



	<b>Assessment of speciation through the analysis of <i>K</i>-edge XAFS of heavy metals: the type-case of antimony in ancient glassy materials</b>	<b>Experiment number:</b> ME-735
<b>Beamline:</b> BM 29	<b>Date of experiment:</b> from: 4 Dec 2003 to: 9 Dec 2003	<b>Date of report:</b> 2004.02.16
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Sakura Pascarelli	<i>Received at ESRF:</i>
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## Report:

The study of ancient decorative building materials with cultural value is a challenge to material scientists once it is usually necessary to apply only non-destructive techniques. *Glazed ceramic tiles – azulejos*, from the original Arab designation – have been used throughout the last five centuries in Portugal as decorative panels in the interior of private and public buildings. When recovering such artistic tile panels for exposure in a museum, restoration is usually needed – a task requiring a concise knowledge of materials and colorants used at the time and place of production, so that only conformable new products are employed in tile restoration.

*Yellow colouring* was usually obtained by adding yellow lead antimonate ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ) to prepare the glaze. However, *Sb-speciation in the glaze is still questionable* and the purpose of the XAFS study was just to ascertain the phase(s) incorporating antimony in yellow tile glazes manufactured along XVI-to-XIX centuries.

The *electron configuration* of Sb favours *formal valences* (3+) & (5+). The energy of *K-absorption edge* is expected to display *shifts depending on the valence state(s)* present in the absorbing material. The lone pair of electrons  $5s^2$  – strongly localized in  $\text{Sb}^{\text{III}}$  – favours an asymmetric environment and unilateral positioning of ligands in  $\text{Sb}_2\text{O}_3$  oxides. Simultaneously, the energy perturbation of  $4d^{10}$  electrons due to chemical bonding in  $\text{Sb}^{\text{V}}$  is expected to induce *intensity variations* and/or *energy shifts* in *XANES post-edge details*. A similar situation holds for Pb, recognized as a network former/modifier and a charge compensator. Furthermore, an yellow colour in Sb natural oxides (minerals) is always connected with the coexistence of both valence states, while lead antimonate owes its yellow colour to lead speciation in this pyrochlore-type phase.

The instrumental set-up of BM-29 beamline was used to collect absorption spectra in transmission mode at Sb *K*- and Pb *L*<sub>III</sub>-edges. Well crystallized *minerals* and *synthetics* with known phase constitution were used as *model compounds* for various speciations of both metals. A total of 93 useful summed spectra were obtained for Sb and 100 for Pb, collected from model compounds, tile glazes and tetrahedrites.

Small fragments of glaze were directly irradiated. Model compounds (including synthetic  $\text{Sb}_2\text{O}_3$ ) were pelletized with BN. Selected minerals were: yellow *cervantite* with  $\text{Sb}^{3+}$  in pyramidal and  $\text{Sb}^{5+}$  in octahedral

coordination (with minor ordoñezite,  $\text{ZnSb}_2\text{O}_6$ ); whitish minerals *valentinite* and *senarmontite* containing only pyramidal  $\text{Sb}^{3+}$ ; and a poorly defined yellow antimony oxide affine to pyrochlore, *stibiconite* (fig.1).

An energy shift of 4 eV was observed for the Sb *K*-absorption edge in *glaze fragments* (fig. 2) indicating the presence of both species ( $3+$  &  $5+$ ). Combined with X-ray diffraction data, this result shows that the *yellow colour* obtained by adding lead antimonate as raw material is due to the presence of  $\text{Sb}^{5+}$  hosted by a *dispersed nanophase with pyrochlore structure* [1]. To model XANES spectra, *ab initio* calculations were performed with the FEFF8 code [2] using a full multiple scattering approach.

Further work on Pb *L*<sub>III</sub>-edge is in progress.

Fig. 1

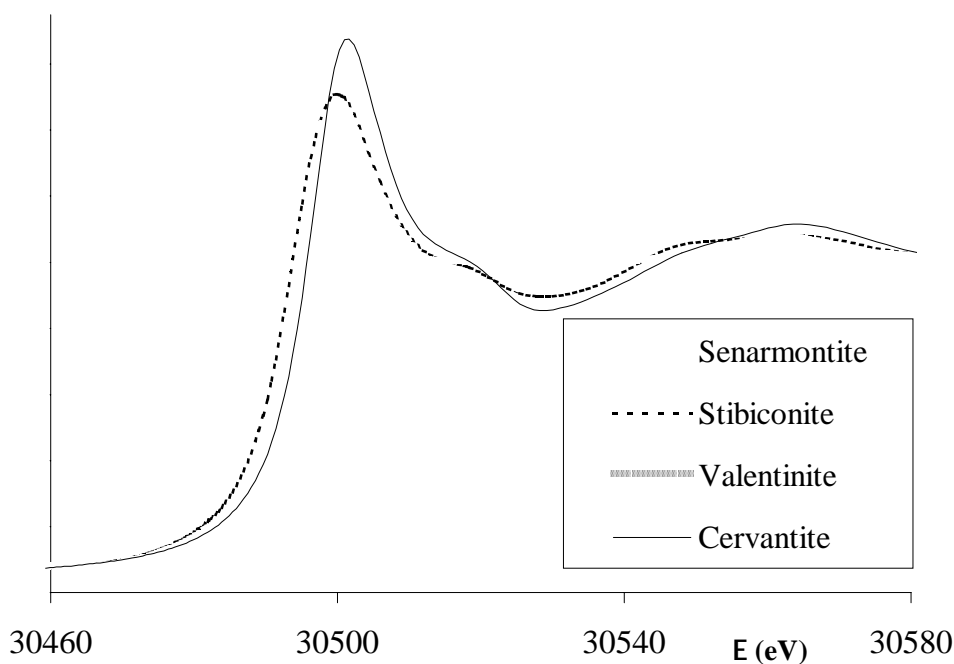
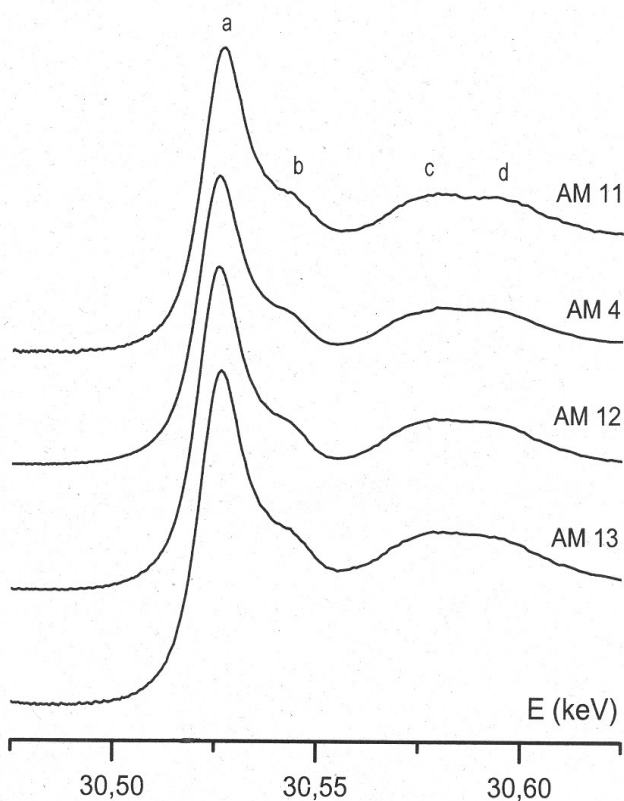


Fig. 2



#### References

- [1] M.O. FIGUEIREDO, T.P. SILVA, J.P. VEIGA, J. MIRÃO & S. PASCARELLI (2004). Speciation of antimony in ancient tile glazes: a XAFS study. *14<sup>th</sup> ESRF Users Meetg.*, 8-13 February, Grenoble.
- [2] A. ANKUDINOV, B. RAVEL & J. REHR (2000) Manual of FEFF8.10 program. *The FEFF Project* Dept. Phys., Univ. Washington, USA, 62 p.