ESRF	**Experiment title:** The Role of Fuser Metals in the Ageing of Tile Glazes: a Problem in Conservating an European Cultural Heritage	**Experiment number:** CH-621
Beamline: ID22	**Date of experiment:** from: 4-Feb-99 (7h) to: 7-Feb-99 (7h)	**Date of report:** 25-Feb-2000
Shifts: 9	**Local contact(s):** A. Simionovici	*Received at ESRF:* - 3 MAR. 2000

Names and affiliations of applicants (* indicates experimentalists):

- M.O. Figueiredo*, Cryst. Miner. Center / IICT & CENIMAT, Materials Science Dept., New University of Lisbon (UNL), Caparica, Portugal
- J.P. Veiga*, CENIMAT, Materials Science Dept., FCT / UNL, Portugal
- J. Mirao*, Geosciences Dept., University of Evora, Portugal

Report:

The aim of the experiment was essentially *to study the speciation and coordination environment assumed by metallic elements added as fusers and cromophores* in the manufacture of blue-and-white glazes applied in Portuguese artistic tile panels from the 17th and 18th centuries as well as those incorporated in archaeologic glass beads of unsual format whose origin and period of manufacture are still uncertain [1].

Amongst the fusers, the most used metals were lead and zinc, the latter assumed to enter the silica glass as a substitute for silicon in the vitreous tetrahedral framework.. Nice blue colourings have been attained by adding to the glass/glaze variable amounts of either copper or cobalt, depending on the material itself but also on the period of manufacture. Therefore, the type of cromophore may be an important feature in dating the cultural artifact under study. Accordingly, XAFS experiments were at first focused on the *crystalchemical role of zinc and copper in tile glazes and copper-rich glass beads.*

The BFO of ID22 microprobe assured the focusing the monochromatic beam on a suitable spot size over the sample. XRF spectra were first collected using an excitation energy of 11 keV to allow for the selection of useful areas to be irradiated for XAFS experiments.

Model compunds for various zinc and copper speciations and coordinations were studied: metallic zinc (Zn^0), zincite (ZnO, with Zn^{2+} in tetrahedral coordination), smithsonite ($ZnCO_3$, with Zn^{2+} octahedrally surrounded by oxygens), cuprite (Cu_2O, a framework of $[O^tCu_4]$ tetrahedra with Cu^+ in linear coordination) and covellite (CuS, with copper atoms in both tetrahedral and triangular coordinations by sulphur).

Five glaze samples of blue-and-white tiles and one of white glaze were analised, together with two multilayer glass beads (blue and green, described elsewhere [2]). A total of 14 XRF and 21 XAFS spectra have been collected.

K-edge XANES spectra were collected with success on various points of each sample displaying different colouring intensities and variable degrees of ageing. For the moment, attempts to obtain good EXAFS spectra were less effective.

Fig 1 compares the Zn *K*-edge XANES spectra of model compounds with two spectra from blue-and-white tile glazes dating from the 16th century (AZ-8) and the 17th century (AZ-26). Zinc was foreseen to have tetrahedral coordination in amorphous (according to XRD data) glazes like the sample AZ-26; conversely, an octahedral environment was expected for the partially crystalline glaze AZ-8. These expectations appear to be confirmed by XAFS data.

Fig. 2 illustrates Cu *K*-edge XANES spectra obtained for the two model compounds, for a blue glass bead (ref. RPN/92/2084) with three concentric layers of varied colouring intensity and also for an externally green bead with starshaped polycrome cross section (RPN/96/6000). The crystalchemical situation of copper atoms hosted in these old glasses seems to differ from the studied minerals in speciation and/or coordination. Indeed, a clearly perceptible detail in the edge ramp and the post-edge oscillation features do not appear in the XANES spectra of selected model compounds.

A publication at present under preparation will report on these conclusions.

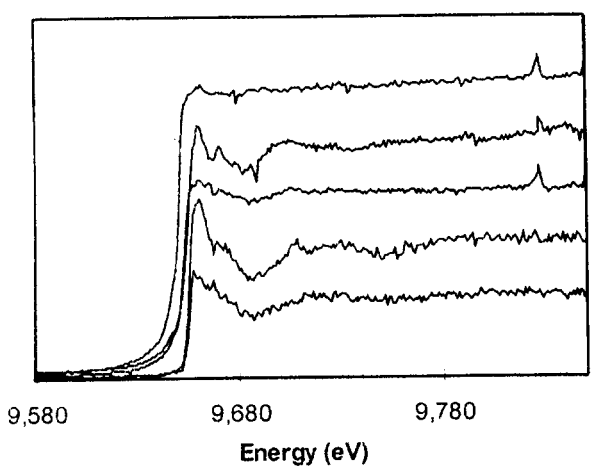

Fig.1 - Zn *K*-edge XANES spectra. Top to bottom: zinc metal, $ZnCO_3$, ZnO glazes AZ-8 and AZ-26 .

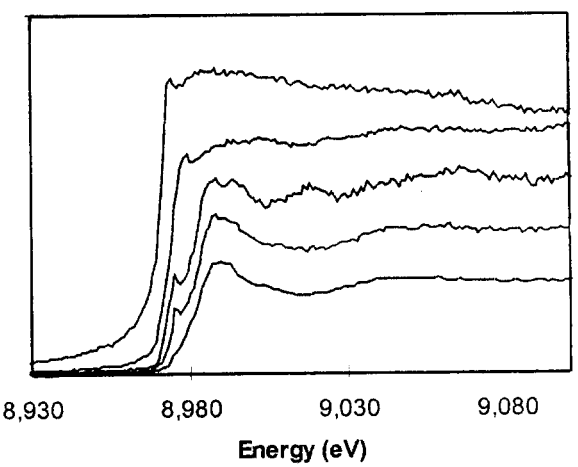

Fig 2 - Cu *K*-edge XANES spectra. Top to bottom: Cu_2O , CuS , beads nr. RPN/96/6000 (red and green layers) and nr. RPN/92/2084 (blue layer).

References

[1] FIGUEIREDO, M.O., VEIGA, J.P. & PEREIRA da SILVA, T. (1999). *Non-destructive chemical characterization of cultural materials using synchrotron radiation X-ray fluorescence*. Proceedings ART'99 - 6th International Conf. on "Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage", Rome/Italy, Vol. 3, 1767-1779.

[2] RODRIGUES, M.C. (1999). *Contributions for the study of glass beads of mediterrannean origin collected in Lisbon ("Baixa Pombalina")* In Portuguese. Proceedings II Thematic Colloqium "Lisboa Ribeirinha", July 1997, Edt. Lisbon City Hall, 197-225.