ESRF	**Experiment title: Sb K-edge and Pb L-edge speciation study through XANES in historical Portuguese tile glazes**	**Experiment number**: HG-100
Beamline: BM 25 A	**Date of experiment**: from: 17th June 2017 to: 20th June 2017	**Date of report**: 4th Nov 2017
Shifts: 9	**Local contact(s)**: Eduardo Salas-Colera	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

João Pedro Veiga * (Main proposer), Maria Margarida Lima, Elin Fiueiredo *(participant in the experimente but not in the original application), CENIMAT/I3N, FCT|NOVA, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

Mathilda Larsson Coutinho, VICARTE, FCT|NOVA, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

Teresa Pena Silva *, LNEG National Laboratory for Energy & Geology, Estrada da Portela, Bairro do Zambujal Apartado 7586 Alfragide, 2720-866 Amadora, Portugal

Report:

Fragments of unique majolica-type polychrome high relief tiles from 19th century Portuguese manufacture, precursors of the Art Nouveau period in Portugal, from the UNESCO World Heritage Pena National Palace (Sintra, Portugal), previously characterized by the group using XRD, µ-PIXE, µ-Raman, Optical Microscopy and VP-SEM [1], along other glazes from tile fragments of Portuguese origin were irradiated at beamline BM25A. These glazes display a silica-lime-alkali glass with the addition of low melting point metals namely Pb (contributing to transparency and brilliance of the glaze) and chromophores based on Sb, Co, Mn and Ni. An opacifier based on Sn was added to make the glaze opaque-white, resulting in the formation of a dispersed SnO_2 crystalline phase.The purpose of this experiment was to ascertain the speciation of Pb (fuser metal) in the vitreous matrix of these ancient tile glazes using XANES and to monitor the chemical state of chromophore Sb to clarify their role in pigment incorporation (still under dispute by several authors) and the possible relationship(s) between their chemical evolution and the ageing mechanisms of the glaze.

A total of 22 glaze fragments or glazed ceramic fragments were characterized by XANES. Also irradiated was a set of model compounds for XANES we used metallic antimony (formally Sb^0 but with pyramidal linkage to three neighbouring atoms in a trigonal layer-type crystal structure) and well crystallized minerals, namely: valentinite (Sb_2O_3) and stibnite (Sb_2S_3) both with Sb^{3+} also in pyramidal coordination by the ligands, oxygen and sulphur; ullmannite (NiSbS), with pyrite-type crystal structure and S=Sb bonding; cervantite (α–Sb_2O_4), containing octahedral Sb^{5+} ; and bindheimite, the pyrochlore-type double oxide $Pb_2Sb_20_7$. Lead models were oxide minerals where lead ions assume various coordination geometries: litharge, red α-PbO, with Pb^{2+} ions coordinated by four coplanar oxygen anions placed on the same side in a pyramidal arrangement, compensated by the lone pair of $6s^2$ electrons; plattnerite, brown β-PbO_2 with Pb^{4+} in a relatively regular octahedral

coordination within a rutile-type crystal structure; minium, tetragonal reddish Pb_3O_4 where both valence states and coordination environments are displayed by lead.
Energies ranging from 13 keV (Pb L_3 edge) to 31 keV (Sb *K*-edge) were used for collecting XANES spectra and characterizing Sb and Pb speciation through *K*- and *L*-edges respectively.
The clarification of the role of Pb and Sb in glazes, still in discussion, through speciation of fuser metals and colourants in ancient tile glazes and glasses is currently under way.
The comparison with XANES spectra from model compounds is currently being performed and will suggest the structural role of additives currently under debate as glass network former or modifier or integration in crystalline colouring phases.
Theoretical modelling of Pb and Sb spectra using the FEFF [2] code based on a multiple scattering approach for the interpretation of observed edge features will allow to disclose the coordination environment effectively assumed by these elements in this type of ancient materials. Figures 1 a) and b) illustrate two spectra from model componds for the XANES study.

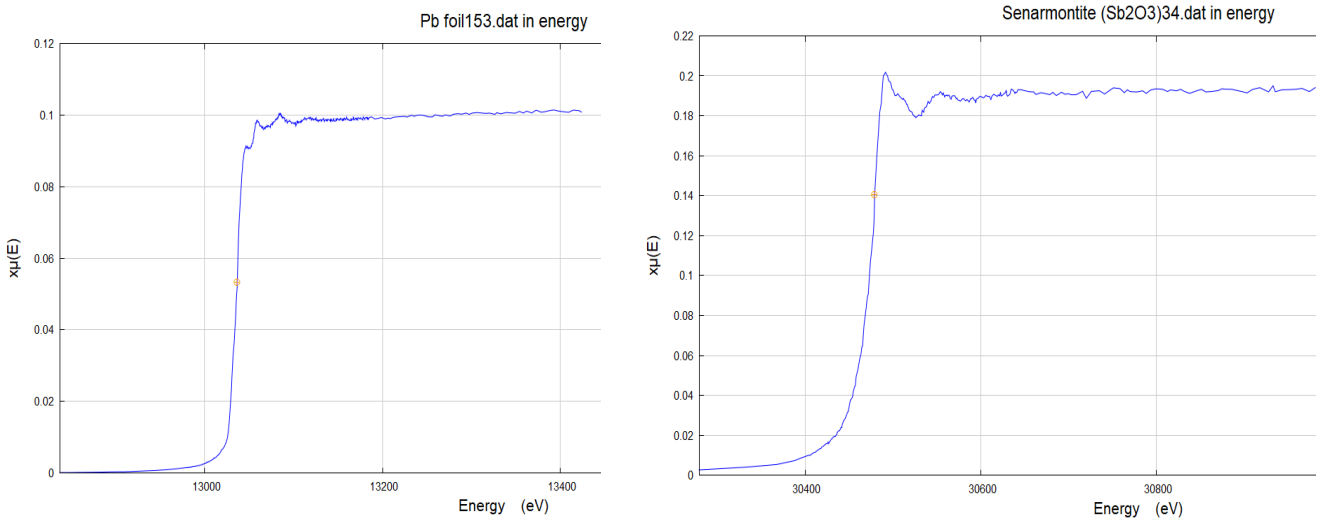

Figure 1 – a) Pb L3 edge XANES spectrum from the Pb foil; b) Sb K edgeXANES spectrum from Senarmontite.

Taking profit from the present experimental campaign an assessment was done on the possible use of XANES and SRXRF by characterizing 4 samples from the Fogo Volcano in Cape Verde Archipelago for a future proposal for beamtime at the ESRF and 1 sample of Portuguese Azul Valverde limestone for iron speciation through XANES (in the meantime both submitted to the ESRF in the last call and currently under evaluation). In the same manner 3 samples from Cassiterites from Portuguese mines were analized to ascertain their adequability for historical characterization of mining through speciation of elements such as tin, niobium and tantalum for a future proposal (in the meantime also submitted to the ESRF during the last call and currently under evaluation).

References:

[1] M.L. Coutinho, J. P. Veiga, L. C. Alves, J. Mirão, L. Dias, A. M. Lima, V. S. Muralha, M. F. Macedo (2016) Characterization of the glaze and in-glaze pigments of the nineteenth-century relief tiles from the Pena National Palace, Sintra, Portugal. Applied Physics A 122 696.

[2] Ankudinov, A.L. *et al.* 2000. Manual of FEFF8.10 Program. *The FEFF Project*, Dept. Physics, Univ. Washington, Seattle, USA, 62 pp.