GEOCHEMICAL PATTERNS AND FIRING TECHNOLOGY RESEARCH ON CERAMIC GLAZED TILES FROM THE 17th – 20th CENTURIES (LISBON REGION, PORTUGAL)

M. Isabel Dias, IST/ITN, Univ. Técnica de Lisboa, EN 10, 2686-953 Sacavém, GeoBioTec, Univ. Aveiro; isadias@itn.pt

M. José Trindade, IST/ITN, Univ. Técnica de Lisboa, EN 10, 2686-953 Sacavém, GeoBioTec, Univ. Aveiro; mjtrindade@itn.pt

Leonel Ribeiro, Instituto de História de Arte/FCSH/UNL, PISAL/DSPC/DPC/DMC/CML, Rua do Machadinho nº20, 1249-150 Lisboa, leonel.d.ribeiro@cm-lisboa.pt

M. Isabel Prudêncio, IST/ITN, Univ. Técnica de Lisboa, EN 10, 2686-953 Sacavém, GeoBioTec, Univ. Aveiro; iprudenc@itn.pt

M. Teresa Bispo, ESEAG, Instituto de História de Arte/FCSH/UNL, PISAL/DPC/DMC/CML, Rua do Machadinho nº20, 1249-150 Lisboa, maria.bispo@cm-lisboa.pt

Laura Trindade, Instituto de História de Arte/FCSH/UNL, PISAL/DSPC/DPC/DMC/CML, Rua do Machadinho nº20, 1249-150 Lisboa, laura.trindade@cm-lisboa.pt

Pedro Flor, Universidade Aberta, Rua da Escola Politécnica, 147, 1269-001 Lisboa. Instituto de História de Arte/FCSH/UNL, Av. de Berna 26c, 1069-061 Lisboa, pedfaf@sapo.pt

Susana Varela Flor, Instituto de História da Arte da Fac. Letras da Universidade de Lisboa / RTEACJMSS, Alameda da Universidade, 1600-214 Lisboa, susanavarelaflor@sapo.pt

Fernando T. Rocha, Campus Universitário de Santiago, Univ. Aveiro, 3810-193 Aveiro, GeoBioTec, Univ. Aveiro; tavares.rocha@ua.pt

ABSTRACT

A set of 17th – 20th century glazed tiles supplied by the Department of Cultural Heritage tile collection, Lisbon City Hall, is studied in this work. The tiles were described and classified in a chronological point of view and analytical work includes chemical and mineralogical characterization of the ceramic bodies and mortars by instrumental neutron activation analysis and X-ray diffraction.

Most tile bodies consist mainly of quartz, gehlenite and calcite in variable proportions; commonly these main phases are accompanied by high temperatures phases, namely wollastonite or diopside, pointing to a Ca- or Mg-rich raw material, and mullite (in one sample) indicating the use of non-carbonated raw materials. Small amounts of K-feldspar and hematite are present in most tiles, whereas analcime, plagioclase, vaterite and cristobalite are found in just a few samples.

Chemical composition points to a certain homogeneity within 18th century tile bodies; the 20th century samples analysed are heterogeneous and have a different rare earth elements (REE) pattern, two are enriched in the first transition row elements, pointing to higher amounts of ferromagnesian minerals, and the other has lower amounts of Na, Fe, Cr and Co, and higher of Cs, light rare earth elements (LREE), Th and U suggesting high aluminium silicates content. The 17th century samples have a more heterogeneous chemical composition and higher contents of As and Na, which is explained by the presence of analcime. The ancient tiles have a general depletion of chemical elements, probably due to a dilution effect of the higher calcite content.

The mortars are all lime rich, but the 20th century ones have a general enrichment in all elements, and more k-feldspar and mica.

KEYWORDS: *Azulejos*, Glazed tiles, mineralogical composition, chemical composition, firing temperatures

1.   INTRODUCTION

The Portuguese glazed tiles (*azulejos*) are one of the most important building and decorative materials of the last four centuries, with important impact in the immovable and movable cultural heritage. They are very well studied in an art history point of view, and even some works concerning their knowledge in the ceramic bodies' composition exist [1][2][3], more compositional studies are needed in the *chamotte* basis of those tiles, especially considering the chronological and contextual issues. Consequently, there is an overall lack of chemically defined reference groups that characterize tiles body productions, especially those comprising a wide range of chemical elements, particularly trace elements, which are well known fingerprints in ancient ceramic materials studies [4][5], particularly glazed tiles [6].

In the framework of research collaboration with the Department of Cultural Heritage (DHC), Lisbon City Hall, glazed tiles from Lisbon buildings are studied in an interdisciplinary approach aiming with this work a chemical and mineralogical characterization of tile bodies. This knowledge will able to better understand tile bodies' behaviour to external agents, contributing to better define degradation progress and more adequate conservation strategies. This information may also be useful in restoration and treatment work regarding the materials employed in the tiles preparation.

Glazed tiles from various epochs, places and contexts, supplied by the DCH tile collection, are studied in this work. They include tiles from mid-seventeenth century to the first half of the twentieth century, and they came from Lisbon and Arrábida. Also available mortars of those tiles are analysed. Mortars can have different binder types (lime, gypsum and mud), but lime mortars are the most commonly found.

This work focuses on the mineralogical and chemical composition of both body and mortars of glazed tiles, and related production technologies, especially those concerned with firing temperatures. Thus this work will provide the necessary knowledge of the compositional/technological features of various types and periods of tiles and possible chronological relationships.
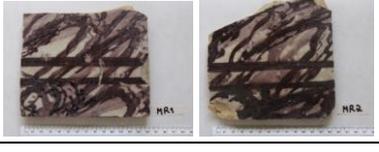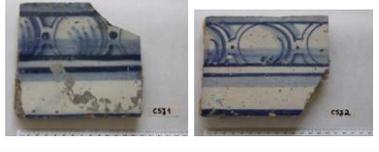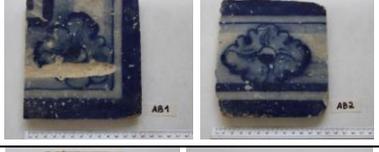

2.   MATERIALS AND METHODS
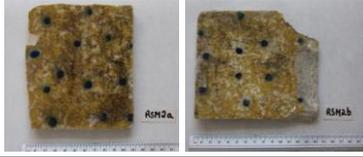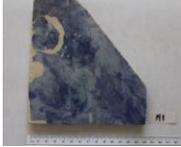## 2.1. Tiles samples

From the DCH tile collection 28 ancient glazed tiles were selected belonging to Lisbon and Arrábida (Setubal) buildings (Table 1). Prior to grinding, glazes and exterior surfaces were removed mechanically by means of a tungsten carbide abrading tool, leaving only the inner part (body) of the tile for analysis. This step served to minimize contamination of the ceramic matrix by glaze and mortar. In addition mortars were sampled when available, so only a total of five sample mortars are studied. Obtained samples were then grounded to a fine powder and homogenised.

The ceramic bodies analyzed are generally characterized by a light yellow-cream to orange (SE1, SE2) colour with a fine to medium texture, and thickness varies from 7 mm to 13 mm. The 20th century tile bodies have a finer granulometry; the RSM1 18th century tile is the coarser one, with inclusions up to 5 mm. In a few cases there are heterogeneities in the ceramic matrix, such as yellow-cream and brown inclusions, some of them grog. The 17th century tiles have the more heterogeneous matrix, with inclusions of several sizes.

The mortars have coarse textures, with visible quartz and calcite inclusions, some of them up to 8 mm.

Table 1 - Glazed Tiles and mortars analysed from the DCH collection

Photo	Reference	Description/Chronology	Context	Max. Body Thickness (mm)
	T2P T1A* T2A*	Polychromed tile with floral motif (in relieved). 2nd quarter 20th cent. *Mortar samples	Indoor Unknown location	10
	FA1 FA2	Tile beaded with winding foliage 1st quarter 20th cent.	Indoor Unknown location	7 7
	FL1	Tile pattern (common) in stylized floral motif, in blue on white enamel, stamped Last quarter 19th cent.	Outdoor Unknown location	11
	MR1 MR2	Tile from the bottom of a Wall. Imitating marble. Last quarter of the 18th	Indoor Unknown location	12 12
	CSJ1P CSJ2P CSJ1A* CSJ2A*	Tiles with "eggs" edging. 3rd quarter of 18th cent. *Mortar samples	Outdoor Palace of the Kitchens of the St. Jorge Castle, Lisbon	10 10
	G1	Tile with *Pombalino* floral pattern 3rd quarter of 18th cent.	Outdoor Palace of the Kitchens of the St. Jorge Castle, Lisbon	11
	AB1 AB2	Tile with floral ornament edging 3rd quarter of 18th cent.	Indoor Palace of the Kitchens of the St. Jorge Castle, Lisbon	12 12
	ABS1 ABS2	Tile with "cushion" and marbled 3rd quarter of 18th cent.	Indoor Palace of the Kitchens of the St. Jorge Castle, Lisbon	12 12
	RSM1	Tile from the bottom of a Wall. Sponged yellow on white enamel 3rd quarter of 18th cent.	Indoor Palace of the Kitchens of the St. Jorge Castle, Lisbon	9

	MA2	Tile from the bottom of a wall with curved ornaments;sponged listed in blue and white 3rd quarter of 18th cent.	Indoor Unknown location	9
	RSM2A RSM2B	Tile sponged in yellow With blue dots 2nd half 18th cent.	Indoor S. Mamede Street, 5 Lisbon	11 11
	SE1 SE2	Tile from the bottom of a wall with "cushion" in blue on white enamel Middle 18th cent.	Indoor Canastras Street Lisbon	11 11
	M1	Tile from the bottom of a wall with "cushion" marbled blue and white Middle 18th cent.	Indoor Unknown location	11
	GB1	Tile (common) with floral motif on a blue and white enamel 1st quarter 18th cent.	Indoor Unknown location	10
	BA1 BA2	Tile white glazed Late 17th – early 18th cent.	Outdoor Dome of the Chapel of the Bom Jesus- Convent of Arrábida, Setúbal	12 12
	AA1P AA2P AA1A*	Tile pattern with floral and other ornaments; blue and yellow on white enamel. 17th cent. *Mortar samples	Indoor Hospital Real de Todos os Santos, Lisbon	12 13

2.2. Methods

The chemical composition was determined by instrumental neutron activation analysis (INAA), using the Portuguese Research Reactor, Sacavém, Portugal, as neutron source. Powdered specimens were stored in polyethylene vials for chemical analysis. Samples are prepared for long irradiations together with reference standard samples (GSD-9 and GSS-1) from the Institute of Geophysical and Geochemical Prospecting (IGGE). One long irradiation and two gamma counts are performed. Two gamma-ray spectrometers are used: (i) one consisting of a 150 cm^3 coaxial Ge detector connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. This system has a FWHM of 1.9 keV at 1.33 MeV; and (ii) the other, consisting of a low energy photon detector (LEPD) connected through a Canberra 2020 amplifier to an Accuspec B (Canberra) multichannel analyser. The concentrations of the following elements was obtained: Na, K, Fe, Sc, Cr, Co, Zn, As, Ga, Br, Sb, Rb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, U. Details concerning the measurement and processing of the gamma spectra can be found elsewhere [4][7].

The mineralogical composition was obtained by X-ray diffraction (XRD), using a Philips X'Pert Pro diffractometer, with a PW 3050/6x goniometer, CuKα radiation, and fixed divergence slit, operating at 45 kV and 40 mA. The powdered samples were prepared as non-oriented aggregates and used to obtain the diffraction patterns. Scans were run from 3º to 70º 2θ, using a step size of 0.02º 2θ and a scan step time of 1.20 s.

3. RESULTS AND DISCUSSION

3.1. Mineralogical composition and firing technology

In general tile bodies' raw materials are a mixture of crystalline minerals like clay minerals, quartz, feldspars, calcite and dolomite. The three later ones can make part of the original raw material or deliberately added to promote the fusibility upon firing, as well as to lighten the color of the paste. Other impurities may also be found.

Mineralogical composition of the analysed ceramic bodies from the 17th till the 20th century consists mainly of quartz (SiO_2), gehlenite ($Ca_2Al_2SiO_7$) and calcite ($CaCO_3$) in variable proportions; commonly these main phases are accompanied by wollastonite ($CaSiO_3$), but in rare cases there is diopside ($MgCaSi_2O_6$) in considerable amounts (20th century tiles – FA1, FA2) and in trace amounts in one sample (19th cent. tile – FL1) instead of wollastonite, suggesting the presence of magnesium in the raw materials, probably a Mg-rich carbonate (Fig. 1). Trace amounts of K-feldspar and hematite are present in most tiles, whereas analcime ($NaAlSi_2O_6.H_2O$), plagioclase, vaterite ($CaCO_3$ – polymorph of calcite) and cristobalite (SiO_2 – high temperature polymorph of silica) are found in just a few samples: analcime is found in tiles from the 17th (AA2P) to the beginning of 18th century (BA1, BA2), and vaterite is present in tiles from the 18th century (M1, MR1, MR2, G1, RSM1) and cristobalite in trace amounts in tiles from the 18th (RSM1) and 20th cent. (T2P). One tile from the 20th century (T2P) has a completely different composition, with a ceramic body mainly with quartz and minor mullite ($Al_6Si_2O_{13}$) and cristobalite (Fig. 2), indicating the use of non-carbonated raw materials, in opposition to all the other analysed tiles.

Regarding the firing technology used in the analysed set of Portuguese glazed tiles, the identified mineralogical associations able to propose range of firing temperatures reached in the ceramic body production of these tiles, and a certain chronological differentiation can be found. The tile body T2P sample from the 20th cent. has high temperature mineral phases, like mullite, indicating firing temperatures of at least 1000ºC. The FA1 and FA2 20th century samples have a similar mineralogical composition, indicating the presence of a magnesium rich carbonate (or other Mg-rich mineral), both pointing to firing temperatures of at least 900ºC. The FL1 sample from the 19th has a similar composition of FA1 and FA2, but has less high temperature phases, as calcite is still detected, pointing to a range of lower firing temperatures (around 800ºC). Concerning the tiles from the 18th cent., mineralogical composition of bodies enhances in general the gehlenite as dominant mineral, followed by quartz, and also the presence of calcite. So, all these 18th cent. samples were made with a calcium carbonate rich raw material, with the same firing range of temperatures around 900ºC, but as some of them have still high amounts of calcite (together with gehlenite), or they were produced with more calcite rich raw materials, or they haven't reach so high temperatures. The composition of the four tile body samples from the 18th–17th centuries have similar mineralogical association to the 18th century tiles, pointing to calcite rich raw materials, firing temperatures of around 900ºC, but have a different mineral that is analcime. This is a zeolite mineral which presence is usually explained by alteration processes [11], consistent with the fact that these tiles are the more ancient ones.

Most of the analysed tiles point to a carbonate rich raw material, calcium or magnesium rich; nevertheless, we are aware that some of the calcite may have a diverse origin: (i) incomplete de-carbonation in the body of the ceramic tile during firing; (ii) re-carbonation of un-reacted calcium oxide

and contamination with soluble CaO/CaCO$_2$ from the mortars. But as most of them have light yellow-cream colour pastes, the most probable explanation is the presence of high level of carbonate phases in the raw ceramic materials, as they promotes high porosity due to de-carbonation during firing, lowering the vitrification temperature (700-800ºC) [12] and producing lighter coloured ceramic pastes.
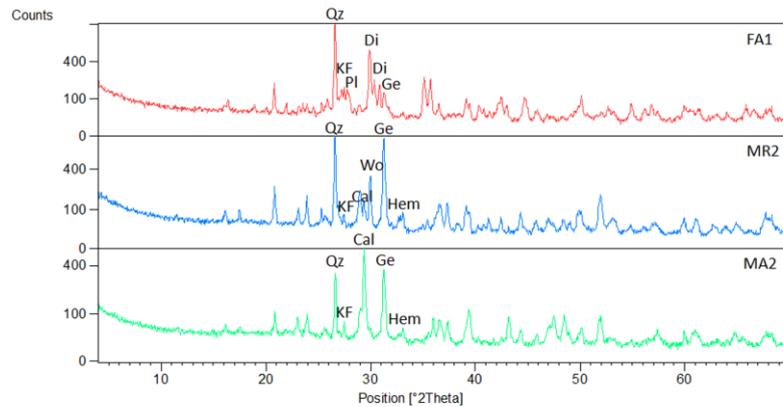

Fig. 1 – X-ray diffraction patterns of main mineralogical associations found in the set of analysed tile bodies. Qz: Quartz; KF: K-feldspars; Pl: Plagioclase; Cal: Calcite; Di: Diopside; Ge: Gehlenite; Wo: Wollastonite; Hem: Hematite.
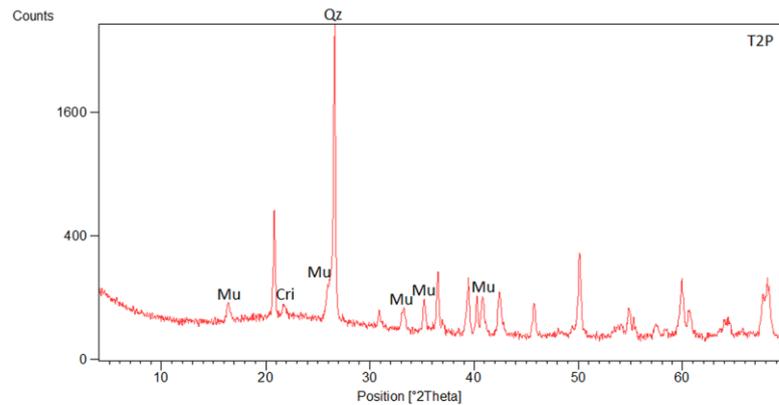

Fig. 2 – X-ray diffraction pattern of a 20th century tile body enhancing the presence of mullite (a high temperature aluminium phase). Qz: Quartz; Mu: Mullite; Cri: Cristobalite.
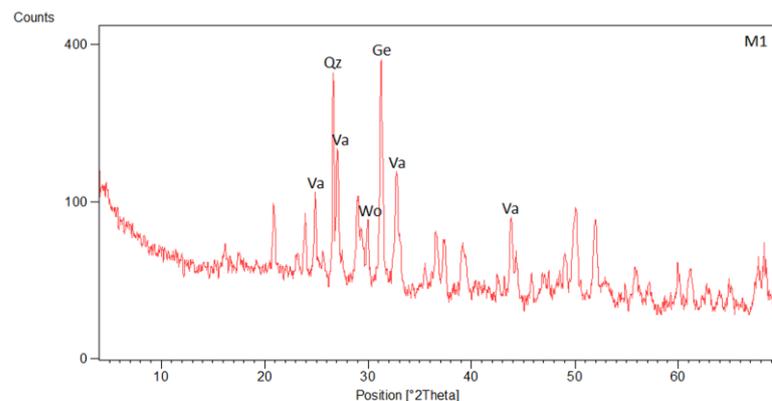

Fig. 3 - X-ray diffraction pattern of a 18th century tile body enhancing the presence of vaterite (a polymorph of calcite). Qz: Quartz; Ge: Gehlenite; Wo: Wollastonite; Va: Vaterite.

Regarding the five mortar samples analyzed, they are mainly composed of quartz and calcite, with minor amounts of k-feldspar; plagioclase and mica were also found in the 20th century mortars and gypsum occurs in one 18th century mortar (CSJ1A). The 20th century mortars (T1A and T2A) have higher amounts of k-feldspars and are the only ones with mica. The 17th mortar (AA1A) only has trace amounts of k-feldspars. In addition, XRD allowed us to establish that no high temperature phases were attained in the technological procedure of the making of mortars, so the burning of the calcareous stone to obtain the lime paste formed from the binder, was done at temperatures lower than 800ºC (presence of micas and absence of high temperature calcium silicate phases). This procedure and mineralogical composition was already observed in lime mortars from Sta Eulalia de Bóveda monument (NW Spain) from the Romanesque, Paleochristian and Late Medieval periods [13].

3.2. Chemical composition

The chemical results obtained by INAA points to a certain compositional homogeneity of tile bodies, especially of those from the 18th century (Fig. 4). Some samples are detachable from the others, particularly the 20th century samples: T2P is the only non-carbonated sample, rich in aluminium silicates, with lower amounts of Na, Fe, Cr and Co, and higher of Cs, light rare earth elements (LREE), Th and U; FA1 and FA2 tile bodies, also from the 20th century, have a similar chemical composition, but different from the T2P sample, with higher amounts of most elements, particularly K, Fe, Sc, Rb, Cs, Ba and Th; on the other hand also FA2 sample can be distinguishable from FA1 due to higher amounts of Ga and medium rare-earth elements (MREE). These chemical differences found in FA samples when compared with the other carbonated samples, reflect the distinctive mineralogy, as they are the only ones pointing to a magnesium rich raw material (i.e. Mg-carbonate, as mentioned above due to the presence of diopside). The FL1 19th century tile has in some elements similar behaviour as FA samples; this may be due to the fact that FL1 have a similar mineralogical association also with the presence of diopside. The chondrite normalized [14] REE distribution patterns also enhance some differences between tile samples, being the more ancient tiles depleted in all REE; also differences are enhanced within the 20th century samples, presenting T2P the higher REE fractionation; the 17th and 18th century tile bodies, have a similar REE pattern (Fig. 5).

The 17th cent. tiles are detachable from the 18th cent. tiles particularly by the much higher amounts of As (Fig. 4), and also by slightly higher amounts of Na. The higher Na content is related with the presence of analcime, only detected in these more ancient tiles, which may be explained by alteration processes, as documented in previous studies [11], accompanied by the leaching of potassium from the matrix, with a subsequent enrichment of Na with analcime crystallization [15][16].

Although a certain chemical consistency was found for the 18th century tile bodies, smooth differences can be detected, namely the S. Jorge Castle samples are generally enriched in Na (with the exception of two samples) (Fig. 6). Also a small group of samples have slightly distinctive chemical composition, with lower amounts of several elements, particularly Na, Sm, Yb and Th (Fig. 7; samples G1, M1, ABS2, MA2, RSM2B, CSJ1P), and no particular correspondence was found with location, as well as, no particular mineralogical features were found.

The enrichment observed in some elements by 20th century sample T2P is certainly related with the more phyllosilicate abundance of this sample, on the other hand the 18th and 17th samples have a general depletion in chemical elements, and are all calcite rich, what might be explained by a carbonate diluting effect.
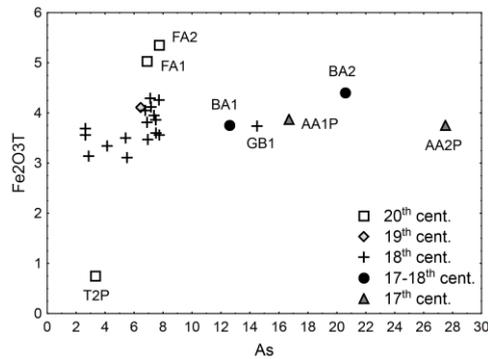
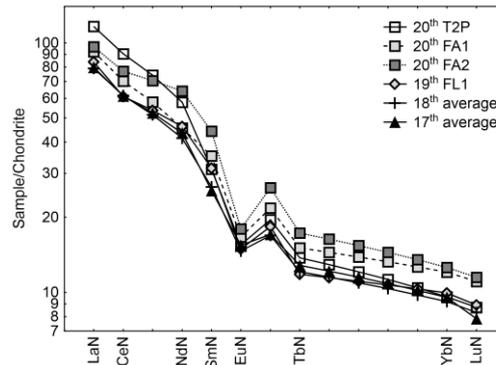Fig. 4 – Fe$_2$O$_3$T *vs* As biplot of tile bodies.

Fig. 5 - REE distribution patterns from the tile bodies of the 20th, 19th century and the average of 18th and 17th centuries, normalized to chondrites [14].
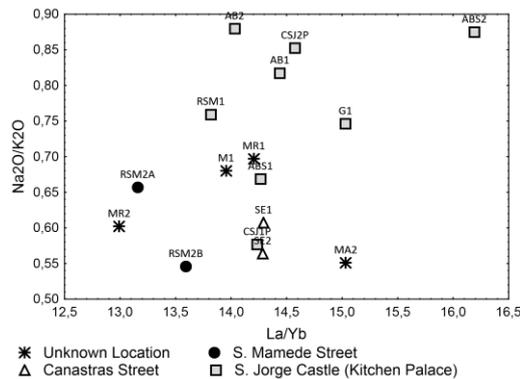

Fig. 6 – Na$_2$O/K$_2$O *vs* La/Yb biplot of 18th century tile bodies, according with location.
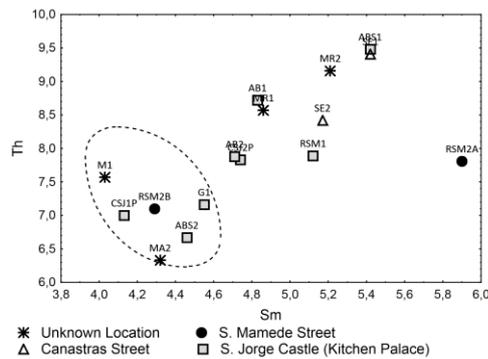

Fig. 7 – Sm *vs* Th biplot of 18th century tile bodies, according with location. Dot ellipse gathers the group of samples generally depleted in several elements.

Regarding the chemical composition of mortars, as mentioned above we were only able to analyse five samples, corresponding to mortars of tiles T1 and T2 (20th cent.), CSJ1 and CSJ2 (18th cent.) and AA1 (17th cent.). As expected, the mortars from the same tiles location have similar chemical composition. Although mineralogical composition was not able to clear differentiate mortar samples, chemical composition able to gather the 20th century mortars (T1A+T2A), and to separate them from the other two *S. Jorge Castle* tile mortars (CSJ1A+CSJ2A) from the 18th century, and the mortar sample from *Hospital Real de Todos os Santos* tile (AA1A) from the 17th century. To enhance these chemical differences we have used the k-means method in order to produce exactly 3 different clusters of greatest possible distinction, so, we would examine the means for each cluster on each dimension to assess how distinct our clusters are (Fig. 8). The mortars from the 20th century tiles (T1A+T2A) are enriched in the majority of the chemical elements obtained, particularly K, Rb, Cs, Ba, Th and U, which is related with the higher proportions of k-feldspars and the presence of mica in these two samples, and they are depleted in Cr, Co and As. The 18th century mortars are depleted in most of the elements, particularly in Na, Fe, Sc, Co, Zn, Ga and REE. The more ancient mortar (17th) is especially enriched in Co and As and depleted in K, Rb, Cs and Ba, which is related with the lower amounts of k-feldspars and the inexistence of mica.
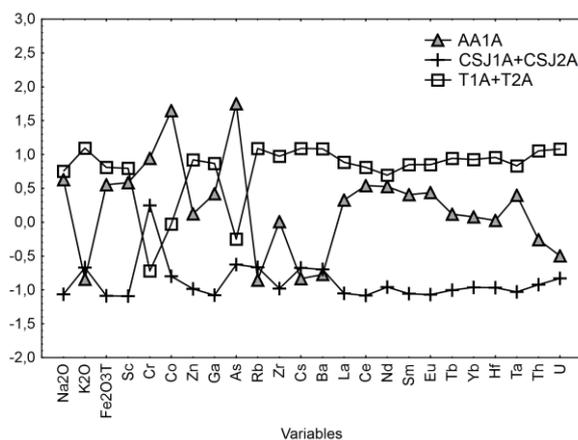

Fig. 8 – Plot of means for each cluster of mortar samples (K-means clustering method).

4. CONCLUSIONS

The compositional study of the tile bodies from various buildings in Lisbon and Setubal able to distinguish different raw materials and production technologies, namely firing temperatures, on the making of these tiles.

The mineralogical associations existing in body tiles shows that quartz, gehlenite, and in some cases wollastonite and diopside, are the main components. Nevertheless, mineralogical composition able to establish differences among the several glazed tile bodies, suggesting the use of compositionally distinct raw-materials, on the case of the 20th century tile T2P the resource to an aluminium-silicate rich material, on the others from the 20th and 19th centuries the resource to a Mg-rich raw material, most probably Mg-carbonate; on the more ancient ones no general mineralogical distinction was possible, pointing to a calcite rich raw material. Also different firing temperatures are suggested, reaching the T2P 20th century tile the highest temperature (1000ºC), and all the others within a range of 800-900ºC.

Chemical compositions of analysed tile bodies point to a certain chemical homogeneity in the 18th century samples. The 20th century tile samples are clearly detachable from the ancient ones, and from each other, suggesting the resource to two main types of raw materials, one more enriched in

aluminium silicates and the other with higher amounts of ferromagnesian minerals, reflected in the higher concentration of the first transition row elements. The ancient tiles have a general depletion of chemical elements, most probably due to a dilution effect of calcite. The 17th century tile bodies have a more heterogeneous chemical composition and have the highest amounts of As; they also have higher Na contents, which is explained by the presence of analcime (detected by XRD) which might have crystallized during alteration processes associated to these more ancient tiles. The REE patterns reinforce the use of the same type of raw materials for the 17th and 18th century tile bodies, being the differences detected related with diverse firing temperatures. In the case of the 20th century tile bodies, REE patterns also support the resource to two types of raw materials for the T2P, and FA1+FA2. Concerning the compositional studies of analysed tile bodies it is important to emphasise that a chronological correspondence was found, but no correlation was established with an outdoor or indoor location. Another interesting aspect is the more general Na enrichment of S. Jorge Castle tile bodies.

Regarding the mortars composition, they also have some chronological differences. Even they are all lime mortars, the 20th century ones have a general enrichment in all elements, and k-feldspar and mica richness. Chemical and mineralogical results confirm a calcite binder and mineralogical associations indicate a technological procedure involving the burning of the calcareous stone at temperatures lower than 800ºC to obtain the lime paste.

For a better characterization and broader comprehension of the production techniques and used raw materials of these 17th – 20th glazed tiles, to complement the tile bodies composition evaluation performed in this work, more studies will be predicted, namely the composition and colour of the glaze surfaces, their textural characteristics and decoration techniques.

5. REFERENCES

[1] CARVALHO, A.P., VAZ, M.F., SAMORA, M.J., PIRES, J. *Characterisation of ceramic pastes of Portuguese ancient tiles.* Materials Science Forum, vol. 514-516, 2006, 1648-1652.

[2] COROADO, J. and GOMES, C. *Physico-chemical characterization of ceramic glazed wall tiles dated of the 17th century, from the "Convento de Cristo", in Tomar, Portugal.* Proceedings of the 7th European Metting of Ancient Ceramics (EMAC'03). Trabalhos de Arqueologia 42, 2005, 33 - 39.

[3] PEREIRA, S.M., MIMOSO, J.M., SILVA, A.S. *Physical-chemical characterization of historic Portuguese tiles.* Relatório 23/2011-NPC/NMM, LNEC, 2011.

[4] DIAS, M.I. and PRUDÊNCIO, M.I., *Neutron activation analysis of archaeological materials: an overview of the ITN NAA Laboratory.* Portugal. Archaeometry, vol. 49.2, 2007, 383-393.

[5] DIAS, M.I., PRUDÊNCIO, M.I., GOUVEIA, M.A., TRINDADE, M.J., MARQUES, R., FRANCO, D., RAPOSO, J., FABIÃO, C.S., GUERRA, A. *Chemical tracers of Lusitanian amphorae kilns from the Tagus estuary (Portugal).* Journal of Archeological Science, 37, 2010, 784-798.

[6] PRUDÊNCIO, M.I., DIAS, M.I., BURBIDGE, C.I., ESTEVES, L., TRINDADE, M.J., MARQUES, R., CARDOSO, G., FRANCO, D. *Portuguese glazed tiles (16th-18th centuries): INAA, XRD and luminescence for raw materials characterization and production technologies of the ceramic bodies, and chronology.* 39TH Int. Symposium on Archaeometry, Leuven, Belgium, Abstract Book, 2012, 406.

[7] PRUDÊNCIO, M.I., GOUVEIA, M.A., CABRAL, J.M.P. *Instrumental neutron activation analysis of two French geochemical reference samples basalt BR and biotite Mica-Fe.* Geostandards Newsletter, X, 2006, 2931.

[8] WOLF, G., KÖNINGSBERGER, E., SCHMIDT, H.G., KÖNINGSBERGER, L.C., GAMSJAGER, H., *Thermodynamic aspects of vaterite-calcite phase transition.* J.Therm.Anal.Calorim.,60, 2000, 463-472.

[9] MORI, Y., ENOMAE, T., ISOGAI, A. *Preparation of pure vaterite by simple mechanical mixing of two aqueous salt solutions.* Materials Science and Engineering, C 29, 2009, 1409–1414.

[10] NIJLAND, T.G., LARBI, J.A., VAN HEES, R.P.J., LUBELLI, B., ROOIJ, M. *Self healing phenomena in concretes and masonry mortars: a microscopic study*. Proceedings of the First International Conference on Self-Healing Materials 18-20 April 2007, The Netherlands, 2007, 1-9.

[11] IÑAÑEZ, J.G., SPEAKMAN, R.J., BUXEDA I GARRIGÓS, J., GLASCOCK, M.D. *Chemical Characterization Of Tin-Leadglazed Pottery From The Iberian Peninsula and The Canary Islands: Initial Steps Toward a Better Understanding Of Spanish Colonial pottery In The Americas*. Archaeometry, 51, 4, 2009, 546–567.

[12] TRINDADE, M.J., DIAS, M.I., COROADO, J., ROCHA, F. *Mineralogical transformations of calcareous rich clays with firing: a comparative study between calcite and dolomite rich clays from Algarve, Portugal*. Applied Clay Science, 42, 2009, 345-335.

[13] SANJURJO SÁNCHEZ, J., TRINDADE, M.J., BLANCO-ROTEA, R., BENAVIDES GARCIA, R., FERNÁNDEZ MOSQUERA, D., BURBIDGE, C., PRUDÊNCIO, M.I., DIAS, M.I. *Chemical and mineralogical characterization of historic mortars from the Santa Eulalia de Bóveda temple, NW Spain*. Journal of Archaeological Science, vol. 37, Issue 9, 2010, 2346-2351.

[14] HASKIN, L.A., HELMMKE, P.A., PASTER, T.P., ALLEN, R.O. *Activation Analysis in Geochemistry and Cosmogeochemistry* (A.O.Brunfelt & E.Steinnes, eds.), Universitetsforlaget, Oslo, 1971, 201-218.

[15] BUXEDA, J., MOMMSEN, H., TSOLAKIDOU, A. *Alterations of Na, K and Rb concentrations in Mycenaean pottery and a proposed explanation using X-ray diffraction*. Archaeometry, 44 (2), 2002, 187–98.

[16] SCHWEDT, A., MOMMSEN, H., ZACHARIAS, N., BUXEDA I GARRIGÓS, J. *Analcime crystallization and compositional profiles – comparing approaches to detect post-depositional alterations in archaeological pottery*. Archaeometry, 48 (2), 2006, 237–51.