A technical comparison of three renaissance azulejo panels from the workshops of Lisbon

João Manuel Mimoso; Sílvia R. M. Pereira; Alexandre N. Pais; Maria Augusta Antunes; Ana Margarida Cardoso; Maria de Lurdes Esteves; António Candeias

ABSTRACT

This study of the early production of faience azulejos in Lisbon relies on three panels or groups of panels of known Portuguese origin: the incomplete and dispersed panels in Graça church, signed by João de Góis and presumably datable to 1560-1570, the panel called Nossa Senhora da Vida today conserved in the Museu Nacional do Azulejo (National Azulejo Museum) bearing a text that we believe identifies João de Góis as the workshop master and datable to ca. 1580, and the panels that line São Roque chapel in Lisbon, dated "1584" and signed "Francisco de Matos".

In this article we compare the information obtained from the microscopic observations and instrumental analyses of samples collected from tiles of the several panels aiming to determine their common characteristics and most relevant differences.

RESUMO

Este estudo da produção inicial de azulejos de faiança em Portugal toma como referência três painéis ou grupos de painéis de origem comprovadamente portuguesa: os painéis dispersos e incompletos da antessacristia da Igreja da Graça em Lisboa, assinados com o monograma de João de Góis e presumivelmente datáveis entre cerca de 1560-1570, o painel da antiga Capela de Nossa Senhora da Vida da demolida Igreja de Santo André, hoje conservado no Museu Nacional do Azulejo, onde existe um texto que acreditamos identifica João de Góis como o mestre da oficina que o produziu e datável a cerca de 1580, e os painéis que ainda hoje revestem a Capela de São Roque na Igreja da mesma invocação em Lisboa, datados de 1584 e assinados "Francisco de Matos".

Neste artigo comparam-se as informações obtidas num estudo realizado sobre os três conjuntos, utilizando observações de microscopia eletrónica e análises instrumentais de amostras de azulejos dos vários painéis, tendo como objetivo a determinação de características comuns e das diferenças mais relevantes.

João Manuel Mimoso
LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, Portugal, jmimoso@lnec.pt

Sílvia R. M. Pereira
LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, Portugal / Laboratório HERCULES - Universidade de Évora, Portugal

Alexandre N. Pais
Museu Nacional do Azulejo, Lisbon, Portugal

Maria Augusta Antunes
LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, Portugal

Ana Margarida Cardoso
Laboratório HERCULES - Universidade de Évora, Portugal

Maria de Lurdes Esteves
Museu Nacional do Azulejo, Lisbon, Portugal

António Candeias
Laboratório HERCULES - Universidade de Évora, Portugal

KEYWORDS: Renaissance majolica / Early azulejo production in Lisbon / João de Góis / / São Roque church in Lisbon / Characterization of early Portuguese azulejos

ACKNOWLEDGEMENTS

The parish Priest of Santo André e Sta. Marinha à Graça Jorge Tomaz Dias, and Miguel Ângelo da Silva of Graça church are gratefully acknowledged for supporting this research.

Teresa Morna, Director of the Museu de São Roque, João Miguel Simões of Museu de São Roque, the remarkable Irmandade de São Roque represented by André Martins da Silva, are gratefully acknowledged for supporting and authorizing a limited sampling of the magnificent panels of the São Roque chapel in São Roque church.

Communication produced as an outcome of Project FCT-AzuRe - Estudos no Azulejo Português para Candidatura a Património da Humanidade (PTDC/EPH-PAT/5096/2014) funded by FCT, the Portuguese Foundation for Science and Technology. S. Pereira also acknowledges FCT for her Post-Doc Grant (SFRH/BPD/116807/2016).

LNEC Research Project 0202/111/19747.

1. INTRODUCTION

In the Holy Inquisition process against the Flemish João de Góis, he is specifically referred in 1561 as "oleiro de málaga e azulejos" (potter of faience and azulejos) [1]. This is the first presently known reference in Portugal to such a craft and he, said to have arrived in Lisbon a few years before, the earliest faience azulejo manufacturer in the country whose signed production has been identified.

A study of the beginning of the production of faience azulejos in Lisbon may rely on three early panels or groups of panels of confirmed Portuguese origin: the incomplete and dispersed panels at Graça church signed by João de Góis and presumably datable to the mid-1560s [2]; the panel of the demolished Nossa Senhora da Vida chapel bearing a text found by us that seemingly identifies João de Góis as the workshop master and datable to ca. 1580 [3]; and the panels that line São Roque chapel in Lisbon, of which the presumably oldest panel is dated "1584" and signed "Francisco de Matos" [4]. Thus the three groups are presumed to represent a span of ca. 20 years at a time when the Portuguese inclination for faience azulejos was gaining roots.

The present article presents a technical comparison of those three groups aiming to establish common characteristics with which other productions may be compared, towards the establishment of a comprehensive list of productions of the same workshop or technological circle.

2. TECHNOLOGICAL NOTES

2.1. The glaze of azulejos

The main components of the staniferous glaze used in faience azulejos since their early manufacture in Portugal, during the third quarter of the 16th century, are: sodium (Na, a fusing agent); silicon (Si, the main component of the glaze); potassium (K, also a fusing agent); tin (Sn, the opacifier promoting the whiteness of the otherwise transparent glaze); and lead (Pb, the other main component of the glaze acting as the principal fusing agent that lowers the fusion temperature of silica from ca. 1700 ^{o}C to less than half that value) [5]. Other elements routinely found in the glazes in contents higher than 1 wt. % are: magnesium (Mg); aluminium (Al); and iron (Fe).

Three points to note when studying glazes are: i) the all-important Si/Pb ratio, a parameter that determines the temperature at which the glaze can be fired (the lower the ratio, the lower the temperature needed); ii) the nature and size of the inclusions in the glaze, such as feldspars and grains of sand, which are digested during firing in a way that the remainders left in the glaze are related with their initial content, granulometry and firing conditions (it should be noted that the degree of digestion is also reflected in the final composition of the glaze); and finally iii) the digestion by the molten glass of clay minerals in the contact area with the biscuit leading, over cooling, to crystalline growths of lead-rich K-feldspars in the interface whose magnitude depends on the compositions and firing cycle [6; 7].

2.2. The biscuit of azulejos

The biscuit is rather more complicated than the glaze because the raw materials are sedimentary clays/marls in which many chemical elements are found, including rare-earth elements. The major elements routinely found are: calcium (Ca); the main components of sodium/potassium aluminium-silicate minerals (Na, Al, Si and K); and also Mg, Fe and titanium (Ti). The biscuit may also incorporate up to 10 % in weight of Pb, particularly in the region nearest to the interface with the glaze.

When there was not a suitable marl with the appropriate characteristics of moldability and thermal retraction over cooling to be compatible with the glaze, the pastes were prepared by mixing clays, marls and possibly a source of calcium until a proper result was achieved [8].

2.3. The technology of faience azulejos

Faience azulejos are a layered material in which a previously fired ceramic base (the biscuit) is overlaid by a layer of raw glass, which may be painted with pigments able to withstand temperatures of over 1000 ^{o}C, and is subsequently fired a second time to a white opaque colour. During this second firing, the glass becomes a glaze by connecting to the biscuit in a very durable manner as long as there is a degree of compatibility between them. That compatibility stems from both the compositional possibility for a strong bond to develop over firing, and a similar thermal retraction rate of both materials on cooling after the glaze hardens, otherwise the glaze would either crack (crazing) or peel (shivering).

It is reasonable to suppose that once a workshop had one or more viable formulations, either by trial-and-error or because its master brought with him the "secret" from his apprenticeship in some other workshop, it would stick to them unless better formulations were later acquired [8; 9]. Such approach is also mentioned with contempt by Bastenaire-Daudenet looking back at his experience as head of a French workshop in the late 18th century when trial-and-error was being supplanted by the scientific approach [10].

In the Hispano-Moresque tiles (mostly from the first three quarters of the 16th century) the low Si/Pb ratio in glazes, often less than 50% [11; 12], means that they could be successfully fired at a relatively low temperature. It can also be noted that, in some Hispano-Moresque tiles, there are very noticeable crystalline outgrowths from the biscuit to the glaze [11; 12]. These neo-formed crystals are a consequence of the glaze composition and firing cycle (temperature and duration) and have been duplicated in reproduction studies [6; 7]. As the manufacture of azulejos in Portugal progressed from the 16th to the 17th centuries, the ratio Si/Pb increased [11]. This development likely derived from an improved firing technology at higher temperatures and, by using less lead for the same weight of cheaply available siliceous sand, the production costs were lowered. Concomitantly, the Ca/Si ratio in the biscuits is seen to increase as well, possibly to adjust to the new glaze formulations, also allowing to reduce the content in expensive tin – a light cream biscuit requires less tin to form a perfectly white glaze than the brown-red biscuits often seen in 16^{th} century tiles.

Of the utmost importance when studying geographical provenance of glazed ceramics is the notion that there were only two materials almost certainly of local origin, as long as they were available, as was the case in Lisbon: i) siliceous sand for the glazes; and ii) suitable marl and clays for the biscuits. Therefore, the biscuit is of prime interest for geographical provenance studies because it should be fully local while the glaze incorporates local sand but also materials eventually imported from afar. To complicate matters, the glaze also digests and incorporates material from the biscuit over firing [7]. Any particular composition of the local sand beds may still stand against this background but it may also be lost in such a diverse glassy matrix.

When there were several workshops in the same vicinity, they would likely source marl and clay from the same geological strata and consequently the biscuits are good indicators of geographical provenance but do not necessarily allow the singling out of workshops. But since glaze compatibility was required and it could be achieved in a number of ways by varying the relative contents of the raw materials, the composition of glazes as well as the morphology of inclusions may help identify specific workshops. Finally, the firing cycle imparts to the glaze inclusions and to the glaze/biscuit interfaces distinct morphologies that may be correlated with specific kilns.

3. EXPERIMENTAL

3.1. Samples

The samples used in this study formed three groups collected from:

- the renaissance panels of Graça church (Figure 1). Samples from this group bear the reference Az013;
- the Nossa Senhora da Vida panel from the collection of Museu Nacional do Azulejo (Figure 2). Samples from this group bear the reference Az032;
- the lining of São Roque chapel dated "1584" (Figure 3). Samples from this group bear the reference Az068.

The individual test items from each group were assigned an alphanumeric identification added to the reference.

Details about the sampling locations in the panels may be found, respectively, in references [2], [3] and [4].

Figure 1. Two aspects of the azulejo panels in Graça church from where samples Az013 were collected

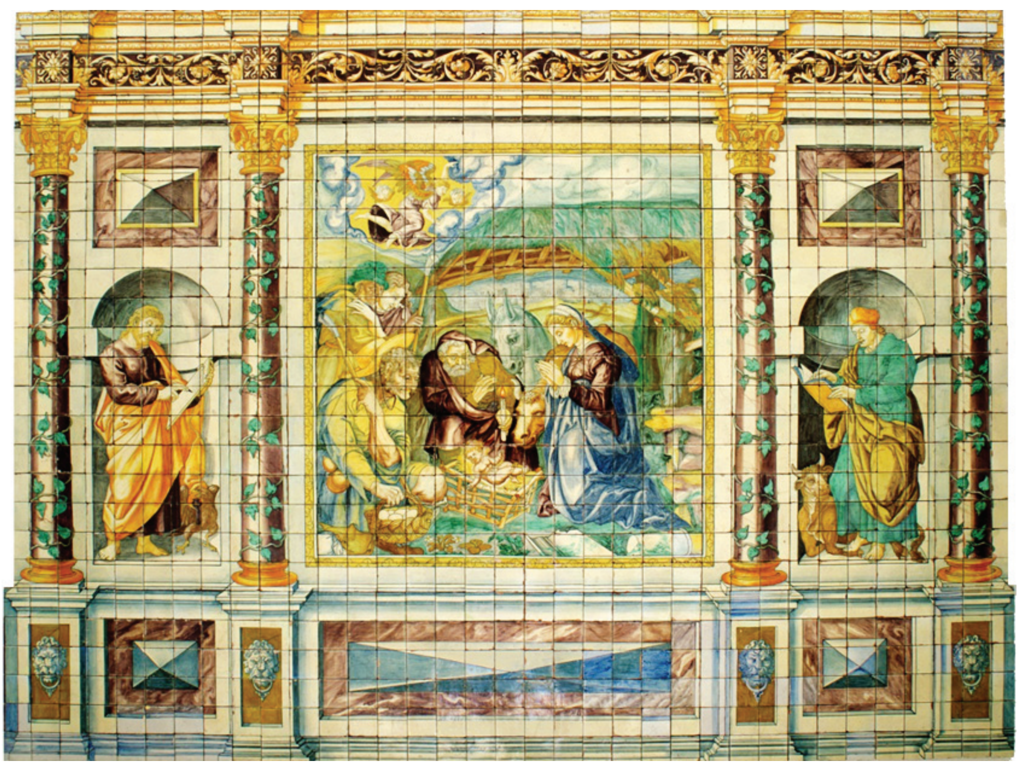

Figure 2. The lower part of the Nossa Senhora da Vida azulejo panel from which samples Az032 were collected

Figure 3. The signed panel on the Gospel side of São Roque chapel from which samples Az068 were collected

3.2. Equipment and technical methodology

The small samples detached from the azulejos with a scalpel were stabilized in epoxy resin, lapped and polished to obtain a flat surface for observation and analysis by scanning electron microscopy coupled with an X-ray energy-dispersive spectrometer (SEM-EDS).

Optical observation and acquisition of sample images used a Leica DFC295 digital camera attached to a Leica M205C stereomicroscope.

SEM-EDS observations and analyses were made at the HERCULES Laboratory in Évora using a HITACHI 3700N SEM coupled to a BRUKER XFlash 5010 EDS. The specimens were uncoated and the observations were made in backscattered electrons mode (BSE) with a chamber pressure of 40 Pa and at an accelerating voltage of 20 kV. The acquisition of X-ray spectra was done with the detector set at ca. 8 mm working distance.

The selection of areas for EDS analysis avoided inclusions in the glaze or biscuit representing more than ca. 5 % of the full area analysed. The preferred area sizes for analytical purposes were ca. 200 x 200 μm^2 for glazes and 500 x 500 μm^2 for biscuits but acceptable repeatability was verified in areas four times smaller. For comparison purposes, only the elements usually representing the major contents were considered, excluding tin (Sn) in the glaze and lead (Pb) in the biscuit due to their variability with the area chosen (in the case of Sn because of local aggregations of SnO_2 crystals; in the case of Pb because its content in the biscuit increases with proximity to the interface with the glaze). The results of the EDS analyses are given in weight % of each element identified.

Principal component analysis (PCA) was made of EDS results using the SPSS® software platform by IBM Analytics.

3.3. Results

3.3.1. Glaze morphology

Figure 4 compares sections of samples with yellow or orange paint from all panels. The transparent areas seen over the paint in sections prepared from the Az013 Graça church samples reveal the use of *coperta*, a final layer of transparent glaze sprinkled over the rather dull yellow or orange areas to restore the gloss and protect the superficial colour from abrasion. The sections of samples from the São Roque church and Nossa Senhora da Vida panels do not depict any *coperta*.

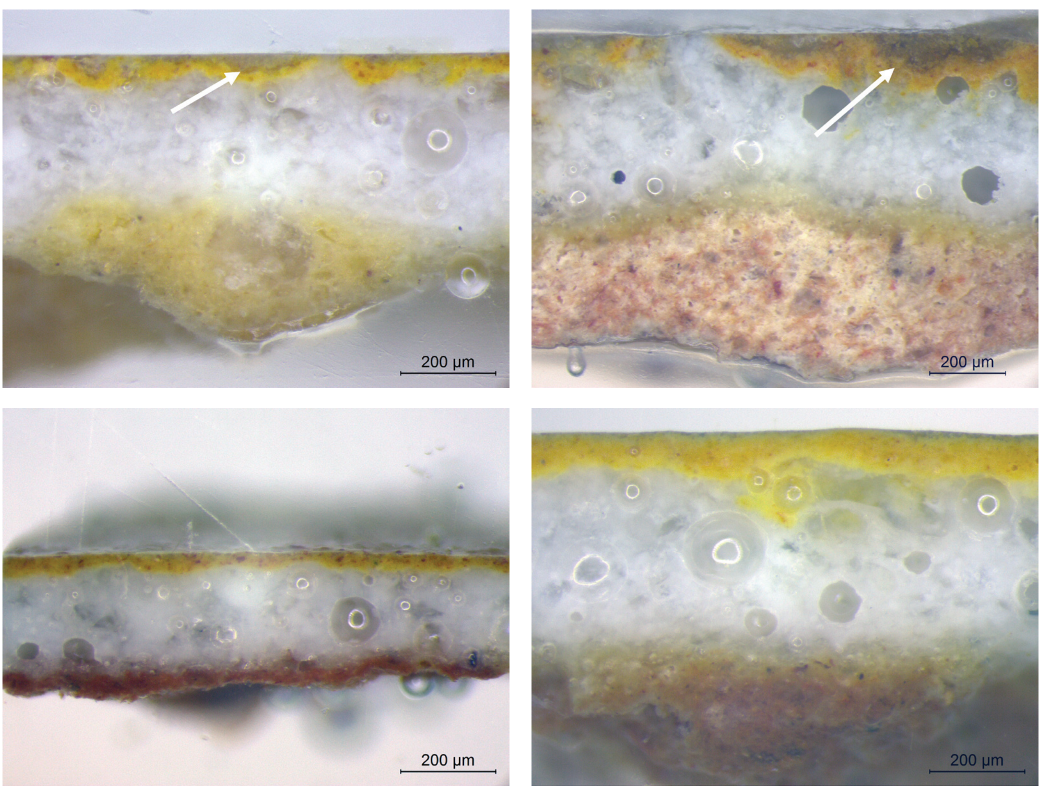

Figure 4. Top to bottom: use of sprinkled *coperta* in samples Az013/01 (left side) and Az013/L3 (right side) – the arrows indicate spots where drops of transparent glaze fell; absence of *coperta* in samples Az032/03 (left side) and Az068/02 (right side)

Figures 5, 6, and 7 illustrate SEM images of sample sections from the several panels, establishing the main micro-morphologic characteristics associated with the glazes. All depict in common the presence of few inclusions in the glazes, predominantly grains of silica, often large, and a glaze-biscuit interface characterized by the presence of abundant crystals of neoformation.

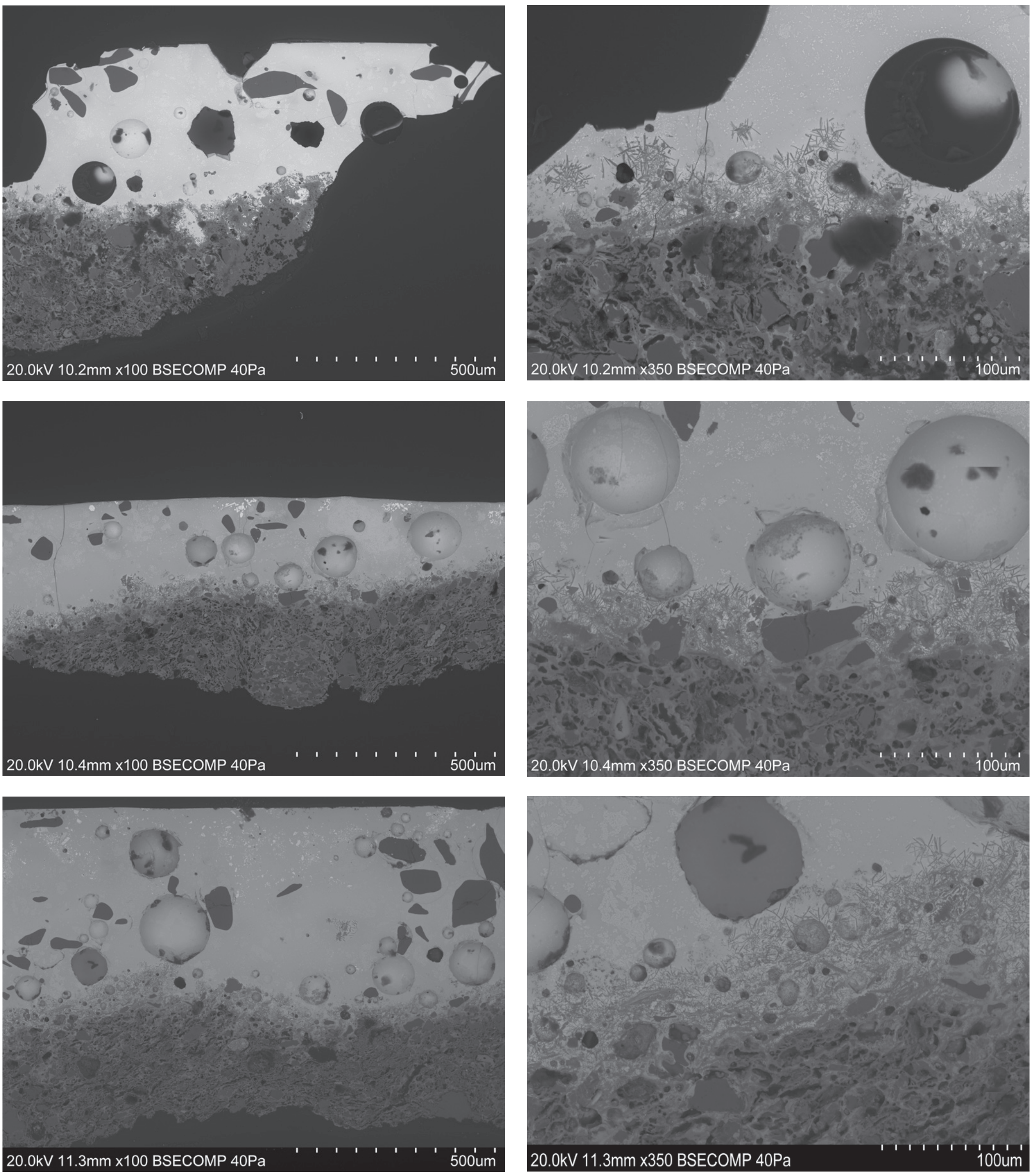

Figure 5. SEM images showing the glaze and the interfacial micro-morphology in azulejos of Graça church panels – from top to bottom: samples Az013/L1; Az013/L2; and Az013/L3 from tiles adjoining the monogram of João de Góis

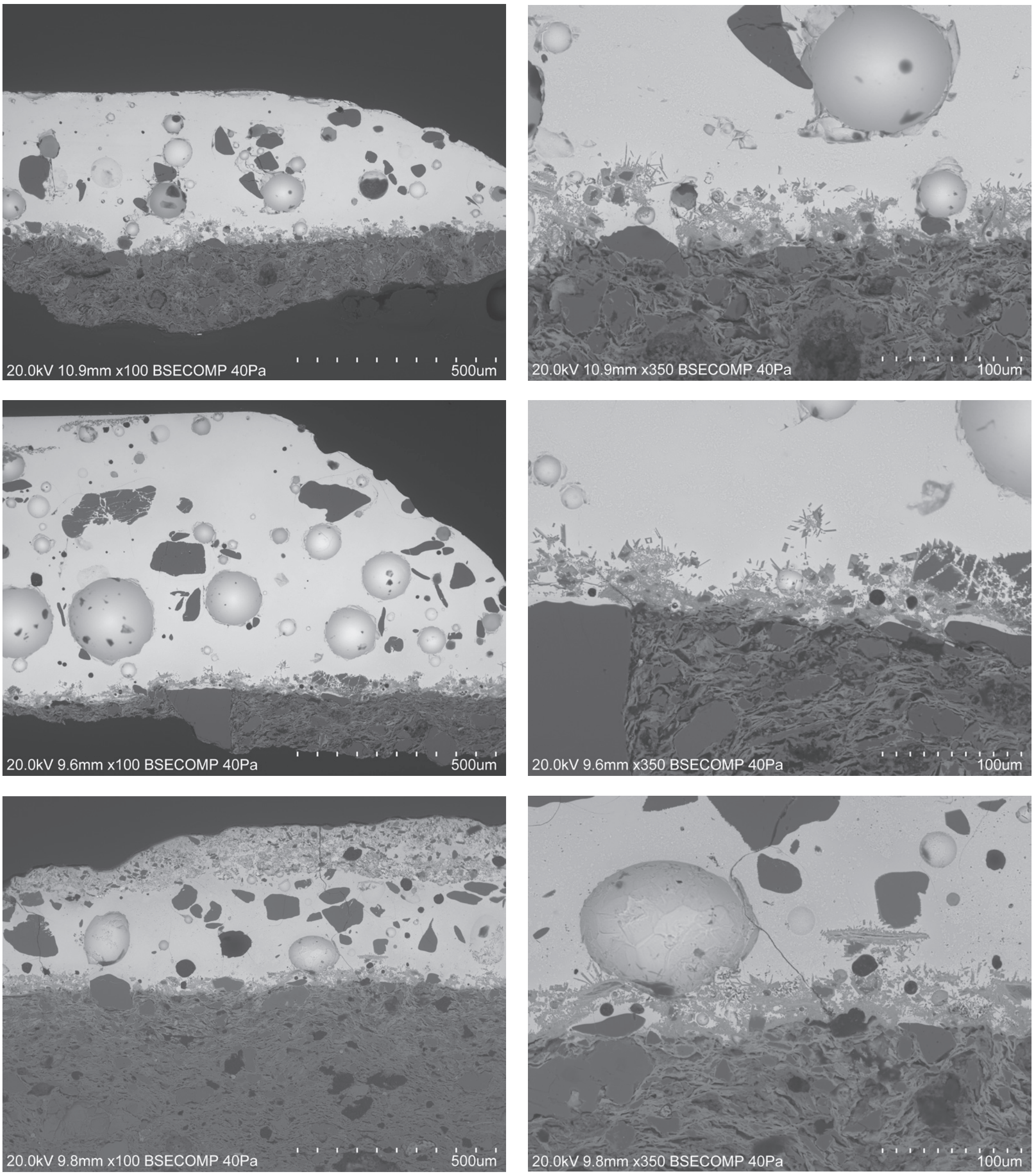

Figure 6. SEM images showing the glaze and the interfacial micro-morphology in azulejos of Nossa Senhora da Vida – from top to bottom: samples Az032/01; Az032/02; and Az032/08

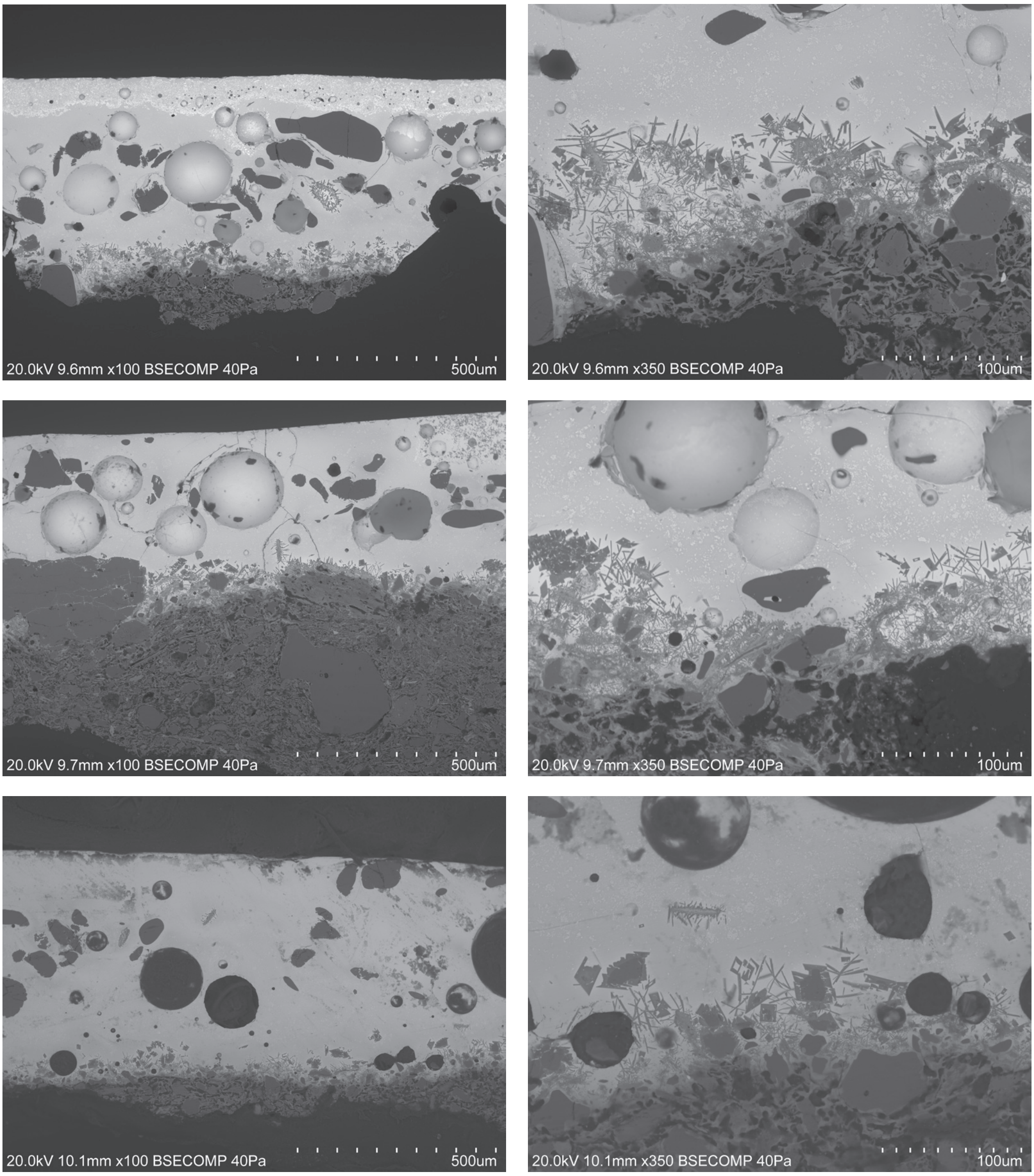

Figure 7. SEM images showing the glaze and the interfacial micro-morphology of azulejos from São Roque chapel – from top to bottom: samples Az068/02; Az068/03; and Az068/13 from tiles of the signed panel

3.3.2. Glaze composition

Table 1 includes the semi-quantitative results of glaze analyses by EDS in weight %. Sn was excluded for the reasons pointed out in section 3.2. The amount of oxygen was calculated through the remaining elements stoichiometry considering their most commonly considered oxides (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, Fe_2O_3 and PbO). The results were normalized to 100 % and the table also indicates the ratios Si/Pb.

Table 1. Semi-quantitative composition (% w/w) of the glazes determined by EDS (weight of the elements normalized to 100 %) and Si/Pb ratio

	Sample	Na	Mg	Al	Si	K	Fe	Pb	O	Si/Pb
Graça church	**Az013/01**	1.6	0.3	2.3	23.2	2.9	0.7	36.0	32.9	0.64
	Az013/03	1.9	0.8	4.3	17.9	1.6	1.6	42.0	29.8	0.43
	Az013/04	1.9	0.9	3.5	16.3	1.4	1.2	47.4	27.4	0.34
	Az013/07	1.8	0.8	2.4	21.1	2.4	0.8	39.5	31.2	0.53
	Az013/T1	1.0	0.3	2.7	17.9	1.0	0.7	48.7	27.6	0.37
	Az013/T2	1.7	0.7	3.2	19.4	2.2	0.6	42.2	30.0	0.46
	Az013/L1	1.2	0.4	2.9	19.5	1.7	0.5	44.2	29.5	0.44
	Az013/L2	1.1	0.5	3.3	20.2	1.9	1.1	41.2	30.7	0.49
	Az013/L3	1.3	0.5	3.3	19.0	1.6	0.8	44.1	29.4	0.43
Nossa Senhora da Vida	**Az032/00**	0.9	0.5	2.4	14.5	0.9	0.6	56.1	24.1	0.26
	Az032/01	1.4	0.7	2.6	15.3	0.8	0.6	53.3	25.3	0.29
	Az032/02	0.8	0.7	2.9	16.5	1.2	0.6	50.6	26.6	0.33
	Az032/04	0.7	0.2	3.7	23.8	2.6	1.1	33.6	34.4	0.71
	Az032/05	0.9	0.5	2.7	15.0	0.7	0.8	54.5	24.9	0.28
	Az032/06	1.1	0.5	2.3	15.6	1.0	0.7	53.5	25.2	0.29
	Az032/08	0.7	0.2	4.2	20.5	1.5	1.0	40.5	31.4	0.51
São Roque chapel	**Az068/01**	1.2	0.7	2.7	18.3	1.9	0.5	46.5	28.3	0.40
	Az068/02	1.2	0.8	3.3	18.6	2.0	0.8	44.3	29.1	0.40
	Az068/03	1.3	0.8	3.5	17.6	1.9	0.9	45.6	28.4	0.39
	Az068/05	0.8	0.5	3.0	18.3	1.6	0.7	46.6	28.4	0.39
	Az068/06	1.0	0.5	2.7	18.7	1.4	0.6	46.8	28.5	0.40
	Az068/08	1.1	0.6	4.2	19.2	2.2	1.2	41.0	30.5	0.47
	Az068/09	0.9	0.4	2.4	16.2	0.8	0.7	53.1	25.7	0.30
	Az068/10	0.8	0.4	3.7	19.4	1.2	1.0	43.8	29.9	0.44
	Az068/11	1.0	0.3	4.3	21.9	1.9	1.1	36.7	32.9	0.60
	Az068/12	0.8	0.1	3.8	19.0	2.7	1.1	42.8	29.7	0.44
	Az068/13	0.7	0.1	2.3	19.4	1.4	0.8	46.6	28.7	0.42
	Az068/14	1.0	0.4	2.7	18.7	2.0	0.5	46.2	28.5	0.40

Figure 8 shows the results of a log-based principal component analysis (PCA) of the glazes of all samples, considering the analytical results in Table 1, through a plot in the plane of the two first principal components (PC1 and PC2). PC1 explains 48 % of the variation and is controlled in the positive sense by the contents in Si, K, Al and Fe and in the opposite sense mostly by the content in Pb, as can be seen from the loadings plot of

Figure 9 in which the projections of the vectors on an axis show the contribution of each element to the respective principal component. PC2 explains 24 % of the variation and is controlled in the positive sense mostly by the contents in Na and Mg and in the opposite sense mostly by the content in Si (Figure 9).

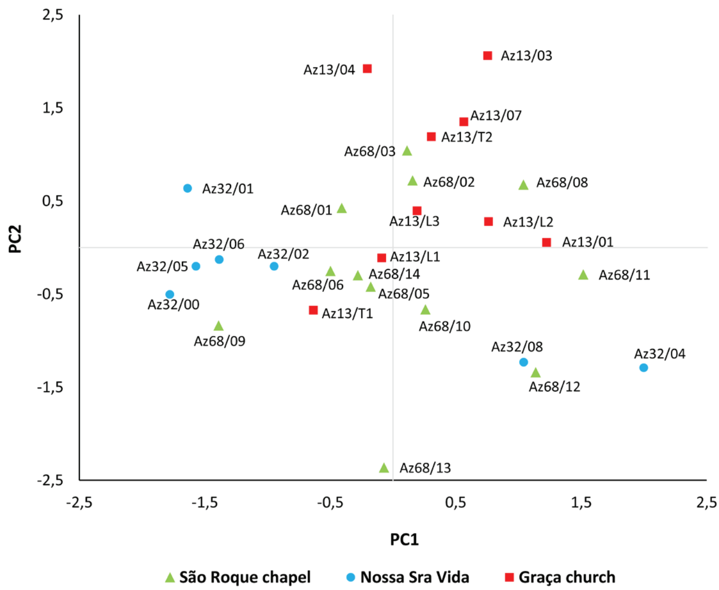

Figure 8. Score plot of PCA analysis of the glazes in which samples are code-coloured according to their origin

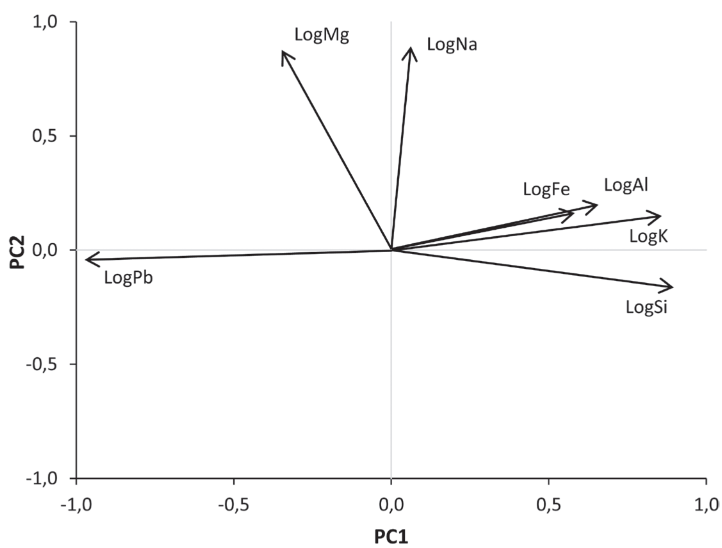

Figure 9. Loadings plot of PCA analysis of the glazes

3.3.3. Biscuit composition

Table 2 includes the semi-quantitative results of biscuit analyses by EDS in weight %. Pb was excluded for the reasons pointed out in section 3.2. The amount of oxygen was calculated through the remaining elements stoichiometry considering their most commonly used oxides (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO and Fe_2O_3). The results were normalized to 100 % and the table also indicates the ratios Ca/Si.

Table 2. Semi-quantitative composition (% w/w) of the biscuits determined by EDS (weight of the elements normalized to 100 %) and Ca/Si ratio

	Sample	Na	Mg	Al	Si	K	Ca	Fe	O	Ca/Si
Graça church	Az013/01	1.8	4.2	8.4	21.1	2.1	15.0	4.2	43.2	0.71
	Az013/03	1.9	2.6	9.4	20.4	2.4	17.0	3.5	42.8	0.83
	Az013/04	1.6	1.6	8.4	26.5	2.5	10.8	3.2	45.5	0.41
	Az013/07	1.4	3.9	8.6	23.8	1.4	12.5	3.7	44.7	0.52
	Az013/T1	1.5	1.6	8.4	26.2	3.4	10.2	3.5	45.2	0.39
	Az013/T2	1.3	2.2	9.3	21.4	1.4	17.0	4.1	43.4	0.79
	Az013/L1	1.3	1.7	8.4	26.5	2.6	10.6	3.3	45.5	0.40
	Az013/L2	1.2	1.4	8.3	26.8	3.2	9.2	4.4	45.5	0.34
	Az013/L3	1.4	1.7	8.3	25.5	2.5	12.2	3.6	44.9	0.48
Nossa Senhora da Vida	Az032/00	1.5	1.7	10.5	25.3	3.8	6.4	5.3	45.4	0.25
	Az032/01	1.2	2.2	9.1	24.6	2.7	9.5	5.9	44.9	0.39
	Az032/02	1.1	1.5	8.7	28.8	2.7	6.9	3.5	46.7	0.24
	Az032/04	1.8	1.4	9.7	23.2	4.0	10.8	5.2	44.0	0.47
	Az032/05	1.2	1.7	12.7	25.4	4.2	2.6	6.0	46.2	0.10
	Az032/07	1.3	1.5	10.3	25.9	3.8	6.5	5.1	45.7	0.25
	Az032/08	1.4	1.8	10.7	23.6	3.6	9.3	4.8	44.7	0.39
São Roque chapel	Az068/01	1.0	1.1	9.2	25.3	5.0	8.7	4.8	44.7	0.34
	Az068/02	1.4	1.3	8.9	27.5	3.4	8.6	2.9	46.0	0.31
	Az068/03	1.3	1.3	7.7	28.9	2.5	8.7	3.2	46.4	0.30
	Az068/05	1.0	1.1	7.3	27.8	3.0	10.7	3.4	45.6	0.39
	Az068/06	1.3	1.4	8.5	27.9	2.6	9.0	3.3	46.1	0.32
	Az068/08	1.5	1.3	9.3	24.9	3.7	10.2	4.4	44.7	0.41
	Az068/09	1.7	1.8	9.1	27.1	2.9	7.1	4.3	46.0	0.26
	Az068/10	1.7	1.4	10.0	26.2	3.2	7.2	4.5	45.7	0.28
	Az068/11	1.4	1.7	10.0	23.0	3.5	12.5	3.7	44.1	0.54
	Az068/12	1.3	1.6	9.1	24.1	2.9	12.4	4.2	44.4	0.52
	Az068/13	0.7	0.9	7.9	28.5	4.0	8.7	3.2	46.0	0.31
	Az068/14	1.4	1.2	8.3	29.9	3.4	6.1	2.8	47.0	0.20

Figure 10 shows the results of a log-based principal component analysis of the biscuits, considering the analytical results in Table 2, through a plot in the plane of the two first principal components (PC1 and PC2). PC1 explains 42 % of the variation and is controlled in the positive sense by the contents in Mg, Ca and Na and in the opposite sense by K and Si, as can be seen from the loadings plot of Figure 11. PC2 explains 33 % of the variation and is controlled in the positive sense mostly by the contents in Al and Fe, and in the opposite sense by Si and Ca (Figure 11).

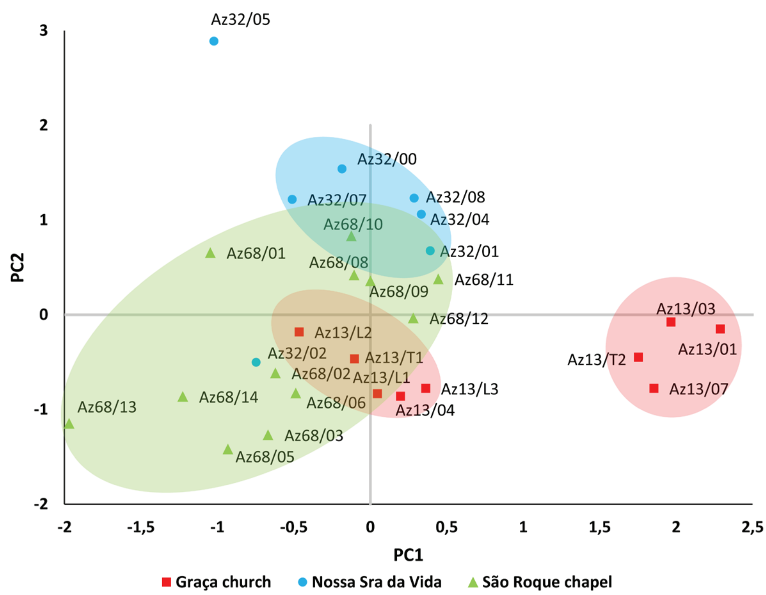

Figure 10. Score plot of the PCA analysis of the biscuits with tentative clustering

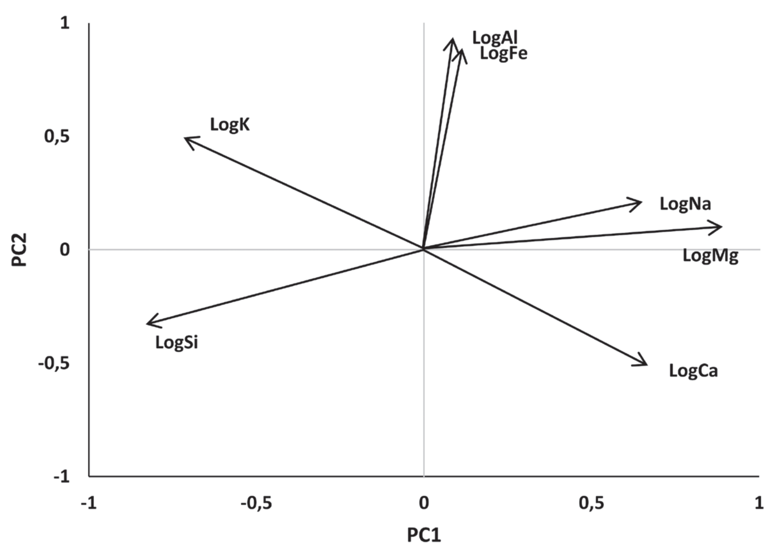

Figure 11. Loadings plot of the PCA analysis of the biscuits

3.3.4. The dark outlines of figures

The outlines of figures in the panels of Graça church (not illustrated) are sketched with a dark paint that does not offer any particularly remarkable morphology, either under the optical microscope, or the SEM. However, the dark outlines in the other two panels, exemplified by samples Az32/08 and Az068/03 of which Figure 12 illustrates sections in optical microscopy, have a peculiarity that we had not found before. In the corresponding SEM-BSE images (Figures 6 bottom left and 13 left) they are seen to contain a large number of small particles made up of low atomic weight elements (and for that reason seen as dark inclusions).

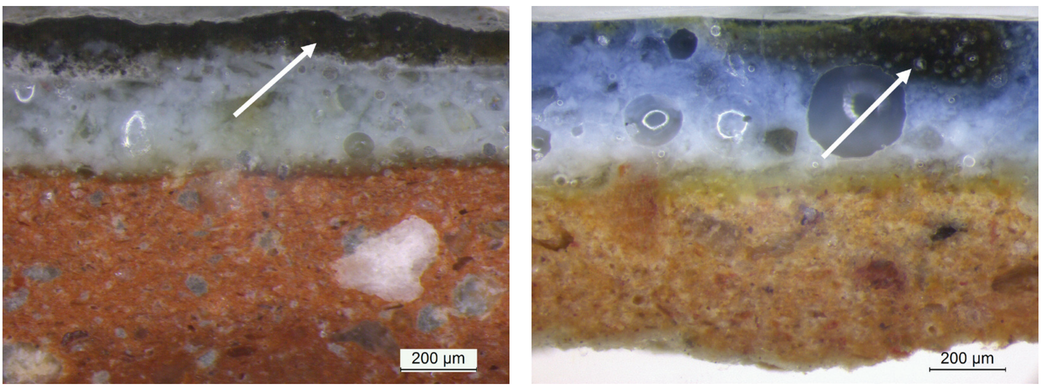

Figure 12. Optical microscopic images of cross sections of samples Az032/08 (left side) and Az068/03 (right side) depicting areas corresponding to the dark outlines (white arrows)

The particles in the outline paints (left side of Figure 13) were likely added to a smalt containing the pigments to make a paste with which the lines were painted. Besides the elements of the matrix, a high content in Ca was found in these particles, together with a higher content in Si than can be explained by the matrix (right side of Figure 13). Analyses by Raman spectrometry were inconclusive, however the calcium silicate *wollastonite*, presumed to be a possible mineral composition of the inclusions, was not detected. For the moment we may only state that the particles are of a mineral rich in Si and Ca.

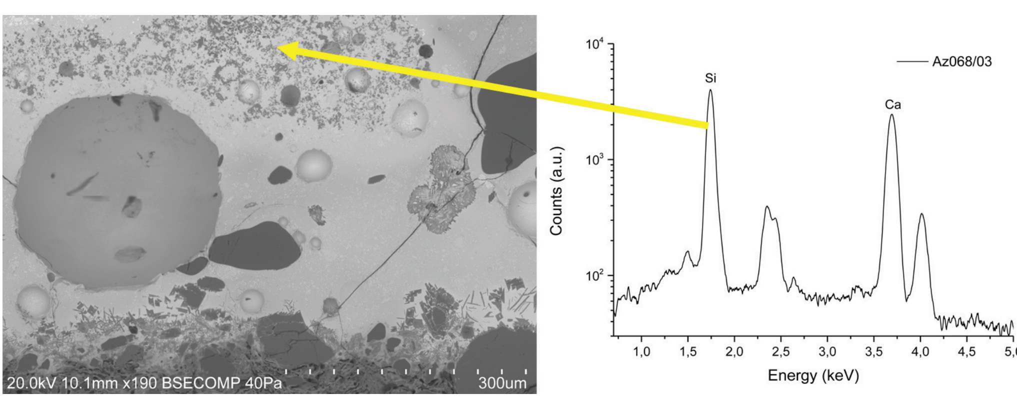

Figure 13. Selection of a particle of the inclusions added to the pigment in Az068/03 and relevant part of the resulting EDS spectrum

It will be noted that, in the São Roque panel, the outlines are largely level with the glaze surface (right side of Figure 12 and Figure 13) as is expected of a sketch on a raw glaze. However, in Nossa Senhora da Vida, some outlines are clearly protruding from the glaze surface (left side of Figure 12 and bottom left of Figure 6). The dark inclusions in this sample were also analyzed with similar results [3] but the fact that the outline protrudes from the glaze surface suggests that it may have been painted over an already fired glaze, which was then re-fired.

The mineral addition represents the sort of technological resource that may help pinpoint the production of a single workshop. Besides the two cases referred, we also found the same mineral additions when we studied azulejo-plaques from the garden of *Palácio e Quinta da Bacalhoa* in Azeitão [13]. Figure 14 depicts one such plaque and a SEM-BSE image of a section in which inclusions with the same analytical signature are seen spread this time through the whole glaze, presumably to increase the viscosity of the molten glass.

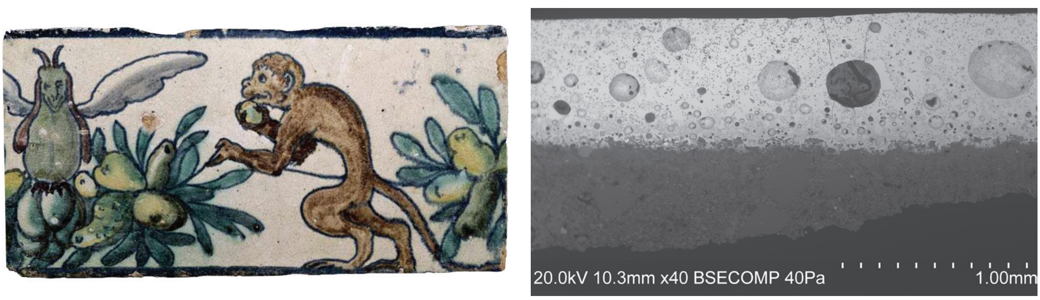

Figure 14. Azulejo plaque from *Quinta da Bacalhoa* (coll. Museu Nacional do Azulejo, inv. MNAz 53) and SEM-BSE image of a section in a white area of the same plaque

3.3.5. The yellow pigments

An extensive study of the pigments used will be published hereafter, however it must be noted that in both Graça church and Nossa Senhora da Vida we identified the use of a Sb+Pb+Sn light yellow pigment [14] that we have also found in azulejos imported from Antwerp [15]. Figure 15 depicts EDS spectra corresponding to yellow areas in each panel covered by the present study. In both Graça church and Nossa Senhora da Vida the unusual Sb+Pb+Sn yellow pigment was found, as seen by the presence of the conspicuous Sn peak, while in São Roque the only yellow found was the common Sb+Pb *Naples Yellow*.

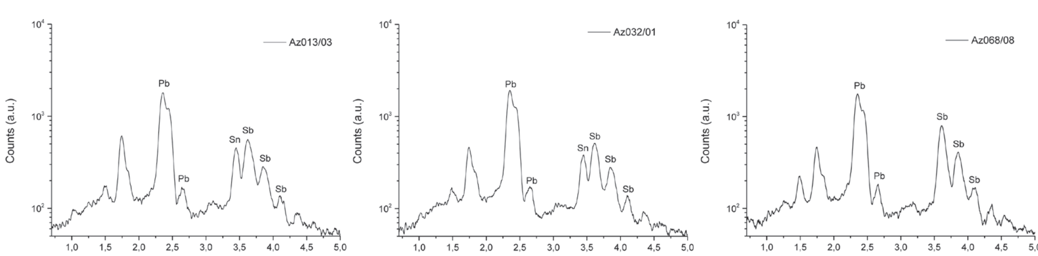

Figure 15. Partial EDS spectra of the yellow pigment in samples of the three panels covered by the present study – notice the lack of the Sn peak in the yellow used at São Roque

It should also be noted that in the first two panels mentioned a remarkable wealth of colours and hues was used, particularly greens, blues and yellow/oranges (Figures 1 and 2). Not on the panels of São Roque, where the colours are the plain Naples yellow and then the usual cobalt blue, manganese violet and copper green with a few other (such as the brown of the dog fur or the greenish dark blue of some outlines) obtained from simple mixtures of pigments. Actually, the palette depicted by the whole lining of São Roque chapel is basically the same that would be used in Portuguese azulejos throughout the 17th century.

4. DISCUSSION

The glazes of all samples studied are closely related by their low Si/Pb ratio (usually under 0.5) and comparable morphologies (Figures 5, 6, 7). The low Si/Pb ratios separate them clearly from the typical 17th century compositions which usually have Si/Pb ratios around or over 1.0 [11] while the inclusions and interfacial morphologies suggest they were all fired in similar conditions, possibly even in the same kiln. The composition of the glazes of all three panels is also comparable, notwithstanding the extended chronology they represent. Up to now we have not encountered the combined characteristics found here in any other group of faience azulejos we have studied, neither Portuguese productions of later centuries, nor 16th century Seville productions[1] or azulejos from the workshops of Antwerp [11; 15], granting a marked difference for tiles produced in Lisbon at this time, seemingly stemming from the technology introduced by the workshop of João de Góis [1; 2] and which we may therefore take together as *the technological circle of João de Góis*. Accordingly, the PCA of the glazes does not allow a clear clustering: samples from the three panels are mixed together (Figure 8). Still, the distribution is not wholly random and the Nossa Senhora da Vida samples (except Az032/04 and Az032/08) are seen to be slightly skewed to the left of the PCA1 vs. PCA2 plot when compared to the rest (Figure 8). This results from these samples having, in average, a higher content in Pb and a correlated lower content in Si and K (Table 1) than samples from the other panels. A higher content in Pb would be expected from an older production because it could then be fired at a lower temperature, but Nossa Senhora da Vida is not the oldest in the group. This fact suggests that Nossa Senhora da Vida may have been produced to a more exacting specification and the high content in Pb that certainly lead to a higher cost may have been intended to ensure a reduction of defects of the surface that might impair the overall aspect, combined with higher gloss [16; 17].

The use of *coperta*, as seen in the panels of Graça church (Figure 4 top), was probably superseded by the use of better yellow smalts (a mixture of the pigment with finely ground glass or its components, giving the result seen in the bottom row of Figure 4) and *coperta* was considered superfluous by the time the other two panels were produced.

For the biscuits, an aggregation in clusters seems feasible. The fact that the biscuits from different panels are not identical is what may be expected from their diverse chronologies and the natural variability of the marls or clays used in the preparation of the ceramic pastes. Clustering in PCA plots is always the result of subjective decisions and in this case,

1 A comparative study with 16th century faience azulejo productions of Seville will be published at a later time, but a number of samples have already been studied, the oldest of which a pattern used in *Santa Clara* convent in Seville, dated from 1576, that depicted a completely different glaze morphology.

bearing in mind the uncertainty on the quantification of the composition of the biscuits particularly at the scale of our study, we considered Az032/02 and Az032/05 as outliers, left out of the four proposed clusters in Figure 10. It is remarkable that, although samples from both the panels of Nossa Senhora da Vida and São Roque chapel can be aggregated in individual clusters, Graça church can better be represented by two different clusters of which that at the right side of the plot of Figure 10 includes Az013/01, Az013/03, Az013/07 and Az013/T2. These four samples are characterized by biscuits with Ca/Si ratios above 0.5, higher Ca and Mg and lower K contents than the average. Those relevant disparities suggest that the azulejos that make up the Graça church panels may actually represent two different chronologies [2].

The peculiar addition of a finely ground mineral to form a paste with which the dark outlines of figures are painted, suggests independently a connection between Nossa Senhora da Vida and São Roque and also with the azulejo plaques that decorate the garden of Palácio da Bacalhoa in Azeitão.

The use of a rare yellow pigment including tin in its composition connects Graça church with Nossa Senhora da Vida and suggests that the pigment may have been purchased from Antwerp [15]. The fact that by 1584, when the lining of São Roque was started, the pigment, together with a wealth of hues of other colours, seemingly was no longer available, may be connected with the so-called *Sack of Antwerp* on November 1576 that laid the city waste, cut short its economic prosperity, and very likely interrupted the supply of art materials.

5. CONCLUSIVE NOTES

The results presented here demonstrate that there are collective attributes allowing to group 16th century azulejos produced by the workshops of Lisbon within what we may call *the circle of João de Góis*. This is not an artistic circle, but rather a technological one, highlighting the fact that at this time, when the manufacture of faience azulejos in Lisbon was in its early years, there might be a considerable number of painters but likely few potters mastering the means needed to produce quality panels. Those workshop masters (if indeed more than one) shared a common technique (glaze compositions and firing cycle) which identifies *the Circle*.

The results have shown that there is significant variation in the composition of the biscuits, maybe stemming from the fact that the ceramic pastes were produced from marls or clays from different pits and varying depths. However, the composition of the glazes remains stable throughout the period, probably because it represented a reasonable assurance of good results when firing the tiles according to a set cycle involving a single kiln. The very distinctive morphology of the glazes, particularly as pertains the development of neoformed crystals in the glaze-biscuit interface, is probably more a consequence of the firing cycle than of the composition of the glaze itself. This point has to be borne in mind when assessing later productions that lack the same interfacial development: different glaze morphologies may result from diverse firing cycles in different kilns, rather than characterize singly a workshop.

The morphology of the glazes will likely be immediately affected when a different firing cycle is adopted, but the elemental composition of the glazes and biscuits does not change substantially when a different kiln is used. However, when a higher firing temperature is obtained, the ratio Si/Pb may be increased to save on the cost of lead. Once more results become available, these and similar considerations may help establish the progressions and chronological sequences that marked the spread of the production of faience azulejos in Portugal.

BIBLIOGRAPHIC REFERENCES

1. PAIS, A. et al. – *The beginning of the production of majolica azulejos in Portugal – João and Filipe de Góis in 16th century Lisbon* in Studies in Heritage Glazed Ceramics, No. 1, pp. 1-24, LNEC, Lisbon, Portugal, February 2019.
2. PAIS, A. et al. – *Study of the azulejo panels in Graça church signed by João de Góis* in Studies in Heritage Glazed Ceramics, No. 1, pp. 47-66, LNEC, Lisbon, February 2019.
3. PAIS, A. et al. – *The 16th century nativity azulejo panel called "de Nossa Senhora da Vida"* in Studies in Heritage Glazed Ceramics, No. 1, pp. 67-76, LNEC, Lisbon, February 2019.
4. MIMOSO, J. et al. – *A research on the azulejo panels of the São Roque chapel in Lisbon* in Studies in Heritage Glazed Ceramics, No. 1, pp. 93-112, LNEC, Lisbon, February 2019.
5. RAVAGLIOLI, A. & KRAJEWSKI, A. – *Chimica Fisica Tecnica e Scienza dei Materiali Antichi Ceramici e Vetrosi, Museo Internationale della Ceramiche*, pp. 219-229, Faenza, Italy, 1989.
6. PEREIRA, S. et al. – *Influence of the production technology on the morphological characteristics of azulejos* in Proc. Int. Conf. Glazed Ceramics in Cultural Heritage (GlazeArt 2018), pp. 140-149, LNEC, Lisbon, 2018.
7. MOLERA, J. et al. – *Interactions between Clay Bodies and Lead Glazes*, Journal of the American Ceramic Society, Vol. 84, No. 5, pp. 1120-1128, May 2001.
8. ESTEVES, M. – *Estudo do fabrico e da degradação de azulejos portugueses históricos*, PhD thesis, pp. 41-49, Universidade Évora, Portugal, 2016 (available through the Internet).
9. CAMPAGNE, C. – *Een verkeerde loop in 't vuur: an initial investigation into what Dutch archival sources can tell us about techniques and problems in the production of 17th and 18th century Dutch tin-glaze tiles*, in Proc. Int. Conf. Glazed Ceramics in Architectural Heritage (GlazeArch 2015), LNEC, Lisbon, 2015.
10. BASTENAIRE-DAUDENET, F. – *L'Art de Fabriquer la Faïence Recouverte d'un Émail Opaque Blanc et Coloré,* pp. 11-13 & 27-32, Paris, France, 1828.
11. MIMOSO, J. et al. – *A comparison of the earliest faience tiles produced in Lisbon with earlier and later types,* in Studies in Heritage Glazed Ceramics, No. 1, pp. 25-46, LNEC, Lisbon, February 2019.
12. COENTRO, S. – *An Iberian Heritage: Hispano-Moresque architectural tiles in Portuguese and Spanish collections*, PhD thesis, pp. 60-62 & 132-135, Universidade Nova de Lisboa, 2017 (available through the Internet).
13. RASTEIRO, J. – *Inícios da Renascença em Portugal – Palácio e Quinta da Bacalhoa*, Estampa XXVII, Figura 22, Lisboa, 1898.
14. SECCARONI, C. – *Giallorino – Storia dei pigmenti gialli di natura sintetica*, pp. 78-90 & 180-211, De Luca Editori D'Arte, Roma, Italy, 2006.
15. MIMOSO, J. et al. – *Analytical study of tiles of presumed Flemish origin from the Palace of the Dukes of Braganza in Vila Viçosa* in "From Flanders. The azulejos commissioned by D. Teodósio I, 5th Duke of Braganza, pp. 64-74, Museu Nacional do Azulejo & Fundação da Casa de Bragança, Lisbon 2012.
16. WACHTMAN, J. – *Materials and Equipment – Whitewares Manufacturing,* p. 146, John Wiley & Sons, 2009.
17. NORSKER, H. & DANISCH, J. – *Glazes for the self-reliant potter*, Deutsches Zentrum fur Entwicklungstechnologien (GATE-GTZ), Eichborn, 1993.