositional data obtained by X-ray fluorescence (XRF) spectroscopy. Technological choices, such as the type of raw materials, the firing conditions and the surface coating techniques, are probed by X-ray diffraction and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX).

In this work, an approach integrating the above techniques was used to explore the manufacture technology of red gloss pottery from ancient Cassope (4rth-1rst century BC), Epirus (**Fig. 1**).

A set of 24 potsherds was selected for analysis, considered to represent local pottery production (2nd-1rst century BC), according to a previous compositional study and chemical grouping of a large collection of red gloss pottery recovered from the excavations in Cassope [1].

Fig. 1: A map showing the location of ancient Cassope, in Epirus.

MATERIALS & METHODS

The concentrations of 17 major, minor and trace elements were determined in the ceramic bodies using radioisotope-induced energy-dispersive X-ray fluorescence (EDXRF) spectroscopy.

X-ray diffraction (XRD) patterns were obtained for representative potsherds using a D8 Advance Brüker diffractometer operating with CuKα (λ = 1.5406 Å) radiation and a secondary beam graphite monochromator. Powder samples were scanned over an angular 2θ range from 5 to 60º, in steps of 0.02º (2θ) at a rate of 2 s per step.

Fresh-fractured sections of selected sherds were examined under a field-emission scanning electron microscope (SEM, FEI Inspect F) coupled with an EDX spectrometer. The elemental compositions of the ceramic bodies and surface slips were assessed by scanning five different areas in each case and using a ZAF correction to account for matrix effects.

RESULTS & DISCUSSION

The EDXRF analysis showed that the examined potsherds generally possess a calcareous fabric (see **Table 1**). The ancient potters were aware of the better moulding and shaping properties achieved using calcareous pastes, prepared either by selecting naturally Ca-rich clays or by tempering with calcite. For the production of pottery with surface coatings, high calcium contents were particularly favoured, in order to obtain a light-coloured body, on which a dark decoration ensured a more aesthetic appearance. In addition, calcareous pastes yield fabrics with a particularly stable microstructure over a wide temperature range and, thus, could guarantee a consistent product quality, sparing the need for a strict control of firing conditions.

Table 1: Compositions determined by EDXRF.

Element	M	σ(%)	Min	Max
K (%)	1.51	19.1	0.67	2.28
Ca (%)	6.80	31.0	3.36	10.6
Ti (%)	0.61	17.1	0.37	0.88
Cr	164	22.2	83	253
Mn (%)	0.16	18.7	0.07	0.21
Fe (%)	7.96	10.6	4.95	9.99
Zn	136	22.7	71	225
Pb	54	52.8	8	121
Rb	55	36.7	9	117
Sr	227	19.9	138	328
Y	23	15.0	16	28
Zr	135	15.2	95	165
Nb	16	19.3	10	20
Ba	230	18.1	126	286
La	15	21.1	10	25
Ce	36	10.1	31	44
Nd	10	17.2	8	12

M = average values from 24 sherds; σ = standard deviations (in % of M); Min-Max = concentration ranges. Data in μg g^{-1}, unless otherwise indicated.

Selected XRD patterns are shown in **Fig. 2**. The main minerals identified include quartz (Q), plagioclase (P), potassium feldspar (F) and diopside (D). A firing temperature of at least 850ºC may be estimated for all sherds, based on the development of diopside. Diopside is a high-temperature Ca/Mg silicate that forms upon complete decomposition of primary calcite around 800-850ºC.

Depending on the presence and intensity of the illite/muscovite (I/M) peaks, even higher temperatures - possibly reaching 1000ºC - may be suggested for certain sherds. Minerals of the I/M group decompose between 700 and 1000ºC, although the (110) reflection at 19.8º2θ is not essentially affected below 900-950ºC.

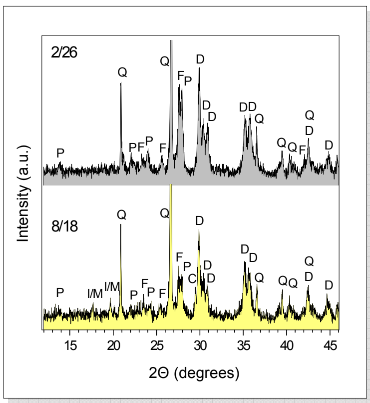

Fig.2: X-ray diffractograms for sherds 2/26 and 8/18. See text for explanation of mineral phases.

SEM examination showed that the sherds possess a fairly regular coating, which, in several places, reveals the underlying body. The coating is well vitrified and varies in thickness from around 8 μm down to 5 μm (**Fig. 3**). The microstructure of the ceramic body exhibits initial-to-extensive vitrification, implying firing temperatures in the range 850-1050°C.

The SEM-EDX analyses point to a decrease of the alkaline earth content and an increase of the alkali content and the Al/Si ratio in the slips compared to the bodies (**Fig. 4**). Depletion of Ca and Mg results from the removal of carbonates, in order to enhance the quality of the slip layer, while K and Na-enrichment is important for promoting vitrification of the surface. Higher Al/Si ratios are consistent with the removal of coarse quartz grains and the increase in the relative amount of clay minerals.

The overall trend indicates that the coating was prepared from a fine illitic suspension, different from the calcareous clay used for the body. Combined with appropriate firing temperatures, the slip composition was adequate to achieve a good quality surface gloss.

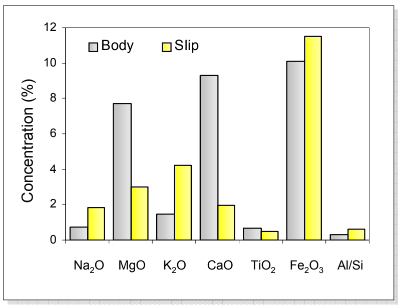

Fig. 4: Comparison between body and slip compositions determined by SEM-EDX.

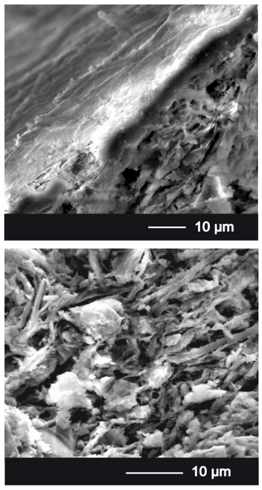

Fig. 3: SEM images of a selected sherd showing the main body and the body-to-slip interface.

References

[1] C. Papachristodoulou, K. Gravani, A. Oikonomou, K. Ioannides, 2009. On the provenance and manufacture of red-slipped fine ware from ancient Cassope (NW Greece): evidence by X-ray analytical methods, *in preparation*.

Acknowledgments

Measurements were carried out at the EDXRF and XRD units, UoI and in the SEM-EDX facility at the Institute of Materials Science, NCSR "Demokritos".

Contact information

E-mail: xpapaxri@cc.uoi.gr
Website: http://omega.physics.uoi.gr