Portuguese 16th to Early 18th Century tin Glazed Ceramics Found at the Tagus Estuary Saltpans

Vieira Ferreira LF[1*], Ferreira Machado I[1,2], Gonzalez A[3], Pereira MFC[4], Casimiro TM[5]

[1]IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

[2]Polytechnic Institute of Portalegre, P-7300-110 Portalegre, Portugal

[3]ARQA, Associação de Arqueologia da Amadora, Rua Doutor Azevedo Neves, 37-39, Moinho, 2700-277 Amadora, Portugal

[4]CERENA- Centro de Estudos em Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

[5]Instituto de História Contemporânea e Instituto de Arqueologia e Paleociências da Universidade Nova de Lisboa, Departamento de História, Avenida de Berna 26-C, 1069-061 Lisboa, Portugal.

*Corresponding author:** Vieira Ferreiraa LF, IBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

Abstracts

Salt was extracted from saltpans, in the South shore of Tagus River by evaporation of the salted sea water which penetrates into the estuary. The walls and the bottom of those saltpans were made of local clays to retain the sea water, and ceramic sherds have been used to endure those walls and also to allow people to walk on the saltpans' walls. Those sherds constitute an example of the ceramics production in Lisbon workshops, starting in the mid-16th century and reaching high levels of quality in the 17th and 18th century.

A detailed archaeometric study of 14 selected sherds dated from the 16th to the early 18th century has been made and the conjugation of the information provided by the micro-Raman, XRD and XRF experiments for those sherds and clays collected locally, allowed us the characterisation of the Lisbon ceramics in that period.

Three main groups could be identified in the ceramic bodies; all made with locally collected clays of Miocene origin. In the first group, the potters used raw materials from the clay sources located at Santa Catarina area in Lisbon, most probably mixed with Lapa clays, which were fired at a high temperatures, ranging from 850ºC to 950ºC. Gehlenite and quartz are the dominant minerals of these ceramic bodies. In the second and third groups of Lisbon ceramic bodies, made with Prazeres clays, diopside was also detected but with variable amounts of gehlenite. Clay formations mineralogy mainly include kaolinite, muscovite/illite, quartz, calcite, and feldspars (albite and microcline).

Keywords: 16th to early 18th Portuguese Ceramics; Tagus estuary saltpans; MRS; XRF; XRD

Introduction

In the South shore of the Tagus River salt extraction from saltpans was a traditional activity, by evaporation of the salted sea water which penetrated into the estuary. Salt was used as an exportation commodity sold to countries in Northern Europe and the New World fisheries being essential for the development of fish industry. Written records reveal that this trade was developed as early as the 15th century, increasing in the 16th and 17th centuries and continuing into the 20th century, originating from places such as the Tagus estuary, Setúbal and Aveiro among others [1-5]. This was the time when Portugal became a global empire with contacts, settlements and colonies located from Japan to Brazil initiating a global trade of products originating in Africa, South America and Asia and re-exporting those goods to other countries in Europe [7-9]. Salt was also a major asset in this global strategy since it was fundamental in the preservation of food on board of the Portuguese ships [1,2].

This paper studies 14 sherds found in the saltpans' walls dated from the 16th to the 17th century (or early 18th). This was the criterion of selection. The collection of finds recovered in the saltpans corresponds to thousands of sherds dated from this period thus the selection will permit the study of the evolution of production from its early stages to a consolidated industry in the 17th century and its progressive decline in late 18th century when industrial productions will start to occupy their place in the city. No sherds of industrial production were included in this paper and all the 14 sherds were manufactured in traditional pottery workshops.

Tin glaze ware production

Portuguese tin and lead glaze wares dating from the 16th to the 18th century were studied in detail by Tânia [4,5,6], establishing an accurate chrono-stylistic evolution based on shape and decoration, determining six production moments, in this way helping archaeologists for studies in post-medieval archaeological contexts.

Although tin and lead glaze wares were made in three different areas of the country (Lisbon, Coimbra and Vila Nova), the major production centre, responsible it seems for at least half the Portuguese production, was Lisbon. Decorative influences from Europe and the East created unique aesthetic patterns distributed to several places around the world. Decorations were not static and since the early 16th century until the early 20th century these are in a constant change.
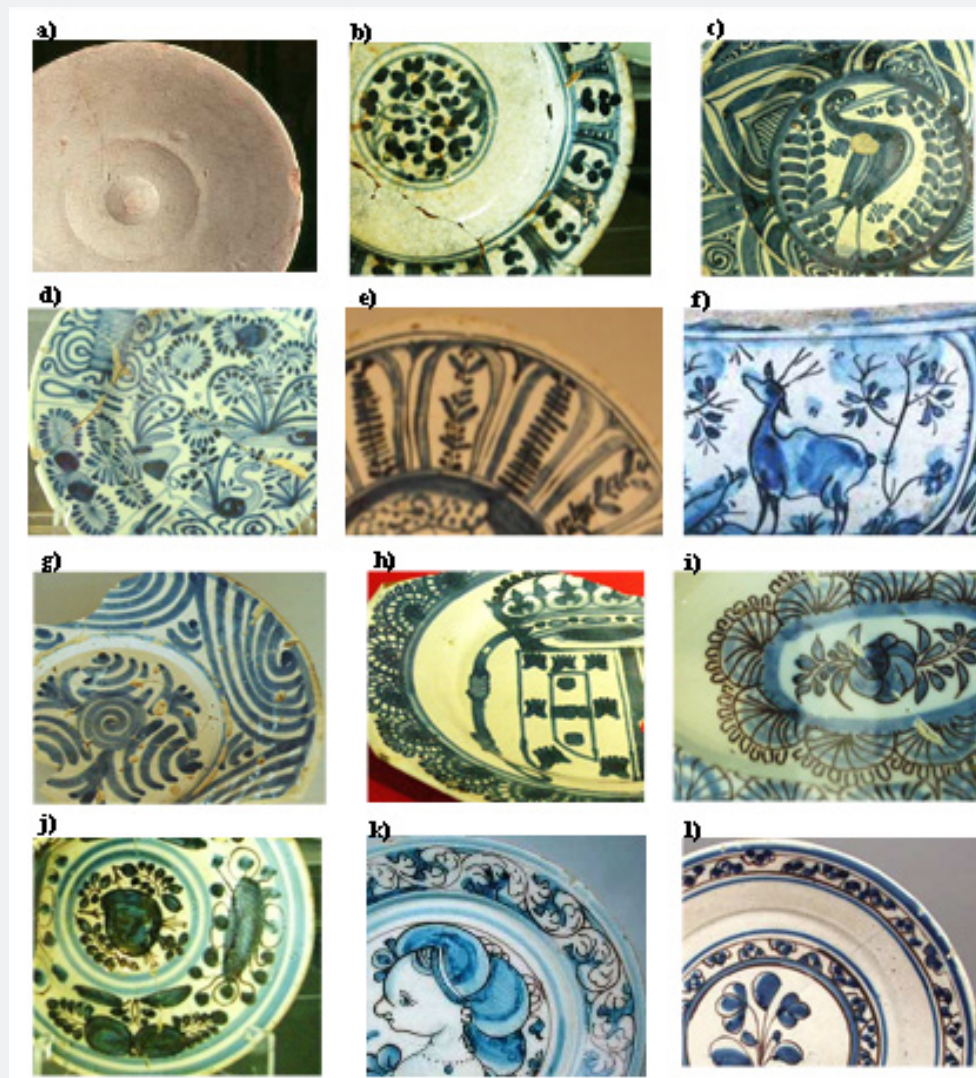

Figure 1: Representative examples of the decorative patterns of the Portuguese ceramics from the 16th to the early 18th century, presented by chronologic order.

In the 16th – early 18th century period that this paper focus on, Lisbon would dictate these changes and would influence the production in the other two production sites. This means that despite the possibility of recognizing the production of different centres there is a general Portuguese style. Figure 1 summarizes the decorative patterns' evolution from 16th to early 18th century Lisbon productions: a) is a white tin glazed dish with recessed bottom, made in the 16th century b) is also a plate from the 16th century, in a moment when blue starts to be used in decoration; c) was produced from about 1570 to 1640, and corresponds to blue on white frames with geometrical decoration; d) was produced in the beginnings of the 17th century. These plates were a copy of the Ming porcelain plates, which were imported from China by the Portuguese merchants, being quite common is Lisbon in those days; e) is a blue on white floral fern decoration, produced somewhere between 1635 and 1660; f) corresponds to a first moment of manganese pigment use with "fine drawings" of Chinese inspiration; g) is a plate decorated with concentric circles, produced somewhere between 1640 and 1710; h) corresponds to blue on white lace decoration produced in the 1650 to 1720 period; i) during the same period some of these laces were outlined with manganese pigment; j); manganese pigment was also used to outline other motifs of oriental inspirations such as aranhões 1660-1700; k) blue and purple on white with a baroque garland in the rim 1660-1720; l) blue and purple could also be used to draw beads between 1660 and 1760.

Following previous work on the topic of Portuguese ceramics produced in the 16th and 17th centuries [10-13]. we present now new data, aiming further insights in the spectroscopic characterization of the glazes, pigments and ceramic bodies of the Lisbon pottery in the above referred period. Non-destructive or micro-destructive techniques were used as our main tools, namely: micro-Raman spectroscopy (MRS), X-Ray Fluorescence Emission (XRF) and X-Ray Diffraction (XRD). Raw materials (clays) were collected from different locals in Lisbon, namely from Santa Catarina, Santos-o-Velho, Prazeres and also Lapa area (not far from Prazeres), all of Miocene origin. These sources are located in the western area of Lisbon [14]. The mineralogical and elemental contents of the clays were evaluated and compared, as collected and also after firing in an electric furnace (at 750ºC, 850ºC and 950ºC for 8 hours).

Archaeological Context

Built as early as the 15th century the Tagus River saltpans continued to be explored until early 20th century. Nowadays, these are in most cases abandoned and the walls suffered great erosion and subsequent destruction. Without the proper supervision the stone boulders are widely visible and small sherds of tin glazed pottery, redwares, porcelain, Italian majolica, glass, ceramic pipes, and many other ceramic objects are outcropping to the surface. These are fundamental in understanding when these saltpans were constructed and how these were maintained over time, a period which ranges from the Middle Ages to a contemporary chronology. Saltpans in the Tagus estuary are known to exist at least since the Roman period. Fish products were one of the main activities of this area and salt is fundamental in its production [15]. At least since the Middle Ages saltpans were built by raising earth clay walls and creating square "tanks" where the salted water would evaporate. To increase the building strength of those clay walls medium sized stones and ceramic sherds were mixed into the clay. These materials ensure construction workability and contribute to improve the structural resistance of the saltpans' walls, also allowing the circulation of people and carts so the salt could be recollected. Due to the proximity of Lisbon, one of the major production centers of various types of ceramics objects in medieval and early modern age, most ceramic sherds used in saltpans' construction were produced in Lisbon. Although this paper focuses on tin glaze wares, the ceramics found within the saltpans' walls are variable. Coarse wares and lead glazed wares produced in the Tagus estuary area, as well as imported objects from China and other European countries are also found.

The sherds used in the consolidation of the saltpans' walls seem to originate not directly from workshops but from domestic garbage. Lisbon ceramics were widely consumed all over the country and especially in the River Tagus area. The variability of the collection with different types of quality, decorations and forms over a long period of times suggests its origin from boulders assemblages. It is an interesting debate trying to understand how these were taken into the saltpans area since no dwellings exist nearby. These may have come from the nearby villages of Montijo or Barreiro or most likely from Lisbon. The transport of domestic garbage from Lisbon into the south margins of the river, getting rid of the undesirable waste, is a well-known practice since medieval times.

Archaeologists from Moita municipality often monitor the saltpans' erosion and recover the ceramic fragments used in the saltpans construction. Figure 2 shows a schematic map indicating the location of the referred saltpans (6 and 7), main villages around the saltpans and Lisbon city itself. Also the location of several clay sources and kilns North and South of Tagus River (in use from the 16th to the early 18th centuries) is pointed [13].

Geological Context

The Lisbon region presents two main different geological areas: one is located North of Tagus River, with Cretaceous, Paleogenic (basalt complex of Lisbon) and Neogenic (Miocene) formations [14,16-18]. South of Tagus River also some Miocenic outcrops can be found. However this second region is quite different from the first one, and corresponds to an area of Plio-pleistocene deposits. It should be emphasized that in the Lisbon region, Miocene clays can be found North and South of Tagus River, while Pliocene clays only exist South of Tagus River [14,16-18]. Further details on the geological context for the Lisbon ceramics can be found in references [16,17].

Figure 2: Schematic map indicating the location of the saltpans (6 and 7), main villages around the saltpans and Lisbon city. Also the location of several clay sources and kilns North and South of Tagus River (in use from the 16th to the early 18th centuries) is pointed.

Lisbon clay sources are traditionally grouped as West Lisbon and East Lisbon, for white or red clays respectively [14]. In Lisbon area, we collected clays in the areas of Prazeres, Sant'Ana à Lapa (Lapa parish), Santos-o-Velho, Santa Catarina and Travessa dos Oleiros, all of them in the West Lisbon. These raw materials were used since the 16th century [13,14,19-22].

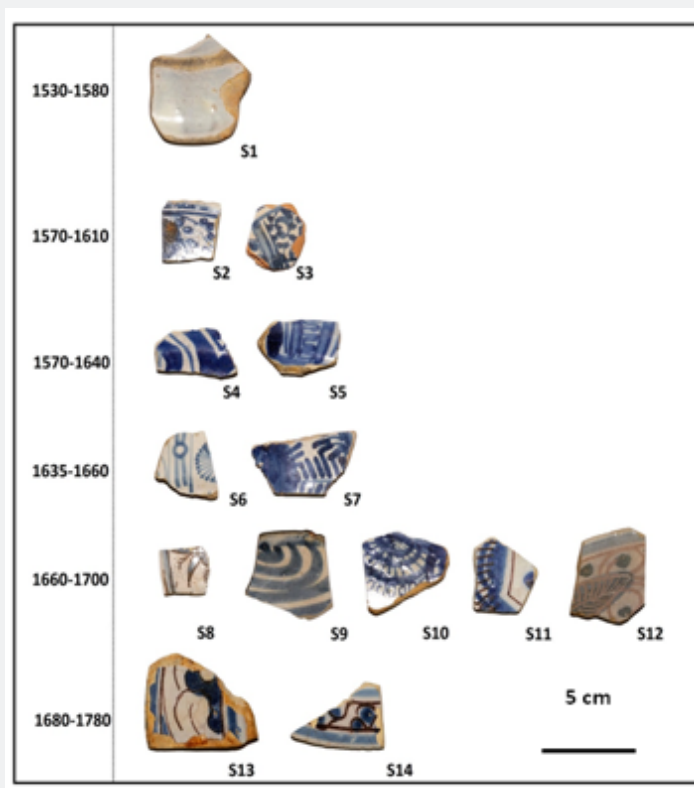## Materials and Methods

Samples

Figure 3: Samples 1 to 14 (sherds) found at the Tagus estuary saltpans. Sherds are presented by chronologic order.

In this study we present results for 14 pottery sherds, shown in Figure 3, and labelled as S1 to S14. Most sherds present a yellowish/greyish ceramic body, with the exception of S3 and S10 that present a more reddish hue. In all cases a lead glaze was used. The oldest ceramics exhibit a white or blue on white surface decoration. Only after the middle of the 17th century the purple colour was introduced in the pottery decoration in the Lisbon workshops.

Experimental Techniques under use

The XRD experiments, micro-Raman, and XRF spectroscopies and details regarding the firing procedures of the collected clays are described in previous publications of our group [10-13,16,17,22,23].
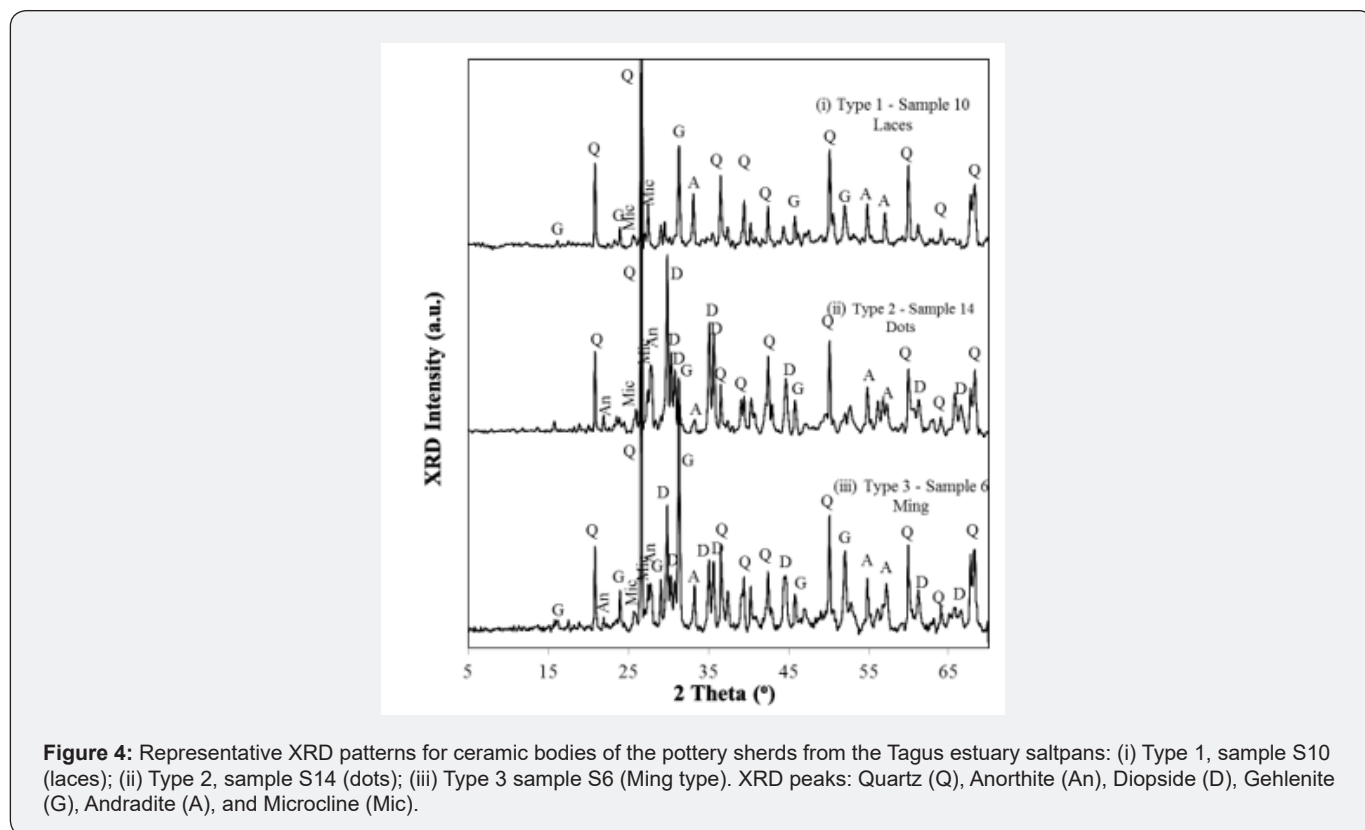
Results and Discussion

XRD studies

XRD technique has provided relevant information on the mineralogical composition of the 14 sherds under investigation, which was crossed with the Raman data, allowing us to correlate the clay sources with the ceramic bodies' mineral compositions for all the Lisbon sherds collected from the Tagus estuary saltpans. All diffractograms are normalized to the quartz peak at $2\theta = 21.0$ (constant intensity), to allow comparisons of the relative amounts of all the other minerals. The main XRD peaks observed for each sample are presented in Table 1.

Table 1: XRD main peaks used to identify the minerals in the diffractograms of samples S1 to S14.

Quartz - Q, SiO_2, $2\theta = 21.0, 26.7, 36.7, 46.0, 50.2, 60.0, 64.1, 68.2$,
Gehlenite - G, $(CaO)_2Al_2O_3SiO_2$, $2\theta = 16.2, 17.6, 24.3, 29.3, 31.4, 37.2, 44.5, 52.2, 61.3$,
Andradite - A, $Ca_3Fe^{3+}{}_2(SiO_4)_3$, $2\theta = 20.9, 29.6, 33.3, 36.5, 46.5, 55.0, 57.1$,
Microcline - Mic, $K\,Al\,Si_3O_8$, $2\theta = 20.9, 25.7, 27.5, 42.0, 50.8$,
Muscovite - M, $KAl_2(Si_3Al)O_{10}(OH)_2$, $2\theta = 8.8, 17.8, 19.8, 26.7, 45.3$,
Calcite - CC, $CaCO_3$, $2\theta = 23, 29.4, 47.5$,
Anorthite - An, $CaOAl_2O_3(SiO_2)_2$, $2\theta = 22, 27.5, 27.9$,

Ceramic Bodies

Figure 4 shows the three XRD pattern main types of ceramic bodies detected in the sherds under study.

Figure 4: Representative XRD patterns for ceramic bodies of the pottery sherds from the Tagus estuary saltpans: (i) Type 1, sample S10 (laces); (ii) Type 2, sample S14 (dots); (iii) Type 3 sample S6 (Ming type). XRD peaks: Quartz (Q), Anorthite (An), Diopside (D), Gehlenite (G), Andradite (A), and Microcline (Mic).

Type 1 ceramic pastes, curve (i) of Figure 4, exhibit quartz, gehlenite, andradite and microcline as major mineral components. Quartz (Q, SiO_2) was the major component, but also huge amounts of gehlenite a calcium alumino-silicate (G, $(CaO)_2Al_2O_3SiO_2$), andradite (A, $Ca_3Fe^{3+}_2(SiO_4)_3$), a calcium and iron silicate, microcline, a potassium alumino-silicate (Mic, $K\,Al\,Si_3O_8$) were detected in the diffractograms. Gehlenite formation indicates firing temperatures (Tf) above ~800ºC. The non-existence of muscovite, (M, $KAl_2(Si_3Al)O_{10}(OH)_2$), indicates Tf above ~850ºC, as we have shown before in [16]. Seven samples from Figure 3 are Type 1, namely S1, S2, S4, S7, S8, S9 and S10. Non presence of calcite (CC, $CaCO_3$) implies also Tf ≥ 850ºC [24].

Type 2 ceramic pastes, shown in curve (ii) of Figure 4, evidence several major differences from Type 1, namely the presence of anorthite (An, $CaOAl_2O_3(SiO_2)_2$) and also of very large amounts of diopside, (D, $CaMgSi_2O_6$), a calcium and magnesium silicate, in this way establishing a clear difference from Type 1 ceramics. The presence of diopside requires the existence of magnesium in the raw materials and also firing temperatures above ~850ºC [16,17,24]. Finally, the large amounts of anorthite shown in curve (ii) of Figure 4 are an evidence for very high firing temperatures in the kiln (above ~900ºC - 950ºC) and also of long-lived firing [16,17,24]. The high amounts of diopside are the main feature of Type 2 ceramic pastes. At the same time small amounts of gehlenite can also be detected, as well as microcline and andradite, the latter one in smaller quantities when compared with Type 1 case. Only two samples from Figure 3 are Type 2, namely S3 and S14.

Type 3 ceramic pastes (curve (iii) of Figure 4), show a similar mineral composition as Type 2, but in this case the amount of the detected gehlenite is significantly larger than the one existing in Type 2 ceramics, while the amount of diopside decreases. Most probably this means that the clay source for Type 2 and Type 3 ceramics is the same and it was the variation in the magnesium and calcium contents in the initial raw materials, corresponding to local stratigraphical facies variations, that establishes the differences in the final mineral compositions obtained after firing the pottery in the kilns of the pottery workshops (diopside requires magnesium to be formed and gehlenite requires more calcium [13]. The kiln temperature needed for gehlenite formation (≥ about 800ºC) is slightly lower than that needed for diopside formation. Again the absence of muscovite in both cases implies firing temperatures above ~850ºC. Six samples from Figure 3 are type 3, namely S5, S6, S11, S12 and S13.

The study of the diffractograms of the Lisbon clays used to produce all these ceramics was therefore mandatory and we will now present it. It points to clays collected in Lisbon from Travessa dos Oleiros (at Santa Catarina area) for Type 1 ceramics, and for Prazeres clays for Type 2 and Type 3 ceramics.

Collected Clays

Diffractograms of the Travessa dos Oleiros clays as collected are presented in Figure 5 (Curve (i)), and also of the same clays after firing at 850ºC for 8 h in an electric furnace (Curve (ii)).

Travessa dos Oleiros clays were collected in an area where a 16th-17th century pottery workshop existed, in the Santa Catarina area [22]. In the case of curve (i) calcite was detected and this mineral exists in the Travessa dos Oleiros clays in very large amounts. These clays also exhibit microcline, muscovite and quartz. Muscovite is a phyllosilicate, common in many clays in the Lisbon area. After firing at 850ºC new minerals were formed, with special relevance to gehlenite. Andradite and lime (L, CaO) could be detected in this sample immediately after the heating process. Water (humidity) reacts with lime, and this component disappears from the pastes easily.

The influence of the kiln's temperature in the disappearance of muscovite in the heated samples was studied before [16]. and always occurs totally for temperatures above ~850ºC. The thermal decomposition of the calcium carbonate originated the formation of lime, by CO_2 release. Since CaO is highly reactive with water, it can easily disappear by forming the calcium hydroxide after reacting with water. No calcium carbonate was found, meaning that carbonation (reaction of lime with CO_2 to reform Calcite) is certainly negligible in the present case.

In the case of the diffractogram of curve (iii), from Prazeres clays as collected, one should point the existence of kaolinite, (K, $Al_2Si_2O_5(OH)_4$), and also exhibits albite (Alb, $NaAlSi_3O_8$), which only exists in much smaller quantities in the Travessa dos Oleiros clay. After firing at 950ºC, curve (iv) of Figure 5, we were able to detect the formation of anorthite and diopside, but no formation of mullite ($3Al_2O_3\,2SiO_2$ or $2Al_2O_3\,SiO_2$). This temperature selection was justified because it allows the formation of anorthite and diopside, but not of mullite [24,25] as we could observe in this study. However, one can see that large amounts of anorthite were formed after firing, while the peaks for muscovite, kaolinite and albite disappeared. Also studying different samples from the clay source of Prazeres, we could observe the formation of different relative amounts of diopside and gehlenite. All these data point to the use of Prazeres clays for Type 2 or Type 3 ceramic bodies, and also shows that the temperature of the kilns had not exceeded 950ºC.

Raman micro spectroscopic studies

Coloured pigments of the sherds' surfaces:

The Raman spectra obtained for the different colours of the glazed surfaces for sherds S1 to S14 are presented in Figure 6 (i) to (vii), while the data for ceramic pastes (analysed as powders removed from the sherds) are presented in Figure 7 (i) to (vi).

Curve (i) in Figure 6 was obtained from the white glaze of sample S1, a sherd from a 16th century plate. The bending band of SiO_2 (δ_{Si-O}) exhibits a maximum at 462 cm^{-1} and the stretching band (υ_{Si-O}) at 996 cm^{-1}. Clearly this latter value indicates a lead based glaze [25,26]. The ratio of the bending band area relative to the stretching band is about 0.5, pointing to a relatively low temperature of the kiln, about 800 ºC [25]. This value is in accordance with the formation of gehlenite as XRD studies presented before indicated.
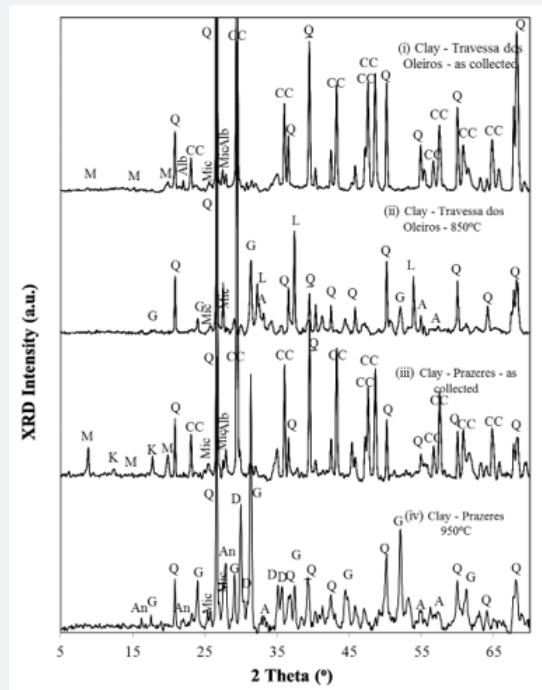
Figure 5: Diffractograms for clays collected in the western region of Lisbon: (i) Travessa dos Oleiros clay, as collected from the clay source; (ii) Travessa dos Oleiros clay, fired at 850ºC for 8 hours; (iii) Prazeres clay, as collected from the clay source; (iv) Prazeres clay, fired at 950ºC for 8 hours. XRD peaks: Quartz (Q), Gehlenite (G), Diopside (D), Anorthite (An), Albite (Alb), Microcline (Mic), Lime (L), Calcite (CC), Kaolinite (K) and Muscovite (M).
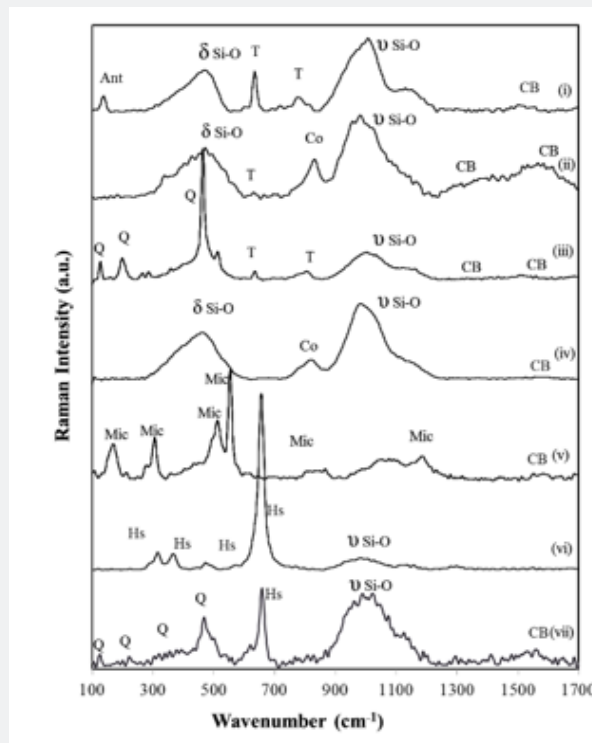

Figure 6: Raman spectra from the glazed surface of the sherds from Tagus estuary saltpans. (i) Sherd S1, white glaze; (ii) Sherd S2, blue glaze; (iii) Sherd S6, white glaze; (iv) Sherd S6, blue glaze; (v) Sherd S10, white glaze, (vi) Sherd S14, purple glaze; (vii) Sherd S13, purple glaze. Tin oxide (T), Quartz (Q), Anatase (Ant), Cobalt silicate (Co), Microcline (Mic), Hausmannite (Hs) and Carbon Black (CB).
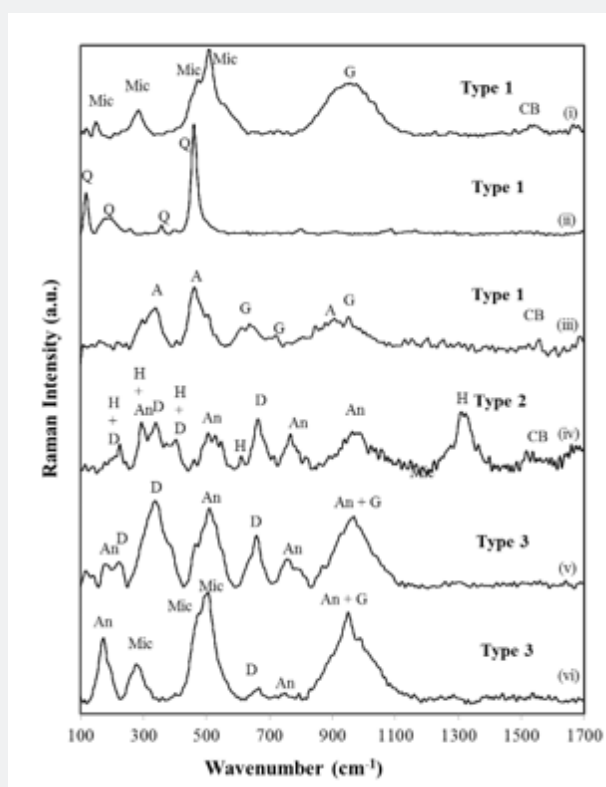
Figure 7: Raman spectra from the ceramic bodies of the sherds from the Tagus estuary saltpans. (i) Sherd S1 – White plate; (ii) Sherd S2 – Blue and white plate; (iii) Sherd S8 – "Fine drawings"; (iv) Sherd S14 - Dots; (v) Sherd S6 – "Ming"; (vi) Sherd S12 - Spiders. Anorthite (An), Andradite (A), Diopside (D), Microcline (Mic), Quartz (Q), Hematite (H) and Carbon Black (CB).

Several peaks located at 632 and 775 cm^{-1} could be detected, the main Raman peaks for tin oxide (T, SnO_2), the pigment responsible for the white colour of the glaze. Also the presence of anatase (Ant, TiO_2, main peak at 143 cm^{-1}) should be strength, which may also contribute for the white hue of this glaze.

Curve (ii) in Figure 6 is from sherd S2, blue area of the blue and white decorated plate. The small peak located at 631 cm^{-1}, indicates the presence of SnO_2, and a larger peak at 832 cm^{-1} indicates cobalt silicate as the blue pigment included in the glassy matrix, as observed in previous faiences made in Lisbon workshops in the 16th and 17th centuries [10,11,22,23]. The ratio bending band area/ stretching band area is now about 0.6, pointing again to a relatively low temperature of the kiln, about 850ºC [25].In this case some carbon black was detected as pointed in curve (ii) of Figure 6, the Raman bands located at the long wavenumber part of the spectrum.

Curve (iii) in Figure 6 is from the white glaze of the "Ming" sherd (S6 sample), the peaks at 126, 200 and 462 cm^{-1} clearly indicating crystalline silica, in this case quartz. Tin oxide exhibits peaks at 634 and 772 cm^{-1}. Curve (iv) in Figure 6 is also from the "Ming" sherd, now for the blue glaze. The main feature is the cobalt silicate signature at 829 cm^{-1}.

Curves (v) of Figure 6 was obtained in the white area of the laces sample (S10), and the presence of microcline (Mic) is clear, and its peaks are superimposed on the bending band and stretching bands of SiO_2.

Curves (vi) and (vii) of Figure 6 were chosen to indicate that the purple colour is due to the presence of a manganese pigment, in this case Hausmannite (Hs, 314, 367, 474 and 657 cm^{-1} peaks), which can dominate the Raman spectrum (curve (vi) or simply be superimposed on the bending band of SiO2 of the glaze (curve (vii)).

i. Ceramic Bodies

Firing conditions and origins of the pottery sherds from the Tagus estuary saltpans could also be establish using the micro-Raman studies of the ceramic bodies.

Curve (i) of Figure 7 refers to sherd S1, a Type 1 ceramics, and it exhibits microcline and gehlenite. Curve (ii) of Figure 7 refers to another Type 1 ceramics, S2, and in this case it is quartz that could be clearly identified. Curve (iii) is now from sample S8, also a Type 1 Lisbon ceramics. Here it is andradite and gehlenite that can be identified. All these informations match very well with the minerals detected in the diffractogram of the Type 1 ceramic bodies presented before in Figure 4, in this way confirming the mineral identifications provided by the diffractograms.

In curve (iv) of Figure 7, which refers to sample S14 (dots decoration) a Type 2 ceramic body, it was possible to identify anorthite, diopside, hematite and some carbon black. Anorthite indicates high kiln temperatures, about 950ºC [22-25,27-29]. The main peaks are located at 192, 286, 471, 505, 765 and 979 cm^{-1}. Diopside main peaks are located at 255, 320, 389, 660 and 999 cm-1 and its formation may occur at lower temperatures, at about ~850ºC [24,29]. Several peaks located at 224, 297, 412, 611, 662 and 1319 cm^{-1} could also be detected, due to the formation of hematite (H, Fe_2O_3), showing that oxidizing conditions existed in the kiln during firing.

The Raman spectra of Type 3 ceramic bodies are also included in Figure 7, curve (v) for sample S6, the "Ming" sherd and curve (vi) for sample S12, the spiders sherd. Diopside, anorthite, gehlenite and microcline were identified, showing again that in this case the high temperature of the kiln enabled the formation of some anorthite, which coexists with the other minerals that are formed at lower temperatures, i.e. gehlenite and diopside.

The diffractograms presented as curves (i) and (iii) from Figure 5 – clays as collected from Travessa dos Oleiros and Prazeres clay sources, respectively, also provided an important information, namely that some albite (Alb, ($NaAlSi_3O_8$)), a sodium alumino-silicate exist there. After firing in the kiln albite was totally transformed, and in the case of Type 2 and 3 ceramic bodies some anorthite was formed. Microcline, the potassium alumino-silicate, with the Raman main peaks close to albite, was detected both in the clays and remains in the ceramic bodies after firing in the kiln.

All these ceramic bodies indicate the use of Lisbon Miocene clays, and also show that in the case of the Prazeres clay source, the firing temperature of the pottery raw materials was high, as the formation of anorthite reveals. For temperatures around 950ºC anorthite is formed and it was detected in the case of Type 2 and 3 ceramic bodies. Also gehlenite and diopside exist, although in different relative amounts.

Type 1 pastes are also of Miocene origin, and were made using different raw materials from Travessa dos Oleiros or Santa Catarina, which are very rich in calcium carbonate, or these mixed with Lapa clays, which are very poor in calcium carbonate. In this case lower kiln temperatures when compared with Type 2 and 3 cases were used since no anorthite formation was detected. Some of the minerals in the raw materials remained unchanged, namely microcline and only gehlenite is formed in large amounts.

XRF studies

XRF analyses were performed for all ceramic bodies of the 14 samples under study. Only about 10 mg of powder were removed from each sherd. Table 2 presents these data, expressed as weight % of the indicated oxides for major and minor elements, and parts per million (ppm) for trace elements. Also the glazes of all sherds were analysed, and some results are presented as supplementary material in Table S1.

The ratio

$$R = (SiO_2 + Al_2O_3 + K_2O) / CaO$$

Table 2: Chemical composition of the powdered ceramic pastes of the Tagus saltpans' ceramics obtained by XRF, wt.% for major and minor constituents and ppm for trace elements.

Samples	MgO	Al2O3	SiO$_2$	K$_2$O	CaO	TiO$_2$	Fe$_2$O$_3$	Mn	Rb	Sr	Zr	Nb	R(*)
S1	1.98	11.33	50.22	3.34	21.39	1.55	10.03	394	37	380	174	23	3
S2	nd/nq	13	50.25	2.88	23.48	1.4	8.89	325	31	237	165	21	2.8
S3	1.66	12.54	56.58	3.72	13.45	1.35	10.59	298	57	178	141	20	5.4
S4	1.7	11.99	43.19	1.78	32.5	1.3	7.47	nd/nq	30	252	184	24	1.8
S5	2.1	12.26	47.33	1.58	26.78	1.4	8.47	nd/nq	29	422	180	26	2.3
S6	2.21	14.35	43.68	1.78	25.93	1.35	10.59	415	45	330	197	32	2.3
S7	nd/nq	13.73	52.11	3.08	20.04	1.73	9.24	nd/nq	37	431	153	28	3.4
S8	1.99	10.42	47.58	1.97	30.06	1.16	6.75	nd/nq	34	319	131	23	2
S9	2.23	11.13	45.62	1.93	29.61	1.38	8.03	nd/nq	26	245	160	23	2
S10	1.86	12.08	58.34	3.05	13.04	1.67	9.86	nd/nq	27	442	167	28	5.6
S11	2.35	11.31	48.53	1.5	26.92	1.22	8.1	nd/nq	30	289	217	25	2.3
S12	1.66	12.66	51.53	2.48	21.58	1.5	8.49	nd/nq	41	488	248	27	3.1
S13	2.16	12.11	48.74	1.68	23.46	1.33	10.42	nd/nq	24	342	181	23	2.7
S14	2.94	12.54	48.37	1.46	25.34	1.27	8.01	nd/nq	30	300	184	23	2.5

(The estimated error for major elements (Si and Al) was ≤ 3%, for minor elements (K, Ca and Fe) ≤ 4% and for trace elements ≤ 8%)

(*) Ratio, $R = (SiO_2+Al_2O_3+K_2O)/CaO$

(nd: not detected; nq: not quantified).

Table S1: Chemical composition of the glaze pigments of the Tagus saltpans' representative ceramics obtained by XRF, wt.% .(nd: not detected; nq: not quantified).

	Glazes	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SnO_2	PbO
S1	White	nd/nq	3.89	33.737	1.04	27.306	2.43	nd/nq	0.11	0.13	0.41	nd/nq	nd/nq	nd/nq	nd/nq	2.78	4.45	23.716
S2	Blue	1.29	4.52	46.32	1.14	19.8	5.44	0.48	0.14	0.08	1.65	0.74	0.44	nd/nq	0.02	2.27	3.26	12.41
S6	White	1.33	4.71	49.53	0.96	18.11	3.72	nd/nq	0.24	0.09	0.56	nd/nq	0.02	nd/nq	nd/nq	1.23	3.26	16.23
S6	Blue	nd/nq	3.76	43.39	1.12	22.14	2.96	nd/nq	0.11	0.11	1.87	0.33	0.11	nd/nq	0.01	2.16	3.24	18.69
S13	Purple	1.39	5.09	38.25	1.07	21.98	4.02	nd/nq	0.15	1.53	0.63	nd/nq	0.03	nd/nq	nd/nq	1.8	4.55	19.52
S14	White	nd/nq	4.27	44.46	0.94	23.11	3.71	nd/nq	0.16	0.36	0.4	0.02	0.04	nd/nq	nd/nq	1.67	4.24	16.62
S14	Purple	nd/nq	5.24	36.45	0.99	23.49	3.56	0.19	0.13	3.76	1.28	0.08	0.07	0.02	0.01	1.77	4.53	18.43

was used here to quantify the relative amounts of the structural and most abundant components of the ceramic pastes, (SiO_2 + Al_2O_3 + K_2O), related to calcium fractions (CaO). This methodology was used previously in other recent publications from our group [12,13,16,17,22,23]. Table 2 presents the R values for all Tagus saltpans' sherds. Table 3 presents similar values for the raw materials obtained from several Lisbon clay sources, commonly used in Lisbon workshops from the mid-16th to the early 18th centuries, in the western part of Lisbon [12-14,22,23]: Prazeres, Travessa dos Oleiros, Santa Catarina, Santos-o-Velho and Sant'Ana à Lapa.

Table 3: Chemical composition of the raw materials (clays as collected) used to produce pottery in the western part of Lisbon city, obtained by XRF, wt.% for the major and minor constituents and ppm for trace elements. (nd: not detected; nq: not quantified).

Samples	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Mn	Rb	Sr	Zr	Nb	R(*)
Prazeres	1.5	11.61	45.44	3.58	30.48	0.73	6.61	nd/nq	48	95	96	11	2
Santa Catarina (SC)	2.2	8	35.71	3.13	44.36	0.66	5.87	nd/nq	39	249	97	11	1.1
Travessa Oleiros	nd/nq	6.67	33.11	2.28	48.01	0.68	4.51	nd/nq	28	141	96	9	0.9
Santos-o-Velho	2.76	3.42	17.33	0.49	68.91	0.43	2.07	258	9	240	51	7	0.3
Sant'Ana à Lapa (SL)	1.28	11.85	71.09	4.54	2.76	1.32	7.8	nd/nq	65	60	215	17	31.7
50% SC + 50% SL	1.97	10.47	50.46	4.02	24.22	1.12	7.66	nd/nq	60	167	162	17	2.7
30% SC + 70% SL	nd/nq	11.72	58.46	4.39	16.11	1.24	8.01	nd/nq	65	139	177	18	4.6

(The estimated error for major elements (Si and Al) was ≤ 3%, for minor elements (K, Ca and Fe) ≤ 4% and for trace elements ≤ 8%)

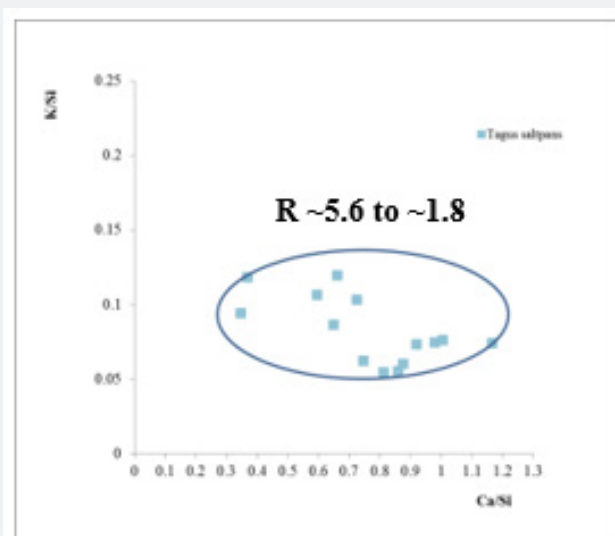(*) Ratio, R = (SiO_2 + Al_2O_3 + K_2O)/ CaO.

Figure 8: Scatterplot of K/Si versus Ca/Si count ratios for the pastes of the Tagus saltpans' ceramics. The contents of K and Ca measured by XRF were normalized to the Si content.

From the analysis of the R values from Table 2, which refer to samples S1 to S14 presented in Figure 3 and the R values presented for the clays (as collected from the clay sources, Table 3), one can see that Prazeres clays were in many cases used without temper i.e., without mixing with clays from other sources [30]. The initial amount of calcite in those clays was suitable to produce a good ceramic body after firing in the kiln's workshop. However, in the cases of Santa Catarina, Travessa dos Oleiros and Santos-o-Velho, the R values point to mixtures with the Sant'Ana

à Lapa clay. It is important to stress that the Sant'Ana à Lapa clay, used as collected, does not produce a ceramic paste compatible with the one observed in the samples S1 to S14.

Figure 8 presents a scatter plot of K/Si versus Ca/Si (% wt ratio) for all the 14 sherds under study. A previous normalization of the K and Ca contents to Si content, the main component of the body of the ceramics, was made, avoiding errors from empirical measurements and data treatment procedures [31] (Figure 9).
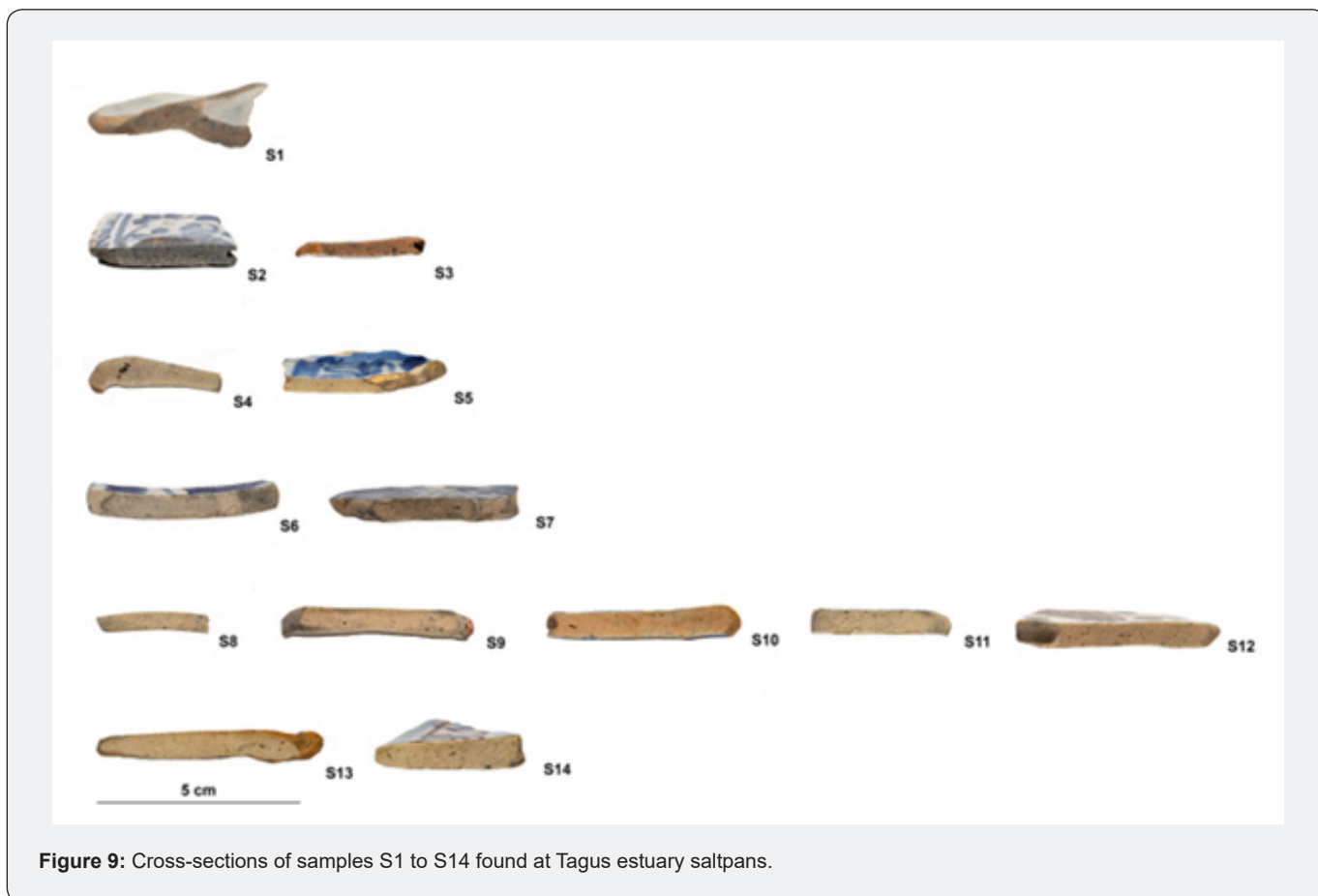

Figure 9: Cross-sections of samples S1 to S14 found at Tagus estuary saltpans.

The ratio R lays in a band of ~5.6 to ~1.8 for the 14 ceramics' pastes inside the ellipse, clearly indicating its Miocene Origin, as previously observed for studies of Lisbon ceramics [12,13,16,22]. These R values establish a clear difference for the ceramics produced south of Tagus River with Pliocene clays, where the R parameter lays in a very large range (usually ~150 to ~500), meaning the total absence or much reduced amount of calcite in the raw material of this origin [13].

Conclusion

Sherds from pottery produced in Lisbon workshops, starting in the mid-16th century and reaching high levels of quality in the 17th and early 18th century, were used as aggregates in the walls of the saltpans located South shore of Tagus River.

The mineralogical study of the ceramic bodies of those pottery sherds revealed three types of pastes: in Type 1, quartz, gehlenite and andradite were detected as major mineral components, indicating relatively low firing temperatures in the kiln, ~850ºC. In Types 2 and 3, high amounts of anorthite were detected, muscovite was absent and some diopside and gehlenite were also present, indicating a kiln temperature of about 950ºC. Also, firing was long enough to enable the formation of anorthite.

Clays used in several common pastes of the sherds found at Tagus saltpans were collected at Prazeres clay sources, as the R values and diffractograms indicate. In some other cases clays from Santa Catarina, Travessa dos Oleiros or Santos-o-Velho may also have been used but now tempered with Lapa clays, where the calcite weight percentage is much more reduced, as indicated for

the R values presented in (Tables 2 & 3). In this study, 7 sherds are of Type1 pastes, 2 samples are of Type 2 and 5 are of Type 3, all of Miocene origin.

The Raman assignments confirmed most XRD mineral identifications for Types 1, 2 and 3 ceramic bodies, and also provided additional information on the glazes: the pigments used in all sherds were identified on the white, blue and purple glazes on the surface of the sherds: tin oxide in the white surfaces, cobalt silicate for the blue and Hausmannite, a manganese oxide for the purple traces of the decoration.

All the data presented in this work provide complementary archaeometric informations on Lisbon's pottery production (faience) from the mid-16th century to the 17th and early 18th centuries, following previous studies on this topic by our Group.

Acknowledgements

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