Ancient glazed ceramic tiles: a long-term study from the remediation of environmental impacts to the non-destructive characterization of materials

M.O. Figueiredo
Dr. Sci. /Senior Researcher, LNEG, Geol. Data Centre, & CENIMAT/I3N, Fac. Sci. Technol., New Univ. Lisbon, 2829-516 Caparica, Portugal, *ondina.figueiredo@ineti.pt*

T. Pereira da Silva
Ph.D. /Researcher, CENIMAT/I3N & LNEG, Geol. Data Centre, 2721-866 Alfragide, Portugal, *teresa.pena@ineti.pt*

J.P. Veiga
Ph.D. /Auxiliary professor, Dept. Materials Sci., Fac. Sci. Technol., New Univ. Lisbon, 2829-516 Caparica, Portugal, *jpv@fct.unl.pt*

SUMMARY: Since the involvement in a national research project[1] in 1995-1997 with the partnership of the National Tile Museum in Lisbon, until a recent European project[2] with partners from Mediterranean countries which cultural patrimony entails glazed ceramic tiles, the authors have been active in the non-destructive characterization of ceramic and vitreous materials used to manufacture ancient decorated tiles (16th-19th century) through the access to the European Synchrotron Research Facility (ESRF, Grenoble/France). As an input to the preservation of this important cultural patrimony through the improvement of restoration techniques, a synopsis is presented of the work so far developed.

KEY-WORDS: tiles, ceramics, glazes, XANES

INTRODUCTION

"Ceramics" is the general designation for any inorganic non-metallic material obtained through a thermal processing of natural lithologic raw materials at relatively high temperature. It then covers ceramic materials in a strict sense, including silicate refractory materials with limited interest within the cultural heritage (see the triangular sketch bellow).

The production of ceramics was the first industry implemented by Man in the Neolithic period. The raw materials are essentially clays plus finely divided quartz (sand) and feldspars, the latter controlling the rheology of the raw ceramic paste along the thermal processing: red ceramics (bricks and roof tiles) arise from illite-rich clays, while firing kaolinite gives rise to faience (mainly composed of mullite, an aluminous silicate displaying variable composition). Depending on the mineralogical constitution, clays retain variable amounts of water liberated along firing at distinct temperature ranges:

- fluid water (liquid) retained in pores between clay particle aggregates (low temperature);

- molecular water adsorbed at the surface of particles or crystallites (medium temperature);
- combined water hosted by the crystal structure of clays as neutral molecules (H_2O) or ionic hydroxyl groups (OH^-) liberated at higher temperatures in the thermal processing.

The firing process of ceramic pastes then gives rise to a significant decrease in volume, concomitant with the development of a percolating pore system in the fired product. “Porosity” is then the ceramics constitutional feature that ultimately constrains permeability and mechanical properties, being responsible for many alteration and degradation processes currently undergone by ceramic materials. As sketched bellow, the overall behaviour of ceramics depends on its chemical constitution and bulk properties, both physical and mechanical.

Ceramics

Chemistry	**Bulk properties**	
	Physical	**Mechanical**
SiO_2, Al_2O_3,	Porosity	Elasticity
CaO, MgO,	Permeability	Compressive strength
FeO, K_2O,	Density	Tensile strength
Na_2O, TiO_2,	Hardness	
MnO, P_2O_5,	Colour	
LOI & SO_2		

For common ancient ceramics, the main mineral constituents are gehlenite, $Ca_2Al_2SiO_7$ and anorthite, $CaAl_2Si_2O_8$, beyond quartz (SiO_2), minor belite (β-Ca_2SiO_4) and eventually carbonates – calcite, $CaCO_3$, and/or dolomite, $CaMg(CO_3)_2$. Once limestone commonly integrates the ceramic raw materials, the fired products may also contain magnesian components – namely, äkermanite, $Ca_2MgSi_2O_7$, a phase isostructural with gehlenite and forming with it a solid solution that may also include iron, thus corresponding to the general chemical formula $Ca_2(Al,Fe,Mg)(Si,Al)_2O_7$. Mg-silicates (e.g., diopside, $CaMgSi_2O_6$) may also be formed at high enough firing temperature when magnesium is well represented in the raw materials, as occurs for ancient Chinese ceramics and actual porcelain. Phase constitution ultimately constrains the physical and mechanical properties of ceramics.

GLAZED CERAMIC TILES

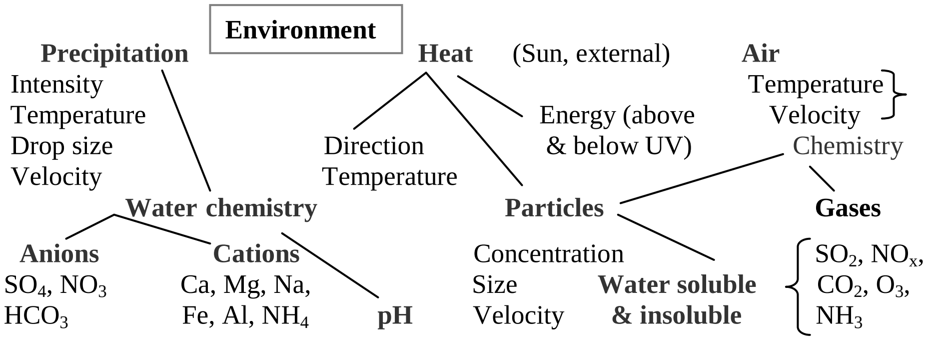
Ceramic tiles or simply “tiles” (“azulejos” in Spanish and Portuguese, from the original Arab designation “*al-zuléija*” or “*al-zulaiju*”) configure a paradigmatic case of ceramics with wide application in the architectural cultural heritage. They deserve a particular attention around the Mediterranean Basin where they have been used for long to decorate important buildings, either covering façades or forming artistic decorative panels, often located in the outside of architecturally relevant constructions.

Usually square in shape and not much thick, *tiles* are composed of a *ceramic stratum* or base over which a *vitreous glaze* was deposited by further processing, this giving rise to an impermeable glassy and brilliant surface. *Fuser metals* (namely, lead and zinc) plus glass *modifiers* assuring the stabilization of non-vitrifying components are usually added; *colorants* (chromophore elements, mainly transition metals like copper, manganese or cobalt) are incorporated to obtain the nicely decorated and coloured glaze surfaces of ornamental tiles.

Ancient tile glazes are essentially calco-sodic siliceous glasses. Often, they are not transparent vitreous materials, turning opaque by the addition of specific compounds. The most common *opacifier* formerly used in tile manufacture was tin oxide (cassiterite, SnO_2), in industrialized recent productions replaced by zircon ($ZrSiO_4$), a compound with higher refractive index.

ENVIRONMENTAL IMPACTS

Environmental actions upon outside-exposed tile panels are mainly driven by the sun, both due to heat and to photonic effects (particularly UV radiation) motivating discoloration, and by rain plus air currents and humidity. According to the sketch bellow, the chemistry of raining water, the size and drop velocity are important features, as well as the nature of the gases carried in the air (especially in cities with a high level of pollution) and air-transported particles.



Porosity plus permeability of the ceramic body underlying the glaze in decorative tiles are in the origin of deterioration under exposure to the environment (Fig. 1). But other physical properties play also an important role in tile durability, like hardness and density of both glaze and ceramics. Furthermore, the mechanical behaviour of the ceramics supporting the decorated glaze depends on its elasticity, which determines tensile and compressible strengths. The differential expansion of the ceramic body relatively to the non-elastic glass forming the glaze may give rise either to a network of fissures – a phenomenon known as "craquelé" of the glaze – or ultimately to the detachment of glaze portions (Fig. 2).

The influence of water – not only rain, but also liquid water or vapour ascending through the porous system of the ceramics – mainly depends on water chemistry (particularly acidic anions in solution) and implies the corrosive attack of mineral components by extracting soluble elements susceptible of forming salts at the outer surface as efflorescent products or ultimately precipitate within pores and vacuoles (Fig. 3). Whatever the case, removing these soluble salts is the first step in any tile restoration and conservation procedure [1-3].

Micro-organisms may also play a significant role in tile alteration and degradation processes by developing noteworthy communities within ceramics under favourable conditions. For instance, algae may be observed as greenish stains on mortars originally underlying removed tiles in walls exposed to the environment as illustrated by figure 2.

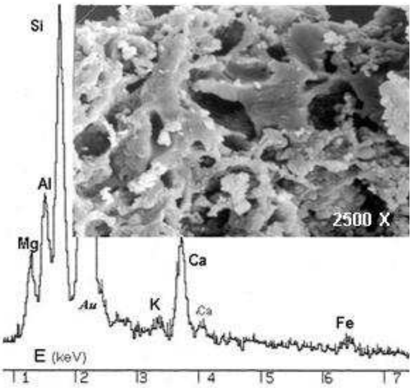


Fig. 1 – Microstructure of the ceramic body from a XVI century tile showing a framework of imbricate gehlenite crystals (SEM micrograph, left), identified through the presence of major Si, Al, Ca, Mg plus minor K, Fe present in the X-ray emission spectrum (SEM-EDS; *Au* from sample preparation). The porous system of the ceramics is further illustrated by the image on the right.

Fig. 2 – Environmental impact on ceramics illustrated by the state of blue-and-white tiles from an internal wall façade at a XVIII century church prior to restoration and having remained for various years without roof. Expansion of the ceramic body due to water infiltration has given rise to fissures at the glaze surface ("craquelé") and to glaze detachment, as well as to salt precipitation (see below) and "efflorescences".

Ageing of ancient tile glazes (usually calco-sodic silica glasses) and subsequent deterioration by the environmental agents proceeds through successive steps, starting with the partial *devitrification* of the glassy matrix of the glaze giving rise to the formation of cristobalite (low temperature form of silica easily detected by X-ray diffraction) and subsequent precipitation of newly-formed crystalline phases under the form of minute, nanoscale grains within the vitreous matrix or as larger crystal aggregates inside vacuoles (Fig. 3).

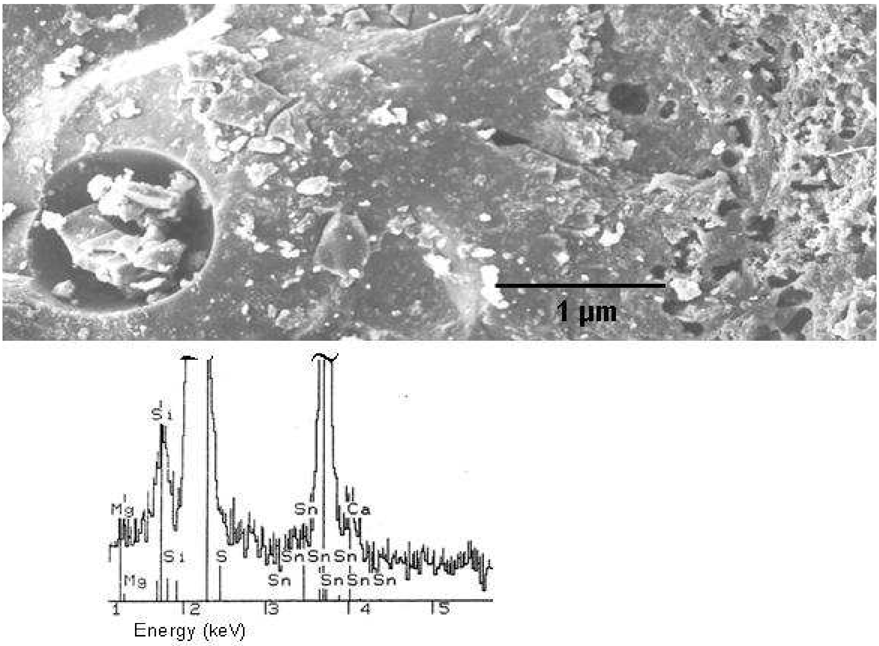


Fig. 3 – SEM micrograph collected from a blue-and-white tile from the internal wall façade of S. Salvador Church illustrating the junction between the glaze and the ceramic body. The crystals hosted within a vacuole in the glaze were analysed by SEM-EDS: the tabular, pseudo-cubic crystals contain tin and calcium, being most possibly an hydroxide, $CaSn(OH)_6$; the clusters of minute grains contain mainly calcium (calcite, $CaCO_3$).

COMPATIBILITY OF RESTORATION PRODUCTS: A CONDITION FOR TILE DURABILITY

It becomes clear from what has been described that the removal of soluble salts retained within the pore system of the ceramic body is mandatory prior to undertaking any restoration treatment of an ancient tile.

The choice of consolidation products is also critical for the durability of the restoration procedure. When comparing the X-ray diffraction patterns of ancient and actual glazes (fig. 4) it becomes apparent that their phase composition is very different. Beyond the vitreous phase, modern glazes contain crystalline zircon ($ZrSiO_4$), the dominant component of commercial materials for tile restoration; conversely, ancient counterparts differ significantly in phase constitution, being composed of a siliceous glass (uplifted background in the diffraction pattern, with a maximum close to the dominant Si–Si distances in the glass, d ~ 3.3 Å) plus SnO_2 (cassiterite, a common glaze opacifier) and minor crystalline silica phases (e.g., quartz leftover from glaze manufacture and/or cristobalite arising from glaze ageing by partial devitrification).

These comments emphasize the need for a detailed appreciation of the degradation state of the ancient tile and for a careful diagnostic of glaze composition before attempting to design a suitable conservation strategy.

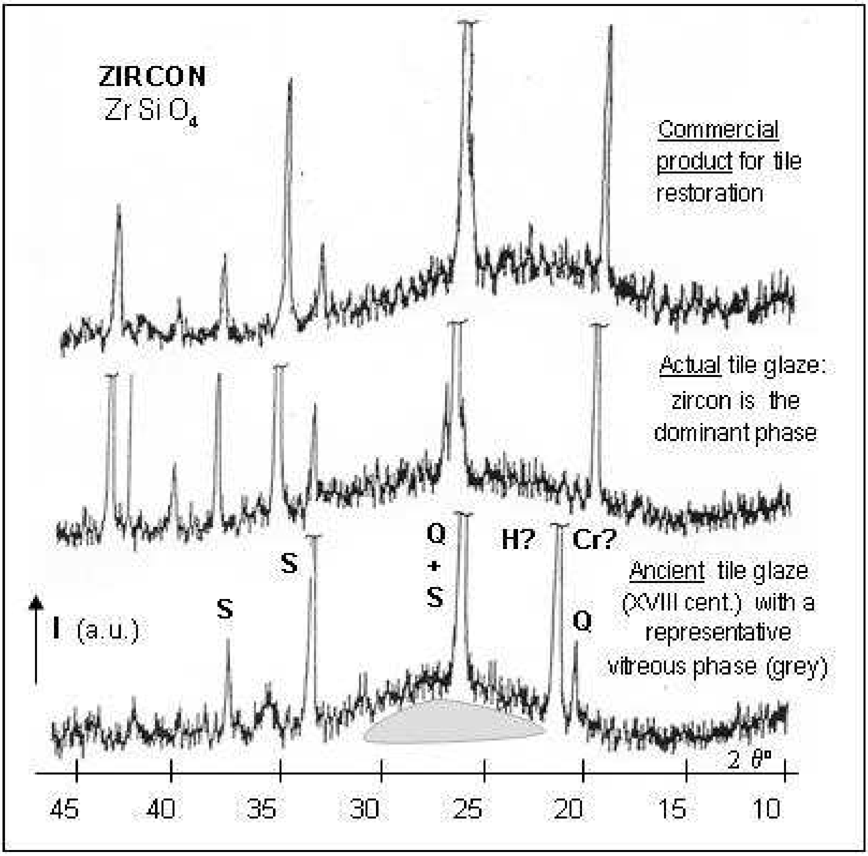


Fig. 4 – X-ray diffraction (XRD) spectra (Cu Kα radiation) collected in a non-destructive way from irradiated glaze fragments, comparing the phase constitution of ancient and actual tile glazes with a commercial product frequently used in tile restoration processes. The contribution of siliceous glass to the diffraction pattern of the ancient glaze is indicated in grey. Diffraction lines from crystalline phases are assigned: cassiterite (SnO_2, **S**), plus quartz (**Q**), and a single line arising from the joint contribution of two glaze degradation phases, $CaSn(OH)_6$ (**H** ?) plus cristobalite (**Cr** ?).

NON-DESTRUCTIVE CHARACTERIZATION OF TILE GLAZES

The study of ancient cultural materials usually requires the use of non destructive methodologies, rendering most valuable the conjugate application of various techniques based on X-rays: diffraction (XRD) for phase identification, fluorescence spectrometry (XRF) to characterize the elemental composition and absorption spectroscopy (XAS) to ascertain the speciation state of constituting chemical elements. While XRD and XRF are easily accessible laboratory techniques that have been even adapted to portable equipments, the spectroscopic procedures require the use of synchrotron radiation (SR) in large scale installations [4].

The chemistry of tile glazes is rather complex due to the addition of metals with low melting point capable of being homogeneously incorporated in the glass and chromophore elements. Speciation of both fuser metals and colorants in ancient tile glazes and glasses may account for chemical affinities and correlations in phase behaviour, thus contributing to clarify the ageing mechanisms [5-6].

Concerning the fuser metals, zinc has a dominant network-forming role, allowing for reducing the addition of network-modifiers and displaying a stabilizing role and improving mechanical properties and chemical durability; lead contributes to enhance glaze transparency and brilliance, having been extensively used in ancient decorated tiles.

Ancient tile glazes of Portuguese manufacture (Fig. 5) were first studied for bulk chemical characterization using X-ray fluorescence induced by synchrotron radiation (SRXRF) and thereafter applying X-ray absorption near-edge spectroscopy (XANES) to assess speciation state(s) of fuser metals and chromophore cations.

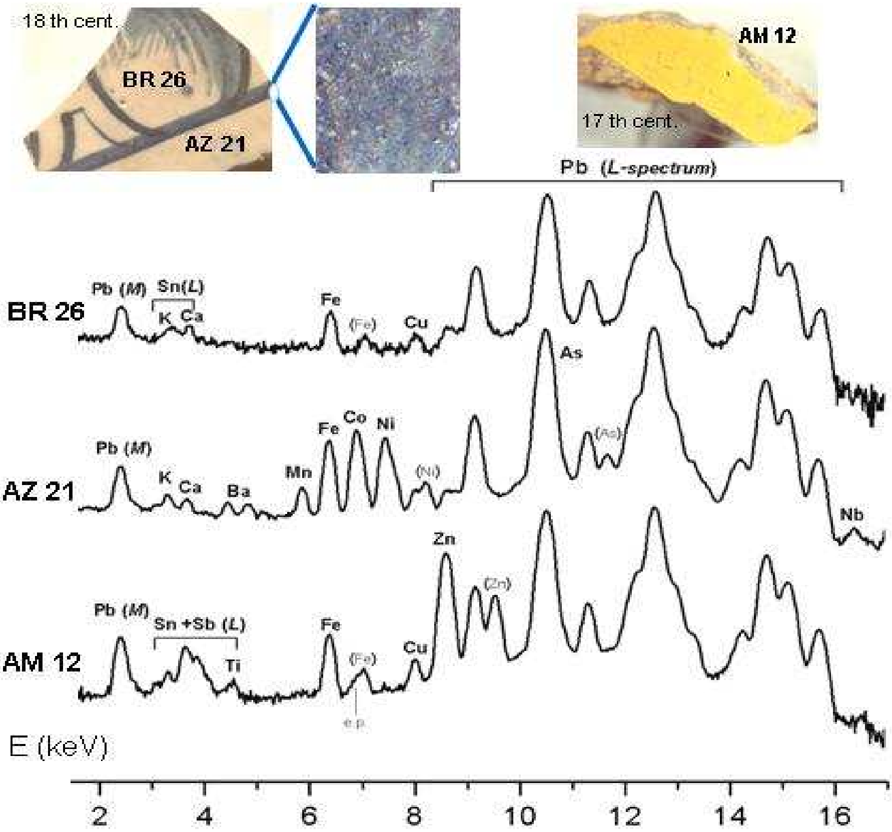


Fig. 5 – Synchrotron radiation X-ray fluorescence (SRXRF) spectra collected from the coloured glaze fragments reproduced above. Diagnosis *K*- and *L*-lines of various elements are assigned: all glazes contain lead – a fuser metal (along with zinc, noticed only for the yellow glaze AM 12 which contains antimony as chromophore element). The colouring of glaze AZ 21 is due to cobalt – a common blue pigmenting metal.

An X-ray absorption approach to lead-rich, tin-opacified yellow glazes of majolica-type ancient tiles (17th-19th centuries) disclosed the possibility of an antimony oxide being the only responsible for colouring rather than the originally added yellow pigment (bindheimite, $Pb_2Sb_2O_7$). Sb *K*-edge XANES spectra (Fig. 6) collected from these glazes were compared with similar spectra from well crystallized Sb-oxide model minerals configuring various speciation states of Sb-ions and theoretically modelled using a full multiple scattering approach; the best fit was attained for identical contributions of Sb^{3+} in pyramidal coordination and Sb^{5+} with octahedral environment, thus excluding the presence of lead in the yellow colouring phase [7,8].

Lead-rich glazes displayed identical Pb L_3-edge XANES spectra (Fig. 7), irrespective of the colour of the glaze and the period of tile production, demonstrating the identity of lead formal valence plus coordination environment and supporting the conclusions that lead is hosted by the glassy matrix even in yellow glazes and that it lead ions assume coordinations higher than usual for silica glasses in ancient tile glazes (silica-lime-alkali glasses) [9, 10]. Conversely, the XANES study at Zn *K*-edge performed on blue-and-white glazes from 16-17th century [11] pointed towards a tetrahedral coordination of Zn^{2+} ions, thus supporting a network-former role.

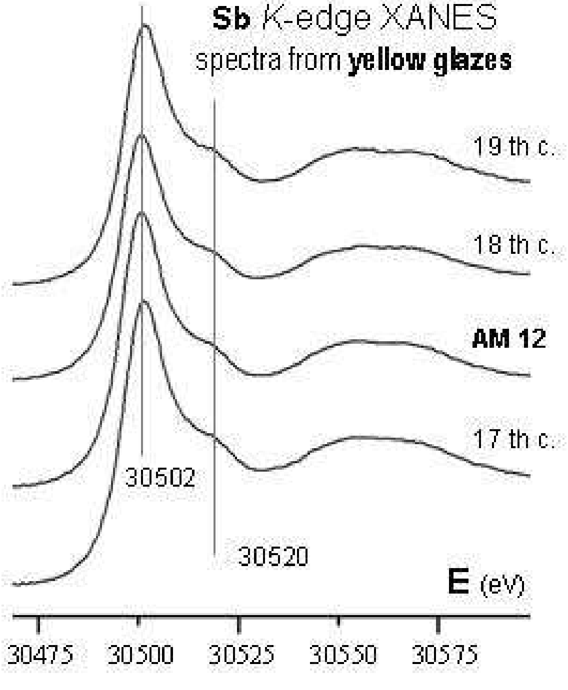


Fig. 6 – X-ray absorption near-edge spectra which features show that antimony is hosted by the glassy matrix of yellow glazes in a similar way irrespective the period of manufacture.

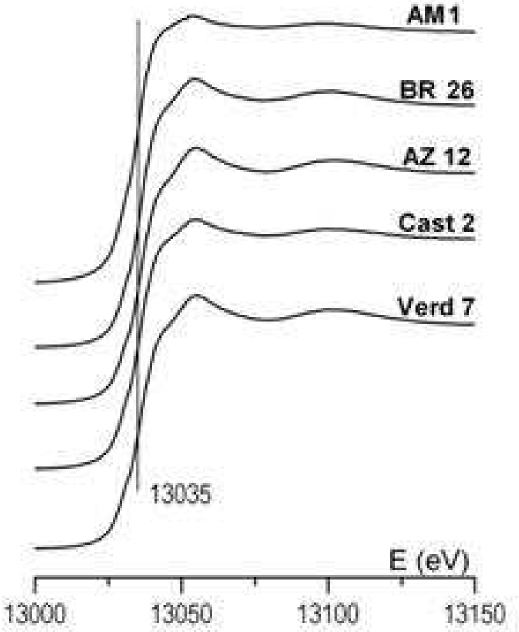


Fig. 7 – XANES spectra showing that lead is hosted by the glassy matrix in 2+ valence state (L_3-edge at 13035 eV) whatever the glaze colour, that is, with identical coordination environment in all glazes

FINAL COMMENTS

As expressed in the Preamble, the present contribution summarizes the results of a fifteen years study on materials characterization applied to ancient decorated tiles – a valuable cultural patrimony in the Mediterranean area. Actual developments of such study are centred on the characterization of chromophore speciation states in glazed ceramics.

Future advances on the application of novel techniques to the conservation of this important cultural patrimony will desirably focus on the use of neutron beams and gamma radiation to inactivate microbiota inside the pore structure of the ceramics without damaging the decorated glaze.

Acknowledgements

- PRAXIS/ 2/ 2.1/ HIS/ 13/ 94, with the financial support from Foundation for Science and Technology, Ministry of Science, Technology and Higher Education (FCT/MCTES).
- Proj. INCO-CT-2006-518697 “Valorisation of Monumental Heritage through Higher Education and Professional Training. Socioeconomic Study & Analysis of National Policies on EU-MED-DEV Countries & EC Directives”.

List of quoted publications

[1] COSTA PESSOA, J., FARINHA ANTUNES, J.L., FIGUEIREDO, M.O., FORTES, M.A. - *Removal of soluble salts from ancient tiles*. Studies in Conservation, 41, 1996, 153-160.

[2] BORGES, C., CAETANO, C., COSTA PESSOA, J., FIGUEIREDO, M.O., LOURENÇO, A., MALHOA GOMES, M., SILVA, T.P., VEIGA, J.P. - *Monitoring the removal of soluble salts from ancient tiles by ion chromatography*. Journal of Chromatography A, 770, 1997, 195-201.

[3] COSTA PESSOA, J., FIGUEIREDO, M.O. – *A contribution from Chemistry to the diagnostic of conservation problems* (in Portuguese). Monumentos, 10, Dir. Geral Ed. Mon. Nac., 1999, 38-41.

[4] FIGUEIREDO, M.O., VEIGA, J.P., PEREIRA da SILVA, T. - *Non-destructive chemical characterization of cultural materials using synchrotron radiation X-ray fluorescence*. Proceedings ART 1999, 6th Int. Conf. Non-destructive Testing and Micro-analysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Rome/Italy, 1999, 1767-1799.

[5] FIGUEIREDO, M.O., VEIGA, J.P., PEREIRA da SILVA, T. - *Ageing of high-lead glazes in XVI-XVII century tiles*. Proceedings ART 2002, 7th Int. Conf. Non-Destructive Testing and Micro-Analysis for the Diagnostics and Conservation of Cultural and Environmental Heritage, edts. ICR & AIPnD, Antwerp/Belgium, 2002, 8 pp. (ISBN 0-444-50517-2).

[6] FIGUEIREDO, M.O. - *Study and characterization of cultural ceramic materials: the paradigmatic case of decorated tiles* (in Portuguese). Azulejo, 8-11, Nat. Tile Museum (MNA, Lisboa), 2003, 11-20 (ISSN 0872-170X).

[7] FIGUEIREDO, M.O., VEIGA, J.P., SILVA, T.P., MIRÃO, J.P., PASCARELLI, S. - *Chemistry versus phase constitution of yellow ancient tile glazes: a non-destructive insight through XAS*. Nuclear Instruments and Methods B, 238, 2005, 134-137.

[8] FIGUEIREDO, M.O. – *Extended vs. local structure in Sb-pyrochlores: an illustration of the valuable interplay between Crystallography and XAFS*. X-ray Absorption Fine structure – XAFS 13, AIP Conf. Proceedings, 882, 2007, 205-207.

[9] FIGUEIREDO, M.O., SILVA, T.P., VEIGA, J.P. - *A XANES study on the structural role of lead in glazes from decorated tiles, XVI to XVIII century manufacture*. Applied Physics A (Mat. Sci. & Processing), 83, 2006, 209-211.

[10] VEIGA, J.P., SILVA, T.P., FIGUEIREDO, M.O. - *Coordination environment of lead in coloured glazes from ancient tiles: an EXAFS approach through the Pb L_3-edge*. EMAC'07, 9th Europ. Meeting on Ancient Ceramics, Budapest/Hungary, 24-27 October, 2007 (Poster, abstract P-52).

[11] VEIGA, J.P., FIGUEIREDO, M.O. - A XANES study on the structural role of zinc in ancient tile glazes of Portuguese origin. X-ray Spectrometry, 37, 2008, 458-461.