EUROPEAN SYNCHROTRON RADIATION FACILITY
ESRF User Office
BP 220, F-38043 GRENOBLE CEDEX, France
Delivery address: 6 rue Jules Horowitz, 38043 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Application for beam time at ESRF – Experimental Method

Aims of the experiment and scientific background

Ancient ceramic was very often covered by a substance which was deposited for protection or decorative purposes. What do we learn when studying this layer located on top of an ancient ceramic? This questioning is part of a research programme (Communauté de Travail des Pyrénées) which started in March 2004 and gathers the following European regions around the Pyrenees: Aquitaine, Aragon, Catalonia and Midi-Pyrenees. This research programme is dedicated to the study of thin decorative layers covering ceramics of Antique times. The goal is to combine physical and chemical analyses for studying these decorations, at the micrometer scale. This archaeometric investigation aims at bringing complementary data to the former approach archaeologists can carry.

Previous studies (at Barcelona, Bordeaux, Toulouse, Saragossa) have shown that this thin layer of decoration has, in the majority of cases, turned to glass but also includes new generated crystals (nanometric to micrometric size), unmelted crystals, holes due to gas desorption. Moreover the interface which is located in between the so-called glaze and the earthenware seems to provide new data regarding the firing conditions and more generally the technical know-how of ancient potters.

In this application we intend to answer to the following: i) what type of adhesion is there between the decorative layer (glaze) and the substrate (earthenware) ? ii) can we interpret the nature of crystals located at the interface glaze/substrate ? ii) Do these crystals provide information on the firing processes of the ceramic object?

Figure 1 presents a SEM-EDX-CL (cathodoluminescence) study (published) showing data obtained with cross-section of a glazed ceramic of Islamic period (12th c. AD, Portugal). The BSE image is focusing on the glaze and its interface with the substrate. It indicates clearly the paste (black), the glaze (white), some crystals inside the glaze (black) and holes (black). EDX mapping (left in fig 1) show that some cations have been exchanged between the paste and the glaze during firing (Ca, Fe, Pb). CL spectrometry (right in fig 1) suggests that some crystallized zones are mixed with non-crystallized ones at the interface (the more intense and well defined the signal, the more crystallized the area). Investigation is also carried out on laboratory-made samples. Figure 2 shows a detail of the interface glaze-substrate in SEM. Raman spectrometry (fig 3) indicates the possible nature of the crystals. SR facilities will help in providing an interpretation for the nature of the crystals and the nature of the impurities, thanks to its better spatial resolution and lower detection thresholds.

Experimental

1- X ray fluorescence (with lower thresholds than with SEM-EDX) for chemical speciation
2- X ray diffraction patterns on spots of around 3 microns to identify the phases and assess the crystallinity.

A series of ancient ceramics and lab-made samples need to be investigated: 4 ancient ceramics (10th-12th c. AD from al-Andalus, i.e. Spain and Portugal; see fig. 1); 4 modern reproductions (with known parameters such as firing conditions and nature of the raw materials used for the substrate and the glaze)

5 line profiles (length~100 microns each, 3 microns step and resolution) per sample are needed in both XR fluorescence and diffraction across the interface

Beamline requested = ID22 or ID18F

# of shifts requested = 6 (2 for alignment and 0,5/sample)

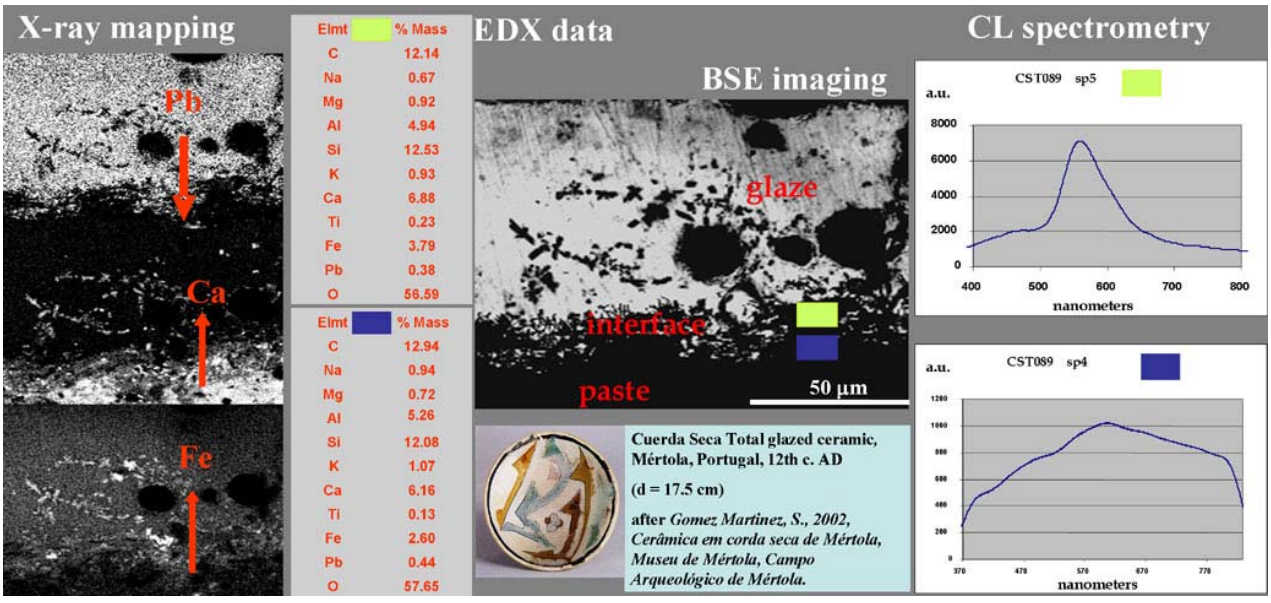

Fig 1: SEM-EDX-CL of a cross-section of ancient glazed ceramic

Expected results

Identification of the crystals located at the interface glaze/substrate

Localization of crystallised / non-crystallized areas at the interface glaze/substrate

Interpretation of the manufacturing process : number of firings, top temperature of firing

Explanation of the adhesion between the glaze (glass) and the ceramic substrate.

Focus

Analysing the devitrification crystals present at the glaze/substrate interface of double and single fired samples enables to discriminate the firing process (one or two sessions of). In the doubled fired sample, only one type of silicate crystals is found: a lead containing pyroxene. In the single fired sample, two types of crystals are observed: high lead containing white crystals identified as feldspars and grey crystals which appear to be a mixture of feldspars and pyroxenes.
The next step is to make a µ-XRD profile under X-ray synchrotron radiation on the very same zone.

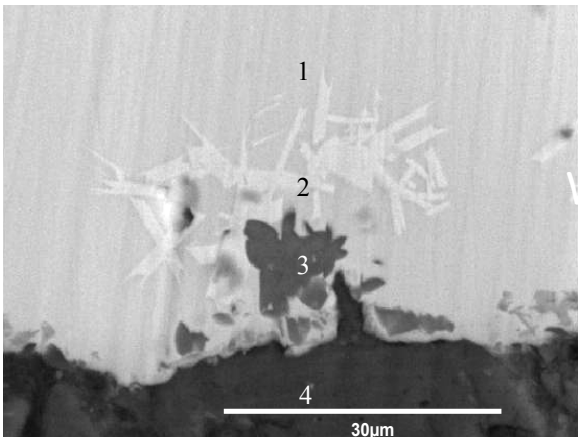

Fig. 2: BSE image of the glaze/substrate interface of a single fired sample. 1: glaze; 2: white crystals; 3: grey crystals; 4: ceramic substrate

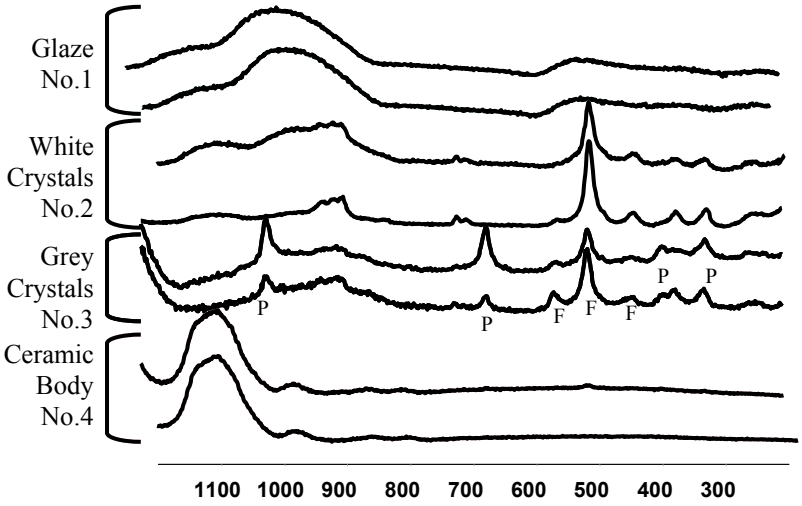

Fig. 3: Characteristic Raman spectra (633nm laser) of the different zones in Fig. 1 at the glaze/ceramic substrate interface of a single fired sample. The four peaks P at 323, 387, 665 and 1014 cm^{-1} are characteristic of pyroxene ($XY(Si, Al)_2O_6$). The three peaks F at 480, 513 and 558 cm^{-1} are characteristic of feldspars ($XAl_{Si}3O_8$ / $YAl2Si_2O_8$)

The consequences are of interest in the knowledge of the production technics (History of Technics), and also in the field of conservation of ancient ceramics. Alteration processes would find some interpretation when considering the quality of adhesion between the different materials involved in a ceramic. **The results will take place in the PhD of Claire Pacheco, dedicated to the study of interfaces in ancient ceramic decorations.**

References from the teams involved in the research programme

- Molera, J.; Pradell, T.; Salvadó, N.; Vendrell-Saz, M., 2001, Interaction between clay bodies and lead glazes during firing *Journal of the American Ceramic Society*, 84 (5), 1120-1128.
- Ph. Sciau, L. Vendier, E. Dooryhee, 2002, La diffraction des rayons X est-elle adaptée à l'étude des engobes des sigillées. In Céramiques de la Graufesenque et autres productions, Hommages à Bettina Hoffmann (dir. A. Verhnet, éditions monique mergoil,), 171-179.
- L. Vendier, Ph. Sciau, E. Dooryhee, 2002, Etude par diffraction des rayons X des vernis rouges des sigillées du sud de la Gaule. Les ateliers de la Graufesenque. J. Phys. IV France 12, Pr6, 189-196.
- T. Pradell, J. Molera, J. Roque, M. Vendrell-Saz, A. D. Smith, E. Pantos and D. Crespo , 2005, Ionic-Exchange Mechanism in the Formation of Medieval Luster Decorations, Journal of the American Ceramic Society, 88 (5), 1281
- Chapoulie R., Déléry C., Daniel F., Vendrell M., 2005, Cuerda seca ceramics from al-Andalus, Islamic Spain and Portugal (10^{th}-12^{th} c. AD). Investigation with SEM-EDX and Cathodoluminescence, ARCHAEOMETRY, 47, 3, 519-534.
- R. Chapoulie, F. Daniel, Cathodoluminescence in Archaeometry through case studies: classification of Chalcolithic ceramics from Syria, English glass stems (XVI-XVIIth c.AD), and glass/paste interface of glazed Islamic ceramics (X-XIIth c.AD). In Proceedings of 35^{th} International Symposium on Archaeometry, Saragossa, 3-7 may 2004, *in press*