Towards the quantification of trace metals in pottery shards for discriminating different workshops in Southern Italy

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INTRODUCTION

The technology of production of red-figured pottery found at Locri Epizephiri (Southern Italy) has been under study for more than 10 years [1, 2]. The numerous vases and fragments excavated on the site were attributed to Attic or Southern Italian (mainly Locrian or Sicilian) workshops on grounds of stylistic criteria [3]. Previous archaeometric studies by means of SEM-EDX and ICP-OES analyses [4, 5] unveiled a pattern, based on major elements concentrations, that allows discriminating between the Greek and the Italian origin.

Instead, provenance markers for distinguishing Calabrian from Sicilian samples could lie in the trace element composition of the very thin vitrified gloss on the pottery shards. It is in fact reasonable that different workshops would have used raw materials from different sources to obtain their products; considering the different geological contexts of the two areas as well, this would in turn lead to a different trace composition of the coating.

With such a small target – as the coating layer measures only some 20 microns in thickness – a microbeam is then mandatory for performing PIXE quantitative analysis.

EXPERIMENTAL

The 8 pottery samples (3 Attic, 3 Locrian and 2 Sicilian) analysed in this work were small shards prepared as cross sections: embedded in resin, they have been polished to expose the interface between the coating layer and the body and then carbon-coated to make them conductive.

Micro-PIXE measurements were carried out at the AN2000 microbeam facility using 2 MeV protons. The focused beam was about 5 μm in size and the current detected on sample during acquisitions was ~ 1 nA. An aluminium funny filter [6] with a small hole in the centre was placed in front of the detector window in order to analyse both light and heavy elements.

The optimal procedure for the analysis of the black slip was developed. Firstly, a wide map of the surface of the shard is acquired in raster scan mode; then the area is reduced to a 50×50 μm^2 square, focused on the coating layer that is easily detectable from the iron elemental map (figure 1). The spectrum destined to quantitative processing is then acquired over a 50 μm X line that runs along the coating layer. At least three line acquisitions in different positions are performed on the gloss for each sample, alongside with an additional point on the ceramic body for comparison.

For calibration purposes in the quantitative approach, two certified ceramic standards (NIST 98b and SARM 69) have been additionally measured in the same way. The standards, originally in powder form, have been prepared as pressed pellets and heated at 900 °C, the maximum firing temperature estimated for the pottery in study [4].

RESULTS AND DISCUSSION

Preliminary observations of the maps for major elements (figure 1) confirm the general trend already identified for vitrified clay slips: a lower content of silicon, calcium and sometimes magnesium and a higher content of aluminium, iron and potassium in the slip with respect to the body [4].

A qualitative comparison of the gloss spectra, normalised on Fe content, shows some intensity differences between Attic and Southern Italy samples (a representative example is reported in figure 2). The chlorine signal often detected is due to the embedding resin composition and can be neglected. Markers for the discrimination of Locrian samples from Sicilian ones could be identified in Cr, Ni, Cu, Sr and Zr, but a more accurate distinction will be achieved with the completion of the quantitative analyses in progress.

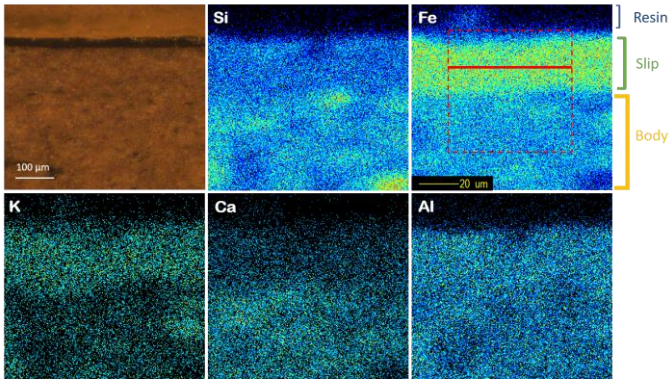

Fig. 1. Optical microscope image of the sample in cross section (top left) and μ-PIXE acquisitions on the black slip. Fe maps are used for guidance and the final data are acquired along the 50 μm-long red line. All reported PIXE maps are equally scaled.

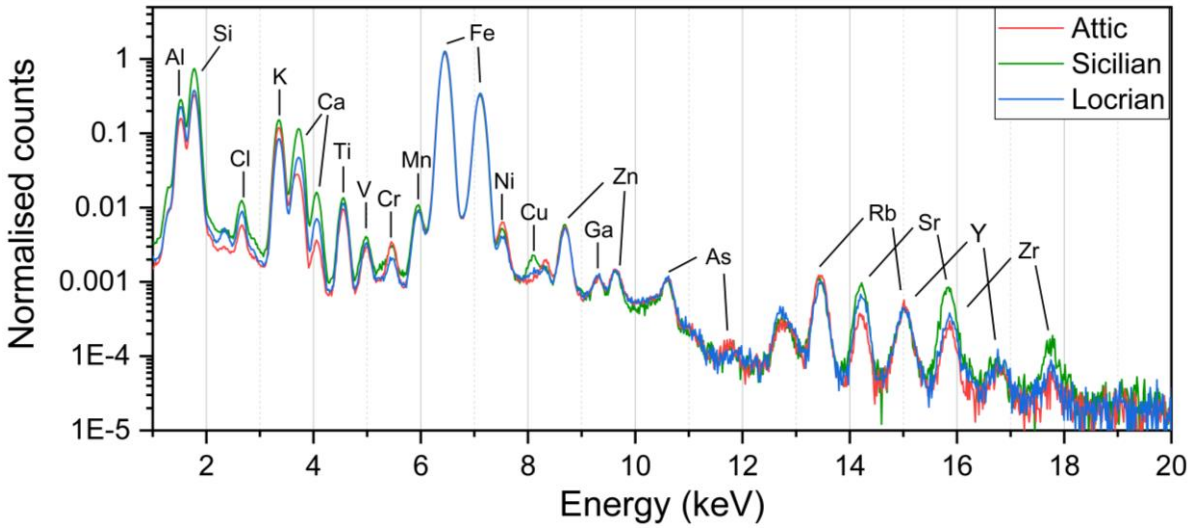

Fig. 2. Comparison of representative μ-PIXE spectra of black slips for the three different pottery provenances taken into account. Spectra in logarithmic scale are normalised on Fe counts to enhance possible differences in trace elements.

CONCLUSION

Micro-PIXE measurements have been carried out on red-figured pottery shards to identify trace elements as markers for manufacturing workshops discrimination. The optimal analytical approach, to be used also in future measuring sessions, has been determined. Moreover, from preliminary qualitative results, differences in concentration for metals such as Cr, Ni, Cu, Sr and Zr arise. The ongoing quantitative analysis of the data, supported by a calibration with standards, will possibly clarify the role of these and other trace elements in the differentiation between Locrian and Sicilian workshops.

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