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Evolution of azulejo glaze technology in Portugal from the 16th to the onset of the 19th century

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ABSTRACT

Azulejos have been applied to architectural settings in Portugal for the last five centuries and represent one of its most unique art forms. In this article a group of representative samples regarding the chronology and typology of the majolica azulejos produced by the Lisbon workshops from the second half of the 16th century (beginning of majolica azulejos production in Portugal) up to the first quarter of the 19th century (after which more industrialized manufacturing processes were introduced) are studied. SEM-EDS was used to obtain morphological and chemical information on the glazes, ceramic bodies, and their interfaces. The results show that a major shift from lead-rich to lead-alkali glazes occurred in the transition from the 16th to the 17th century, while from then to the end of the studied period the same basic technology prevailed. The Lisbon tiles production is also considered in the European context.

1. Introduction

Portuguese glazed ceramic tiles (azulejos) are one of the most original contributions of Portugal to the European cultural heritage. Portuguese majolica azulejo production was initiated in Lisbon and is rooted in a long tradition of glazed lead-tin based ceramics practice within Europe. Since the middle ages that archaic forms of majolica [1–5], lustre-ware [4,6–10], and Hispano-Moresque wares and tiles [11–15] were actively produced in the Iberian Peninsula and highly acclaimed and traded throughout all Europe [16]. However, it is believed that the production of majolica tiles only began in Portugal in the second half of the 16th century, initiating a cultural tradition and heritage that has continued until the present day.

Majolica, lustre-ware and Hispano-Moresque techniques all apply tin-lead glazed technology (at least in part of the ceramic's decoration) however their production technology differs. With the majolica technique a tin-lead glaze layer is applied over the ceramic body, after which pigments (or smalt) suspensions are applied on the top of the glaze layer. A final firing procedure is performed to fuse the decorated layer, revealing the actual decoration colour scheme. With the lustre technique, a previously fired white tin-lead glazed ware, while sometimes having on-glaze decoration with pigments or smalt (as with the majolica technique), is further decorated by applying a mixture containing metal copper and/or silver compounds and fired a third time in a reducing atmosphere to form the metallic nanoparticles that originate the shine effect. With the Hispano-Moresque technique, the design is obtained by applying integrally coloured glazes, including white tin-lead glaze, on designated areas of the ceramic body. While other terms (such as maiolica, faience, delftware or talavera) are also used to designate the production of tin-glazed ceramics, in this article the term majolica will be generally applied.

The origin and subsequent diffusion routes of the tin-glazed technology are still unclear. However, it is generally accepted that the technology was known in Iraq since before the 9th century and from there the technology spread to North Africa and Eastern Mediterranean countries [17]. In the 9–10th centuries tin-glazed ceramics were introduced from North-Africa into the Iberian Peninsula with possible local production said to occur from the 10th century on (Fig. 1) [1,10,18]. At that time, the Islamic rule of the Iberian Peninsula highly influenced the ceramic aesthetic and technology, originating a prolific production and trade of archaic majolica, lustre wares and Hispano-Moresque tiles [16,19,20]. In the beginning of the 13th century the tin-opacified lead glaze

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technology diffused from Spain and possibly from the South of Italy into North and Central Italy (Fig. 1) resulting by the mid-15th century in the development of majolica of an exceptional quality [17,21]. The success of the artistic forms of the *istoriato* wares [21] and sculptural Della Robbia glazed ceramic workshops during the Renaissance had consequences all over Europe, ultimately leading, by the end of the 15th and throughout the 16th century, to the emigration of Italian potters towards the northern Europe and the Iberian Peninsula (Fig. 1), who were looking for new markets and opportunities to establish new workshops [17,21]. The exceptional Italian majolica technology is believed to have been transferred by the Italian potters Francisco Niculoso and Guido Andries in the 1490s, first to Spain [20,22] and around 1508 to Antwerp [23]. During the 16th century the Flemish-Italian majolica-style production, including tile panels was well established and commercialised throughout Europe, leading to a new wave of technology transfer thorough the migration of Flemish potters within Europe (Fig. 1) [24]. During the 16th and 17th centuries, after the expulsion of the Moorish rulers to North Africa in 1610 [20], a change of taste developed from the success of Italo-Flemish majolica style [16] a decline in the production of lustre-ware and Hispano-moresque tiles went together with an increase in the production of fine majolica ware and tiles.

Both before and during the 16th century, Hispano-Moresque azulejos (Cuerda seca and arista types) were common Spanish imports in Portugal [22,25,26]. Italo-Flemish style majolica tile panels are however known to have also been imported in the second half of the 16th century from Antwerp (1558) [22,24] and Seville [22,27]. These imports have certainly stimulated the beginning of the majolica tile production in Portugal.

In this article five distinctive Portuguese tile production periods from the second half of the 16th century up to the beginning of the 19th century will be considered:

1.1. 16th century (Renaissance): the beginning of majolica tiles production in Portugal

The Portuguese manufacture of tin-lead majolica tiles is believed to have been started in Lisbon in the second half of the 16th century by the Flemish potter Hans Goos (João de Góis in its Portuguese adopted name) [28]. The first written record regarding the production of azulejo in Portugal is present at the Holy Inquisition order of arrest of João de Góis, in 1561, where he is mentioned as "oleiro d'azulejos e malegueiro" (potter of tiles and majolica tableware). While their work is still unidentified, other potters working with tin-glazed ceramics such as João de Góis' brother Filipe de Góis, João Fernandes, Pero Fernandes and Francisco Jácome were known to be active in Lisbon around that time [28,29]. The Lisbon azulejo productions between the 1560's up to the end of the 16th century are distinct being characterized by their Renaissance style and use of Italo-Flemish inspired patterns, high artistic quality and exuberant use of colours (see Fig. 2 and Figure A.1).

1.2. 17th century (Pattern and Figurative)

At the end of the 16th to the beginning of the 17th century, the use of colour, while still being polychromatic, changed to a somewhat less exuberant *palette.* At the same time there was an increase in the production of patterned tiles. The patterns tiles were mainly composed of single elements and modules (being composed of 2 ×2 up to 12 ×12 tiles), usually representing geometric decorations, sometimes of vegetal inspiration. Figurative or ornamental panels also depicted exotic fauna, flora and religious themes as well as hunting and mythological subjects (Fig. 2, Figure A.1).

1.3. 18th century (Cycle of Masters)

By the end of the 17th century, the fashion for blue and white Chinese porcelain and the success of Dutch tiles and Delft ware derivatives took Europe by storm, leading to the almost exclusive production of blue

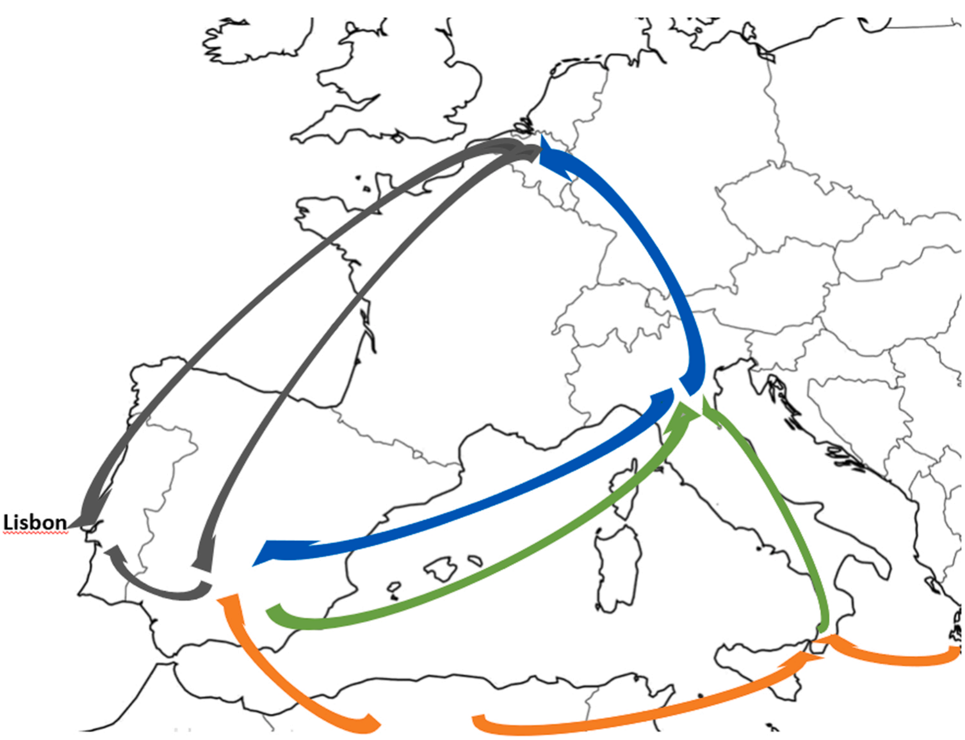

Fig. 1. Possible tin opacified lead glaze technology transfer routes. Legend: 10th centuries tin glaze technology transfer to the South of Iberian Peninsula and South of Italy, 13th century technology transfer from Spain and south Italy to Northern-Central Italy, end of the 15th - beginning of 16th century perfected Italian majolica technology transfer to North Europe and Spain, second half of the 16th century Flemish majolica technology transfer to Spain and Portugal (Lisbon).

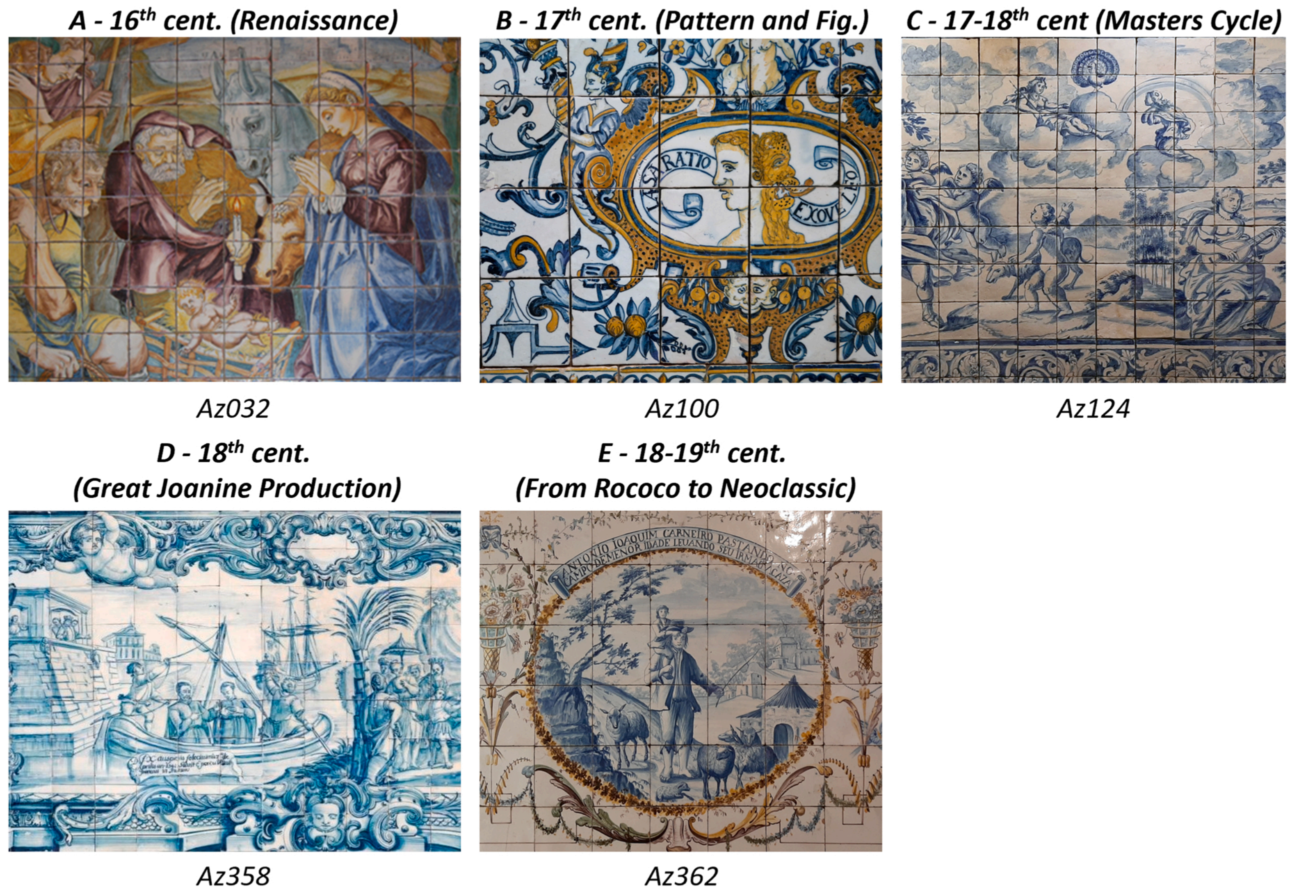

Fig. 2. Representative images of the studied tiles. Periods A-E.

and white tiles, including in Portugal. The restoration of the Portuguese monarchy resulted in a period of renovation and construction of palaces and religious buildings leading to an increased demand for azulejos [22]. The import of Dutch tiles characterized by a finer artistic work with a pristine white, regular surface and detailed figurative depictions [22,30] originated a reaction by the Portuguese workshops to accommodate the resulting demand for a higher artistic quality. Established easel artists, as well as gifted mural painters, were consequently hired in order to assure a higher quality of pictorial rendition [22]. King Pedro II repeated ban on tile imports (1687–1698) further stimulated the national artistic production [22,30] so that the period between the last quarter of the 17th century through the first quarter of the 18th century become known as the Golden Age of the Portuguese azulejo production, the so called "Ciclo dos Mestres" (*Cycle of Masters*) [31]. The earliest artist to be encompassed within that cycle was the Spanish artist Gabriel del Barco, but soon local artists were involved, such as Manuel dos Santos, Antonio de Oliveira Bernardes and his son Policarpo de Oliveira Bernardes, as well as the Master (or Masters) who signed superb panels with the monogram "P.M.P". These artists contributed to the development of an exuberant and professional decorating style, based on a free and pictorial use of engravings (Fig. 2, Figure A.1).

1.4. 18th century (Great Joanine Production)

During the reign of King John V there was a great demand for decorative panels, for palaces, churches and monasteries. The azulejo production in Lisbon increased considerably leading to workshops oriented towards high volume productions and the development of more rational production processes [32]. This period is known as the "Grande Produç ão Joanina" (*The Great Joanine Production*) lasting from the 2nd quarter of the 18th century up to the last decade of the century. The panels were still painted in blue on white but were now characterized by a repetition of iconographies and preponderance of highly elaborated decorative frames (Fig. 2, Figure A.1).

1.5. 18th-19th century (from Rococo to Neoclassic)

After the 1755 earthquake, which caused massive damage throughout Lisbon, a huge effort was directed towards the rebuilding of the town in a more rational urban style by the then prime minister, the Marquis de Pombal. This aim, together with his drive towards the industrialization of the country, led to an increase in azulejos serial production. The *"Real Fábrica de Louça do Rato" (Royal Ceramic Factory of Rato),* hereafter called the Rato Factory, started to manufacture tiles around 1771 and had an important role in the implementation of modern production technologies and the dissemination of the know-how to other factories in the country [22,31,33]. Aiming to obtain high quality and artistically-rich production the factory worked simultaneously on artistic teaching, research into new products and technologies, and the promotion of production based on economic rationality [22]. New patterns such as the Pombalino (1755–1780) and D. Maria styles (1780–1808) brought back the use of more colours than blue. By the second half of the 18th century Rococo and later the Neoclassical influence was increasingly appreciated together with panels depicting pastoral and figurative scenes [30]. At the beginning of the 19th century there was social unrest resulting from the French invasions as well as the competition from imported, novel and more industrialized tiles, resulting in a decrease in the demand for traditional decorative tiles. Many workshops dramatically reduced their production and eventually ceased their activities altogether (including the Rato Factory in 1835 [33] or were restructured, implementing more industrialized procedures and/or novel materials and tile production techniques (Fig. 2, Figure A.1).

In this article the technological evolution of the majolica azulejos production by the workshops of Lisbon from the 16th century (beginning of tile production) to the early 19th century (when more industrialized procedures and new materials were adopted) was studied considering the European majolica production context.

2. Material and methods

2.1. Materials

A group of 28 examples of azulejos produced in Lisbon between the second half of the 16th century and the first quarter of the 19th century were selected as being representative of the five production periods considered in this study:

A) 16th cent. - Renaissance (second half of the 16th century);
B) 17th cent. - Pattern and Figurative (from the beginning of the 17th century to ca. 1680 s);
C) 17th-18th cent. - Cycle of Masters (from 1680 s to ca. 1720 s);
D) 18th cent. - Great Joanine Production (from 1720 s to ca. 1760);
E) 18th-19th cent. - From Rococo to Neoclassic (second half of the 18th century up to the first quarter of the 19th century).

A: the selected representative azulejos of this restricted production period were the Graça Church grotesque azulejo panels signed by João de Góis (Az013) [28,34]; “Nossa Senhora da Vida” (Our lady of life) (Az032) [35,36]; the panel with ferroneries and a dog lining the São Roque (Saint Roch’s) chapel that are dated 1584 and signed by Francisco de Matos (Az068) [37]; the 1592 dated heraldic panel from Alcácer do Sal fountain (Az334) [38], and the also recently discovered linings - hidden behind the altar front - of Setubal Cathedral (Az199) [39]. B: the chosen tiles included pattern tiles (Az001 and Az005) but also the figurative panels (Az092, Az100, Az151, Az052). C: panels by the Masters Gabriel del Barco (Az124 and possibly Az208); António and Policarpo de Oliveira Bernardes (Az121), Manuel dos Santos (Az212), the P.M.P monogrammist (Az122) and an unsigned work (Az120) [30]. D: characteristic blue over white figurative panels with elaborated decorative frames (Az358, Az360, Az123, Az361 and Az359). E: illustrative panels in the Rococo style (Az363, Az367), D. Maria style (Az365) and azulejos with Neoclassical influences from the Rato Factory (Az362, Az364, Az366).

Table 1 summarizes the information of the samples studied. These were mainly retrieved from tile panels located at Museu Nacional do Azulejo - MNAz (National Tile Museum), in Lisbon. Pictures from the selected tile panels can be found in Fig. 2 and Figure A.1.

2.2. Methods

For optical and scanning electron microscopic analysis (SEM-EDS), small fragments (around 1 mm^3) from the tile panels were collected, embedded in epoxy resin (Epofix from Struers), lapped and polished. The optical microscope used was a Leica M205C stereomicroscope attached to a Leica DFC295 digital camera. The SEM-EDS analysis was undertaken using a Tescan Mira3 field emission SEM coupled to a BRUKER XFlash 6|30 EDS. The specimens were uncoated, and the observations were made in backscattered electrons mode (BSE), with a chamber pressure of 10 Pa, an accelerating voltage of 20 kV and an X-ray spectra acquisition working distance of 15 ± 1 mm. SEM-BSE images at different magnifications (100x, 350x, 950x) were acquired. As some samples present a yellow pigment layer on the top of the white glaze layer, the EDS analyses were done exclusively on the white areas of the glaze avoiding the pigmented areas. The EDS analysis were therefore

Table 1
Information regarding the tile panels from periods A to E.

Sample	Date	Artist/Factory	Name/Description	Sidexdepth (mm)	Location
A - 16th cent. (Renaissance)					
Az013	1560 s	João de Góis	Graça grotesques	130 × 16	Graça church, Lisbon
Az032	1580 ca.	João de Góis[a]	Our Lady of life	132 × 15	MNAz, inv. 138 Az
Az068	1584	Fr. Matos	Ferroneries and a dog	132 × 17	São Roque chapel, Lisbon
Az199	1586 ca.	João de Góis[a]	Allegory of time	-	Setúbal cathedral, Setúbal
Az334	1592	João de Góis[a]	Heraldic panel	130-15	Public fountain, Alcácer do Sal
B - 17th cent. (Pattern and Figurative)					
Az003	1600–1620	-	Angel frame tile	130 × 14	LNEC, inv. Az003
Az005	1610–1630	-	Pattern tile (2 ×2)	143 × 15	MNAz, inv. 3188 Az
Az100	1635 ca.	-	Maneirist panel	135 × 14	MNAz, inv. 136 Az
Az052	1660–1667	Manuel Francisco pottery[b]	Leopard hunt	134 × 15	MNAz, inv. 137 Az
Az001	1660–1680	-	Camellia pattern (4 ×4)	143 × 14	MNAz, inv. 147 Az
Az151	1660–1680	-	Allegory of “St Amaro”	142 × 14	St. Amaro hermitage, Lisbon
C - 17th-18th cent. (Cycle of Masters)					
Az120	1680–1700	unknown	Caryatid angel	140–123 × 15	St. António chapel, Vialonga
Az124	1695 ca.	Gabriel del Barco	Ovid methamorphoses	142 × 13	MNAz, inv. 900 Az
Az208	1700	Gabriel del Barco[c]	Panoramic Lisbon view.	137 × 14	MNAz, inv. 1 Az
Az212	1706–1723	Manuel dos Santos	Handrail with balusters/putti	140 × 13	MNAz, inv. 6991/3 Az
Az121	1715–1720 ca.	Oliveira Bernardes	Our lady - ceiling	139 × 13	Nossa Sr. dos Remédios hermitage, Peniche
Az122	1720–1730	“PMP”	The meal	140 × 12	MNAz, inv. 6343 Az
D - 18th cent. (Great Joanine Production)					
Az358	1720–1740	-	Departure of St. Fr. Xavier	141 × 13	MNAz, inv. 9785 Az
Az360	1720–1740	-	Pluto Panel	141 × 12	MNAz, inv. 9748 Az
Az123	1730–1750 ca.	-	Spears and trumpets	140 × 12	LNEC, inv. Az123 Az
Az361	1730–1750	-	Mythological scenes	140 × 13	MNAz, inv. 7014 Az
Az359	1760–1770	-	Adoration of the Magi	141 × 13	MNAz, inv. 864 Az
E - 18th-19th cent. (From Rococo to Neoclassic)					
Az363	1760–1780	-	Panel of the Sheperdness	142 × 10	MNAz, inv. 736 Az
Az367	1770–1780	-	Panel with a port scene	141 × 12	MNAz, Inv. 7880 Az
Az365	1800 ca.	-	D. Maria pattern panel	138 × 12	MNAz, Inv. 6394 Az
Az364	1805 ca.	Rato Factory	Sitting bench	136 × 10	MNAz, Inv. 6370 Az
Az362	1800–1815	Rato Factory	The hatter A. J. Carneiro	139 × 10	MNAz, Inv. 227/1 Az
Az366	1820–1830	Rato Factory	The lady with a hat	139 × 12	MNAz, Inv. 6943 Az

[a] Attributed to João de Góis workshop or production cicle [34–39];
[b] attributed to Manuel Francisco pottery [40];
[c] attributed to Gabriel del Barco productions [41]. MNAz (National Tile Museum, Lisbon), LNEC (National Laboratory for Civil Engineering, Lisbon).

performed on the bulk white glaze in an area of ca. 300 μm x 500 μm, which contain possible inclusions such as sand grains or feldspar nodules as well as cassiterite particles. In addition, smaller areas (ca. 50 μm x 50 μm) devoid of quartz and feldspar particles were analysed, at least two analyses per sample being performed and averaged. Major elements concentrations were retrieved from the EDS analyses. The results are semi-quantitative, being expressed in weight % of the corresponding elements of the most common oxides (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Fe_2O_3, SnO_2, and PbO) and normalized to 100 %.

3. Results

Portuguese tiles production evolved throughout the 16th to the beginning of the 19th century. Besides the aesthetic modifications in the colour *palette* and painting styles (Fig. 2, Figure A.1) there was a characteristic decrease in the thickness (from ca. 16–10 mm) and an increase in the side length (from ca. 130–140 mm - Table 1) of the tiles. Morphological and chemical-mineralogical alterations in the glaze and glaze-ceramic interface were also registered.

3.1. Glaze micro-structure analysis by SEM

Fig. 3 summarizes the main morphological observations registered through SEM analysis. The presence of quartz sand inclusions within the glaze layer is observed for most of the samples (Fig. 3, Figure B.1). In the 16th century azulejos (Group A) the glaze matrix is rather homogeneous with small cassiterite crystals and few quartz grains which are relatively large although variable in size and not uniformly spread (Fig. 3; Figure B.1–2), confirming what has been reported in previous studies [34,35,37]. During the 17th century (group B) a somewhat larger quantity of smaller quartz inclusions are usually observed, together with the frequent presence of K/Na-feldspars (Fig. 3), especially towards the end of the century (Figure B.1–2). However, after the 18th (groups D and E) century, quartz and feldspar glaze inclusions are seen to increase in number and reduce in size (Fig. 3; Figure B.1–2). These characteristics are especially evident in the inclusions of the samples (Az364, 362 and Az366) from the Rato Factory which are seen to be particularly small and uniformly sized. Another observed microstructural difference is the high dispersion and homogeneity of cassiterite crystals found in the samples from the 16th century (Group A), except for sample Az334 where a somewhat increased clustering is observed relative to the larger heterogeneity and cluster agglomeration on the remaining century samples (Fig. 3). Sample Az212 (Manuel dos Santos) (Figure B.1-C.1) is an exception among all the samples, showing a rather homogeneous glaze which probably corresponds to extra steps of pre-firing and grounding (fritting) of the glaze that had been undertaken.

The use of *coperta* (a transparent glaze layer superimposed on the tin - opacified glaze) is reported since the 11–12th centuries in Tunisian Zirids/Almohads productions [42]. This transparent layer is also often found in Italian and Flemish 16th century tiles [24,43] but up to now never found in the autochthonous Portuguese productions studied.

3.2. Interface analysis by SEM

SEM analysis of the glaze microstructures confirmed the previously reported observations [44] that during the passage from the 16th to the 17th century an abrupt difference occurred regarding the neo-formed crystal interface outgrowths resulting from the reaction between the glaze and the ceramic body during firing. The samples from the 16th century (Group A) depict a large interface layer (ca. 20–80 μm) of needle-shaped crystals in opposition to a non-extant or scarce presence of (minor) crystalline outgrowths (ca. 0–15 μm) in the later centuries Lisbon tiles (Groups B to E) (Fig. 3, A to E; Figure B.3). The chemical analyses of the 16th century interface crystals corroborated what is usually stated in the literature that these are potassic feldspars with a composition similar to sanidine [45]. In some 16th century samples Ca-rich interface crystals can also be found together with the K-felspar crystals, or as a small interface layer in some of the later century samples such as Az208 (Fig. 3, C) and Az365. These Ca-rich crystals are usually attributed to the neo-formation of calcium-silicate crystallites, probably a species akin to wollastonite [25].

3.3. Glaze SEM-EDS analysis

When the SEM - EDS glaze analyses of the glaze inclusions (such as quartz, feldspar and cassiterite grains) performed in large glaze areas were compared with those performed on small glaze areas where the inclusions have been avoided, it was verified that the differences in the overall composition were mainly expressed by the rather obvious increase in silicon content and an improved precision in the tin content when the larger areas including inclusions were considered (Figure C.1). In this article the results obtained from the larger glaze areas (including inclusions) are favoured since they provide a more direct relationship with the final formulation used by the potter whilst the analysis of small areas devoid of inclusions, provide information related to the melted glaze matrix as a result of the firing procedure [46]. Furthermore, larger areas devoid of inclusions were often impossible to demarcate.

Table 2 presents the results from the bulk white tin-glazed areas of the studied samples. The classification used throughout the article to discriminate between different glaze compositions will take into account the amount of the main glaze modifier (lead), such as it has been previously used by Tite [47], where lead–alkali glazes are composed of 10–35 wt % PbO (less than 0.5–0.6 PbO/SiO_2 ratio) and high-lead glazes of more than 35 wt % PbO (more than 0.5–0.6 PbO/SiO_2 ratio). The results from the SEM-EDS glaze analysis (Table 2, Fig. 4) show, as already been previously reported [44], a clear change in glaze composition from high-lead to lead-alkali glazes in the passage of the 16th (Group A) to the 17th century azulejos (Group B) (Table 2, Fig. 4a-b).

From the 17th century on (Groups B to E), it is apparent that lead-alkali glaze recipes were consistently adopted (0.8–1 PbO/SiO_2 for the 16th cent. samples and 0.2–0.5 PbO/SiO_2 for the remaining ones) (Fig. 4a–b). The observed decrease in amount of the lead flux and tin opacifier (Figs. 4c-4d) is correlated to the increase in silicon content (Fig. 4a) and is associated with a rise in the contents of the alkali fluxes (Na + K components) (Fig. 4e). The aluminium content (Fig. 4f) also generally increases with the amount of silicon either due to its possible presence in sand components or as direct result of clay or felspar additions. In all samples, higher levels of K_2O compared to Na_2O (1.2–4.8 K_2O/Na_2O) are encountered without any observable tendency within all the studied periods.

For the tiles produced after the 17th century (Groups B to E), no clear trend regarding the main glaze components could be identified except in the case of the samples from the Rato Factory that on average present a slightly higher PbO/SiO_2 ratio (0.4–0.5) (Fig. 4b) and higher amount of SnO_2 (Fig. 4c-d). However, the analysis of the minor elements present in the glaze (Ca, Mg, Ti and Fe) (Fig. 5) shows an increase of the amount of these elements from the 16th to the 17th century (from Groups A to B) and a continuous decrease from the beginning of the 17th century towards the 19th (Groups B to E). The samples from the last period studied (18th-19th cent – From Rococo to Neoclassic) present significantly lower amounts of these elements (<2 % $CaO+MgO+TiO_2+Fe_2O_3$) in the glaze matrix (Fig. 5).

4. Discussion

4.1. Glaze inclusions

The small size of the cassiterite clusters and rather homogeneous 16th century glaze matrix (Fig. 3, A; Figure B.1) indicate that it was derived from a series of fritting and grinding steps where the lead-tin calcine was probably mixed with a silica-alkali frit, remelted and reground to a fine powder before being applied to the ceramic body,

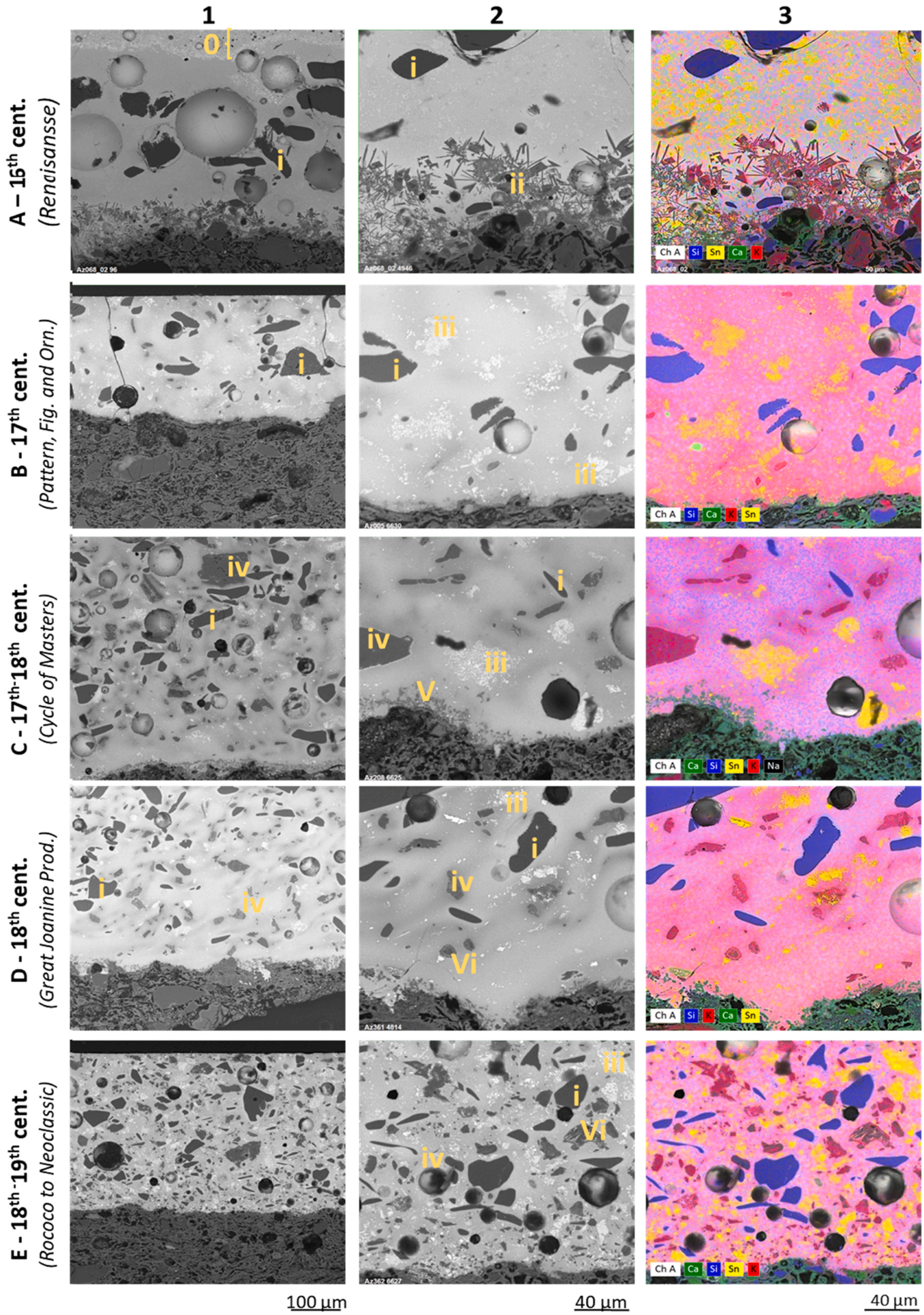

Fig. 3. SEM images of exemplificative samples at 350x and 950x magnifications. From top to bottom: Az068 (Group A); Az005 (Group B), Az208 (Group C), Az361 (Group D), Az362 (Group E). From Left to right: 1) BSE image 350x; 2) BSE image 950x; and 3) Colour map image 950x (Si - Blue, Ca- green, K - red, Sn – Yellow). Legend: 0) Yellow pigment layer; i) quartz sand grain; ii) Neo-formed K-feldspar interface crystals; iii) Cassiterite grains; iv) K-feldspar; v) Na/K-Ffelspar; and vi) Ca-rich crystals.

Table 2
SEM-EDS analysis of the bulk white layer of the lead - tin glazes (ca. 300 ×500 μm) from the A to E groups.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	Fe_2O_3	PbO	SnO_2	CaO	TiO_2	PbO/SiO_2
A- 16th cent. (Renaissance)											
Az013	1,5	0,4	4,8	41,7	1,7	0,5	37,4	10,3	1,4	0,4	0,9
Az032	0,4	0,2	3,9	41,3	1,1	0,6	38,5	13,0	0,9	0,1	0,9
Az068	0,4	0,2	3,7	46,0	1,8	0,5	36,9	8,6	0,9	0,9	0,8
Az199	0,7	0,4	4,2	39,2	1,5	0,7	37,3	12,6	3,0	0,4	1,0
Az334	0,8	0,4	5,2	42,9	1,6	0,6	35,0	11,0	2,4	0,1	0,8
B - 17th cent. (Pattern and Figurative)											
Az003	2,4	0,7	5,8	61,7	6,9	0,8	12,0	7,3	2,0	0,3	0,2
Az005	2,3	0,8	4,8	58,1	6,7	0,6	18,1	6,0	2,1	0,3	0,3
Az100	3,5	1,0	7,0	55,5	5,5	1,1	16,7	6,3	3,0	0,5	0,3
Az052	3,1	0,7	7,1	60,8	4,8	0,6	18,0	3,3	1,2	0,4	0,3
Az001	3,0	0,8	6,9	55,8	7,5	0,8	17,6	4,4	2,8	0,6	0,3
Az151	2,1	0,8	8,2	54,3	9,0	0,9	17,8	3,8	2,4	0,8	0,3
C - 17th-18th cent (Cycle of Masters)											
Az120	2,4	0,6	8,6	64,6	6,7	0,6	9,8	4,1	2,0	0,5	0,2
Az124	2,3	0,1	6,0	58,9	7,8	0,7	16,7	5,6	1,8	0,2	0,3
Az208	3,3	0,3	7,9	61,2	6,8	0,6	15,3	3,3	0,9	0,4	0,3
Az212	2,8	0,2	7,4	56,3	9,5	0,7	15,4	4,9	2,3	0,6	0,3
Az121	2,8	0,2	6,4	57,7	4,7	0,5	21,0	5,6	0,8	0,3	0,4
Az122	1,8	0,2	7,2	57,7	5,9	0,5	21,8	4,1	0,4	0,4	0,4
D - 18th cent. (Great Joanine Production)											
Az358	3,5	0,1	7,8	62,3	6,5	0,5	13,5	4,3	1,0	0,4	0,2
Az360	2,5	0,2	7,0	60,4	7,3	0,5	17,6	3,4	0,9	0,2	0,3
Az123	2,4	0,2	5,7	66,0	6,4	0,3	14,8	3,9	0,3	0,1	0,2
Az361	2,0	0,1	6,4	60,8	7,3	0,5	18,8	3,5	0,4	0,2	0,3
Az359	1,9	0,2	8,6	61,4	9,3	0,7	11,9	4,3	1,1	0,6	0,2
E - 18th-19th cent. (From Rococo to Neoclassic)											
Az363	2,7	0,2	7,6	57,9	7,1	0,5	16,7	6,2	0,7	0,3	0,3
Az367	2,5	0,1	7,5	63,0	6,7	0,4	13,8	5,1	0,7	0,2	0,2
Az365	2,3	0,1	7,2	61,6	7,3	0,5	16,1	3,8	0,8	0,3	0,3
Az364	2,5	0,3	6,2	51,1	6,2	0,3	23,3	9,4	0,4	0,2	0,5
Az362	3,0	0,2	6,5	54,4	5,8	0,6	19,7	8,8	0,8	0,2	0,4
Az366	3,1	0,6	6,8	52,4	6,5	0,4	20,3	9,4	0,4	0,2	0,4

such as mentioned in the 14th century Persian treatise by Abu ʿL-Qasim [48,49]. This glaze matrix homogeneity and small cassiterite clusters in the 16th century samples is in line with what is usually observed in Hispano-Moresque tiles technology [19,50]. Besides the fritting and griding procedure, the cassiterite clustering distribution is dependent on the glaze composition, viscosity and firing temperature, since these influence the compounds solubility, mobility and the crystal nucleation and growth [11]. The use of high-lead glazes on the 16th century versus lead-alkali ones on the remaining centuries, with possible different firing temperatures, can also therefore contribute to the small cassiterite cluster sizes and homogeneous distribution observed. The small amount and relatively large size of the quartz sand grains found dispersed in this otherwise rather homogeneous glaze matrix (Fig. 3, A; Figure B.1) indicate that probably part of the sand was added to the final frit before being applied to the ceramic body [17]. A possible reason would be to increase opacity due to the presence of more crystalline material.

The higher amount of quartz and feldspar inclusions observed in the samples after the 17th century (Groups B to E) is coincident with the decreasing PbO/SiO_2 glaze ratio and the possible direct application of the mixture of the lead-tin calcine and silica-alkali frit (in some cases with additional sand) onto the ceramic bodies without extra fritting of the final mixture such as mentioned in the 16th century Italian Picolpasso treatise [49,51,52]. This increase in quartz and feldspar inclusions in the glaze is especially evident for the samples from the 18–19th centuries (Fig. 3; Figure B.1). This could possibly indicate also changes in their frit/griding procedures.

While there is some discussion regarding the opacifying properties of the quartz grains [17] it is generally accepted that crystallites such as quartz (and feldspars, wollastonite and diopside) together with gas bubbles act as opacifying agents and many have been used already in medieval Mesopotamia productions [53]. The increased number of inclusions observed throughout the studied periods could arguably have a role as opacifiers reducing the need of the large amounts of the expensive tin opacifier (Fig. 3c-d).

4.2. Glaze composition

Studies by Mimoso et al. of tile panels produced within the second half of the 16th century in Lisbon [34,35,37–39,54] have revealed the local use of a distinctive majolica glaze characterised by high-lead, low contents in alkali fusing agents and high amounts of tin, shifting towards lead-alkali glazes in the 17th century [55]. This glaze technology with high contents in lead is in line with what was usually being used in Spanish Islamic influenced wares [1,3–6,9,10,13], in Hispano-Moresque tile technology [14,15,25,26], and the majority of Italian majolica produced before the middle of the 15th century (Fig. 7, Figure E.1) [17,56,57]. However, despite the similar high-lead PbO/SiO_2 ratios, the Hispano-Moresque tile white glazes usually have higher amounts of alkalis and lower amounts of tin [15,25] (Table E.1). After the 17th century up to the beginning of the 19th century, glazes from Lisbon azulejos production consistently belong to the low lead - high alkali type having therefore lower amounts of lead, higher silicon and higher alkali fusing agents. The use of lead-alkali glazes on Portuguese utilitarian majolica and tiles from the 17th and 18th centuries is also confirmed on other reported studies [58–63]. The use of lead-alkali glazes is more in line with what is known until now about the glaze technology generally used after the middle of the 15th century majolica in Italy [17,56,64,65], in the few studies published from 16 to 18th century tiles production in northern Europe [24,44,66,67], and in some studies from the 16th century and later tiles production in Spain [68–70].

The main differences observed between the studied azulejo production periods are evidenced in a Principal Component Analysis graph (Fig. 6). PC1 clearly separates 16th century samples (Group A) from all the others due to the already mentioned higher amount of lead and tin and lower alkalis, Si, and Al (Fig. 3 & 5). PC2 distribution confirms the increased amount in minor elements (Ca, Fe, Ti and Mg, Al), possibly

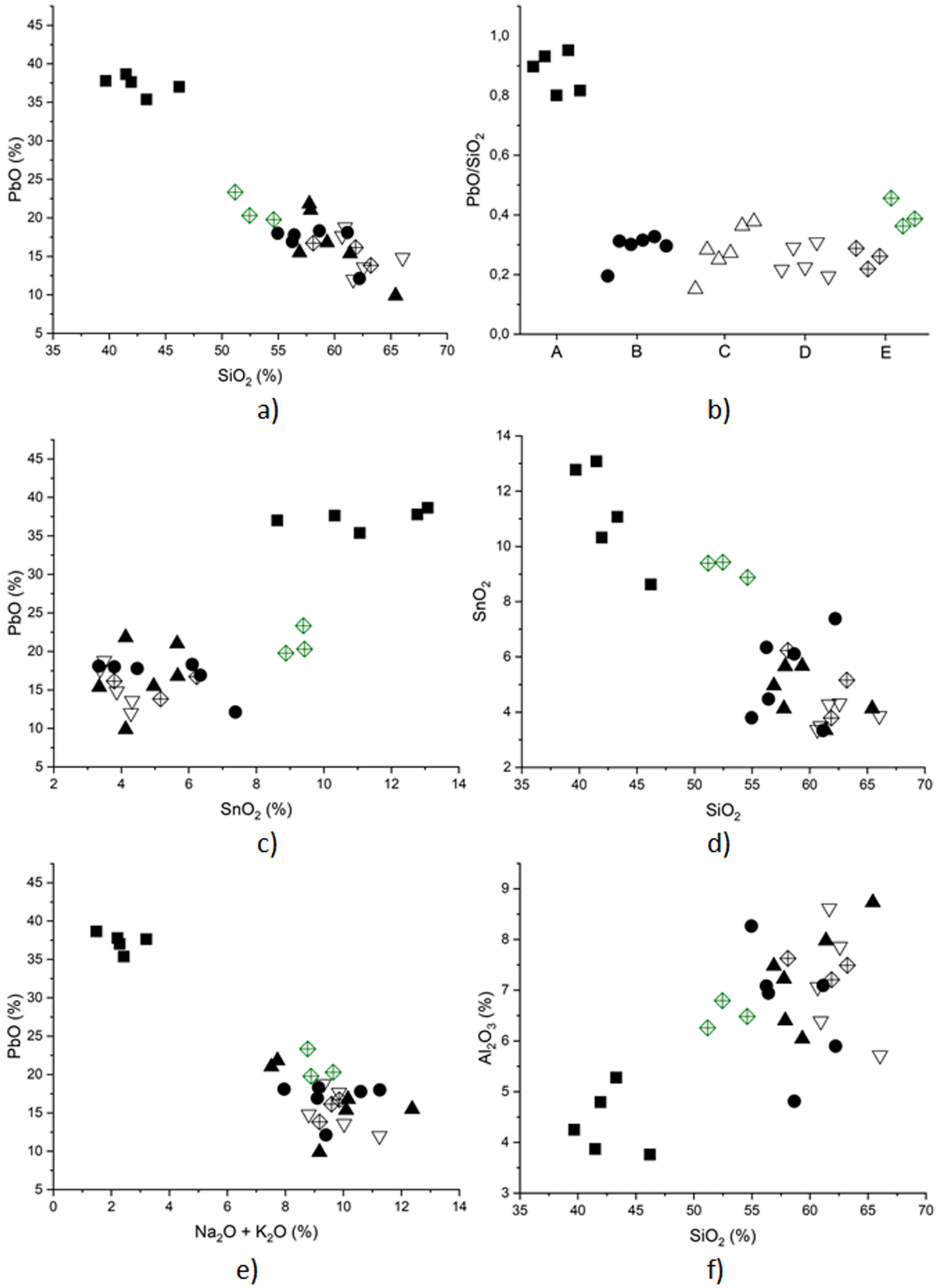

Fig. 4. Binary plots between the glaze composition variables. From left to right and top to bottom; a) % PbO vs % SiO_2; b) PbO/SiO2 ratios vs studied groups; c) % PbO vs % SnO_2; d) % SnO_2 vs % SiO_2; e) % PbO vs% Na_2O + K_2O; and f) % Al_2O_3 vs % SiO_2. Legend: ■ Group A; • Group B; ▲ Group C; △ Group D; ◈ Group E (samples from the Rato Factory are coloured green).

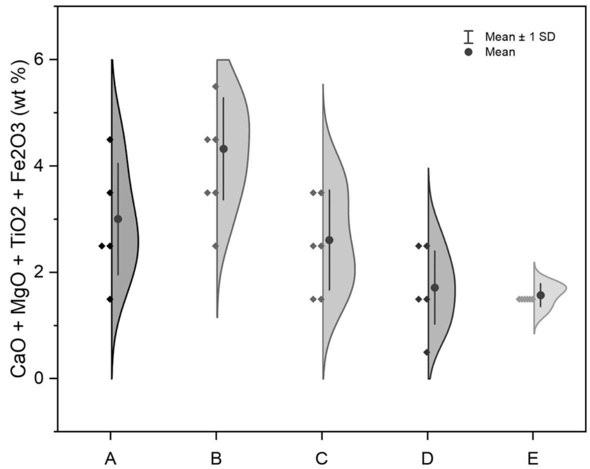

Fig. 5. Half-violin plot representing the content of the minor elements Calcium (Ca), Magnesium (Mg), Titanium (Ti) and Iron (Fe) components present in the tin glaze of the studied samples (Groups A to E).

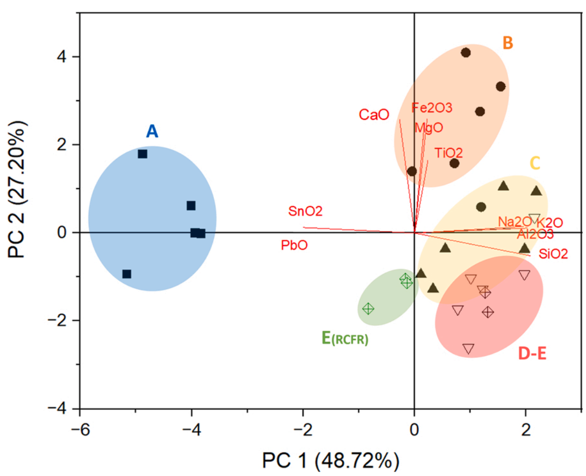

Fig. 6. PCA analysis of the glazes considering glaze inclusions. PC1 explains 49 % of the variation and is controlled in the positive sense by the contents in Al, K, Na and Si components and in the opposite sense by the contents in Pb and Sn. PC2 explains 27 % of variation that is controlled in the positive sense mostly by the contents in Ca, Mg, Ti and Fe. Elipses: Group A -Blue; Group B – Orange; Group C – Yellow; Groups D and E – Red; and Group E tiles from the Rato Factory (ERCFR) - Green. Legend: ■ Group A; • Group B; ▲ Group C; △ Group D; ⊕ Group E (samples from the Rato Factory are coloured green).

resulting from sand-related impurities or clay addition occurred from the 16th century (Group A) - where lower amounts of sand were used - to the 17th century (Group B) (Fig. 3 & 5). The high purity of end of 18 - beg. of 19th century productions is therefore a consequence of optimized methods of raw materials sorting, sifting, washing/settling and of novel purification methods such as the use of magnets to eliminate iron and magnetic iron oxide compounds [71].

The small trend inversion observed towards higher PbO/SiO_2 ratios and higher amount of SnO_2 in the tiles from the Rato Factory (Group E samples Az362, Az364 and Az366) was probably aimed at obtaining a superior gloss (very evident in their tiles) and is an indication of its innovation character and aim of researching and manufacturing products of high artistic and technical quality [33]. However, analysis of further tiles from Rato Factory and other contemporary factories would be necessary to confirm the specificity of this composition change within the factory manufactured products or its adoption by other contemporary operating factories since it is known that the Rato Factory had also the education role and knowledge transfer to the national ceramic industry [33].

The increase of fusing alkali (Na, K) components that is correlated with the decrease of the lead flux (Fig. 3 & 5) compensates for the decreasing PbO/SiO_2 ratio that would otherwise require a too high glaze firing temperature. The higher predominance of K over Na elements in the glazes indicate that the fusing alkali were probably added in the form of potassium bearing compounds such as some plant ashes, wine lees or tartar and less by the addition of common salt. The higher potassium levels found may also be partially due to the larger presence in the glaze of K bearing feldspars compared to Na ones.

Despite the existence of large tin reserves in the centre and north of Portugal, exploited and traded since the Roman period [72], the wider use by Portuguese potters of tin imported from the British Isles is reported since at least the 18th century [72,73]. Tin was the most expensive raw material used in the glaze production and therefore limiting its amount was desirable to cut production costs [72].

The addition of alkalis to lead glazes is reported to improve its colour and the surface hardness [74] producing a glaze less easily scratched and also less sensitive to acid corrosion. Since the small cassiterite crystals scatter light in the blue region of the spectrum and lead glazes simultaneously absorb light in this region, glazes with lower lead content tend to appear whiter and less creamy in colour [17] needing less tin to opacify the glaze (Fig. 3c). High-lead glazes are however known to have higher optical brilliance and reduced risk of crazing due to its lower thermal expansion when compared to more alkali-rich ones [75].

4.3. Glaze – ceramic body Interface

The high temperature attained during the firing process melts the glaze that reacts with the clay body in a complex chemical exchange that produces a mixed composition melt that may result in the formation of a crystal-rich interface. The interface crystals nucleation and growth mechanisms are influenced by the clay body and glaze compositions (and resulting melt mix), the firing temperature, the soaking time (dwell time at maximum temperature), heating and especially the cooling rates. It was observed that with similar compositional glazes, for higher soaking temperature, longer soaking time, and slow cooling rate the resulting interface crystal layer is larger [76,77]. High lead – low silica glazes are reported as being more fluid, with a wider softening range, lower surface and interfacial tension (and therefore better wetting properties) when compared to the probably more viscous lower lead – higher silicon glazes [51,52]. These conditions propitiate a lower interaction between the glaze and ceramic body, lower mobility of the necessary compounds for rearranging in a structured crystal form and therefore a smaller interface crystal zone. The significant effect of the glaze chemical composition shift from high-lead to lead-alkali on the interface crystals formation was proved by us through replicate experiments (results to be published). The alteration observed by altering the glaze composition from high lead – low silica glazes (Group A) to lead-alkali high silica glazes (Groups B-E), together with the higher Al content in the lead-alkali glazes and the possible use of a different firing schedule can likely explain the abrupt decrease of the amount of interface crystals formed.

4.4. Portuguese tile glaze production in the European context

Several archaeometry research studies have been performed by various research groups on tin-glazed ceramics from the 9th to the 19th century. The studies on archaic forms of majolica wares from the 9th to the 15th century in the Iberian Peninsula usually reveals the use of tin-opacified high-lead glazes [1,2]. Also Islamic influenced lustre-ware [4,78] and the tin opacified white areas of Hispano-Moresque items up to the 16th century belong, with some exceptions, to the high-lead glaze type [5,15,25,26]. There is some reported evidence of a generally continuous decrease, within the high-lead glaze type of the PbO/SiO_2 ratio in Iberian glazes from the 9–10th to the 15th centuries [4,11].

From literature studies a decrease in time of the PbO/SiO_2 ratio in the Italian tin-glaze productions (Fig. 7) was also noted. However, the use of tin opacified lead-alkali glazes seems to be rather consolidated after the mid-15th century (Fig. 7). Investigations performed on 16th century *istoriato* wares [79] and other majolica style ceramics also confirm the general usage of lead-alkali glaze type during the Italian Renaissance productions [56,64,65,80].

Regarding Flemish majolica glaze analyses, whose refined majolica technology is believed to have been transferred from Italian potters in the beginning of the 16th century, the few glaze composition studies published indicate the use during the 16th century of glaze compositions closer to the lead-alkali range [24,44]. Studies by van Lookeren Campagne reveal that, such as in Portugal, lead-alkali glazes have also been consistently used in Dutch tile production from the 17th and 18th centuries [66,67].

The Italian potter Francisco Niculoso is believed to have brought the refined majolica technology into Spain in the last decade of the 15th century. Studies using in-situ XRF techniques of his production in Seville, already indicate the use of a lead-alkali glaze type [68,81], in agreement with the common Italian practice from the middle of the 15th century on (Fig. 7). Similar studies using an *in-situ* XRF on the production from the second half of the 16th century by the Sevillian potter Cristobal de Augusta (active ca. 1570–1580) also indicate the use of lead-alkali glazes - even if possibly on the higher end (33 % PbO, with no reporting of the SiO_2 amount) [68]. Recent research by Pleguezelo et al. on the Flemish emigrant potter Juan Flores working in Talavera also shows the use of lead-alkali glazes [69]. Studies by Mimoso et al. on 16th century (dated 1596) tile panels from St Roque Church in Lisbon and attributed to the workshops of Seville also present a composition within the lead-alkali glazes group [70]. Even if the results mentioned tend to indicate a generalized use of lead-alkali glazes in tile production in Spain during the 16th century, Molera presents a study of a set of wares dated from the last decades of the 16th century to the end of first third of the 17th century from Catalonia where the use of high-lead (low end) glazes in both lustre-ware and blue decorated tin-glazed wares was still ongoing [78]. Analyses of some later Spanish majolica wares from the 18th century also indicate the use of lead-alkali glazes [82]. To better unravel the evolution of tin-glaze production within Spain, Italy, France, Flanders, Netherlands and Portugal further systematic archaeometry analysis will be necessary, especially from the 15th to the 17th centuries when an active technology transfer and evolution seem to have occurred.

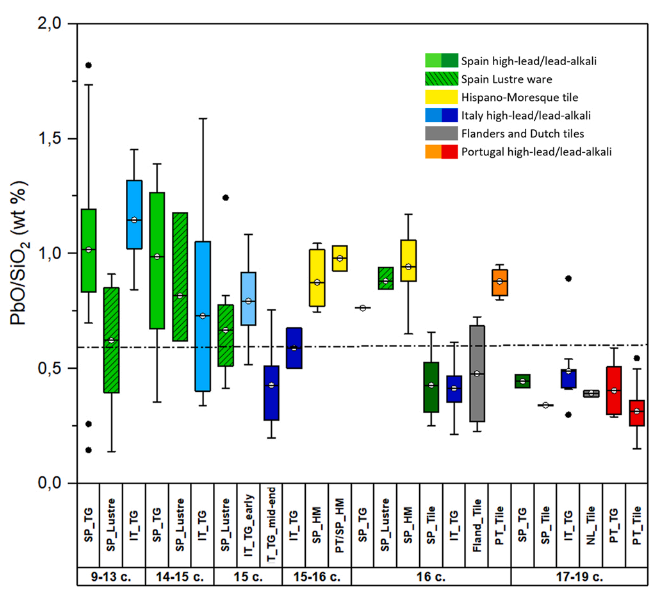

Fig. 7. Box-Plot schematic graph presenting the PbO/SiO2 white tin-glaze composition ratios obtained from our study (PT-Tile) and literature data [1, 3–6,9,10,14,15,17,24,25,56–61,65–70,78,80–86]. Spain (SP), Italy (IT), Flanders (Fland), Netherlands (NL), white tin glaze ware (TG), white tin glaze tile (Tile), Hispano moresque tile (HM). For details of graph data see Table E.1.

Fig. 7 show a schematic view of the main tendencies in tin-glaze composition within Europe from the 9th to the 19th centuries based on results obtained from the literature to which our own results were added (For a PCA analysis of the results please see Appendices D and E). Even if only indicative since different analytical techniques and conditions have been used to obtain the collected data, the results seem to suggest that a generalized use of high-lead glazes in majolica tile production was in place up to the Middle of the 15th - 16th century in majolica ware, Hispano-Moresque and 16th century Portuguese tiles (Fig. 7). The rather consistent use of lead-alkali glazes from the 17th century to the onset of the 19th century is in line with the change in technology that apparently has been initiated by the implementation of an improved majolica production technique by Italian potters in the middle of the 15th century (Fig. 7). The presence of high-lead glazes in the beginning of the Portuguese tiles production (2nd half of the 16th century) points therefore to the use of technology probably rooted on a local glaze tradition.

5. Conclusions

This study provided insight into the chronological evolution in Portuguese tile production from the second half of the 16th to the first quarter of the 19th century. It confirmed the previously observed change from high-lead to lead-alkali glaze compositions between the 16th and 17th centuries [44] and revealed that this later glaze type was consistently used until the beginning of the 19th century. The 16th century samples have a very characteristic morphology, with a homogeneous glaze matrix, relatively large quartz inclusions and a well-developed interface with needle-shaped crystals. After the 16th century, a crystalline interface is barely visible, except for few cases, reflecting the effects of a change in the composition of the glazes and of possibly a different firing cycle. The more homogeneous distribution of tin in the glaze matrix of the 16th century samples indicates the use of well ground frit of the lead-tin calcine and alkali-sand pre-frit mixture with possible later addition of sand (therefore the larger size and angular shape) before the application of the glaze to the ceramic body, a method commonly used in the Islamic ware and Hispano-Moresque tile production. During the following periods, the observed heterogeneous distribution of cassiterite is in line with the usage of less fritting steps in the glaze preparation such as the possible direct application of the mixture of the lead-tin calcine and silica-alkali frit directly to the ceramic bodies without the final mixture fritting. Advancing towards the 19th century, the glaze inclusions are smaller, more homogeneous in size, regularly spread and with a lower presence of minor elements (Ca, Mg, Fe, Ti), which provides evidence of the optimization that has occurred in the production processes including mechanization and optimized raw materials selection and treatment procedures.

A slight compositional change also seems to have occurred between the 18th-19th century, with the use of higher lead in the lead-alkali glazes and higher amounts of cassiterite reflecting the search for high quality and artistic standards by the Rato Factory. However, no major distinctive compositional features could be found in our studies to clearly chronologically distinguish Portuguese tiles from the workshops of Lisbon after the 17th century. A larger systematic study may be necessary to provide significant distinctions between these groups.

The high-lead tin-glazed technology used in the aesthetically appealing 16th century Renaissance style productions may have originated from a singular local tradition. In the 17th century, the use of high-lead tile glazes seems to have halted altogether with the highly artistic, exuberantly coloured tile panel productions in the Renaissance style. The use of lead-alkali glazes in the later centuries has probably derived from a perfected Italian majolica technique that had been diffused throughout Europe by the end of the 15th century, a technology that also started to be current for tile production in Spain. Further studies regarding the composition of 16th century Italian, Flemish, Dutch, Spanish, English, French and North African majolica tiles and ware are necessary to improve the knowledge about the evolution of majolica production within the European context.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jeurceramsoc.2023.01.038.

References

[1] E. Salinas, T. Pradell, The transition from lead transparent to tin-opacified glaze productions in the western Islamic lands: al-Andalus, c. 875–929 CE, J. Archaeol. Sci. 94 (2018) 1–11, https://doi.org/10/gn8pth.
[2] E. Salinas, T. Pradell, Madīnat al-Zahrāʾ or Madīnat Qurtuba? First evidences of the Caliphate tin glaze production of 'verde y manganeso' ware, Archaeol. Anthr. Sci. (2020) 12, https://doi.org/10/gn8px9.
[3] J. Molera, M. Vendrell-Saz, J. Pérez-Arantegui, Chemical and textural characterization of tin glazes in Islamic ceramics from eastern Spain, J. Archaeol. Sci. 28 (2001) 331–340, https://doi.org/10.1006/jasc.2000.0606.
[4] J. Molera, M. García-Vallés, J. García-Orellana, La tecnología de la cerámica islámica y mudejar, Caesaraugusta 73 (1997) 15–41.
[5] R. Chapoulie, C. Delery, F. Daniel, M. Vendrell-Saz, Cuerda seca ceramics from Al-Andalus, Islamic Spain and Portugal (10th−12th centuries AD): Investigation with SEM–EDX and cathodoluminescence, Archaeometry 47 (2005) 519–534, https://doi.org/10/cppx4c.
[6] D. Chabanne, A. Bouquillon, M. Aucouturier, X. Dectot, G. Padeletti, Physico-chemical analyses of Hispano-Moresque lustred ceramic: a precursor for Italian majolica? Appl. Phys. A 92 (2008) 11–18, https://doi.org/10.1007/s00339-008-4458-6.
[7] A. Polvorinos, J. Castaing, Lustre-decorated ceramics from a 15th To 16th century production in Seville, Archaeometry 52 (2009) 83–98, https://doi.org/10/fwrg78.
[8] A. Polvorinos, M. Aucouturier, A. Bouquillon, J. Castaing, J. Camps, The evolution of lustre ceramics from Manises (Valencia, Spain) between the 14th and 18th centuries, Archaeometry 53 (2011) 490–509, https://doi.org/10/fprzzg.
[9] A. Polvorinos, J. Castaing, M. Aucouturier, Metallic nano-particles in lustre glazed ceramics from the 15th century in Seville studied by PIXE and RBS, Nucl. Instrum. Methods Phys. Res B 249 (2006) 596–600, https://doi.org/10/ddh64g.
[10] I. Garofano, M.D. Robador, J.L. Perez-Rodriguez, J. Castaing, C. Pacheco, A. Duran, Ceramics from the Alcazar Palace in Seville (Spain) dated between the 11th and 15th centuries: Compositions, technological features and degradation processes, J. Eur. Ceram. Soc. 35 (2015) 4307–4319, https://doi.org/10/gn7nbk.
[11] M. Vendrell-Saz, J. Molera, J. Roqué, J. Pérez-Arantegui, Islamic and Hispano-Moresque (múdejar) lead glazes in Spain: a technical approach, Geol. Soc. Lond. Spec. Publ. 257 (2006) 163–173, https://doi.org/10.1144/GSL.SP.2006.257.01.13.
[12] Coentro S.X. An Iberian Heritage: Hispano-Moresque architectural tiles in Portuguese and Spanish collections. PhD. Universidade Nova de Lisboa, 2017.
[13] J. Molera, M. Vendrell-Saz, M. García-Vallés, T. Pradell, Technology and colour development of Hispano-Moresque lead-glazed pottery, Archaeometry 39 (1997) 23–39, https://doi.org/10.1111/j.1475-4754.1997.tb00788.x.
[14] L.F. Vieira Ferreira, D.S. Conceição, D.P. Ferreira, L.F. Santos, T.M. Casimiro, I. Ferreira Machado, Portuguese 16th century tiles from Santo António da Charneca's kiln: a spectroscopic characterization of pigments, glazes and pastes: first evidence of tile production in Portugal, J. Raman Spectrosc. 45 (2014) 838–847, https://doi.org/10.1002/jrs.4551.
[15] A.S. Leal, L.C. Alves, S. Coentro, S. Pereira, C. Relvas, T. Ferreira, et al., Chemical, physical and mineralogical characterisation of the Hispano - Moresque tile collection from Lisbon Roman Theatre Museum, Conserv Património 29 (2018) 25–39, https://doi.org/10.14568/cp2017011.
[16] J.C. Conesa, Changing tastes: from lustreware to polychrome tiles. Exported pottery from Valencia in mediterranean area and around (14th to 18th cc.), in: Glazed Pottery Mediterranian Black Sea Reg. 10th-18th Centuries, vol. 2, Stratum, 2017, pp. 31–50.
[17] M.S. Tite, The production technology of Italian maiolica: a reassessment, J. Archaeol. Sci. 36 (2009) 2065–2080, https://doi.org/10.1016/j.jas.2009.07.006.
[18] E. Salinas, T. Pradell, The first glaze production centres in al-Andalus (late 9th-early 10th centuries): Pechina, Cordoba and Malaga, Tecnol. Los Vidrados En. El Oeste Mediterrâneo Tradic. Islâmicas Cristianas (2021) 49–60.
[19] S. Coentro, L. Alves, J. Coll Conesa, T. Ferreira, J. Mirao, R. Silva, et al., White on blue: A study on underglaze-decorated ceramic tiles from 15th- 16th-century Valencian and Sevillian productions. J Archaeol, Sci. Rep. 30 (2020), 102254 https://doi.org/10/gmzd8d.
[20] R.J.C. Hildyard. European ceramics, 1st ed.,, University of Pennsylvania Press, Philadelphia, 1999.
[21] D. Kingery, Painterly Maiolica of the Italian Renaissance, Technol. Cult. 34 (1993) 28–48.
[22] C. Mangucci, A manufactura e a pintura de azulejos em Portugal da produção das primeiras faianças à grande indústria oitocentista. O Revest. Cerâmico Na Arquit. Em Port, Estar, Lisbon, 1998, pp. 19–64.
[23] H. Blake, de nomine Jhesu: an Italian export ware and the origin of maiolica pottery making in the Low Countries. Maiolica North Archaeol. Tin-Glazed Earthenware North-West Eur. C 1500-1600, David Gaimster (1999) 23–56.
[24] J.M. Mimoso, A. Santos Silva, I.M. Martins, D. Costa, S.R.M. Pereira, L. Esteves, et al., Analytical study of tiles of presumed Flemish origin from the Palace of the Dukes of Braganza in Vila Viçosa. In: From Flandres. The azulejos Commissioned by D. Teodósio I, 5th Duke of Braganza (c. 1510–1563), Vila Viçosa: MNAz, Fundação da Casa de Bragança (2012).
[25] S. Coentro, L.C. Alves, C. Relvas, T. Ferreira, J. Mirão, J. Molera, et al., The Glaze Technology of Hispano-Moresque Ceramic Tiles: A Comparison Between Portuguese and Spanish Collections, Archaeometry 59 (2017) 667–684, https://doi.org/10/gnq7k3.
[26] S. Coentro, R.A.A. Trindade, J. Mirão, A. Candeias, L.C. Alves, R.M.C. Silva, et al., Hispano-Moresque ceramic tiles from the Monastery of Santa Clara-a-Velha (Coimbra, Portugal, J. Archaeol. Sci. 41 (2014) 21–28, https://doi.org/10.1016/j.jas.2013.07.031.
[27] J.M. Mimoso, A. Pleguezuelo, M.A. Antunes, Á. Sanchez-Cabezudo, S. Pereira, D. Costa, et al., The 16th century majolica azulejo heritage of Palácio e Quinta da Bacalhôa: imported panels and tiles, Stud. Herit. Glazed Ceram. 3 (2021) 143–179.
[28] A.N. Pais, M. Reis, C. da, J. Campelo, Mimoso, M.Â. Silva, The beginning of the production of majolica azulejos in Portugal - João and Filipe de Góis in 16th century Lisbon, Stud. Herit. Glazed Ceram. 1 (2019) 1–23.
[29] Livro do lançamento e serviço que a Cidade de Lisboa fez a el Rei nosso Senhor no ano de 1565, Câmara Municipal de Lisboa, Lisbon, 1947.
[30] R. Mitchell, Portuguese art: Portuguese Azulejos. Fine Arts Eur. Last 10 Centuries, Michelangelo Proj. / Pixel (2017) 341–360.
[31] S.R.M. Pereira, M. Menezes, K. Campagne, L. van, Importance of technical knowledge for the valorization of azulejo heritage. Intangibility Matters, LNEC, Lisbon, 2017, pp. 55–66.
[32] P. Prostes, J. de Vasconcellos, Industria de ceramica, Bibliotheca de instrucção profissional, Lisbon, 1907.
[33] A.N. Pais, J.P. Monteiro, P. Henriques, Real Fábrica de Louça ao Rato, Palácio Nacional da Ajuda, Lisbon, 2003.
[34] A. Pais, J.M. Mimoso, M. Esteves, L. de, M.Â. Silva, M. Cardoso, M.A. Antunes, et al., Study of the azulejo panels in Graça church signed by João de Góis, Stud. Herit. Glazed Ceram. 1 (2019) 47–66.
[35] J.M. Mimoso, A. Pais, V. Filipe, M. Esteves, L. de, S.R.M. Pereira, M.A.P. de Matos, et al., Analytical study of the 16th century azulejo panel "Nossa Senhora da Vida" and related archaeologic findings, Stud. Herit. Glazed Ceram. 1 (2019) 77–92.
[36] A. Pais, J.M. Mimoso, V. Filipe, M. Esteves, L. de, M. Antónia, P. de Matos, The 16th century Nativity azulejo panel called "de Nossa Senhora da Vida.", Stud. Herit. Glazed Ceram. 1 (2019) 67–76.
[37] J.M. Mimoso, A. Pais, T. Morna, J.M. Simões, M. de Lurdes, A.M. Cardoso, et al., A research on the azulejo panels of the São Roque chapel in Lisbon, Stud. Herit. Glazed Ceram. 1 (2019) 93–112.
[38] J.M. Mimoso, A. Pais, M. Ferreira, M. Esteves, L. de, M.A. Antunes, R. Valona, et al., Instrumental study of the 16th century azulejo panel decorating a public fountain in Alcácer do Sal - Portugal, Stud. Herit. Glazed Ceram. 2 (2019) 19–34.
[39] A. Pais, J.M. Mimoso, P.R. Rosmaninho, M. Esteves, L. de, M. Pereira, M. A. Antunes, et al., Study of a finding of 16th century azulejo panels at the Cathedral of Setúbal in Portugal, Stud. Herit. Glazed Ceram. 2 (2019) 1–18.

[40] J.P. Monteiro, Um gosto português: o uso do azulejo no século XVII. Museu Nacional do Azulejo, Athena, Lisboa, 2012.
[41] M.A.G. da Câmara, Lisboa reencontrada: registos iconográficos na azulejaria de setecentos, Discursos Língua Cult. E Soc. (2003) 167–179.
[42] P. Colomban, G. Sagon, A. Louhichi, H. Binous, N. Ayed, Identification par microscopie Raman des tessons et pigments de glaçures de céramiques de L'Ifriqiya (Dougga, XI-XVIIIèmes siècles), ArchéoSciences Rev. Archéom. 25 (2001) 101–112, https://doi.org/10.3406/arsci.2001.1005.
[43] F. Antonelli, A.L. Ermeti, L. Lazzarini, M. Verità, G. Raffaelli, An archaeometric contribution to the characterization of Renaissance maiolica from Urbino and a comparison with coeval maiolica from Pesaro (the Marches, central Italy), Archaeometry 56 (2014) 784–804, https://doi.org/10/gn4drd.
[44] J.M. Mimoso, S.R.M. Pereira, A. Pais, M.A. Antunes, M. Cardoso, M. Esteves, L. de, et al., A comparison of the earliest faience tiles produced in Lisbon with earlier and later types, Stud. Herit. Glazed Ceram. 1 (2019) 25–46.
[45] J. Molera, T. Pradell, S. Martinez-Manent, M. Vendrell-Saz, The growth of sanidine crystals in the lead of glazes of Hispano-Moresque pottery, Appl. Clay Sci. 7 (1993) 483–491, https://doi.org/10/cgm9qj.
[46] R. Alaimo, G. Bultrini, I. Fragalà, R. Giarrusso, G. Montana, Microchemical and microstructural characterisation of medieval and post-medieval ceramic glaze coatings, Appl. Phys. A 79 (2004) 263–272, https://doi.org/10.1007/s00339-004-2522-4.
[47] M.S. Tite, The technology of glazed islamic ceramics using data collected by the late Alexander Kaczmarczyk, Archaeometry 53 (2011) 329–339, https://doi.org/10/d6h6dm.
[48] J.W. Allan, Abu'l-Qasim's treatise on ceramics, Ashmolean Museum, Oxford, 1973.
[49] M. s Tite, T. Pradell, A. Shortland, Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the Late Iron Age onwards: a reassessment, Archaeometry 50 (2007) 67–84, https://doi.org/10/bk6mnq.
[50] J. Molera, T. Pradell, N. Salvadó, M. Vendrell, Lead frits in Islamic and Hispano-Moresque glazed productions. Mine Microsc. Adv. Study Anc. Technol, Oxbow books, 2009, pp. 11–22.
[51] D.V. Hill, R.J. Speakman, M.D. Glascock, Chemical and mineralogical characterization of Sasanian and early Islamic glazed ceramics from the Deh Luran plain, southwestern Iran, Archaeometry 46 (2004) 585–605, https://doi.org/10.1111/j.1475-4754.2004.00175.x.
[52] J.S. Nordyke, Lead in the world of ceramics: a source book for scientists, engineers, and students, American ceramic Society, Columbus, Ohio, 1984.
[53] M. Maggetti, Technology and provenancing of French faience, Semin Soc. Esp. Miner. 9 (2012) 41–64.
[54] J.M. Mimoso, A. Pais, T. Morna, J.M. Simões, M. de Lurdes, S.R.M. Pereira, et al., Debris of greatness – research on the remains of 16th century Portuguese azulejo panels at Igreja de São Roque in Lisbon, Stud. Herit. Glazed Ceram. 2 (2019) 73–90.
[55] J.M. Mimoso, S.R.M. Pereira, A.N. Pais, M.A. Antunes, M. Cardoso, M. Esteves, L. de, et al., A technical comparison of three renaissance azulejo panels from the workshops of Lisbon, Stud. Herit. Glazed Ceram. 1 (2019) 113–132.
[56] L. Chiarantini, F. Gallo, V. Rimondi, M. Benvenuti, P. Costagliola, A. Dini, Early renaissance production recipes for naples yellow pigment: a mineralogical and lead isotope study of Italian majolica from Montelupo (Florence), Archaeometry 57 (2015) 879–896, https://doi.org/10/gn32hd.
[57] C. Ricci, I. Borgia, B.G. Brunetti, A. Sgamellotti, B. Fabbri, M.C. Burla, et al., A study on late medieval transparent-glazed pottery and archaic majolica from Orvieto (central Italy), Archaeometry 47 (2005) 557–570, https://doi.org/10.1111/j.1475-4754.2005.00219.x.
[58] M. Pereira, T. de Lacerda-Arôso, M.J.M. Gomes, A. Mata, L.C. Alves, P. Colomban, Ancient portuguese ceramic wall tiles ("azulejos"): characterization of the glaze and ceramic pigments, J. Nano Res 8 (2009) 79–88, https://doi.org/10.4028/www.scientific.net/JNanoR.8.79.
[59] L.F. Vieira Ferreira, T.M. Casimiro, Ph Colomban, Portuguese tin-glazed earthenware from the 17th century. Part 1: Pigments and glazes characterization, Spectrochim. Acta A Mol. Biomol. Spectrosc. 104 (2013) 437–444, https://doi.org/10.1016/j.saa.2012.11.069.
[60] L.F. Vieira Ferreira, D.P. Ferreira, D.S. Conceição, L.F. Santos, M.F.C. Pereira, T. M. Casimiro, et al., Portuguese tin-glazed earthenware from the 17th century. Part 2: a spectroscopic characterization of pigments, glazes and pastes of the three main production centers, Spectrochim. Acta A Mol. Biomol. Spectrosc. 149 (2015) 285–294, https://doi.org/10.1016/j.saa.2015.04.090.
[61] S. Coentro, J.M. Mimoso, A.M. Lima, A.S. Silva, A.N. Pais, V.S.F. Muralha, Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos, J. Eur. Ceram. Soc. 32 (2012) 37–48, https://doi.org/10.1016/j.jeurceramsoc.2011.07.021.
[62] Pereira S.R.M., Mimoso J.M., Santos Silva A. Physical-Chemical characterization of historic portuguese tiles. LNEC; 2011.
[63] M.L. Coutinho, J.P. Veiga, M.F. Macedo, A.Z. Miller, Testing the Feasibility of Titanium Dioxide Sol-Gel Coatings on Portuguese Glazed Tiles to Prevent Biological Colonization, Coatings 10 (2020) 1169, https://doi.org/10/gnsjpf.
[64] F. Amato, S. Gualteri, B. Fabbri, La rivolucione tecnica dei "bianchi.", Maiolica Ital. Stile Compend Bianchi (2010) 33–38.
[65] M. Gulmini, F. Scognamiglio, G. Roselli, G. Vaggelli, Composition and microstructure of maiolica from the museum of ceramics in Ascoli Piceno (Italy): evidences by electron microscopy and microanalysis, Appl. Phys. A (2015) 120, https://doi.org/10.1007/s00339-015-9376-9.
[66] K. Campagne, L. van, Understanding 17th-18th century Dutch tin-glaze through the interpretation and reconstruction of historical recipes. Int Conf Glazed Ceram. Cult. Herit, LNEC,, Lisbon, 2018, pp. 150–161.
[67] K.S. Chugunova, I.A. Grigorieva, R.V. Rebrova, A Multi-Analytical Comparative Examination of 18th-Century Dutch Tiles and Russian Imitations. Preliminary Results. Post-Mediev. Pottery Its Bord, Archaeopress, 2018, pp. 237–244.
[68] L. de Viguerie, M.D. Robador, J. Castaing, J.L. Perez-Rodriguez, P. Walter, A. Bouquillon, Technological evolution of ceramic glazes in the renaissance: in situ analysis of tiles in the Alcazar (Seville, Spain), J. Am. Ceram. Soc. 102 (2019) 1402–1413, https://doi.org/10/gnq7kz.
[69] A. Pleguezuelo, A. Sánchez-Cabezudo, J.M. Mimoso, M.A. Antunes, S. Pereira, Á. Silva, Juan Flores: Azulejo works in Spain and connection to the Bacalhôa palace in Portugal, Stud. Herit. Glazed Ceram. 3 (2021) 75–108.
[70] A. Pais, J.M. Mimoso, T. Morna, J.M. Simões, M. de Lurdes, S.R.M. Pereira, et al., The many questions raised by the 16th century Sevillian azulejos in Igreja de São Roque in Lisbon, Stud. Herit. Glazed Ceram. 2 (2019) 51–72.
[71] E. Bourry, A treatise on ceramic industries: a complete manual for pottery, tile, and brick manufacturers, Scott, Greenwood & son, London, 1911.
[72] Sebastian L. A produção oleira de faiança em portugal (séculos xvi-xviii). PHD. Universidade Nova de Lisboa, 2010.
[73] A. Velloso Xavier, Arte da louça vidrada, Na Impressao Regia, Lisboa, 1805.
[74] Z. Al-Saad, Chemical Composition and manufacturing technology of a collection of various types of Islamic Glazes excavated from Jordan, J. Archaeol. Sci. 29 (2002) 803–810, https://doi.org/10/cxs49p.
[75] M.S. Tite, Ceramic production, provenance and use - a review, Archaeometry 50 (2008) 216–231, https://doi.org/10/bzs2pw.
[76] J. Molera, T. Pradell, N. Salvadó, M. Vendrell-Saz, Interactions between clay bodies and lead glazes, J. Am. Ceram. Soc. 84 (2001) 1120–1128, https://doi.org/10.1111/j.1151-2916.2001.tb00799.x.
[77] S.R.M. Pereira, M.A. Antunes, A.M. Cardoso, M. Costa, J. Delgado-Rodrigues, M. de L. Esteves, et al., Influence of the production technology on the morphological characteristics of azulejos. GlazeArt2018 Int. Conf. Glazed Cerâmics Cult. Herit, LNEC, Lisbon, 2018, pp. 140–149.
[78] J. Molera, J. Iñañez, G. Molina, J. Burch, X. Alberch, M. Glascock, et al., Lustre and glazed ceramic collection from Mas Llorens, 16-17 th centuries (Salt, Girona). Provenance and technology, Period Miner. 84 (2015) 45–63, https://doi.org/10/gn3hrx.
[79] G. Padeletti, G.M. Ingo, A. Bouquillon, S. Pages-Camagna, M. Aucouturier, S. Roehrs, et al., First-time observation of Mastro Giorgio masterpieces by means of non-destructive techniques, Appl. Phys. A 83 (2006) 475–483, https://doi.org/10/chfk87.
[80] M.S. Tite, Italian majolica, Old. Potters Alm. 7 (2012) 1–7.
[81] A. Gomez-Morón, A. Polvorinos, J. Castaing, A. Pleguezuelo, Ceramics by Niculoso Pisano and quantitative analysis of glazes using portable XRF, PH Invest. 06 (2016) 1–23.
[82] R. Padilla Alvarez, O. Schalm, K. Janssens, R. Arrazcaeta, P. Van Espen, Microanalytical characterization of surface decoration in Majolica pottery, Anal. Chim. Acta 535 (2005) 201–211, https://doi.org/10/bkwt2x.
[83] S. Sánchez Ramos, F. Bosch Reig, J.V. Gimeno Adelantado, D.J. Yusá Marco, A. Doménech Carbó, Study and dating of medieval ceramic tiles by analysis of enamels with atomic absorption spectroscopy, X-ray fluorescence and electron probe microanalysis, Spectrochim. Acta Part B Spectrosc. 57 (2002) 689–700, https://doi.org/10.1016/S0584-8547(01)00395-0.
[84] J. Coroado, C. Gomes, Physical and chemical characterisation of ceramic wall tiles, dated to the 17th century, from the "Convento de Cristo", in Tomar, Portugal, Trab. Arqueol 42 (2003) 7.
[85] G. Politi, A. Bouquillon, M. Aucouturier, A. Gueli, S.O. Troja, C. Vella, et al., Analysis of lustred ceramics of the Galleria Regionale di Palazzo Bellomo di Siracusa, Italy, Nucl. Instrum. Methods Phys. Res Sect. B Beam Inter. Mater. 331 (2014) 82–88, https://doi.org/10/f594wt.
[86] F. Agua, Á. Sánchez-Cabezudo, A.P. Tudela, M.Á. de, Villegas, M. García-Heras, Archaeometric case-study of tiles of different dates from the Royal Monastery of San Lorenzo de El Escorial (Spain), Bol. Soc. Esp. Cerámica Vidr. 61 (2022) 84–97, https://doi.org/10.1016/j.bsecv.2020.09.001.