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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Black Gloss Technology in Athens during the Classical Period: A Scanning X-ray Microscopy and Full-field TXM-XANES Investigation	**Experiment number**:
Beamline:	**Date of experiment**: from: 16 July 2014 to: 22 July 2014	**Date of report**:
Shifts:	**Local contact(s)**: Marine Cotte and Bernhard Hesse	*Received at ESRF:*

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Florian Meirer – Uni. of Utrecht

Report:

Below is a summary results from July2014 experiment – HG27 - on ID21.

There was a vacuum fault in the beginning, but the ESRF staff caught it quickly and got the beamline up and running promptly. Thanks to preliminary transmission images of sample thin-section, acquired at a few energies around Fe K-edge, we also discovered that some of our samples were too thick to allow X-Ray Absorption Near Edge Spectoscopy (XANES) acquisition in transmission mode, as mandatory for full-field XANES measurements in ID21 geometry. Again ESRF staff provided access to a lab and polishing equipment and we were able to thin most of the samples. With the loss of the time at the beginning, added to that 12+ hours it would take to switch back to scanning fluorescence mode, plus the superb quality of the full-field data we were getting, we decided to stay with the full-field measurement mode for the entire beamtime.

Our goal was to infer the various critical technological processes that must have been utilized to produce the iconic red-black Athenian pottery via detailed materials characterization. Furthermore, by tracking the variation in the material mineralogy and morphology we were hoping for a glimpse into how contemporary competing workshops innovated and modified the basic black gloss technology.

In pursuit of the above goals we collected full-field XANES datasets around the Fe K-edge on 29 cross-sections of Greek pottery sherds.

a) There were three early pieces from late 6th century BCE; one from Corinth and two from Athens, but from black-figure vessels.

b) Thirteen of the sherds were from the early 5th century BCE, attributed to 5 contemporary red-figure workshops located in Athenian Kerameikos.

c)The remaining thirteen pieces were from late 5th century to 3rd century BCE. Two of these pieces were Faliscan (Roman) and Apulian (Southern Italy), but the rest were from an excavation from present day Lattes in southern France, but are believed to be imports from Athens.

This is the first exemple of such vast XANES spectroscopic study concerning ancient ceramics made possible thanks to fullfield capabilities. We, in effect, collected upwards of 20 million XANES spectra on large sample areas and sample corpus sizes. Consequently, data treatment necessitates unsupervised and machined learned datamining approaches and protocols (that may find use in other fields besides the characterization of ancient ceramics), explaining why data processing and analysis are at an early stage.

Preliminary analysis, using Principle Component Analysis (PCA) combined with k-means clustering, and least square linear combination fitting (LCLS) [1], of these datasets have lead to at least three new discoveries. These will be presented at two upcoming conferences – SR2A in Paris in early September 2014 and Materials Science and Technology conference in Pittsburgh in October 2014. We hope to write at least two peer review articles by December 2014 based on these discoveries.

In the following we will briefly discuss our discoveries in three sub-sections: 1) suprisingly complex production protocol employed by the early 5th century Athenian workshops, 2) red slip background in a vessel attributed to Berlin painters, and 3) red-on-red misfires. We will also include data analysis steps into these discussions.

Complex Production Protocol of the Early 5th Century Athenian Workshops:

The result with the widest scope was the discovery that the black gloss (BG) slip from the early 5th century BCE Athenian workshops (see above group a) stands out from the earlier pieces and some of the later pieces as well. The BG slips on these sherds are smoother in surface, thicker and laterally more homogeneous than the slips from the earlier period (group b). And surprisingly, many of them appear to be composed of two distinct layers, based on Fe oxydation states. See Figure 1 for a comparison between one of these sherds (from the workshop of Douris) and an earlier Corinthian piece.

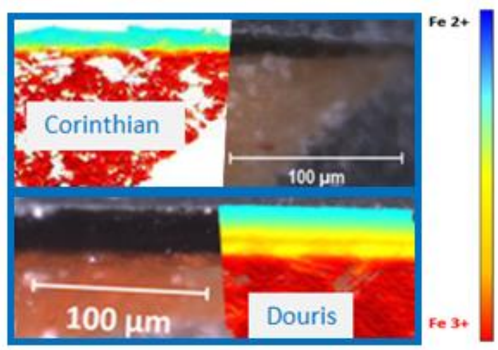

Figure 1: Comparison of BG cross-section from a sherd from Corinth and Douris. Fe valence map and corresponding optical image is shown side-by-side in the same panel.

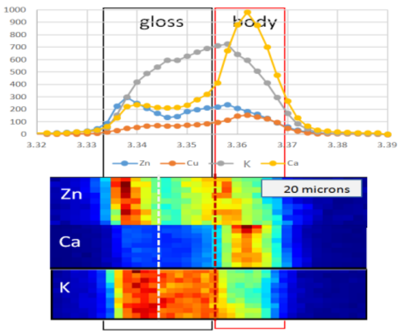

Figure 2: Elemental map (jet color map) from a BG cross-section from a sherd from Brygos obtained via μ-XRF.

Preliminary low resolution (2μm x 2μm) XRF maps (collected at Stanford Synchrotron Radiation Lightsource) on a subset of three of the sherds attributed to the Brygos workshop show a small, but distinct, variation in the concentration of a few trace elements, suggesting the application of two different slip layers (cf. Zn map in Figure 3). This hypothesis is supported, in some of the sherds, by a very narrow oxidation layer between the two main slip layers (e.g., the narrow orange line in Douris in Fig. 2). This could either suggest that a diffusion gap opened up between the two slip layers, but, because of the absence of a visible crack, it more likely suggests that an oxidative firing step separated the application of the second slip from the first.
These results supplemented by low resolution XRF images from SSRL and micro-Raman measurements at selected locations and will be presented at MS&T 2014.

High resolution elemental and tomographic imaging is needed to confirm or confute the existence of two slip layers, and the presence of microcracks at the interface in all pieces from the late 5th century Athens.

Red Slip under Black Slip in Berlin painter Vessel: Multiple Firings:

Out of 25 sherds, we found two unusual pieces where the black decoration was painted on a red slip instead of the body. The first piece was attributed to the early 5th century workshop of Berlin Painter (group b). The second piece was excavated from Lattes (group c) and is unattributed so far. Figure 3 shows the sherd (in a), optical image of the cross-section (b), Fe valence map (c), three Fe-based phases that best match the chemistry (i.e. hercynite, hematie and maghemite) (d), and the corresponding phase map obtained after LCLS fitting using (d) as references(e).

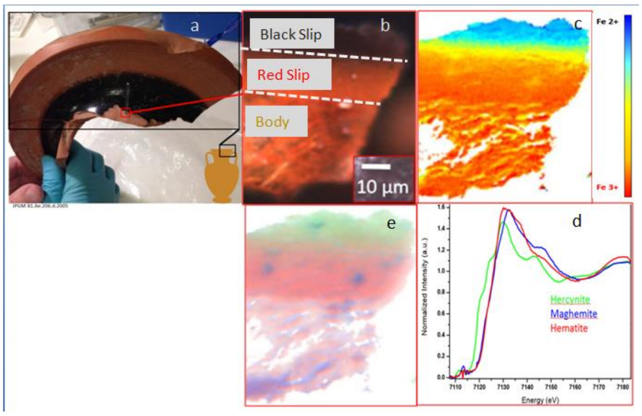

Figure 3:a) Sherd attributed to Berlin Painters showing black slip on red slip, and the location of the cross-section, b) optical micrograph of the cross-section, c) the corresponding Fe oxidation map, d)XANES spectra for the three main phases, and e)LCLS fit indicating that the black slip is mosrly hercynite, the red slip is mostly hematite and the body is mixture of hematite ands maghemite.

Replication and other results suggest that these pieces must have been fired twice, as schematically shown in figure 4 to achieve the mineral phases and the observed distribution. These results will be presented at SR2A.

Figure 4:A schematic two stage firing sequence, first at high temperature followed by application of the second slip and conventional three-step firing sequence needed to produce the mineralogical phases and distribution seen in Figure 3.

Both of these results suggest that the Athenian workshops employed a complex production protocol - involving multiple applications of slip and multiple firings; a production protocol which is claimed as economically unfruitful by established thinking. We are working closely with art historians and conservators, investigating different production protocols in order to establish a deeper understanding of why these pieces were subjected to such an elaborate and economically unsustainable production path way.

Red-on- Red Misfires:

We also looked at a sample (C35) from Lattes (group c) that appears to have a red slip applied on the red body in order to answer the question whether the slip was meant to be black but the piece was misfired, or the creation of red slip was intentional (as in the case of the bottom slip in the sherd attributed to Berlin painters – discussed above.)

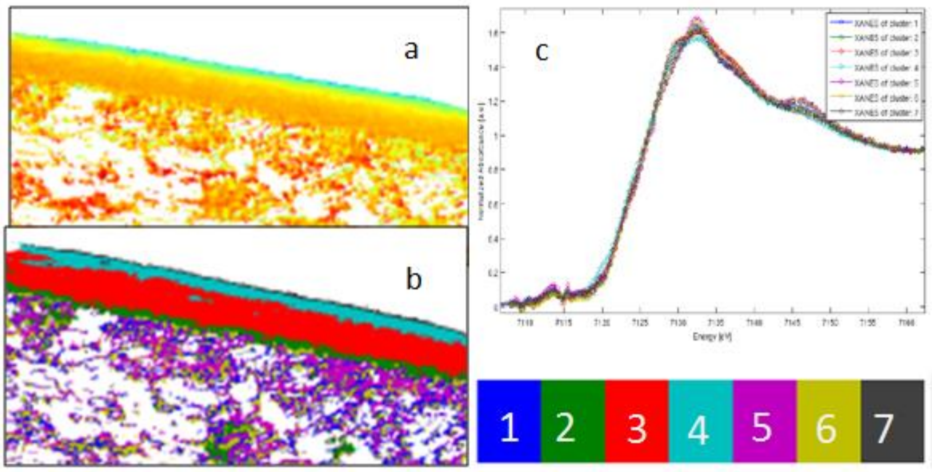

Figure 5:

Fe oxidation state analysis (Fig. 5a) indicates that the surface of the sherd is just slightly reduced in comparision to the rest of the slip and the body. Image segmentation based on XANES similarity using the first three principal components and Gaussian Mixture Modelling (GMM) for clustering in PC space results in the map shown in Fig. 5b. XANES of corresponding clusters are shown in Fig. 5c. (See ref 1 for some of the details on unsupervised datamining of these large multi-dimensional data sets. The segmentation and the corresponding XANES spectra high-light three salients features of this sherd. The first salient feature is that there is not a very significant oxidation or mineralogical differentiation between the body and the bulk of the slip. The second salient feature is that the XANES spectra for cluster 3 (red) has a doubled peaked whiteline, which is a distinctive signature for hematite. Replication studies have indicated that the hematite phase is produced when the sherd is fired in oxidizing conditions at temperatures higher that 900 °C. And finally the thin and just barely reduced surface phase suggests that the sample was subjected to reducing firing conditions. However, measurements of surface densification are needed – either via nano scale tomographic reconstructon or TEM analysis – to confirm that this sample was intended to have a black slip, but was accidentally misfired.

References:

1. F. Meirer, Y. Liu, E. Pouyet, B. Fayard, M. Cotte, C. Sanchez, J. C. Andrews, A. Mehta, and Ph. Sciau, *J. Anal. Atomic Spectro.*, DOI: 10.1039/c3ja50226k, 2013