

## **Influence of the production technology on the morphological characteristics of azulejos**

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*SUMMARY: In this article some aspects of the production technology connected with the preparation of the glaze and of the biscuit and with the firing cycle have been researched in order to better understand their effects on the morphological and chemical characteristics of the glaze and glaze-biscuit interface. Azulejo reproductions have been prepared by using raw and fired ceramic bodies glazed with either a lead-tin raw preparation or with a frit of different quartz grain sizes. The firing temperatures and the duration of the firing cycles have also been varied. The resulting cross-sections of the ceramic reproductions were analysed with SEM-EDS.*

*An increase in the Pb-rich K-feldspars formed at the glaze-biscuit interface is observed as the maximum temperature increases and the cooling rate slows. The use of raw glazes and single firings also promotes the growth.*

*The results led to a better interpretation of the technological fingerprint observed on historic glazed tiles and offer more insight into the early azulejo production technologies and on the nature of the glaze-ceramic interface.*

*KEY-WORDS: majolica reproductions, azulejo, interface, production technology*

## INTRODUCTION

When researching the origin of Portuguese faience azulejos, it was found that the earliest productions of the workshops of Lisbon (maybe a single workshop working since the 1550s up to at least the 1590s) were morphologically identifiable by a peculiar crystalline growth at the glaze-biscuit interface (figure 1) which usually does not occur in later productions. This growth was commonly seen in Hispano-Moresque tiles and has been ascribed to single-fired glazed ceramics. At first sight, the high quality of the painted faience glazes raises doubts on whether a single firing process was used in their production. To help clarifying these doubts, a research project was set, whose first results are here presented.

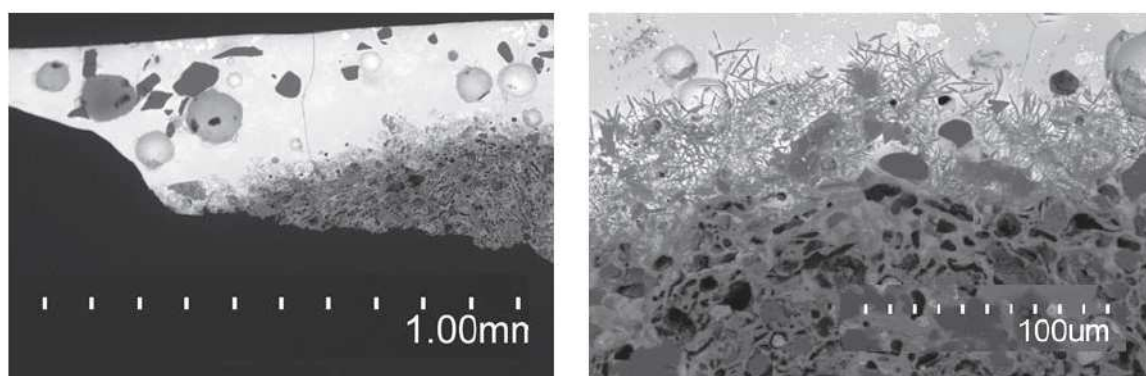


Figure 1: SEM-BSE image of a section of an azulejo from the workshop of João de Góis (Igreja da Graça- Lisboa, ca. 1565)

A better understanding of the glaze-ceramics interactions and the resulting interface is also essential to understand the azulejo as a composite material and consequently its degradation mechanisms, also contributing to develop better conservation attempts. The results of the metamorphosis supervened from the firing process also help to interpret what is seen on actual historic azulejos and to try to unravel their production technology.

During firing, the glaze fuses and interacts with the ceramic body digesting it, decomposing some constituent phases and diffusing its elements into the glaze and vice-versa [1]. When elements digested from the body diffuse into the glaze crystals are formed at the interface. For similar systems these crystals were determined to be lead-rich potassium (K) feldspars similar to sanidine with a typical formula  $K_{0.4}Pb_{0.6}Al_{1.2}Si_{2.7}O_8$  [2, 3]. It is this layer of neo-formed crystals that is commonly considered and measured as the "interface layer". In 2001, and for transparent (non-tin opacified) high-lead glazes (70:30 up to 90:10 PbO:SiO<sub>2</sub> wt%) Molera *et al* have shown that the sanidine-type feldspar crystals form a thicker layer for higher firing temperatures and lower cooling rates [4, 5].

In this article different firing cycles (maximum firing temperature, heating/cooling rates), glaze preparation type (raw or frit glaze, silica granulometry) are researched aiming to verify their effect on the glaze-biscuit interface morphology, when tin-opacified lead glazes with a composition typical of the Portuguese azulejo productions from the last quarter of the 16<sup>th</sup> century azulejos (around 50:40 PbO:SiO<sub>2</sub> wt%) were used.

## MATERIALS AND METHODS

### Ceramic biscuits preparation

A commercial calcareous paste ( $\text{SiO}_2\text{PT}^{\text{®}}$ ) was used for the preparation of the biscuit. Table 1 presents its composition according to the supplier information:

Table 1: Chemical composition of the clay paste used according to the supplier in weight %.

$\text{SiO}_2$ (%)	$\text{Al}_2\text{O}_3$ (%)	$\text{CaO}$ (%)	$\text{MgO}$ (%)	$\text{K}_2\text{O}$ (%)	$\text{Na}_2\text{O}$ (%)	$\text{Fe}_2\text{O}_3$ (%)	$\text{TiO}_2$ (%)	$\text{MnO}$ (%)	LOI (%)
47.8	15.9	12.10	1.73	2.83	0.25	4.0	0.55	0.04	14.5

For testing the effect of single, partial and double firings, glazes (raw and frit) were applied on to clay bodies that were unfired (C0), to biscuits fired at 500°C (C1), and fired at 1000°C (C2).

For firing the biscuits, a firing cycle was used with a heating rate of 100°C/h up to 500°C (C1), 50°C/h between 500 and 600°C and again at 100°C/h up to the 1000°C (C2). Both C1 and C2 biscuits were maintained for 30 min at the maximum temperature (500 and 1000 °C, respectively) and then allowed to cool down naturally.

### Glazes preparation

A typical glaze composition of tiles from the late 16<sup>th</sup> century was tentatively simulated (Table 2). For its preparation, PbO from VWR chemicals, silica powder (FPS 180 and FPS 500) from Areipor, SnO<sub>2</sub> from Merck, K<sub>2</sub>CO<sub>3</sub> from VWR chemicals, and Na<sub>2</sub>CO<sub>3</sub> from Riedel de Haen, were mixed and ground together. According to the supplier, the FPS 500 quartz grain size is lower than 45 μm, with 97 % below 25 μm, while for FPS 180 the grain size is lower than 150 μm, with 45% below 53 μm and 35 % below 75 μm. Table 2 presents the resulting glaze composition expected.

The glaze mixture was both applied “raw” or after a fritting procedure to the different biscuits. For the frit, the powdered glaze mixture was fired to 1000°C and ground to less than 106 μm.

Table 2: Expected chemical composition of the glaze in weight %.

$\text{SiO}_2$ (%)	$\text{PbO}$ (%)	$\text{SnO}_2$ (%)	$\text{K}_2\text{O}$ (%)	$\text{Na}_2\text{O}$ (%)
39	49	7	3	2

### Azulejo preparation

The “raw” and frit glaze powders were suspended in water, at approximately 1:0.5 (glaze:water) and applied by brush to the surface of the different ceramic bodies (C0, C1 and C2) and let to dry overnight. The glazes were then fired according to table 3.

Table 3: Azulejos Firing Cycles (FC)

Batch	Heating rate (≈20-500°C)	Heating rate (500-600°C)	Heating rate (600-Tmax)	Tmax.	Time at Tmax (h)	Cooling rate (>500°C)	Cooling Time (h)
FC1	100°C/h	50°C/h	100°C/h	800°C	0.5	30°C/h	10
FC2	100°C/h	50°C/h	100°C/h	950°C	0.5	30°C/h	15
FC3	100°C/h	50°C/min	50°C/h	950°C	0.5	20°C/h	22.5

## SEM-EDS

The resulting fired samples were cut and polished for observation of their cross-section by SEM-EDS. These observations and analyses were made at the HERCULES Laboratory in Évora using a HITACHI S3700N Scanning Electron Microscope (SEM) coupled to a BRUKER XFlash 5010 Energy Dispersive Spectroscopy (EDS) system. Specimens were observed uncoated and images were taken in variable pressure back-scattering mode (BSE) with chamber air pressure of 40Pa, at an acceleration voltage of 20.0 kV. The spectra acquisition was done in the same conditions with the detector set at ca. 8-9 mm distance from the specimen surface.

## μ-Raman spectroscopy

Micro-Raman analysis was performed using a HORIBA XPlora Raman spectrometer, equipped with a 638 nm diode laser and coupled with an Olympus™ microscope. The system uses a thermo-electrically cooled charge-coupled device detector (CCD). The calibration of the instrument was performed with the Raman band of a silicon crystal at 520 cm<sup>-1</sup>. Raman spectra were acquired in the 100-2000 cm<sup>-1</sup> region with an exposure time of 30 s and 10 accumulations. To avoid thermal damage of the samples, their irradiation was obtained through a 50% filter. The instrument itself was controlled using the LabSpec software. The collected Raman spectra were further processed in GRAMS (ThermoFisher Scientific™).

## RESULTS AND DISCUSSION

### Effect of silica granulometry, firing temperature and paste/ceramic biscuit pre-firing

The effect of silica grain size used for the preparation of the raw powdered glazes was studied at two different temperatures (800°C – FC1 and 950°C – FC2).

The results obtained (Figures in Table 4) show a clear difference in size of the residual non-fused/non-dissolved silica grains in the glaze layer. Silica grains of the two raw batches (coarse- and fine-grained) remain less altered at low firing temperatures (FC1). At 950°C (FC2), especially for the lower size silica grains, the formation of needle-star crystals was observed and these were identified by μ-Raman spectroscopy [6] as cristobalite (Figure 2), a high-temperature polymorph of silica [7]. At this higher temperature and especially for the lower silica grain size glaze, a higher degree of fusion/dissolution of the silica grains into the glaze matrix is visible.

A “clean” glaze layer without any visible silica grains is observed close to the interface, especially evident in the lower silica grain size (FPS500) (Table 4). This clear glaze layer is hypothetically interpreted as a segregation layer caused by the fast filtration of the freshly applied paste (proto-

glaze) induced by the high suction pressure of the porous paste/fired body. This layer was also occasionally found on 16<sup>th</sup> century Portuguese azulejos.

Table 4: Raw-applied glazed replicas made with different grain size silica fired at different firing cycles.

	Coarse silica (FPS180)		Fine silica (FPS 500)	
	C0	C2	C0	C2
FC1 - 800 °C	Not done			
FC2 - 950 °C				

C0 – applied on unfired paste; C2 – applied on a pre-fired paste at 1000°C  
 FC1 and FC2 – glaze firing cycles (picture magnifications are roughly similar)

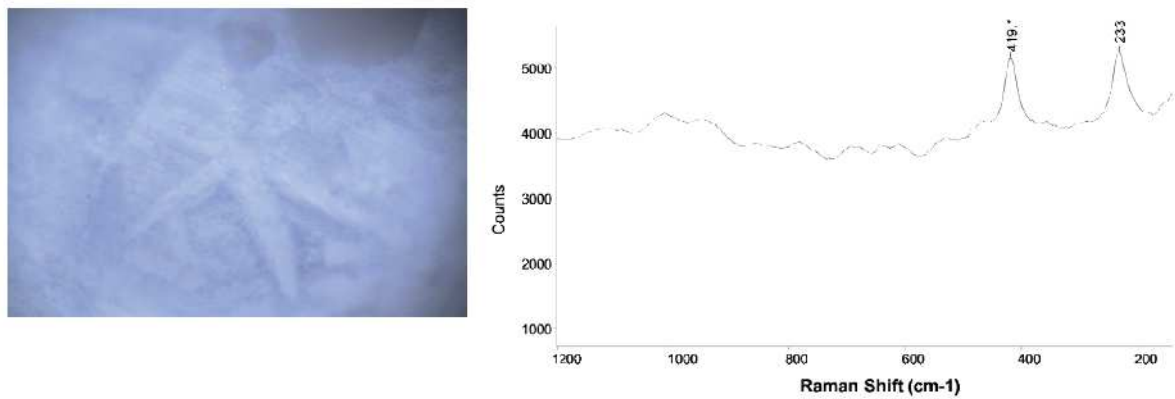


Figure 2:  $\mu$ -Raman spectrum of the needle-star crystal of cristobalite formed during the firing cycle FC1 (950°C).

Table 5: Raw-applied glazed replicas interface made with different grain size silica fired at different firing cycles

	Coarse silica (FPS180)		Fine silica (FPS 500)	
	C0	C2	C0	C2
FC1 - 800 °C		Not done		
FC2 - 950 °C				

C0 – applied on unfired paste; C2 – applied on a pre-fired paste at 1000°C  
FC1 and FC2 – glaze firing cycles (picture magnifications are roughly similar)

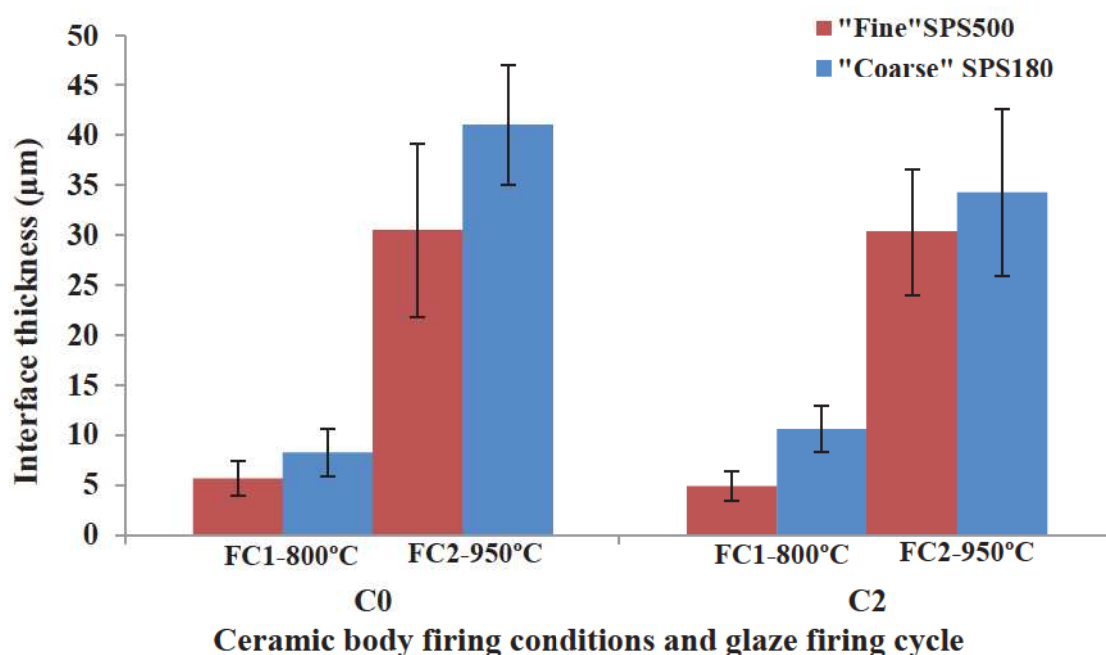


Figure 3: Interface thickness of azulejo replicas prepared with raw-applied glazes prepared with coarse- (FPS180) and fine- (FPS500) grained silica proto-glaze and with firing temperature cycles FC1 (800°C) and FC2 (950°C).

### Comparison of “raw” and frit glazing

When fritting a raw glaze, an extra fusion/dissolution of the quartz grains occurs as a consequence of the two-step heating and grinding of the frit. The resulting glaze may show a total dissolution of the quartz grains into the glass matrix or a decrease of their average size (Table 6). A larger increase of the interface thickness is observed when using a raw glaze when compared to its equivalent frit (Table 7, Figure 4). This may be due to a decrease in the effective Pb/Si ratio that happens in the frit glaze as a consequence of its faster fusion and consequent higher Si content in the fused phase. A similar effect occurs when using silica powders with different grain sizes. In the finer grained powder, silica is dissolved faster and at a higher extent resulting in a lower Pb/Si ratio.

Figure 4 compares the interface thickness for the “raw” and frit glazes applied on to an unfired clay body (C0), on to a biscuit fired at 500°C (C1), and fired at 1000°C (C2). The results show that no significant differences exist between the unfired (C0) and fired at 500°C (C1), while a significant reduction in the interface thickness is visible when using ceramic bodies fired at 1000°C.

At the glaze firing temperature of 950°C the formation of needle-like crystals, probably of cristobalite, could also be observed (Table 6).

Table 6: General view of tiles with raw and frit glaze powders prepared with coarse quartz sand FPS180 after glazing at 950°C, using the firing cycle FC2.

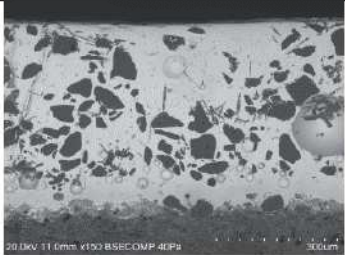
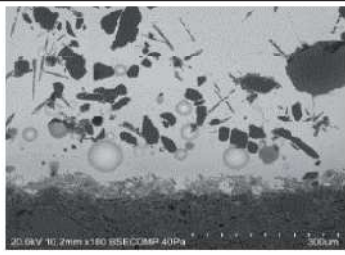
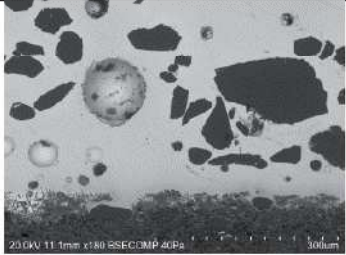
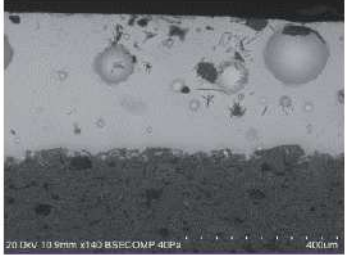

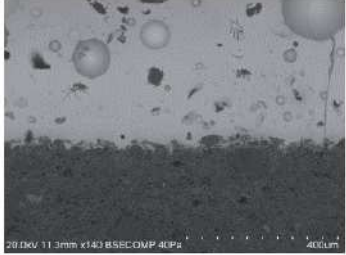
	C0	C1	C2
Raw			
Fri			
C0 – applied on unfired clay body; C1 – applied on a biscuit pre-fired at 500°C; C2 – applied on a biscuit fired at 1000°C (picture magnifications are roughly similar)			

Table 7: Interface of tiles with raw and frit glaze powders prepared with coarse quartz sand FPS180 after glazing at 950°C, using the fire cycle FC2.

	C0	C1	C2
Raw			
Frit			

C0 – applied on unfired clay body; C1 – applied on a biscuit pre-fired at 500°C; C2 – applied on a biscuit fired at 1000°C (picture magnifications are roughly similar)

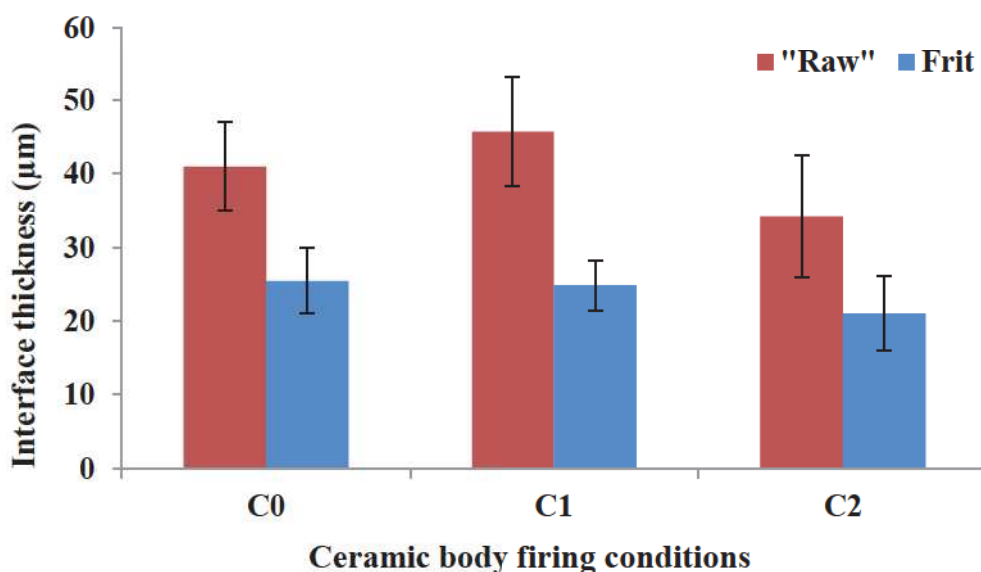


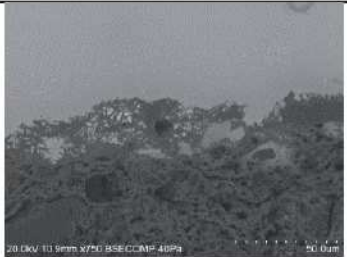





Figure 4: Interface thickness of azulejos prepared with raw and frit glazes with FPS180 silica granulometry and at a maximum firing temperature of 950°C (firing cycle FC2).



### Effect of slower and faster firing cycles

When analysing the results obtained for the fritted (FC2 fast cooling and FC3 slow cooling firing cycles) a slight increase of the interface width is observed, as made evident by the presence of Pb-rich K-feldspar crystals. This effect is slightly more evident when the biscuit was fired at 1000°C (Table 8 and figure 5).

Table 8: Interface of azulejos prepared with a frit glaze after being fired at 950°C according to fire cycle FC2 (slower) and FC3 (faster).

	C0	C1	C2
FC2 - Fri			
FC3- Fri			

C0 – applied on unfired clay body; C1 – applied on a biscuit fired at 500°C; C2 – applied on a biscuit fired at 1000°C (picture magnifications are roughly similar)

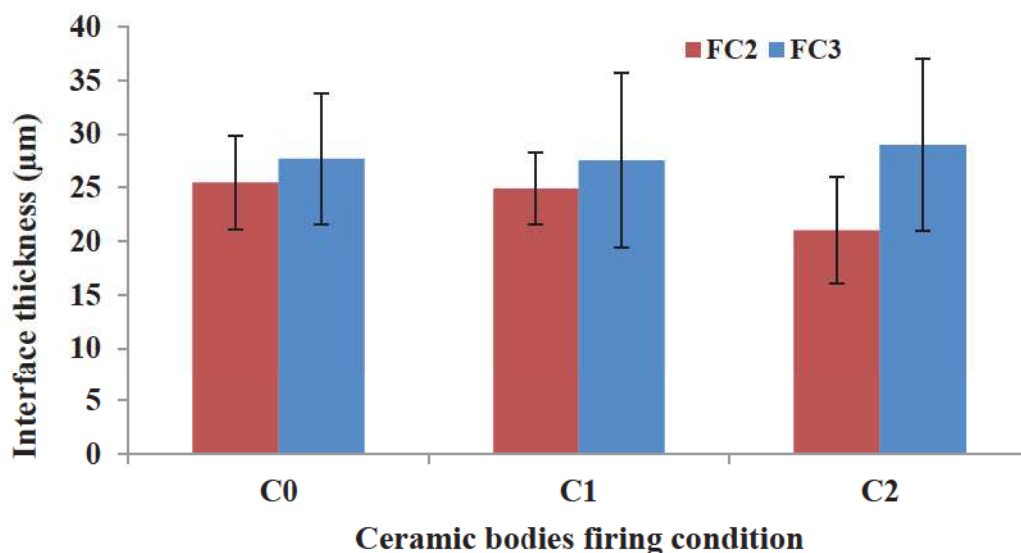


Figure 5: Interface thickness of azulejos prepared with a frit glaze after being fired up to 950°C using the firing cycles FC2 (slower) and FC3 (faster).

## CONCLUSIONS

The effect of firing conditions and glaze-biscuit preparation on the lead-tin azulejos interface morphology has been researched. Our study showed that the cross-sectional thickness and chaotic appearance of the glaze-biscuit interface layer does not, in itself, mean that the tile was single-fired.

Under the test conditions, the interface formed reached higher thickness for higher firing temperature and when using a “raw” vs a frit glaze as well as with a coarser silica powder. Slower heating/cooling rates and the use of single (C0) and partial (C1) pre-firing temperatures also led to higher interface thickness.

These morphological modifications are accompanied by significant chemical changes at both the glaze and ceramic levels, which may help to understand better the interactions between them. These aspects are currently under research and will be communicated in future papers.

## Acknowledgements

S. Pereira acknowledges FCT, the Portuguese Foundation for Science and Technology, for her Post-Doc Grant (SFRH/BPD/116807/2016).

Communication produced as an outcome of Project FCT-AzuRe - Estudos no Azulejo Português para Candidatura a Património da Humanidade (PTDC/EPH-PAT/5096/2014) also funded by FCT.

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