ESRF	**Experiment title:** Manufacturing process of marbled terra sigillata: a full-field TXM-XANES study on thin cross-section of roman potteries at the Ti and Fe K-edge	**Experiment number**: HG-20
Beamline: ID21	**Date of experiment**: from: 20/11/2013 to: 25/11/2013	**Date of report**: 28/02/2014
Shifts: 15	**Local contact(s)**: Marine COTTE	*Received at ESRF:*

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Report:

The first shift was used for the set-up of the configuration for elemental maps with a submicron (0.2x0.6 μm^2) beam focused on the sample. The energy calibration was defined using both Fe (max. of 1st derivative at 7110.75 eV) and Ti (max of 1st derivative at 4966.40 eV) foils in order to fit with the ALS databases [1].

Before the recording of elemental maps this configuration was used to record the XANES spectra of the references (1/2 shift): rutile (Ti edge), anatase (Ti edge) and pseudobrookite (Ti and Fe edges). Then 4.5 shifts were used for XRF mappings on archaeological samples. 5 samples were investigated and for each, 4 zones, including body and slip, were scanned. The results obtained from one zones of the TSGM-D sample are shown in Fig.1.

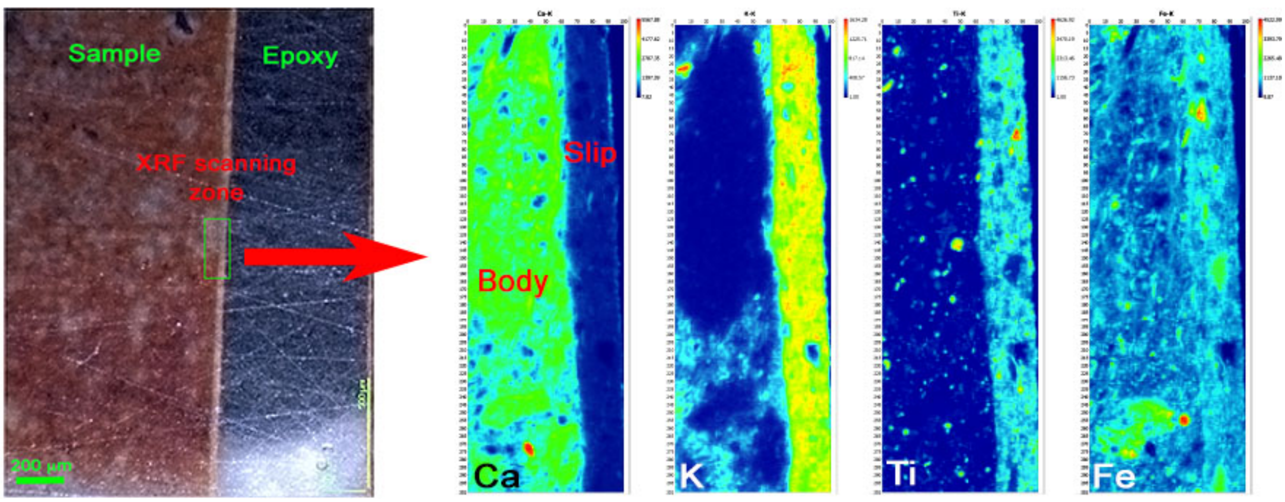

Fig. 1 XRF scanning of a zone of a marbred terra sigillata sample and the obtained elemental maps with a beam energy of 7.2 keV.

The results reveal that the yellow slip of marbled Terra Sigillata was characterized by high Ti and K concentrations and is in agreement with previous studies. The body, similar to the body of classical Terra Sigillata, contains Ca (around 10% in CaO wt.) but the slip is not enriched in Fe as it is in the classical red slip Terra Sigillata, which contains twice the amount of iron. Acquisition with higher resolution was also carried out on some zones to precisely locate the distribution of Fe and Ti in the slip.
Because all analyzed samples showed similar results, XRF mappings were limited to 5 samples and the other shifts were used for TXM XANES investigations (½ shift to set-up and 8.5 shifts to data acquisition). Because of motor problems one shift was lost and finally only 6 samples could be analysed, with two areas for each, both at Ti and Fe K-edges. The data collection at the Ti K-edges took longer than expected; two to three times longer than at the Fe edges due to the lower Ti concentration and non-optimal sample thickness. The sample thickness was optimized for Fe but that meant it was too thick for Ti; an inherent problem for an investigation needing mineralogical data from the same areas collected at two different x-ray energies with significantly different penetration depths.
Part of the data processing was performed during the experiment and in particular the image alignment procedure using the open source software package PyMca. Then the TXM wizard software was used to obtain maps of iron and titanium valences and mineral phases as described in detail in ref [2] for Roman pottery [2]. Figure 2 shows the result for one marbled Terra Sigillata sample at the Ti K-edge. This result shows clearly that the pseudobrookite (PS) is mainly distributed in the slip while the large titanium grains in the body are essentially rutile (R), suggesting that iron and titanium were more closely mixed in the raw clay used for the slip than that used for the body. In addition, from mineral mapping we were also able to deduce that the firing temperature was sufficiently high (≥1050°C) and atmosphere sufficiently oxidizing during both the heating and cooling steps to form and retain pseudobrookite in the slip and the atmosphere was oxidizing both during the heating and the cooling steps. The data processing of the other maps is currently in progress.

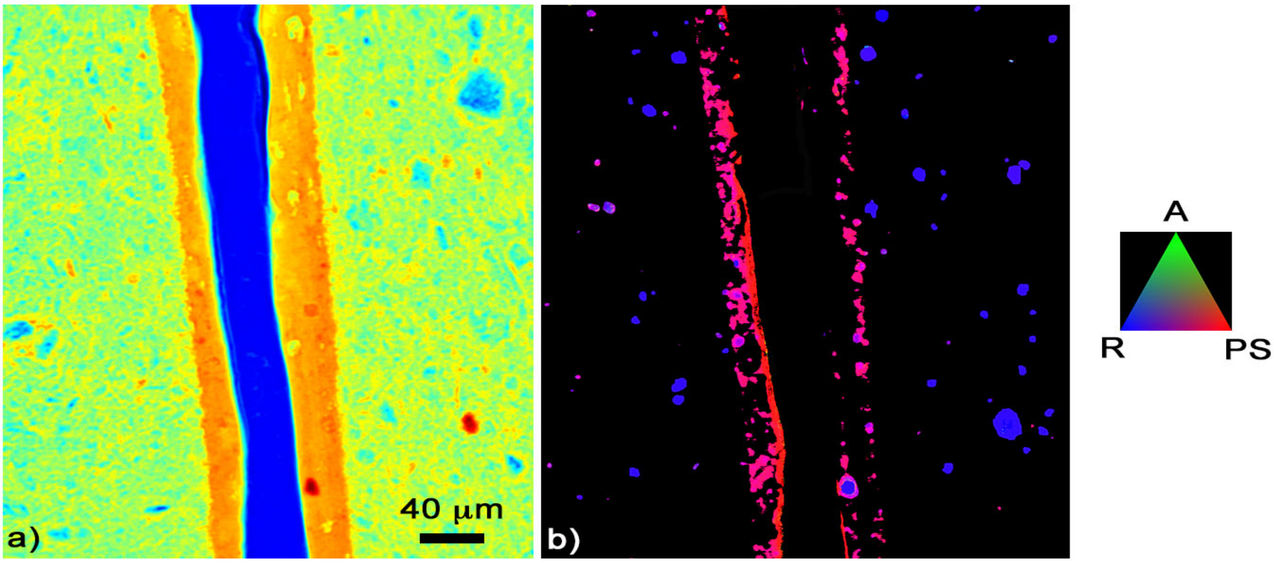

Fig.2 TMX image at 5.2 keV (a) and (b) Ti phase maps deduce from the full-field experiment at the Ti K-edges.

Reference

[1] http://xraysweb.lbl.gov/uxas/Databases/Overview.htm
[2] Full-field XANES analysis of Roman ceramics to estimate firing conditions—A novel probe to study hierarchical heterogeneous materials. F. Meirer, Y. Liu, E. Pouyet, B. Fayard, M. Cotte, C. Sanchez, J. C. Andrews, A. Mehta, Ph. Sciau (2013). J. Anal. At. Spectrom. 28 (12), 1870–1883 (DOI: 10.1039/c3ja50226k).