ESRF	**Experiment title:** A XANES study on heavy metal speciation(s) in sulphosalts: analysis of Ag and Sb *K*-edges plus Bi and Pb L_{III}-edges	**Experiment number**: ME 1130
Beamline: BM-29	**Date of experiment**: from: 4 March 2005 to: 8 March 2005	**Date of report**: 2005.08.30
Shifts: 12	**Local contact(s)**: Dr. Sakura Pascarelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*M.O. Figueiredo, *J.P. Veiga, T.P. Silva, Cryst. Miner. Center/IICT & CENIMAT, Mater. Sci. Dept., Fac. Sci. Technology, New University of Lisbon, 2829-516 Caparica, Portugal

*J. Mirão, Geophysics Centre, Univ. of Évora, Apt. 94, 7002-554 Évora, Portugal

J. Ferreira, INETI, Lab. IGM, Rua da Amieira, 4466-956 S. Mamede de Infesta, Portugal

Report:

The study of heavy metal ions in chemically complex matrices – undertaken by the applicants (experiment ME-735, report dated February 29, 2004) on the speciation of Sb in ancient tile glazes, taking oxide minerals as model compounds [1] – was extended to other heavy metallic elements with the purpose of relating *K*- and L_{III}-edges absorption spectra of metal ions with XANES data previously obtained for the S *K*-edge (experiment ME-821, beamline ID 21, report dated October 13, 2004).

Sulphosalts – and among them, *tetrahedrites* –, are a group of economically valuable minerals, where Ag^{1+} cations may assume triangular coordination while Fe and other divalent metal ions fill structural sites with a tetrahedral environment of sulphur anions. However, the structural position occupied by heavy metal ions in tetrahedrites remains questionable, and the study of Pb, Sb, Bi L_{III}-edges in selected sulphosalts provides data of a major importance to understand the spatial implications of the lone pair of electrons in Pb^{2+}, Sb^{3+} and Bi^{3+} ions, in connection with prevailing electronic state and chemical bonding.

The instrumental set-up of BM-29 beamline was used to collect a total of 69 scans that allowed to obtain 15 high quality XANES spectra and 12 EXAFS spectra, collected in the usual transmission geometry and complemented with fluorescence yield data. Model compounds were pelletized with BN.

Several simple model minerals were thus analysed as well as Pb-rich sulphosalts with known crystal structure. Minerals selected to model Pb state were *minium* (Pb_3O_4) with Pb^{2+} in pyramidal coordination (CN3), *plattnerite* (β-PbO_2) with Pb^{4+} in octahedral coordination, *litharge* (α-PbO) with Pb^{2+} in pyramidal coordination (CN4), *cerussite* ($PbCO_3$) with Pb^{2+} in a less regular coordination. For silver, *argentite* (β-Ag_2S, cubic) and *acanthite* (α-Ag_2S, monoclinic) were selected.

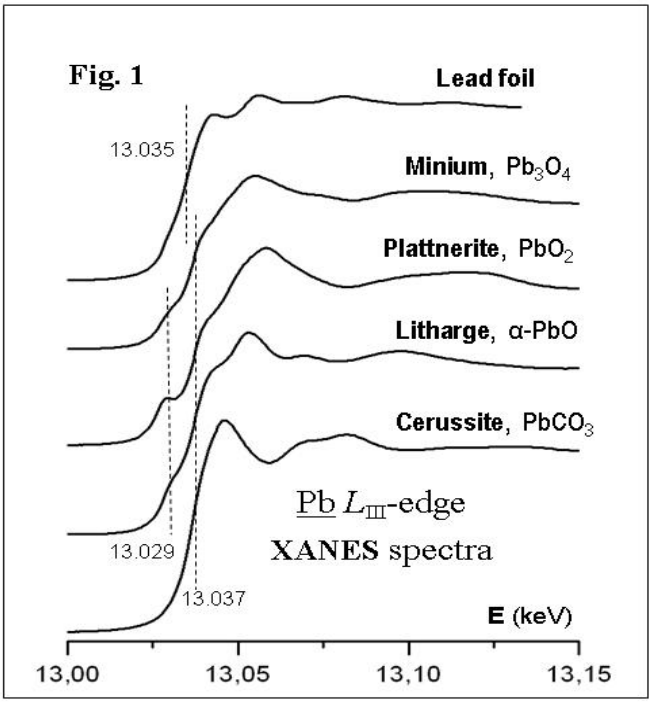
An energy shift to higher energy relatively to the metal was observed for Pb ions in the oxides and in the carbonate, with no noticeable energy difference between formal valences Pb^{2+} and Pb^{4+}, but clear differences in post-edge features were noticed (Fig. 1). Conversely, the energy of Ag *K*-edge in the sulphides argentite and acanthite and in the sulphosalt tetrahedrite coincides with the value for metallic silver (Fig. 2).

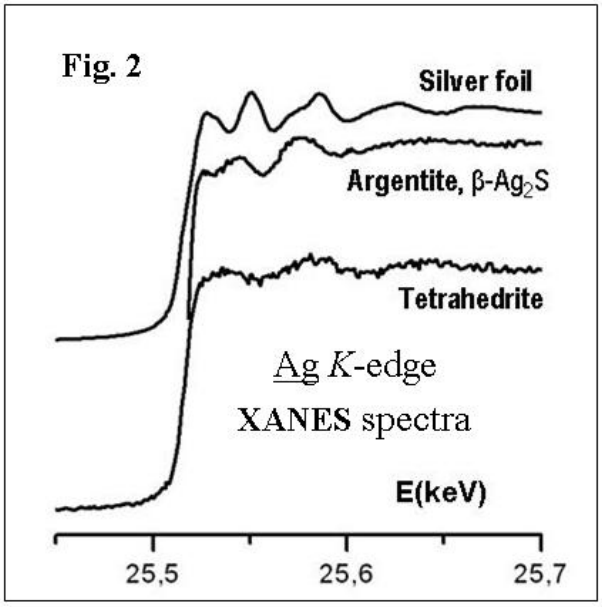
A first attempt to study iron in the usual formal valences 2+ and 3+ was successfully conducted on natural materials with variable structural complexity, including Fe-rich alteration products of volcanic rocks (Fig. 3).

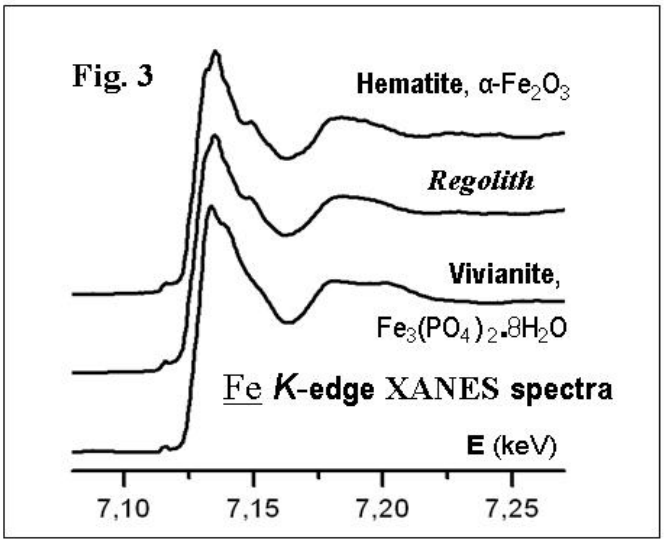
The results on lead will be included in a communication on ancient ceramics accepted for presentation at a forthcoming congress [2], in this way complementing and extending XANES data already in press [3].

Worth remarking is the fact that the joint approach to Sb and Pb in ancient yellow glazes has allowed to clarify the kind of pyrochlore prevailing in the glaze as a dispersed crystalline phase [4].

Further theoretical modelling of *K*-edge XANES spectra using the FEFF code is at present in progress.







[1] M.O. FIGUEIREDO, J.P. VEIGA, T.P. SILVA, J. MIRÃO, S. PASCARELLI (2005) Chemistry versus phase constitution of yellow ancient tile glazes: a non-destructive insight through *XAS*. *Nuclear Instruments and Methods B* (in press).

[2] M.O. FIGUEIREDO, J.P. VEIGA & T.P. SILVA (2005) High-lead glazes in ancient polychrome tiles. *EMAC'05, 8th European Meeg. Ancient Ceramics*, Lyon/France, October 25-28 (accepted as a poster).

[3] M.O. FIGUEIREDO, T.P. SILVA & J.P. VEIGA (2005) A *XANES* study on the structural role of lead in glazes from decorated tiles, XVI to XVIII century manufacture. *Applied Physics A* (in press).

[4] M.O. FIGUEIREDO (2005) Antimony oxides: the pyrochlore-type revisited. *IUCr2005, XX Congr. Int. Union of Crystallography,* Florence/Italy, August 23-31 (poster).