SEM-EDS research on mineral inclusions found in the biscuit of azulejos as a tool for provenance studies

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SUMMARY: Since 2016, the Museu Nacional do Azulejo (Portuguese National Azulejo Museum), the Laboratório Nacional de Engenharia Civil and the HERCULES Laboratory of the University of Evora made a joint effort in the instrumental study of 16th century Portuguese azulejos, aimed at establishing their origin, technology and eventual systematization of workshop productions. The microscopic observation of the biscuits did not hint obviously to widespread mixtures of clays, as are routinely observed in the sections of 17th century azulejos. Therefore, it seems likely that the workshops often used plain marls with a suitable composition to grant compatibility of the biscuit with the glaze and thus their composition is a prime choice to confirm a local provenance. Azulejo samples are collected from panels on the walls and consequently are necessarily superficial and very small. In such samples the biscuit composition as pertains to minor and trace elements is tainted by the penetration of the raw glaze and digestion phenomena over firing. However inclusions of minerals that are infusible at the kiln temperatures remain largely unaltered. A means to discriminate provenance of azulejos based on a morphologic and compositional study of the small inclusions found in biscuit sections, often less than 5µm across, is proposed in this communication. These include mineral inclusions, both with and without repetitive morphologies, and micro-fossils.

This communication reviews the inclusions repetitively found in Portuguese 16th century azulejos as a first step for the construction of a database aimed at exploring their potential as markers of provenance.

RESUMO: Desde 2016, o Museu Nacional do Azulejo, o Laboratório Nacional de Engenharia Civil e o Laboratório HERCULES da Universidade de Évora, num esforço concertado, associaram-se no estudo instrumental de azulejos portugueses do século XVI, procurando estabelecer a sua origem, tecnologia empregue e uma eventual sistematização das olarias envolvidas. A observação microscópica das chacotas não revelou indícios de misturas recorrentes de barros, como é usual observar-se em secções de azulejos do século XVII. Assim, parece provável que as oficinas tenham em geral usado margas cuja composição permitia naturalmente a compatibilidade entre o biscoito e o vidrado, pelo que as suas composições são *uma escolha óbvia para confirmar proveniências locais. Muitos dos provetes utilizados no estudo foram amostradas de painéis completos ou ainda in situ e tiveram que ser, necessariamente, superficiais e de pequena dimensão. Nas secções que resultam da preparação destas pequenas escamas a composição da fracção de chacota presente, tal como a da pequena área de vidrado, estão contaminadas pela interacção entre os dois materiais durante o processo de cozedura o que complica a utilização de elementos de muito baixo teor como indicadores de proveniência. No entanto e na generalidade, inclusões de minerais infusíveis à temperatura de cozedura permanecem inalteradas. Assim, é proposto um método de discriminar proveniências baseado na morfologia e composição de pequenas inclusões encontradas em secções da chacota, frequentemente de dimensões inferiores a 5µm. Estas incluem inclusões minerais, com morfologias que podem ou não ser repetitivas, e microfósseis.*

Esta comunicação enumera inclusões encontradas repetitivamente em azulejos portugueses do século XVI como um primeiro passo para a construção de uma base de dados, destinada a explorar o seu potencial como elementos marcadores de proveniência.

KEY-WORDS: Provenance of ceramics; Early azulejo production in Lisbon; Use of SEM-EDS in the study of majolica; mineral inclusions in ceramics.

INTRODUCTION

16th century azulejos extant in Lisbon were locally manufactured or imported from Spain (Seville is a well-established origin [1]), from Antwerp [2] or from unknown production centres in Italy [1]. Later Portuguese azulejos (from the 17th century onwards) are easily identified on stylistic grounds but in the 16th century the first Portuguese workshops followed the Renaissance taste in patterns and designs and any attribution on that base alone is debatable. Setting aside the technological specificities of workshops that may, or may not, be present, provenance studies should best rely on those raw materials that were certainly of a local origin, in this case the sand used for the glaze and the clays or marl used for the biscuits of which there was ample supply in the Lisbon area.

Analytical studies of the glaze as a marker of geographical provenance stumble upon two main problems: on one side, the glaze incorporates several other raw materials of certainly different provenance (lead and tin compounds) or of unknown origin (e.g. the ashes used as a source of potassium or sodium oxides); and on the other side there is the often neglected fact that the glaze digests the biscuit over firing, incorporating many elements that did not previously exist or else were only residual, as Molera et al. have conclusively demonstrated [3] and the interface seen in figure 4 clearly documents. Therefore, we are left with the biscuit as a presumably best option where to find markers of geographical provenance. These can be found in the chemical composition and in the petrography of the ceramic material. A problem that is specific to azulejos, particularly renaissance productions, is that they are rare and have to be sampled from the walls which they line with the utmost prudence. Such samples include a section of glaze and a small piece of adherent biscuit, often less than 1 mm deep, collected with great care preferably from areas where the glaze is already detaching. Our (as yet unpublished) analytical results from those specks of biscuit in over 30 samples of 16th century azulejos of Portuguese origin have always returned contents in lead of up to 8% in weight (confirming Coentro's results measured on larger specimens [4]), meaning that the components of the glaze enter the biscuit and therefore provenance studies should better concentrate on major components and not trace elements that could have been acquired from the glaze.

There is however another source of potential information on provenance residing in the biscuits: the morphology and composition of the small inclusions found there. These include mineral inclusions, both with and without repetitive morphologies, and microfossil vestiges. Microfossils and petrography in general have already been proposed by several authors in studies of provenance of clays and ceramics (e.g. [5, 6, 7, 8]). We are not aware of any previous work pointing to minerals of rare earth and heavy elements in general for such purpose. Yet, these are particularly easy to spot in electron microscopy, when scanning biscuit sections with back-scattered electrons, because their atomic weight has a counterpart in the whiteness of the image that makes them stand from the background.

When experimenting with a method based in the nature and morphology of the repetitive inclusions to advance the study of the provenance of azulejos applied in Portugal we were faced with the same problem that curtails many such attempts in the field of cultural heritage: the lack of a reliable database of such inclusions found in ceramics of diverse provenance. This communication reviews the inclusions repetitively found in Portuguese 16th century azulejos as a first step for the construction of a database aimed at exploring their potential as provenance markers.

SAMPLES USED

Samples were collected from panels and tiles with known or strongly supported Portuguese origin. Whenever these panels incorporate azulejo units of different characteristics, eventually of different chronologies including later restorations, only the earliest azulejos, usually with red or reddish biscuits (the colour of the biscuits derives both from their composition and the firing cycles) were considered. Confirmation of the antiquity of each sample was based on morphological and compositional characteristics that are unique to this provenance and period and will be individually dealt with in communications presented to this conference. The panels considered were as follows:

2.1. Renaissance panels at *Igreja da Graça* in Lisbon [9], signed with the monogram of João de Góis who was active in Lisbon after ca.1558 - figure 1. Samples from this panel are identified with the code Az013/xx in which “xx” is an alfa-numeric code unique to each test item;

2.2. Renaissance panels lining *Capela de São Roque* in Lisbon, signed “Francisco de Matos” and dated 1584 (a study of these panels will be presented in GlazeArt2018 and be published separately)- figure 2. Samples from this panel are identified with the code Az068/xx;

2.3. Renaissance panel called “de Nossa Senhora da Vida” once in the now demolished *Igreja de Santo André* (Church of St. Andrew) in Lisbon and presently at the Museu Nacional do Azulejo and tentatively dated to ca. 1580 (a study of these panels supporting their Portuguese origin will be presented in GlazeArt2018 and be published separately)- figure 3. Samples from this panel are identified with the code Az032/xx.

Figure 1: An aspect of the dispersed 16th century panel at *Igreja da Graça* in Lisbon

Figure 2: An aspect of the 16th century panel dated “1584” at *Capela de São Roque*, Lisbon

Figure 3: An aspect of the *Painel de Nossa Senhora da Vida* once in the now demolished *Igreja de Santo André* and now displayed at the *Museu Nacional do Azulejo* in Lisbon

SEM-EDS ANALYSIS

The panels were sampled and the samples were stabilized in resin, cut so that a transversal section is obtained and polished for observation and analysis by scanning-electron microscopy coupled with energy-dispersive spectrometry (SEM-EDS). Figure 4 depicts one of the small samples with inclusions of potential interest marked for closer observation and eventual analysis.

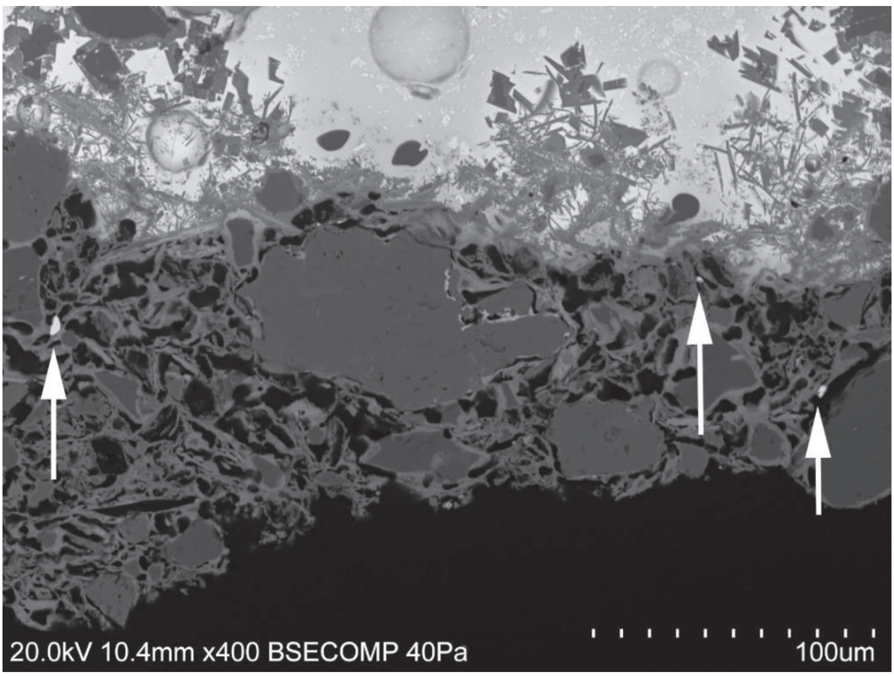


Figure 4: An aspect of part of the biscuit and interface with the glaze of sample Az068/02 (*Capela de São Roque*) with inclusions of potential interest marked for analysis

SEM-EDS observations and analyses were made at the HERCULES Laboratory in Évora using a HITACHI 3700N SEM coupled to a BRUKER XFlash 5010 EDS. Samples were uncoated and observations were made in back-scattering mode (BSE) with air in the chamber at a pressure of 40Pa and at an accelerating voltage of 20.0 kV.

A SYSTHEMATIZATION OF INCLUSIONS FOUND IN THE BISCUITS OF 16th CENTURY PORTUGUESE AZULEJOS

The inclusions can be systematized in three main types: i) morphological mineral inclusions are those that are not fossils but nevertheless have a distinctive morphology; ii) specks of minerals (without apparent morphological content); and iii) presumptive microfossils.

Morphological mineral inclusions

Framboids

The most common inclusions of this type are framboid structures and related micro-spherules (figures 5, 6, 7, 8, 9).

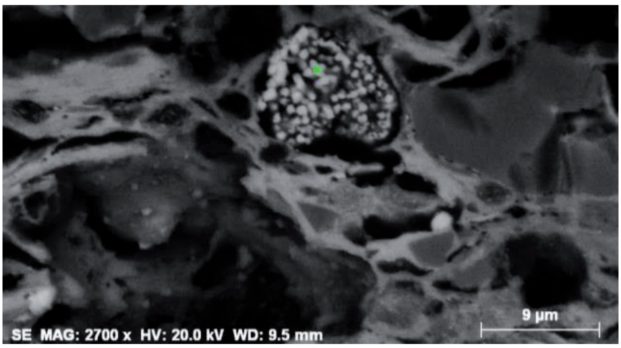
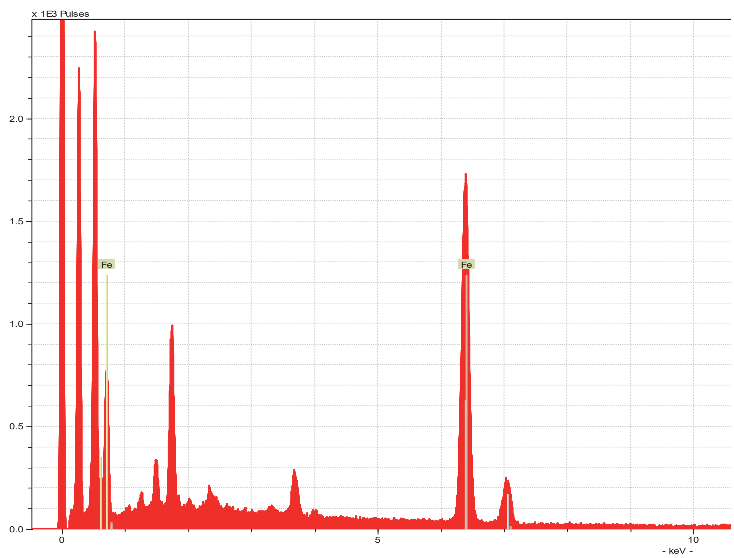


Figure 5: Top: irregular framboid of a Fe-rich mineral (presumably once pyrite) in Az032/01; bottom: EDS spectrum at the spot marked, depicting the characteristic Fe peaks (the other peaks are due to elements in the matrix).



The Pb content in the biscuit is not nil and the coincidence of the K peaks of S with a Pb peak makes it difficult to evaluate how much of the sulphur remains after the firing of the biscuit at over 800 ºC

EDS shows them to be constituted mostly of iron and oxygen (figures 10, 11). Presumably they were originally framboidal pyrite (FeS2) that lost most of its sulphur upon firing of the ceramic and glaze.

Framboidal structures occur when nucleation is faster than crystalline growth and are particularly common in pyrite [10]. They were once thought to need an organic source as a basis for organized nucleation but researchers have been able to reproduce them in the laboratory without such precondition. A review of framboidal pyrite and its synthesis was given by Ohfugi and Rickart [10]. The same authors point to the fact that although not a requisite, structures of organic origin are often found beneath the framboid and indeed several examples found in azulejos point to an organic origin in the circular hollows where they developed or their particular aggregations.

Useful nomenclatures for the several framboid morphologies were given by Merinero et al. [11] and by Sawlowicz [12] and were followed by us.

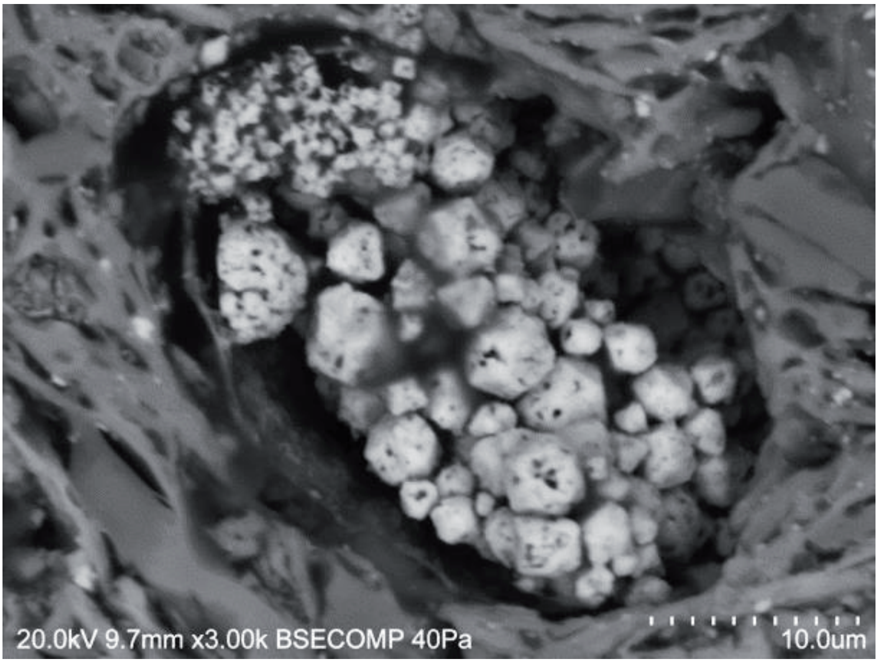


Figure 6: Irregular framboid associated with large euhedral crystals (Az 032/07)

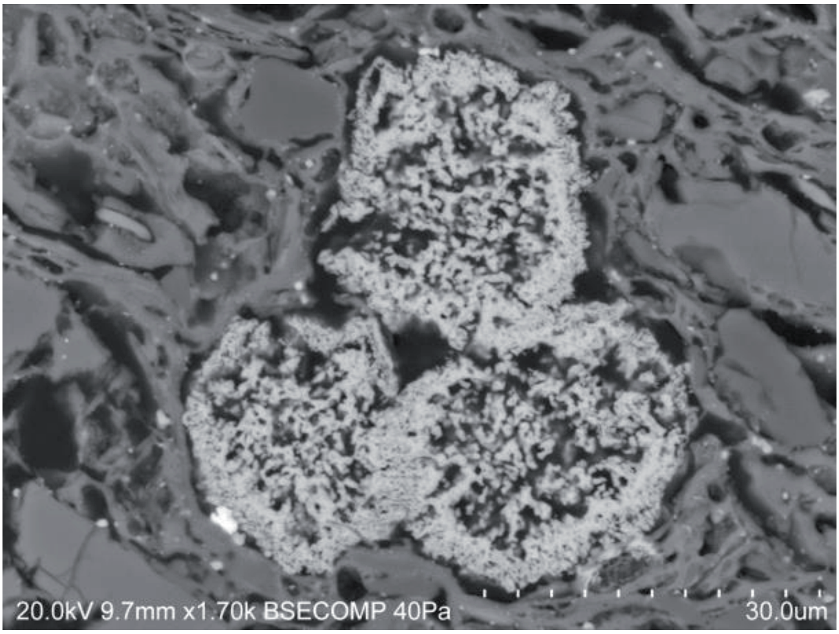


Figure 7: Annular framboids (Az 032/07)

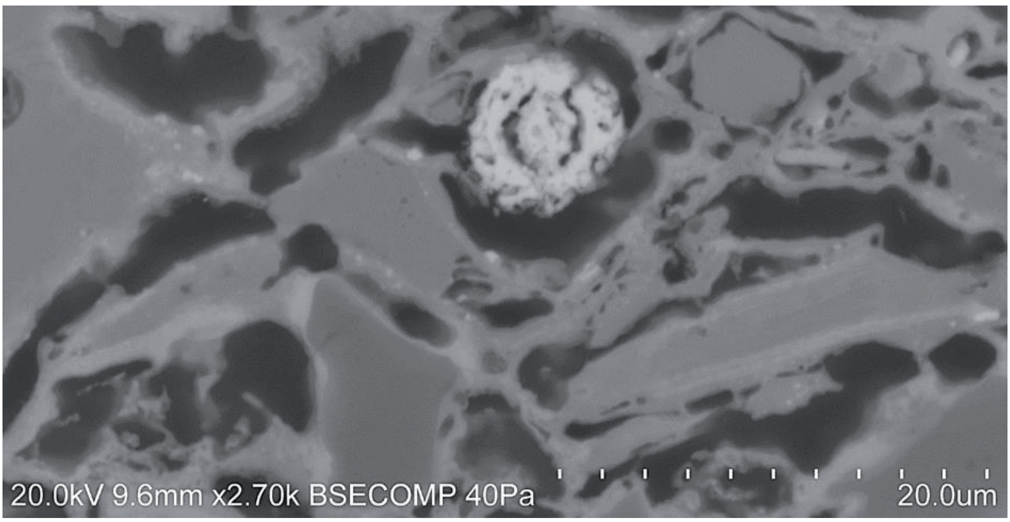


Figure 8: Annular framboid (?) with central area in separation (sample Az068/06)

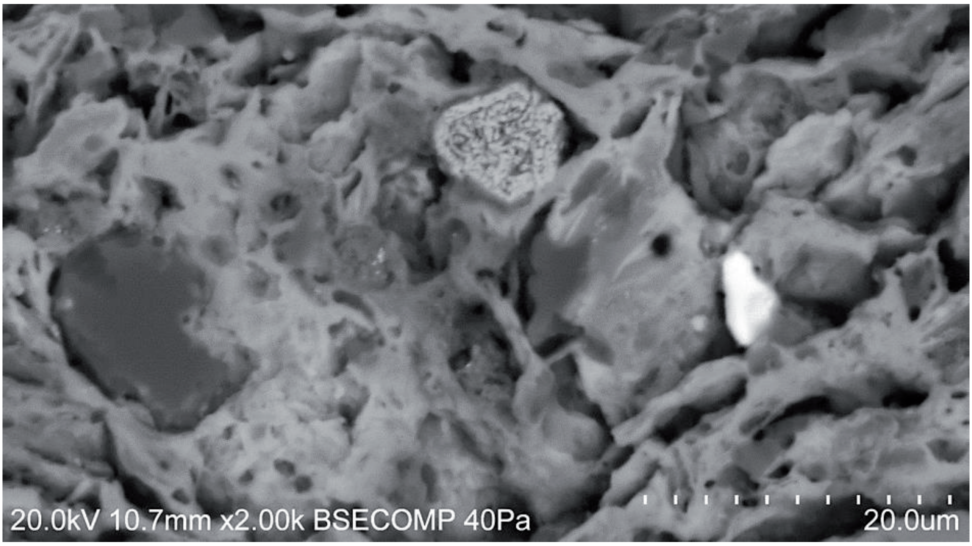
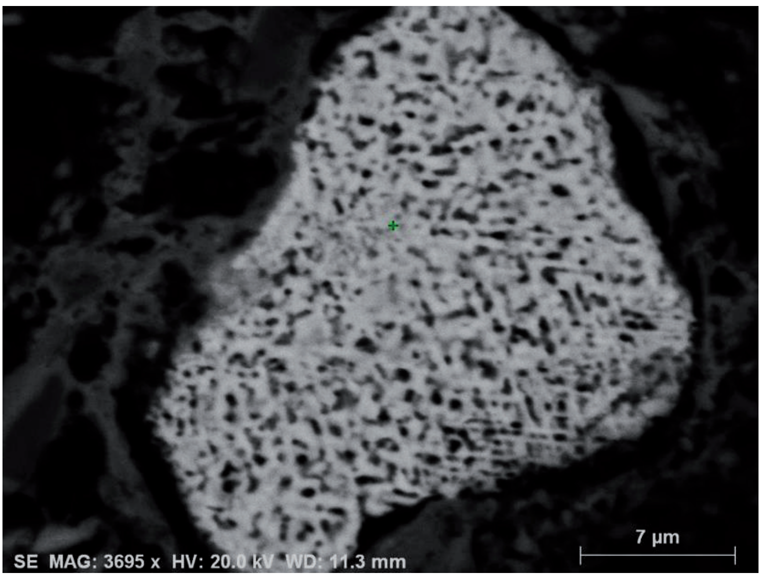


Figure 9: Euhedral-shaped crystal with framboidal core (sample Az032/04)

Structured crystals of an iron-titanium mineral

A mineral rich in Fe and Ti, probably ilmenite ($FeTiO_3$) is common in the shape of small featureless inclusions. Sometimes, however, it is found as needle-like or twinned crystals seen at the bottom right side of the inclusion pictured in figure 10. Here the crystals are agglomerated but twinned crystals also occur free in the ceramic matrix.



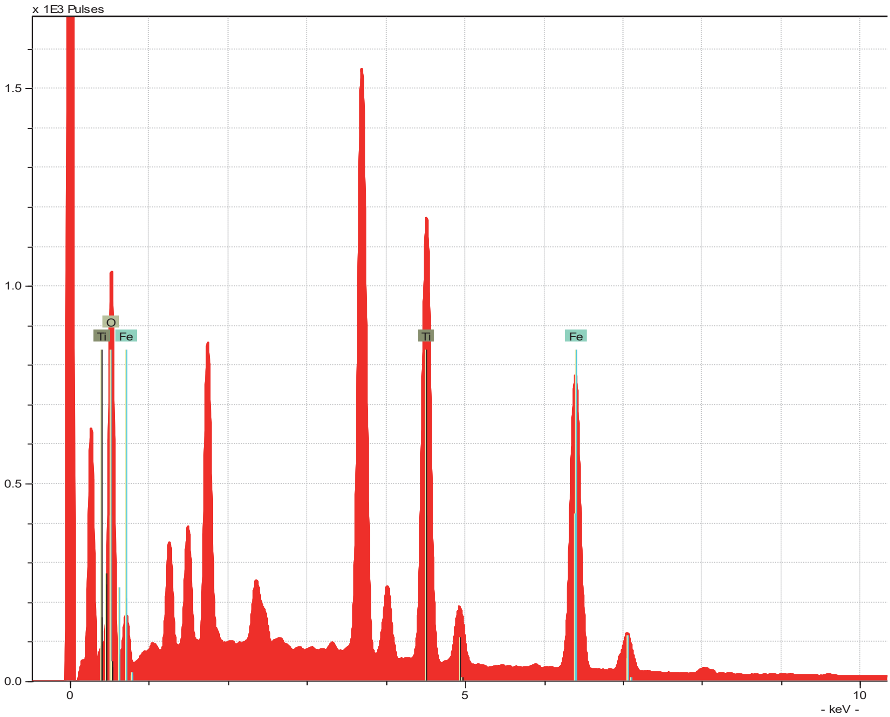
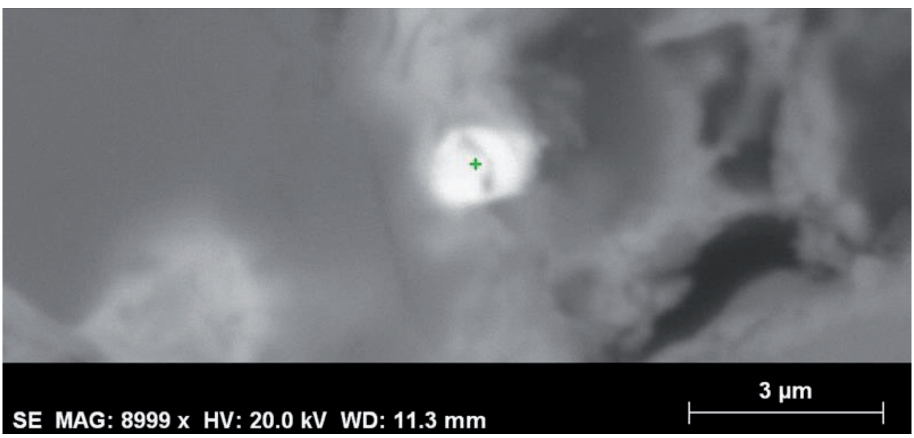


Figure 10: Top: mineral inclusion in the biscuit of sample Az013/07, rich in Fe and Ti; bottom: EDS spectrum depicting the substantial elements (the other peaks are probably due to elements in the matrix)

Zircon crystals

Zircon ($ZrSiO_4$) is relatively common as fragmented crystals but it may also be found as complete crystals (figures 11, 12) in which case they are often readily identified.



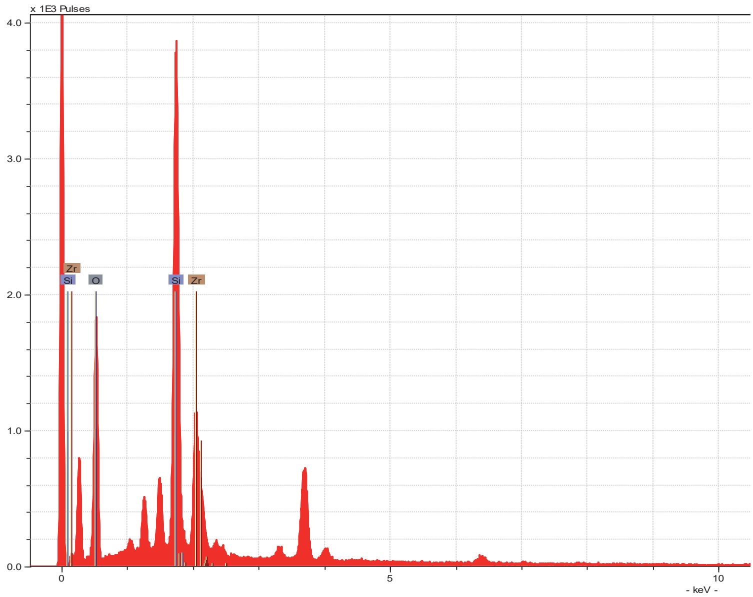


Figure 11: Top: zircon crystal in Az013/07 - such crystals are often seen with an ellipsoidal geometry because their upper face is polished off during the sample preparation; bottom: EDS spectrum at the spot marked depicting the peaks of the relevant elements (the other peaks are due to elements in the matrix)

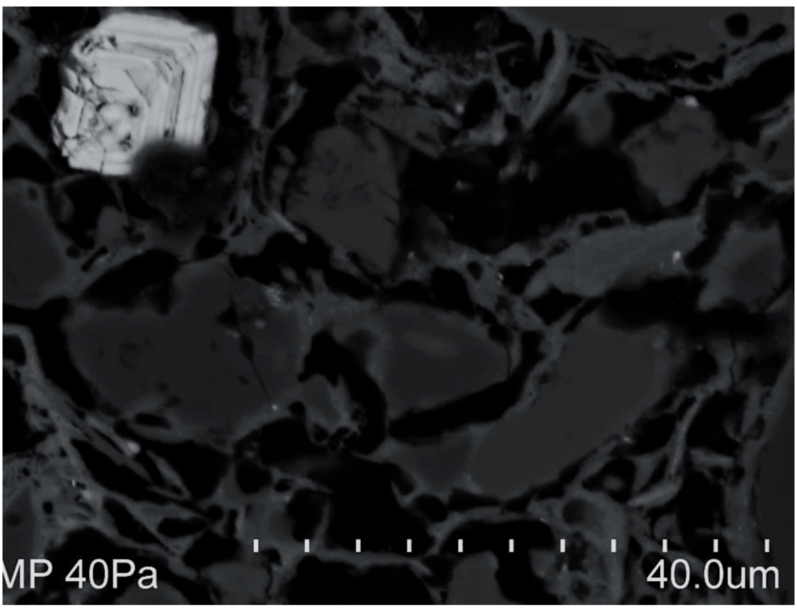


Figure 12: BSE image of a zircon crystal with inner growth marks apparent (Az068/06)

Specks of minerals

Specks of iron and titanium oxides have not been included because their ubiquity renders them of little value as markers of provenance.

The Tagus-Sado river basins began forming in the Cenozoic [13] and the rivers brought with them to what today is the region of Lisbon sediments from the interior of the Iberian Peninsula. These sediments are the origin of a number of inclusions of heavy elements minerals.

Gold

The fact that the Tagus River bears gold is well-known since Antiquity [14]. The occurrence of gold inclusions is not unusual in the biscuits of 16th century azulejos produced in Lisbon (figure 13).

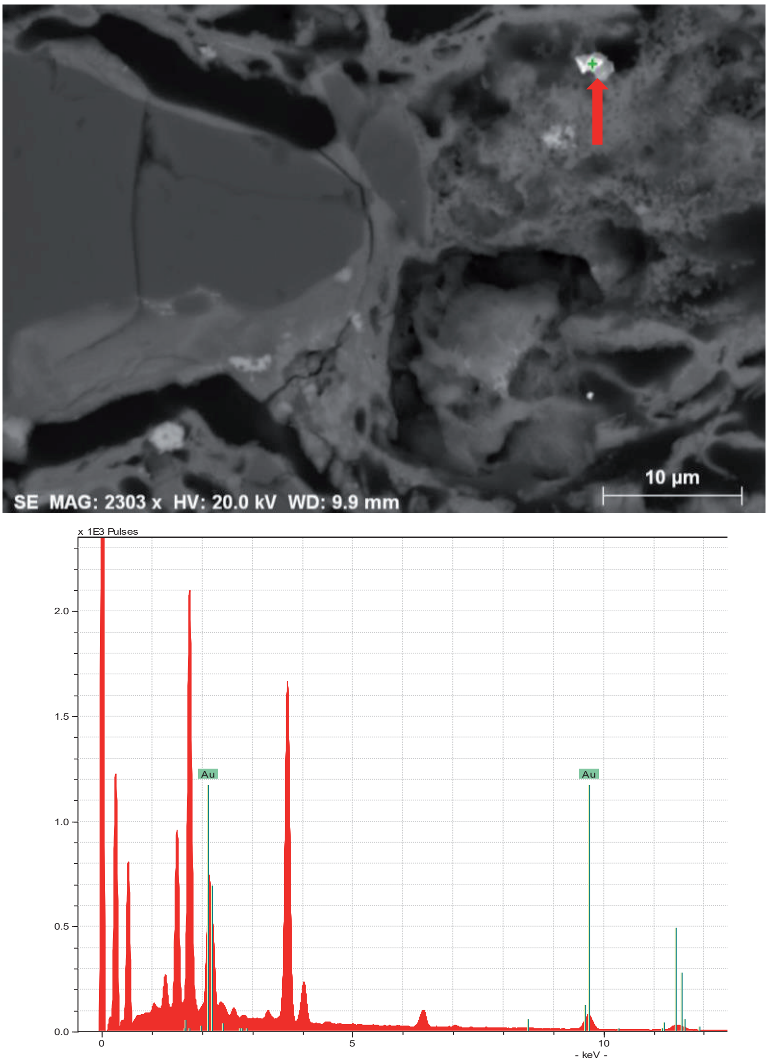


Figure 13: Top: inclusion of gold in Az068/06; bottom: EDS spectrum at the spot marked depicting the characteristic Au peaks (the other peaks are due to elements in the matrix)

Monazite (Ce)

Monazite (Ce) - (Ce,La,Nd,Th) PO_4 - is relatively common in most all samples examined and the inclusions are featureless (figure 14). Two main types are apparent: Th-poor mineral in which the EDS content ratio in weight Th/Ce approaches zero (figure 15 top) and Th-rich mineral in which the ratio in weight is typically > 0.5 (figure 15 bottom). Comparing the EDS spectra of both types of monazite in figure 15, corresponding to monazite (Ce) inclusions in the same sample, the peaks that define the presence of Th (Mα1 and Mβ, indicated in the graphs by the two consecutive vertical marks, the first of which indicated by "Th") are unapparent in the case of the first inclusion but well defined in the second.

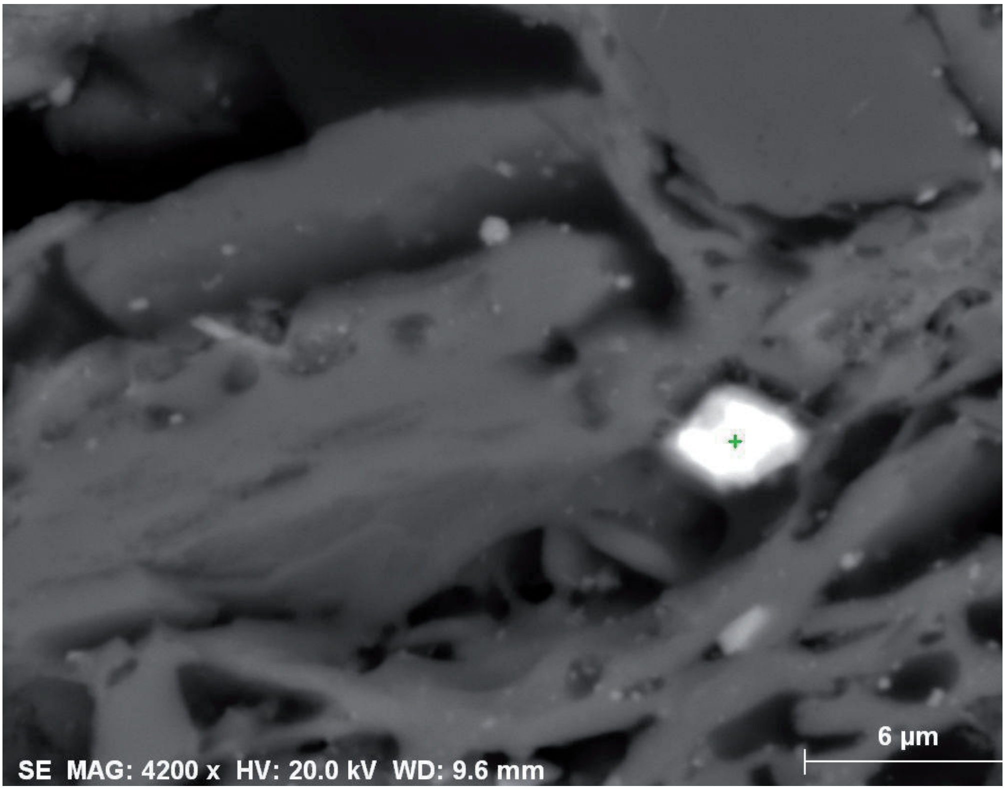


Figure 14: Typical featureless inclusion of monazite in sample Az032/07

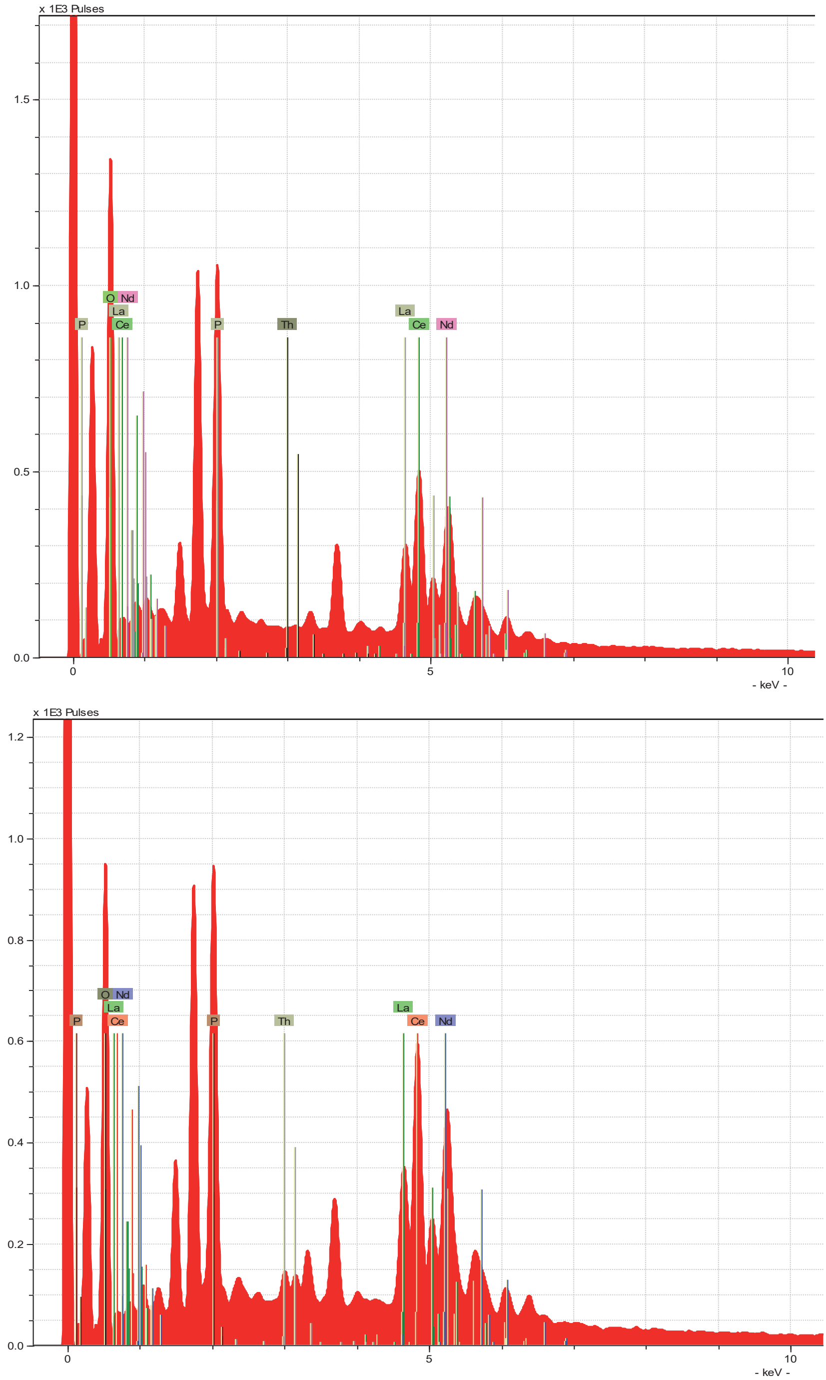


Figure 15: EDS spectra of (Ce) monazite inclusions in Az032/04. Top: Th-poor type; bottom: Th-rich type

Xenotime

Xenotime (YPO_4) inclusions were rarely found in the sections examined. Morphologically they are featureless and similar to monazite (Ce). Besides yttrium and phosphorous (figure 16) the composition of the inclusions found may include U and a variety of rare-earth elements in low contents.

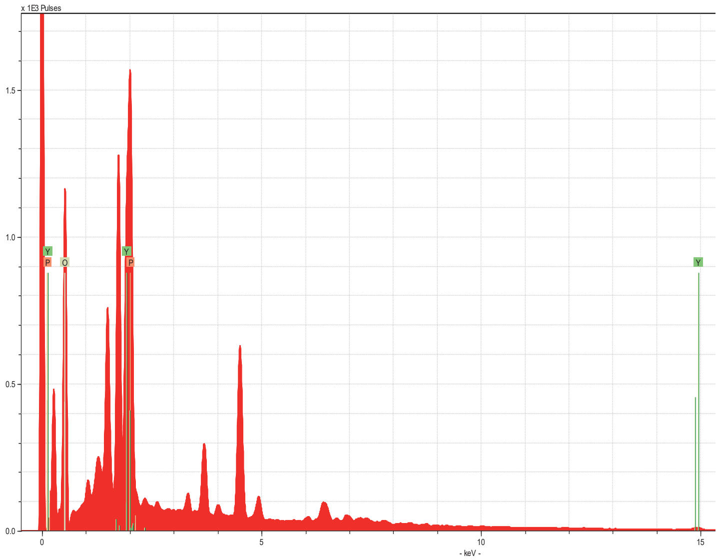
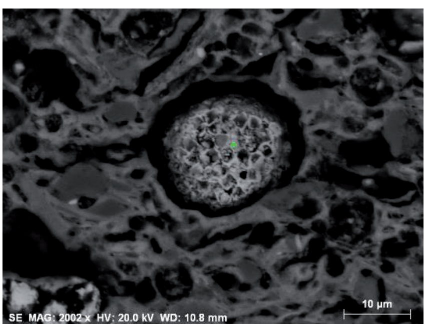
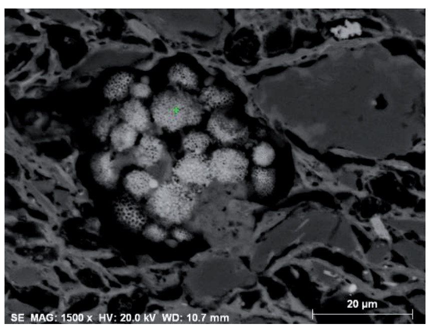


Figure 16: EDS spectrum of a xenotime inclusion in sample Az068/06.

Presumptive microfossils

In this chapter we show a number of mineral structures presumed to be fossils. Framboids are a bouquet of small spheroidal crystals. Fossil-like structures, on the other side, have the same general shape and composition but depict a multitude of what seem to be chambers (figures 17, 18, 19). Often they are lodged in circular holes suggesting biologic activity. In some cases such structures are likely crystalline growths nucleated over the test of a dead animal. They may also result from disappearing mineral framboids whose empty spaces were filled with plastic clay. Whatever their nature, their morphology is repetitive and therefore may serve as a provenance marker.





Figures 17, 18: Fossil-like structures in Az013/04. They are lodged in clear-cut holes and depict a mesh of seemingly empty chambers

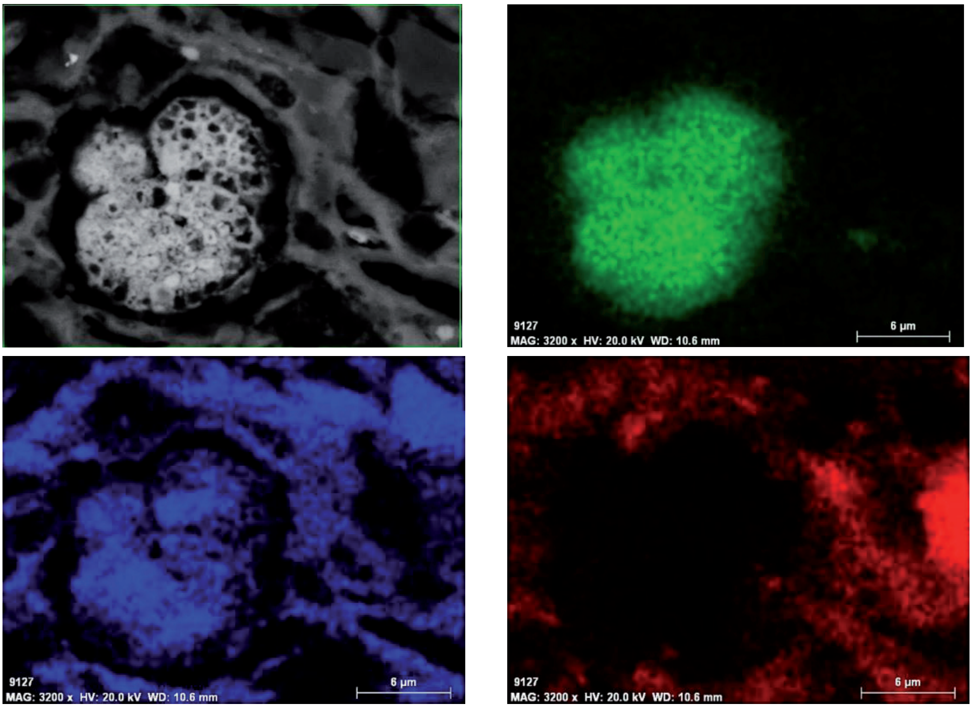


Figure 19: Fossil-like structures with chambers in Az013/04. The composition is similar to that of the framboids - elemental maps correspond to Fe (green), O (blue) and Ca (red)

5. CONCLUSION

We have presented a systematized list of inclusions repetitively found in the biscuits of 16th azulejos produced in Lisbon as well as images exemplifying the several cases. These are by no means exhaustive as we have also identified other rarer mineral inclusions that, through composition and approximate stoichiometric proportions obtained from the EDS semi-quantification, are thought to be pyromorphite - $Pb_5(PO_4)3Cl$ and vanadinite - $Pb_5(VO_4)3Cl$. Other inclusions containing Pb, Bi or Hg may correspond to workshop residues and may also afford additional data on that basis.

The research has to be followed by a more complete survey including accurate compositional analyses of inclusions such as monazite and xenotime, aiming at fingerprinting them from their contents in relevant minor, trace and sub-trace elements. Other geographic sources of majolica tiles such as Seville and Antwerp should also be included, with a view to determine which inclusions may profile each provenance location in the most straightforward manner. So… the results presented today are just the beginning of what we foresee as a promising new area of study in this field.

Acknowledgements

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