1st Portuguese Meeting
SYNCROTRON RADIATION USERS _ ENURS
January 2012, CENIMAT – FCT / UNL, Caparica, Portugal

CHROMOPHORE BEHAVIOUR OF IRON, COPPER, COBALT AND ANTIMONY IN ANCIENT TILE, FAIENCE AND PORCELAIN GLAZES PLUS ARCHAEOLOGICAL GLASS BEADS: AN OVERVIEW ON X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPY STUDIES

M. ONDINA FIGUEIREDO[1,2]*, JOÃO P. VEIGA[1], TERESA P. SILVA[2]

[1] CENIMAT / I 3N, Fac. Sci. & Technology, New University of Lisbon, 2829-516 Caparica,
[2] LNEG, Unit of Mineral Resources & Geophys., Apartado 7586, 2610-999Amadora, Portugal
*mof@fct.unl.pt

ABSTRACT: The modern X-ray sources available at large-scale installation facilities allow for the study of materials through powerful chemical and structural characterization techniques, particularly X-ray absorption spectroscopy. Along the last decade, the non-destructive characterization of a diversity of cultural materials – glazed ceramics (decorated tiles, faiences, porcelains) and glasses (archaeological glass beads) – as well as pigmenting natural materials, has been performed at the ESRF (European Synchrotron Radiation Facility) in Grenoble/France with the support of EU. The electronic situation of chromophore ions and fuser metals was assessed by analyzing the details observed in X-ray near-edge absorption curves (XANES spectra) collected from the subject elements. A brief overview is presented on recently published results.

Keywords: Tiles; glazes; chromophore elements; XANES

1. INTRODUCTION

Synchrotron radiation sources nowadays available at large-scale installations allow for the study of materials through powerful chemical-structural characterization techniques, particularly X-ray absorption spectroscopy.

Using the instrumental setups of beam-lines ID22, ID21 and BM29 (actual BM23) at the ESRF (European Synchrotron Radiation Facility, in Grenoble/France), non-destructive analyses and structural characterization of a great diversity of materials – ceramics, glasses, gems and pigmenting nanominerals – have been performed along the last decade.

The electronic (and eventually magnetic) situation of the constituting atoms in a given material is assessed through the analysis of features and details observed in the near-edge region of X-ray absorption curves (XANES). Conversely, the fine-structure analysis and the theoretical modelling of post-edge oscillations in the extended region of these curves (EXAFS) allow for disclosing information about the number of closest neighbours around the absorbing element in the host material.

A brief summary is presented of the results attained in this domain, focusing particularly the fine-structure analysis of near-edge absorption spectra.

2. EXPERIMENTAL AND RESULTS

The key-factors influencing multiple scattering effects in X-ray absorption experiments – that is conditioning the lay-out of collected XANES spectra – are mainly the symmetry of the structural site occupied by the absorber (particularly the absence of a symmetry centre), the nature and charge(s) of the ligands, and the bond distances.

The present overview focus the results of X-ray absorption experiments performed at the *K*-edge of chromophore transition metals – Fe [1,2], Cu [3,4], Co [5,6], – and at the *L*-edge of antimony [7,8]. The role of fuser metals used in the manufacture of ancient glazes – Zn [9] and Pb [10] – is addressed as well.

The FEFF 8.10 Code [11] was applied with success to simulate XANES spectra on the basis of a theoretical multiple diffuse scattering approach and to compare the simulations with experimental data.

2.1. Iron in mineral pigments

The colourings provided by iron are nicely illustrated by the mineral beryl (ideally $Be_3Al_2Si_6O_{18}$). This mineral displays a remarkable set of gemmological varieties and the role of iron was successfully studied by X-ray absorption near-edge spectroscopy to ascertain the speciation state of the chromophore element [1].

Such spectroscopic approach to the colouring by iron was recently extended to a natural blue pigment, vivianite [2]. The interest on blue iron minerals as pigments for painting was enhanced with the use of vivianite – an hydrated ferrous phosphate $Fe_3(PO_4)_2.8H_2O$ – which in medieval Europe became an alternative to the expensive *lapis lazuli,* with simplified formula $(Na,Ca)_4(AlSiO_4)_3(SO_4,Cl,S)$.

2.2. Copper in archaeological glasses

Let us start by addressing the chromophore role of copper, a metal that originates a great diversity of colourings either in natural compounds (minerals) or in synthetics.

As a contribution to the question about the origin of red coloured ancient soda-lime glasses, an archaeological glass bead from the 16th century was extensively studied [3,4]. This twisted tubular "rosette"-type bead is composed of five layers (fig. 1): external, green; intermediate "rosette", white-red-white; internal, bluish.

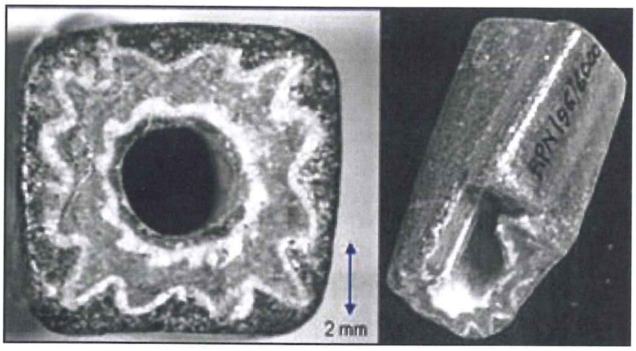

Fig. 1. Two views of the twisted tubular "rosette"-type archaeological glass bead found in 1996 during the excavations conducted in Lisbon Old-City to extend the Underground.

Cu 1*s* XANES spectra were collected from the red layer using the instrumental set-up of the former beamline ID-22, actual μ-FID_{22} – micro-imaging, diffraction and fluorescence beam-line – and compared against spectra obtained from copper metal and cuprite, the natural cuprous oxide (fig. 2).

XANES spectra simulations using the FEFF code for spherical atomic clusters with a radius of ~5 Å for the metal and ~5.3 Å for cuprite allowed interpreting the red colour of the glass as stemming from the presence of copper nanoclusters covered by a monolayer of cuprous oxide [3].

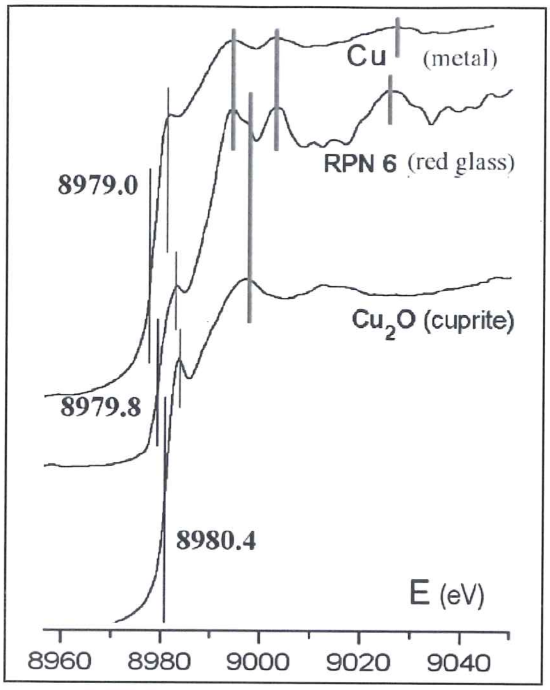

Fig. 2. Cu *K*-edge XANES spectra collected in fluorescence yield (FY) mode

Cu *K*-edge XANES spectra were collected from model oxide minerals with red, blue, green and black colourings, confirming a certain similarity of spectra layout when the chromophore ion is Cu^{2+} (fig. 3).

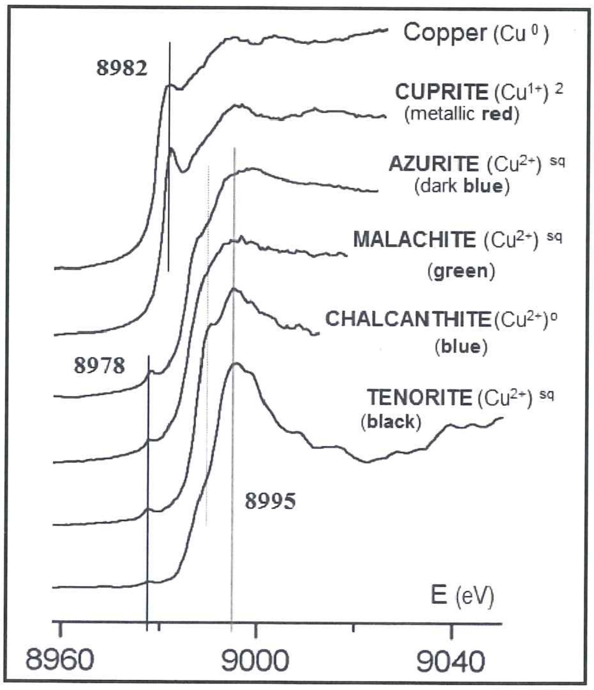

Fig. 3. Cu 1*s* XANES spectra (FY mode) collected from model minerals presenting various colourings

2.3. Cobalt in blue-and-white Chinese porcelains

A study carried out on blue-and-white Chinese porcelains manufactured for the Portuguese market along the 16th-17th centuries [5] has allowed disclosing the dominant role of cobalt as chromophore element, with tetrahedral Co^{2+}ions being responsible for the blue colouring of the porcelain glaze.

These tetrahedral cobalt ions play simultaneously a minor function of network formers in the silica-rich glassy matrix of the ancient Chinese blue-and-white porcelain glaze as confirmed by a recent study [6].

2.4. Antimony in Napples' yellow glaze pigments

Great interest has been focused on antimony oxides in the domain of ancient cultural materials because of metal speciation in relation to colour and its dependence from crystal structure. Using well crystallized minerals as model compounds, X-ray absorption spectroscopy at the Sb *K*-edge has allowed tackling the chemistry and phase constitution of ancient tile glazes manufactured with the Napples' yellow pigment.

Most of antimony oxides occur naturally as yellow minerals and display a variety of structural arrangements resulting from two stable Sb speciations: cervantite (orthorhombic) with Sb^{3+} with a pyramidal environment (CN 3) and Sb^{5+} in octahedral coordination; valentinite (orthorhombic but white) and dimorphous senarmontite (cubic, yellow), both containing also Sb^{3+} in pyramidal coordination (now with CN 4); finally, the very rare mineral stibiconite with octahedral Sb^{5+} ions within a pyrochlore-type atomic arrangement.

Spectral contributions from the two ionic Sb species simulated using a multiple scattering approach through the FEFF code [11] for a cluster of 87 atoms within an atomic array of pyrochlore-type structure ($\sim Sb_4O_{6.5}$) have provided a good fitting between calculated and experimental Sb 1*s* XANES spectra (fig. 4),

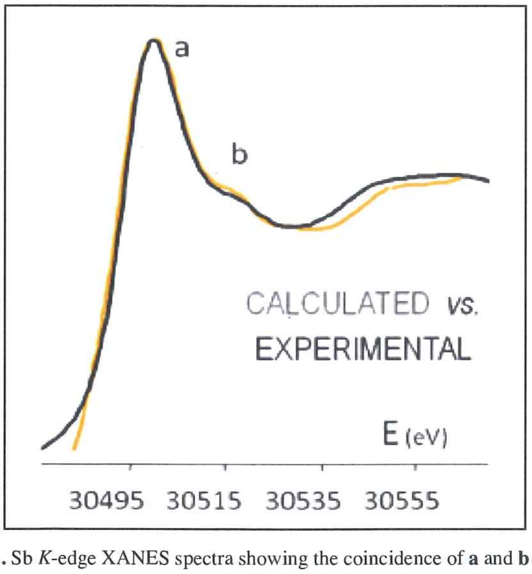

Fig. 4. Sb *K*-edge XANES spectra showing the coincidence of **a** and **b** spectral details

thus demonstrating that antimony alone may be responsible for the yellow colour of ancient tile glazes through a finely dispersed pyrochlore-type Sb-oxide [7,8].

2.5. Fuser metals

The structural role of fuser metals in ancient lead-rich tin-opacified glazes from polychrome ceramic tiles of Portuguese manufacture (16th-18th cent.) was characterized by performing XANES studies at the Zn *K*-edge and at the Pb L_3-edge. Minerals and synthetics with known crystal structures were used as model compounds to configure different speciation states and coordination environments of lead and zinc ions and to interpret the effects upon spectra details.

It was concluded that zinc acts exclusively as a network former [9]. Similarly, lead is hosted by the glassy matrix whatever the glaze colour but plays the structural role of a glass network modifier, possibly assuming a coordination higher than usual for silica glasses [10].

3. FINAL COMMENT

The present contribution is intended to summarize recent relevant results on the characterization of ancient cultural materials (particularly glasses and ceramics) obtained through the application of X-ray absorption spectroscopy at the ESRF.

ACKNOWLEDGEMENTS

The financial support of EU to perform at the ESRF the following X-ray absorption experiments focused on cultural materials is gratefully acknowledged: ME-324 (beam-line ID-22, 2001); EC-87 (beam-line ID-21, 2006); EC-401 (beam-line BM-29, 2008).

REFERENCES

[1] M.O. Figueiredo, T. Pereira da Silva, J.P. Veiga, C. Leal Gomes, V. de Andrade, The blue colouring of beryls from Licungo, Mozambique: an X-ray absorption spectroscopy study at the iron *K*-edge. *Mineralogical Magazine* 72 (2008) 175-178.

[2] M.O. Figueiredo, T.P. Silva, J.P. Veiga, The blue of iron in mineral pigments. A Fe *K*-edge XANES study of vivianite. *Applied Physics A* 99 (2010) 357-361.

[3] M.O. Figueiredo, J.P. Veiga, J.P. Mirão, Modelling the size of red-colouring copper nanoclusters in archaeological glass beads. *Applied Physics A* 83 (2006) 499-502.

[4] J.P. Veiga, M.O. Figueiredo, Copper blue in an ancient glass bead: a XANES study. *Applied Physics A* 83 (2006) 547-550.

[5] M.O. Figueiredo, T.P. Silva, J.P. Veiga, M.I. Prudêncio, M.I. Dias, M.A. Matos, A.M. Pais, Blue pigments in XVI-XVII century glazes: a comparative study between Portuguese faiences and Chinese porcelains. In: J.L. Ruvalcaba Sil, J.R. Trujeque, J.A. Alatorre, A.V. Castro (Eds.), *2nd Latin-American Symp. on Physical and Chemical Methods in Archaeology, Art and Cultural Heritage Conservation* (LASMAC 2009), Univ. Nac.

Autónoma de México, 2010, pp 84-88 (ISBN 978-607--02-2017-3).

[6] M.O. Figueiredo, T.P. Silva, J.P. Veiga, A XANES study of cobalt speciation state in blue-and-white glazes from 16th-17th century Chinese porcelains. *J. Electron Spectroscopy and Related Phenomena* 185 (2012) 97-122.

[7] M.O. Figueiredo, J.P. Veiga, T.P. Silva, J.P. Mirão, S. Pascarelli, Chemistry versus phase constitution of yellow ancient tile glazes: a non-destructive insight through XAS. *Nuclear Instruments & Methods in Physics Research B* 238 (2005) 134-137.

[8] M.O. Figueiredo, Extended vs. local structure in Sb-pyrochlores: an illustration of the valuable interplay between Crystallography and XAFS. *XAFS 13 - X-Ray Absorption Fine Structure,* Eds. B. Hedman & P. Pianetta, *AIP Conference Proceedings* 882, 205-207.

[9] J.P. Veiga, M.O. Figueiredo, A XANES study on the structural role of zinc in ancient tile glazes. *X-ray Spectrometry* 37 (2008) 458-461.

[10] M.O. Figueiredo, T.P. Silva, J.P. Veiga, A *XANES* study on the structural role of lead in glazes from decorated tiles, XVI to XVIII century manufacture. *Applied Physics A*, 83 (2006) 209-211.

[11] A. Ankudinov, B. Ravel, J.J. Rehr, *Manual of the FEFF8.10 program* (The FEFF Project, Univ. Washington, Seattle, USA, 2000)