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M.O. FIGUEIREDO[1,2,✉]
T.P. SILVA[1,2]
J.P. VEIGA[2,1]

A XANES study of the structural role of lead in glazes from decorated tiles, XVI to XVIII century manufacture

[1] Crystallography and Mineralogy Centre, IICT, Alameda D. Afonso Henriques, 41-4°, 1000-123 Lisbon, Portugal
[2] CENIMAT, Materials Science Department, New University of Lisbon, Quinta da Torre, 2829-516 Caparica, Portugal

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ABSTRACT Aged lead-rich, tin-opacified glazes from polychrome tiles manufactured in the 16th–18th century were studied to ascertain the structural role of lead. Glaze fragments with white, blue, yellow, brown and green colouring were analysed using non-destructive X-ray techniques, both laboratorial – X-ray diffraction to identify crystalline components – and synchrotron-based. Elemental analyses by synchrotron radiation X-ray fluorescence were performed at the former LURE photon microprobe (line D15A at DCI, in Orsay). The instrumental set-up of beamline BM29 at the ESRF, in Grenoble, was applied to collect X-ray absorption spectra at the Pb L_3-edge. Natural minerals and synthetics with known crystal structure were used as model oxy-compounds to configure different formal valences and coordinations of lead ions by oxygen anions, and to interpret the effects upon details of X-ray absorption near-edge spectroscopy (XANES) spectra. Experimental evidence supports the general conclusion that lead is hosted by the glassy matrix, irrespective of the glaze colour. Furthermore, it was concluded that lead ions assume coordinations higher than usual for silica glasses, acting as network modifiers in the silica-lime-alkali glasses of ancient tile glazes.

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1 Introduction

Ancient polychrome glazed tiles exposed to the environmental conditions in artistic panels often display ‘ageing’ of the decorative glaze due to partial crystallization and precipitation of newly formed phases out of the vitreous matrix.

The conservation and restoration of decorated tiles sets forth questions of materials’ compatibility that require a deep knowledge about these ancient cultural artefacts, particularly concerning their chemical composition and phase constitution.

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 – fusers like zinc, a non-colouring metal, and lead, a metal that contributes to enhance transparency and brilliance. Colourants with diversified constitution also contribute to increase the chemical complexity of tile glazes.

An opacifier (most frequently tin) was often added to make the glaze white-opaque due to the formation of a dispersed crystalline phase – an oxide (cassiterite, SnO_2) that can be easily detected through the diffraction pattern obtained by directly irradiating the surface of a small glaze fragment, using a common X-ray laboratory apparatus. However, the interpretation of the obtained diffraction pattern is sometimes difficult due to texture effects.

Characterization of phase constitution may require complementary techniques for the direct assessment of element speciation – namely, X-ray absorption spectroscopy (XAS) using synchrotron radiation.

Formal valences 2+ and 4+ are expected for lead ions taking into account the outer electron configuration of the element – $5d^{10}6s^26p^2$. The lone pair of strongly localized $6s^2$ electrons in Pb^{II} usually induces an asymmetric coordination with ligands unilaterally positioned to form a pyramid. Conversely, the energy perturbation of $5d^{10}$ electrons due to chemical bonding in Pb^{IV} will give rise to intensity variations in the post-edge region of the X-ray absorption curve. Accordingly, the Pb L_3 absorption edge is expected to display an energy shift and various details depending on the valence and bonding state(s) of lead present in the absorbing material.

Following a first X-ray absorption near-edge spectroscopy (XANES) approach to antimony speciation in ancient yellow glazes based on the Sb K-edge [1], the present X-ray absorption study at the Pb L_3-edge concerns the assessment of lead speciation in glazes with varied colouring collected from ancient decorated tiles.

2 Experimental

2.1 *Materials*

Small fragments of lead-rich glazes with an underlying thin layer of the ceramic body were collected from decorated tiles manufactured in the 16th–18th century. Phase identification and chemical characterization were performed by direct irradiation of the glaze surface, without any further sample preparation.

Coloured model compounds selected for interpreting XANES spectra were oxide minerals where lead ions assume various coordination geometries: litharge, red α-PbO,

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✉ Fax: +351-21-2957810, E-mail: crysmin@clix.pt

with Pb^{2+} ions coordinated by four coplanar oxygen anions placed on the same side in a pyramidal arrangement [2], 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 [3]; minium, tetragonal reddish Pb_3O_4 where both valence states and coordination environments are displayed by lead [4].

To model Pb^{2+} ions in a high-coordination environment by oxygen anions, due to difficulties in obtaining a sample of the old pigment 'white lead' [5] – a mixture of cerussite [6], $PbCO_3$, and basic lead carbonate, $Pb_3(CO_3)_2(OH)_2$, a compound corresponding to the mineral hydrocerussite [7] – a white chemical product labelled 'spec-pure PbO' currently used as a chemical standard was alternatively used, since the corresponding X-ray diffraction pattern coincides with synthetic hydrocerussite (JCPDS file 13-131).

2.2 *Techniques*

Non-destructive methodologies were preferentially applied in the present study to prevent damaging the small glaze fragments that were observed and photographed under an optical stereomicroscope.

X-ray diffraction to identify the crystalline component(s) of the glaze was performed with a non-automated Philips diffractometer (Bragg–Brentano geometry), equipped with a large-anode copper tube and a graphite crystal monochromator placed in front of the diffracted beam detector.

The photon microprobe of the LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, in Orsay, France), line D15A at the former DCI storage ring, was used to perform synchrotron- radiation-induced X-ray fluorescence (SRXRF) analyses at a microscopic scale. The instrumental set-up [8] was equipped with a solid-state Si(Li) detector and the area to irradiate in the sample (minimum of $0.03\,mm^2$) was positioned with the aid of a laser beam by using a computer-controlled micrometer stage. Excitation energies of 14.6 and 21.6 keV were used for SRXRF spectra collection to optimize the detection of metals with medium atomic number (e.g. Sn and Sb).

Peak assignment was based on the usual diagnostic emission lines: $K\alpha$ in the X-ray emission spectrum of elements with medium atomic number and $L\alpha$ for elements with $Z > 42$. Data handling and processing programs developed at the LURE [9] were used for spectra deconvolution and analysis.

X-ray absorption near-edge spectroscopy (XANES) at the Pb L_3-edge was performed in the ESRF (European Synchrotron Radiation Facility, in Grenoble, France), using the instrumental set-up of beamline BM29 [10] operating in transmission mode with a Si(311) double-crystal monochromator. The experimental energy resolution ($\Delta E/E$) was about 6×10^{-5} (1 eV at the Pb L_3-edge). A lead metal foil was used for energy calibration of collected XANES spectra.

Pellets were prepared by slightly grinding model minerals and compounds and mixing the powdered material with boron nitride in proportions calculated with specific software available at the beamline (XASAM). In this way, the absorption jump was optimized and bulk absorption effects were minimized, improving the display of pre- and post-edge details.

The glaze fragments (flat and about 0.5-mm thick) were irradiated without any further sample preparation.

3 Results and discussion

According to X-ray diffraction data, crystalline SnO_2 (cassiterite) is in general present in ancient tile glazes, particularly in white ones. The occasional presence of cristobalite – the first silica phase to crystallize from a silica-rich vitreous matrix – is indicative of ageing, a conclusion corroborated by the simultaneous occurrence of calcite ($CaCO_3$). A pyrochlore-type phase identified in yellow glazes was fully discussed in a previous publication [1].

Figure 1 reproduces typical SRXRF spectra collected from tile glazes. A high lead content is common to all glazes, independently from the colour and the period of production (16th–18th century). White glazes display a higher tin content (Fig. 1a), while zinc (fuser metal) is more represented in yellow glazes (Fig. 1c).

Colouring agents were also identified in SRXRF glaze spectra: Co in blue glazes (Fig. 1b), Sb in the yellow ones (Fig. 1c), Mn plus Cu in brown glazes (Fig. 1d) and Cu in the green ones (Fig. 1e).

The possible use of a reinforced opacifier in brown glazes was assigned through the Ba L-spectrum (Fig. 1d).

An edge shift of about 2 eV towards higher energy relative to the theoretical value quoted for metallic lead (13 035 eV) was observed in Pb L_3-edge XANES spectra collected from

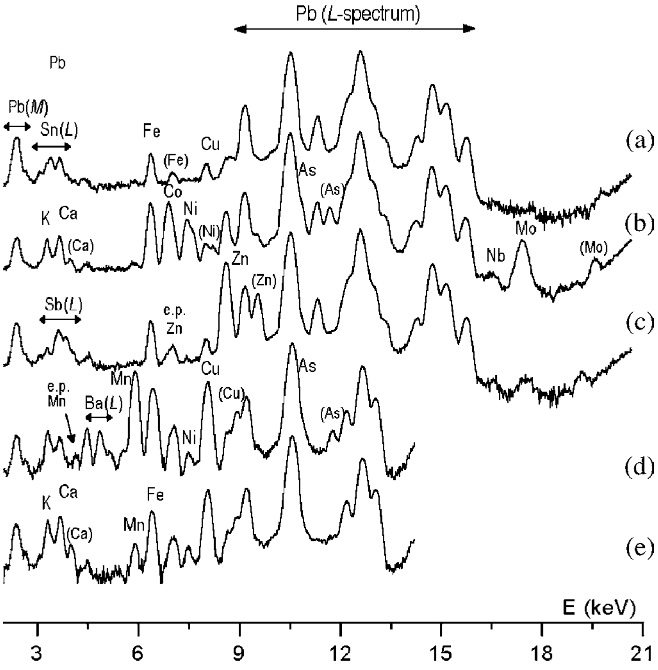

FIGURE 1 SRXRF spectra of tile glazes collected at 21.6 keV (a) to (c) and 14.6 keV (d) and (e). Intensity in arbitrary units, semi-log scale. Diagnosis $K\alpha$ lines for identified elements, plus the L- and the M-spectral regions for heavier metals, are assigned. *Escape peaks* (e.p.) of Zn and Mn $K\alpha$ are indicated, as well as $K\beta$ lines for elements present in higher concentration. Sample nomenclature according to the original labelling of the National Tile Museum (MNA, Lisbon): (a) BR 4, *white*, and (b) AZ 8, *blue*, 18th century; (c) AM 12, *yellow*, and (d) Cast 2, *brown*, 17th century; (e) Verd 7, *green*, 18th century

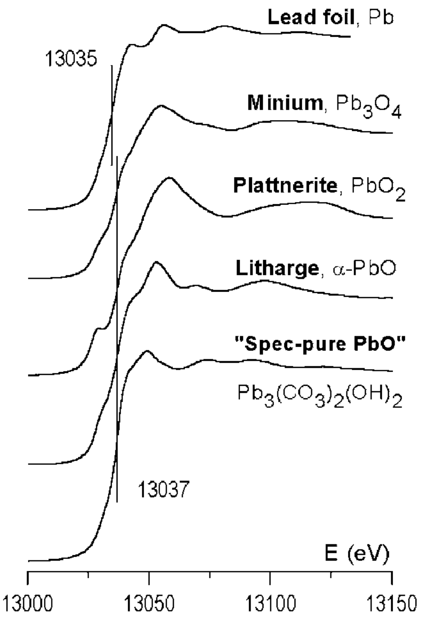

FIGURE 2 Pb L_3-edge XANES spectra of model compounds. Edge energies inferred through the inflection point of absorption curves are assigned

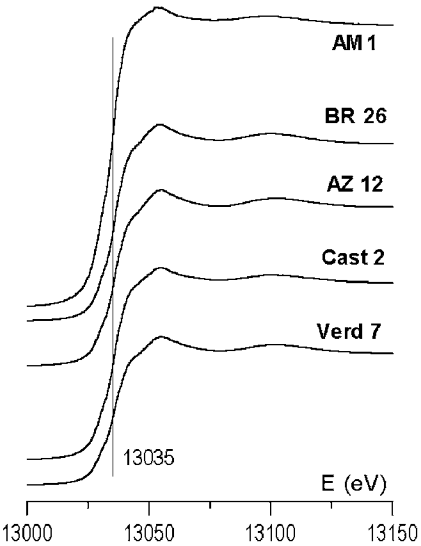

FIGURE 3 Pb L_3-edge XANES spectra of glazes: BR 26, *white* (18th century); AZ 12, *blue* (17th century); AM 1, *yellow* (16th century); Cast 2, *brown* (17th century); Verd 7, *green* (18th century)

model compounds (Fig. 2), including the succedaneum of 'white lead' ('spec-pure PbO').

Despite clear differences in pre- and post-edge details, no difference in edge energy was perceptible within the experimental energy resolution for the various structural situations involving the two formal lead ion valences 2+ and 4+.

On the other hand, differences in pre-edge details and post-edge features are clearly apparent in the XANES spectra collected from model compounds. The fact that lead ions assume different coordination numbers and geometries in the crystal structures of these compounds – white lead synthetics (hydrocerussite) and coloured oxide minerals (litharge, plattnerite and minium) – may account for the diversity of assigned details.

Conversely, the close similarity of XANES spectra collected from tile glazes (Fig. 3) implies the identity of coordination environment for lead atoms in these ancient glasses. However, the common position of the Pb L_3-edge shared by the analysed glazes (13 035 eV, identical to the theoretical value for metallic lead), raises bonding questions that call for further study.

4 Conclusions

Speciation of fuser metals and colourants in ancient tile glazes and glasses may account for chemical affinities and correlations in phase behaviour, thus contributing to clarify the ageing mechanisms.

Ancient lead-rich glazes display identical Pb L_3-edge XANES spectra, irrespective of the colour of the glaze and the period of tile production, as previously remarked. This demonstrates the similarity of lead formal valence plus coordination environment in the studied glazes and supports the conclusion that whatever the glaze colour, lead is hosted by the glassy matrix.

The comparison with Pb L_3-edge XANES spectra from model compounds (oxides and carbonates) suggests that lead plays the structural role of a glass network modifier rather than being integrated in any crystalline colouring agent, even within yellow glazes. Experimental evidence then points towards the general conclusion that lead ions possibly assume coordinations higher than usual for silica glasses [11] in the silica-lime-alkali glasses of ancient tile glazes.

Theoretical modelling of Pb L_3-edge spectra using the FEFF code based on a multiple scattering approach [12] is in progress with the purpose of interpreting edge features observed for model compounds whose crystal structure is well known. The collection of EXAFS data from the herein studied tile glazes is also foreseen in order to disclose the coordination environment effectively assumed by lead in these ancient lead-rich coloured glasses.

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