



Rem: Revista Escola de Minas

ISSN: 0370-4467

editor@rem.com.br

Escola de Minas

Brasil

Rivas Mercury, José Manuel; Costa Pereira, Domingos de Jesus; Silva Vasconcelos, Nazaré do Socorro Lemos; Cabral Jr., Aluísio Alves; Angélica, Romulo Simões  
Chemical and mineralogical characterization of portuguese ceramic tiles in the historic center of São Luís do Maranhão (Brazil): an approximation of the mineralogy and firing temperature of the raw materials

Rem: Revista Escola de Minas, vol. 66, núm. 1, enero-marzo, 2013, pp. 91-98

Escola de Minas

Ouro Preto, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=56425762012>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

## Chemical and mineralogical characterization of portuguese ceramic tiles in the historic center of São Luís do Maranhão (Brazil): an approximation of the mineralogy and firing temperature of the raw materials

### José Manuel Rivas Mercury

Chemical Engineer,  
PhD in Physical and Inorganic Chemistry,  
Professor of the Postgraduate Program in  
Materials Engineering (PPGEM),  
Department of Chemistry (DAQ)  
Federal Institute of Maranhão (IFMA)  
São Luis – MA, Brazil  
rivascefetma@gmail.com

### Domingos de Jesus Costa Pereira

Industrial Chemist in charge of the  
restoration laboratory of the Odylo  
Costa Filho Creativity Center  
Maranhão State Department of Culture (SECMA)  
Historical Center – São Luis – MA, Brazil  
domingoscosta\_pereira@hotmail.com

### Nazaré do Socorro Lemos Silva Vasconcelos

Industrial Chemist, PhD in Chemistry  
from the São Paulo State University – UNESP,  
Professor of the Postgraduate Program in  
Materials Engineering (PPGEM),  
Department of Chemistry (DAQ)  
Federal Institute of Maranhão (IFMA)  
ndsocorro@ifma.edu.br

### Aluísio Alves Cabral Jr.

BSc in Physics, PhD in Materials Engineering,  
Professor of the Postgraduate Program in  
Materials Engineering (PPGEM), Department of  
Physics (CED) – Federal Institute of Maranhão  
(IFMA) – acabraljr@ifma.edu.br.

### Romulo Simões Angélica

Geologist, PhD in Mineralogy and Geochemistry,  
Professor of the Postgraduate Program in Geology  
and Geochemistry of the Geosciences Institute of  
the Federal University of Pará (UFPA)  
at Guamá, – 66075-110 Belém, PA, Brazil  
angelica@ufpa.br

*Caracterização química e mineralógica de azulejos portugueses do centro histórico de São Luís-MA (Brasil): uma aproximação à mineralogia e à temperatura de queima das matérias-primas*

## Resumo

Nesse trabalho, foram caracterizados, pela primeira vez, azulejos históricos portugueses do Centro Histórico de São Luís (CHSL) do Maranhão. A caracterização foi realizada através dos ensaios de microscopia ótica, difração de raios X (DRX) e análise química, visando ao uso dessa informação para a determinação das possíveis matérias-primas utilizadas na sua fabricação, bem como a provável temperatura de queima desses materiais. Os resultados mostraram que a microestrutura desses materiais é constituída por poros de tamanhos variados, apresentando incrustações de calcita e grãos de quartzo de tamanhos inferiores a 500 µm, distribuídos numa matriz de cor rosa-amarelo, onde foram identificadas, por DRX, as fases minerais calcita, gelhenita, wollastonita, quartzo e amorfo. A partir da informação obtida, é possível inferir que as matérias-primas originais estiveram constituídas, provavelmente, por mistura de argilas caoliníticas ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), ricas em carbonatos de cálcio e quartzo ou misturas de argilas caoliníticas, quartzo e calcita. Essas matérias-primas originais não atingiram a temperatura de cocção de 950°C.

**Palavras-chave:** Azulejos históricos, patrimônio cultural, mineralogia, São Luís do Maranhão.

## Abstract

*This work involved the first-ever characterization of antique Portuguese ceramic wall tiles in the Historic Center of São Luis do Maranhão, Brazil. The tiles were*

characterized by optical microscopy, X-ray diffraction (XRD) and chemical analysis to identify the possible raw materials used in the fabrication process, as well as the firing temperature of these materials. The results indicate that the microstructure of these materials consists of pores of varying sizes with calcite incrustations and quartz grain sizes smaller than 500  $\mu\text{m}$  distributed in a pinkish yellow matrix, which were identified by XRD as calcite, gehlenite, wollastonite, quartz, and amorphous mineral phases. Based on this information, it can be inferred that the original raw materials probably consisted of a mixture of kaolinitic clays ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) rich in calcium carbonates and quartz, or mixtures of kaolinitic clays, quartz and calcite, which did not reach the pre-firing temperature of 950°C.

**Keywords:** Cultural heritage, antique ceramic wall tiles, mineralogy, São Luis do Maranhão.

## 1. Introduction

The Portuguese word “azulejo,” which derives from the Arabic “azuleich,” meaning flat smooth shiny blue stone (lapis lazuli), gave rise to what we know today as ceramic tile. This material was widely used as a decorative element in friezes, floors, door frames, domes, tombs, palaces and temples of the vast Muslim empire (Barata, 1955; Simões, 1965; Simões, 1990).

Introduced by Arabs in Spain around AD 711, this material reached its highest expression in Andalusia (Malaga, Seville and Granada), where the Hispanic-Moorish style emerged and spread throughout Spain and Portugal, reaching the Iberian Peninsula, and later, Europe (Simões, 1990; Simões, 1997).

Imports of ceramic tiles from Spain during the 15<sup>th</sup> and early 16<sup>th</sup> centuries enabled the art of ceramic tile fabrication in Portugal to develop to such an extent that, by the end of the 16<sup>th</sup> century, the Portuguese ceramic centers had achieved high technical quality and began to compete with Spanish tiles (Trindade, 2007).

With Spain's overseas expansion and the intensification of its trade with

the new American colonies, Sevillian tiles reached the New World in the early 16<sup>th</sup> century, more specifically the island of Santo Domingo (Dominican Republic) (Sanchez, 1996).

Still under Spanish influence, the ceramic tile culture reached Brazil in the 17<sup>th</sup> century through the Portuguese. Starting in the 18<sup>th</sup> century, Portugal consolidated its position as a major manufacturing center, and popularized the use of tiles on the facades of buildings in the states of Bahia, Pernambuco, Alagoas, Paraíba, Maranhão, Pará, Rio Grande do Sul and Rio de Janeiro (Barata, 1965). Due to their mechanical properties and the effective protection they afforded against the tropical climate, ceramic tiles became very important decorative elements for the Portuguese settlers (Machado, 2003).

Among these states, the city of São Luis do Maranhão (Brazil), founded in 1612 (17<sup>th</sup> century) and listed by UNESCO as a Cultural World Heritage Site in 1997, stands out as the city containing the largest collection of facade tiles in Latin America.

The Historic Center of São Luis (HCSL) also contains tiles from countries

such as Germany, Belgium, Spain, France and Holland. All this artistic and cultural collection is distributed in approximately 3500 civilian and religious buildings, with 312 different patterns (Lima, 2004). However, the effects of time (fungi, algae, bacteria and lichens) have seriously damaged this priceless collection, and in the period of 2004 to 2006 the Odylo Costa Filho Creativity Center recorded a loss of approximately 433 buildings. Additionally, it was found that 30% of the facades present progressively increasing damage (Alcântara, 1980).

This paper describes for the first time the chemical and mineralogical composition and the microstructure of Portuguese tiles of the Historic Center of São Luis (HCSL). The objective of this work was to determine the possible raw materials used in the manufacture of these tiles and the probable firing temperature reached during the pre-firing of these materials, thereby obtaining valuable information for the specific purpose of their restoration and the formulation of new ceramic tiles using local raw materials.

## 2. Materials and methods

Twelve samples, consisting of fragments of Portuguese tiles produced

in the 17<sup>th</sup>, 18<sup>th</sup> and 19<sup>th</sup> centuries, kindly donated by the Costa Filho Odylo

Creativity Center (Lima, 2004), were analyzed.

### Preparation of samples

#### Preparation of biscuit samples

An analysis was made of a fragment from the base of each tile (biscuit), which was washed and brushed using water and mild soap to remove as much as possible of the remains of mortar. The fragments were dried in an air circulating oven

at 110°C until they reached a constant weight, after which a portion of the biscuit near the glaze was removed with a spatula and a scalpel from the inner part of the fragment. The fragments under study are referred to hereinafter as PE01-XIX, PE05-

XIX, PE11-XIX, PE14-XIX, PE27-XIX; PE34-XIX, PE69-XIX; PMJ08-XVIII, CMJ03-XVIII, CMJ-XVII, PM05-XVII and PCM-XVII (where XIX, XVIII and XVII refer, respectively, to the 19<sup>th</sup>, 18<sup>th</sup> and 17<sup>th</sup> century), as illustrated in Figure 1.

All the extracted fragments were crushed in a stainless steel container under a pressure of 50 MPa. The resulting material was then

mixed in an electric agate mortar and ground for 5 minutes in an oscillating micronizer (Retsch MM 200 mixer mill) equipped with an agate jar and

milling elements until the resulting powder passed completely through a 200 mesh (75  $\mu\text{m}$ ) sieve.



Figure 1  
Identification of the tile  
samples from the HCSL.

## Chemical analysis

The samples were placed on a glass disk and their chemical composition was determined by X-ray fluorescence (XRF), using an Axios Minerals sequential spectrometer equipped with a ceramic

X-ray tube with a 2.4 kW Rh anode from PANalytical. Data acquisition and processing were performed, respectively, with SuperQ Manager and IQ+ software (both from PANalytical). The results were

normalized to 100%. Loss on ignition (LOI) occurred at 1000°C (2 h). The glass disc was prepared using 1 gram of sample and 8 grams of the fluxing agent lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ).

## X-ray diffraction

The mineral phases in the samples were identified using a PANalytical X'PERT PRO (PW 3040/60) X-ray diffractometer equipped with a PW3050/60 theta/theta goniometer, a PW 3373/00 ceramic X-ray tube and a Cu anode ( $\text{CuK}\alpha 1 = 1,5406 \text{ \AA}$ ) with long fine focus, 2200 W,

60 kV. A RTMS X'Celerator detector was used. The spectra were processed digitally using X'Pert HighScore version 2.1b software (PANalytical) to analyze the phases quantitatively by the relative intensity ratio (RIR) method and identify the crystalline phases by comparison with diffraction

patterns in the PDF-ICDD database (Powder Diffraction File - International Center for Diffraction Data). Records were collected in the interval of 10 to 70° (2 $\theta$ ) under continuous scanning, applying a step of 0.02° (2 $\theta$ ), 40 mA current, 40 kV voltage, and a count time of 5 s.

## Optical microscopy

The microstructure of the tiles was studied by optical microscopy (OM), using a LEICA DMRX optical microscope

coupled to a LEICA DFC490 digital camera, with 200 X magnification in reflected light mode. The fragments of the samples

were cut and cold-embedded in epoxy resin, and the resin blocks were sanded and polished in an automatic polisher.

## 3. Results and discussion

Table 1 and Figure 2 describe the phases identified by XRD in the tiles under study. The indexed mineral phases were: quartz (PDF 086-0174), wollastonite

(PDF-076-0925), calcite (PDF-086-0174), gehlenite (PDF-074-1607) and perovskite (PDF-089-6949  $\text{CaTiO}_3$ ); the latter was present in smaller quantities only in the

PM-05 and PMJ-08 tiles, both from the 18th century. In addition, it was observed the presence of amorphous phase deduced from the high background in the diffrac-

tograms.

Since the mineral phases identified in all the tiles were identical, the quantitative analysis of crystalline phases by the RIR method was performed on only six fragments, including those containing perovskite (CaTiO<sub>3</sub>) phase. Table 2 lists the results of this analysis.

As can be seen in Table 2, all the samples contained the following mineral phases: quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>), wollastonite (CaSiO<sub>3</sub>) and gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>). Calcite was the predominant mineral in samples PMC-XVII, PMJ08-XVIII, PM05-XVIII, while quartz was found to be more abundant

than calcite in samples PE01-XIX, PE27-XIX, PE34-XIX. The presence of CaTiO<sub>3</sub> crystals was also detected in some of these samples in amounts not exceeding 7 wt%. None of the samples contained other calcium silicates such as larnite (Ca<sub>2</sub>SiO<sub>4</sub>), kilchoanite (Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>), or mullite, hematite and cristobalite (Aras, 2004).

Century	Sample	Quantitative analysis of phases in wt.% (RIR)					
		Quartz	Calcite	Wollastonite	Gehlenite	*CaTiO <sub>3</sub>	Amorphous
19th	PE01	+++	++	++	+	--	++
	PE05	+++	++	++	+	--	++
	PE11	+++	++	++	+	--	++
	PE14	+++	++	++	+	--	++
	PE27	+++	++	++	+	--	++
	PE34	+++	++	++	+	--	++
	PE69	+++	++	++	+	--	++
18th	PM05	+++	++	++	+	?	++
	PMJ08	+++	++	++	+	?	++
	CMJ03	+++	++	++	+	--	++
	CMJ	+++	++	++	+	--	++
XVII	PMC	+++	++	++	+	--	++

Table 1  
Phases identified by X-ray diffraction in the historical tiles of São Luis.

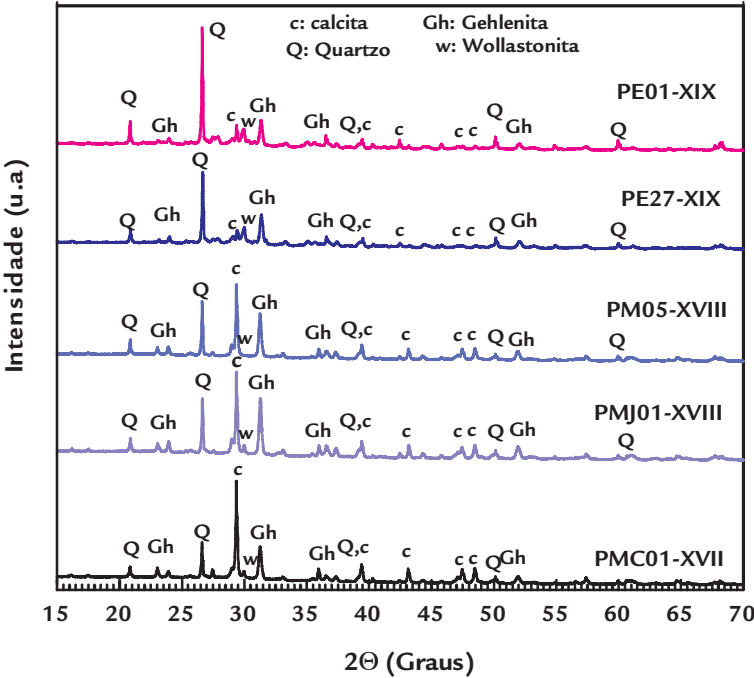


Figure 2  
Diffractograms of the tile samples from the Portuguese historic center of São Luis.

Sample	Quantitative analysis of phases, in wt.% (RIR)					
	Wollastonite	Gehlenite	Quartz	Calcite	*CaTiO <sub>3</sub>	Amorphous
PE01-XIX	16	14	57	13	--	++
PE27-XIX	19	21	50	9	--	++
PE34-XIX	33	29	28	10	--	++
PM05-XVIII	7	13	32	43	6	++
PMJ08-XVIII	10	15	33	35	5	++
PMC-XVII	15	15	14	56	--	++
Total						

Table 2  
Mineral phases identified in the historical tiles of São Luis



Table 3 lists the findings of the chemical analysis of the fragments. Observe that they are constituted primarily of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{SiO}_2$  in variable concentrations exceeding 8, 19 and 32 wt.%, respectively. These high contents of lime ( $\text{CaO}$ ) observed in all pieces (more than 19 wt.%) are in agreement with researches that reported high amount  $\text{CaO}$  in ancient tiles from Spain and Portugal (Antunes, 1992; Ramos et al., 2002; Coroado and Gomes, 2011; Pereira et al., 2011).

These results explain the presence of calcium-rich phases and of amorphous phase formed during the heat treatment of the base of the tile, resulting from the decomposition of the raw materials. The contents of the secondary oxides  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$  did not exceed 5%. Another aspect worth noting is the presence of low  $\text{K}_2\text{O}$  content, which indicates the presence of small amounts of illite in the original raw materials.

Figure 3 depicts the microstructures of the biscuits examined by optical microscopy.

All the samples clearly show the presence of irregular spherical quartz (Q) grains with variable dimensions, which are largest in the PCM-XVII sample (500  $\mu\text{m}$ ). Pores (P) and small calcite (C) clusters are also visible.

Combined with the XRD results and the chemical analysis (see Tables 1, 2 and 3), these data confirm that all the samples contain quartz, which indicates that this mineral has already been in use since the 17<sup>th</sup> century in compositions of ceramic bodies for the fabrication of tiles. When present in large particle sizes, this raw material is used in ceramic body formulations to improve drying and dimensional stability, thus reducing shrinkage after the drying and firing steps (Amorós et al., 2010).

All the samples also contain calcite, whose presence in this material may be explained as follow:

- The temperature or time required for the complete decomposition of calcite in  $\text{CaO}$  and  $\text{CO}_2$  was not attained and small amounts of calcite remain in the core of the ceramic tile un-reacted (An-

tunes, 1995; Vaz et al., 2008; Pereira et al., 2011).

- Re-carbonation of un-reacted  $\text{CaO}$  present in the core of the ceramic tile with  $\text{CO}_2$  coming from air (Ramos et al., 2002; Sanjad et al., 2004; Coroado and Gomes, 2011; Pereira et al., 2011). (Ramos et al., 2002; Sanjad et al., 2004; Coroado and Gomes, 2011; Pereira et al., 2011).

Based on the XRD results and the content of primary oxides ( $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) detected in the chemical analysis, the approximate composition of the tiles can be recalculated, as shown in the  $\text{CaO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  ternary equilibrium phase diagram illustrated in Figure 4.

In Figure 4, observe that all the compositions are located in the  $\text{SiO}_2$ - $\text{CaSiO}_3$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$  compatibility triangle (quartz-wollastonite-anorthite). However, the identified phases (gehlenite-quartz-wollastonite) correspond to non-equilibrium phases, indicating that the heat treatment time and/or temperature were insufficient to reach equilibrium. These results are

Table 3  
Chemical analysis of the historical tiles of São Luís, MA, in wt.%.

Oxide	PMC-XVII	PMJ08-XVIII	PM05-XVIII	PE01-XIX	PE27-XIX	PE34-XIX
$\text{Al}_2\text{O}_3$	7.83	8.62	8.08	12.86	11.44	13.01
$\text{SiO}_2$	33.46	38.64	38.88	54.64	48.26	44.65
$\text{TiO}_2$	0.59	0.74	0.69	0.75	0.83	0.86
$\text{MgO}$	2.53	1.64	1.52	1.36	1.99	1.47
$\text{CaO}$	28.83	30.03	28.79	19.04	21.11	29.82
$\text{Fe}_2\text{O}_3$	3.31	3.33	3.01	4.05	4.18	3.37
$\text{P}_2\text{O}_5$	0.19	0.18	0.20	0.12	0.15	0.25
$\text{Na}_2\text{O}$	0.65	0.61	0.89	0.82	1.55	0.76
$\text{K}_2\text{O}$	1.08	1.01	0.97	2.02	1.75	1.15
Others	0.41	0.57	0.57	0.31	0.68	0.45
LOI	21.12	14.63	16.40	4.03	8.06	4.21
Total	100.00	100.00	100.00	100.00	100.00	100.00

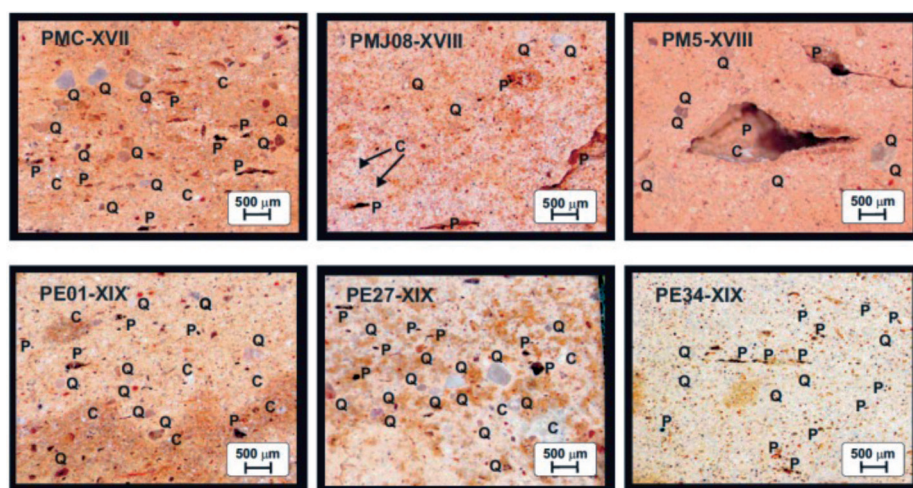


Figure 3  
OM image of fragments of Portuguese tiles from the Historic Center of São Luís. Pore (P), Quartz grain (Q) e Calcite agglomerates (C).

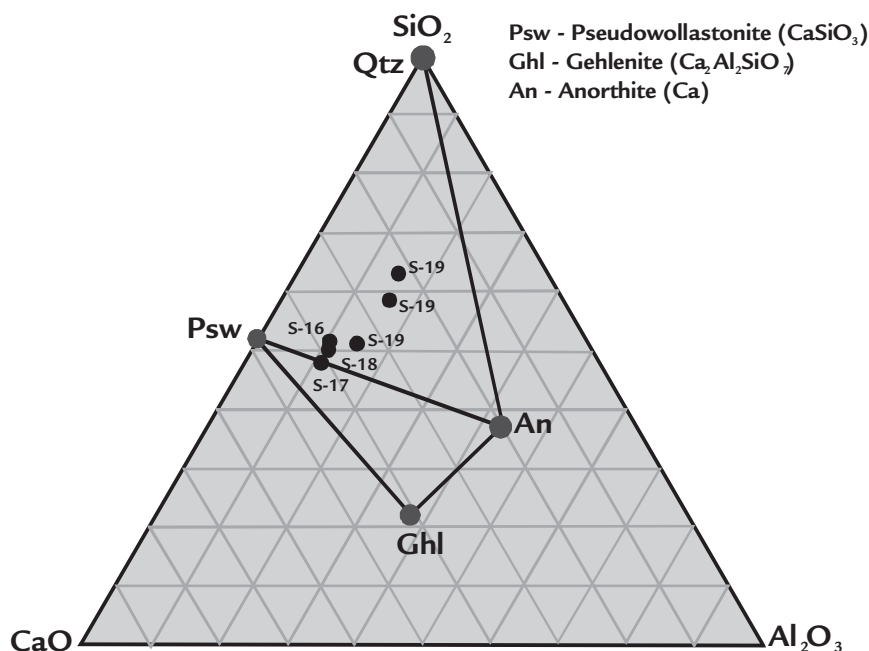
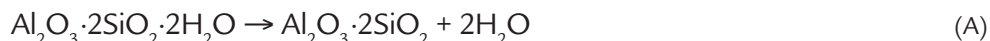


Figure 4  
Schematic representation of the composition of the tiles in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> diagram.

consistent with findings reported in studies of antique ceramic artifacts and mixtures of calcareous clays and artificial mixtures of clay and calcium carbonate in variable proportions (Peters & Iberg, 1978; Kreimyer, 1987; González García et al., 1988; Sanjad et al., 2004; Trindade et al., 2009).

Based on these findings (Tables 1 and 2 and Figure 2), the approximate physical and chemical behavior of the raw material used in the fabrication of the tiles from the HCSL can be explained by means of the following sequence of chemical reactions:



3. In the interval of 600 to 800°C, the

finely divided calcite decomposes, giving

rise to the formation of free lime:



4. At temperatures above 700°C, free lime reacts with metakaolinite to

form calcium silicates and crystalline alumino-calcium silicates (wollastonite

and gehlenite):



As mentioned earlier, the high background in the diffractograms indicates the dehydroxylation of phyllosilicates that occurs between 450 and 550°C. The presence of calcite indicates that this mineral may have been used as a fluxing agent to reduce the melting point, or that it was present as an impurity in the clay. The presence of calcite is a strong indication that the maximum pre-firing temperatures were relatively

low, which is common in antique ceramic materials. Based on data in the literature, it can be stated that the wollastonite (CaSiO<sub>3</sub>) identified in all the samples was formed between 800 and 900°C, by the reaction of amorphous silica resulting from the formation of metakaolinite (450-550°C) with the CaO released through the decomposition of calcite (600-700°C) (Cultrone, 2001). Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) is simi-

larly formed at approximately 700°C, probably due to the reaction of alumina with silica from the decomposition of the clay minerals with CaO (Capel et al., 1985).

Based on the literature and on the findings of this study, it can be stated that the pre-firing temperature of the pastes used in the preparation of the biscuits for these antique Portuguese tiles did not exceed 950°C.

#### 4. Conclusions

The mineral composition of the Portuguese tiles from the historic center of São Luís, MA, consists of a mixture of quartz, gehlenite, wollastonite, calcite and amorphous phases. The X-ray diffraction

results and the chemical analysis led to the conclusion that the raw material used for the fabrication of the tiles from the HCSL possibly consisted of a mixture of kaolinite clays (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) rich in

calcium carbonates or kaolinite clay with calcite additions. It can also be stated that the pre-firing temperature applied in the preparation of the biscuits for these tiles did not exceed 950°C.

## 5. Acknowledgments

The authors acknowledge the Brazilian research funding agencies CAPES (Federal Agency for the Support and Improvement of Higher Education) for its financial support of the project Map of Clays in the State of Maranhão: Recording of Occurrences and Mineralogical

and Technological Characterization of Ceramic Raw Materials, through the academic cooperation program PROCAD AMAZONIA, Geosciences Institute of the Federal University of Pará (UFPA) by the partnerships in the PROCAD AMAZONIA, FAPEMA (Maranhão

State Foundation for Research Support) for its financial support of This Research. We are also indebted to the Odylo Costa Filho Creativity Center (CCOCf) of the Maranhão State Department of Culture (SECMA) for its practical assistance.

## 6. References

- ALCÂNTARA, D. de. *Azulejos portugueses em São Luís do Maranhão*. Rio de Janeiro: Fontana, 1980.
- AMORÓS, J. L., et al. Porous single-fired wall tile bodies: influence of quartz particle size on tile properties. *Jour. Eur. Ceram. Soc.*, v. 30, n. 1, p. 17-28, 2010.
- ANTUNES, J.L.F.. *Caracterização de azulejos do século XVII: estudos para a sua consolidação*. Instituto Superior Técnico, 1992. (Dissertação de Mestrado em Engenharia Química).
- ANTUNES, J. L.F. et al. Characterization of Portuguese 17 th Century tiles. In: international symposium “the ceramic heritage”, world ceramics congress, *Proceedings*. Florence: 1994 e 1995. p. 653-660.
- ARAS, A. The change of phase composition in kaolinite and illite rich clay-based ceramic bodies. *Appl. Clay Sci.*, v. 24, n. 3-4, p. 257-269, 2004.
- BARATA, M. *Azulejos no Brasil, séculos XVII, XVIII, XIX*. Rio de Janeiro: Editora Jornal do Comércio, 1955.
- CAPEL, J., HUERTAS, F., LINARES, J. High temperature reactions and use of Bronze Age pottery from La Mancha. *Central Spain. Miner. Petrogr. Acta*, n. 29-A, p. 563-575, 1985.
- COROADO, J., 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 7<sup>th</sup> European Meeting of Ancient Ceramics (EMAC’03), October 27-31, Lisbon, Portugal. *Trabalhos de Arqueologia*, 42, p. 33-39, 2003.
- CULTRONE, G. et al. Carbonate and silicate phase reactions during ceramic firing. *Eur. J. Mineral.*, v. 13, n. 3, p. 621-634, 2001.
- GONZÁLEZ GARCÍA, F., et al. Arcillas empleadas en la fabricación del azulejo artístico de Sevilla. Propiedades y transformaciones por cocción. I. Materiales que contienen carbonato de calcio”. *Bol. Soc. Esp. Ceram. Vidr.*, v. 27, n. 4, p. 215-223, 1988.
- IBAÑEZ, A., VICENTE, A.P., GONZALEZ PEÑA, J. M., SANDOVAL F. Utilización de una marga dolomítica en la obtención de chamotas anortítica y diópsido-wollastonítica. *Bol. Soc. Esp. Ceram. Vidr.*, v. 29, n. 1, p. 5-8, 1990.
- KREIMEYER, R. Some notes on the firing colour of clay bricks. *App. Clay Sci.*, v. 2, n. 2, p. 175-183, 1987.
- LIMA, Z. *Catálogo dos azulejos de São Luís*. Centro de Criatividade Odylo Costa Filho, Secretaria de Estado da Cultura (SECMA), 2004. 59 p. il.
- PEREIRA, S., et al. Physico-chemical characterization of historic Portuguese tiles, *Relatório 23/2010 DM*, LNEC, 2011. 40 p.
- PETERS, T., IBERG, R. Mineralogical changes during firing of calcium-rich brick clays. *Ceram. Bull.*, v. 57, n. 5, p. 503-509, 1978.
- RAMOS, S. S., et al. Application of XRF, XRD, thermal analysis, and voltammetric techniques to the study of ancient ceramics. *Anal. Bioanal. Chem.*, 373, p. 893-900, 2002.
- SANCHEZ, J.M. La cerámica exportada a América en el siglo XVI a través de la documentación del archivo general de indias. *Materiales Arquitectónicos y contenedores de mercancías. Laboratório de Arte*, n. 9, p. 125-142, 1996.
- SANJAD, T.A.B.C. et al. Caracterização mineralógica de azulejos de Salvador e Belém dos séculos XVI, XVII e XIX. *REM - Revista Escola de Minas*, Ouro Preto, v. 57, p. 255-260, 2004.
- SIMÕES, J. M. S. *Azulejaria portuguesa no Brasil 1500-1822*. Lisboa: Fundação Calouste Gulbenkian, 459 p. il. 1965.



- SIMÕES, J. M. S. Azulejaria em Portugal - sécs. XV-XVI. (2. Ed.). Fundação Calouste Gulbenkian, 1990.
- SIMÕES, J. M. S. Azulejaria em Portugal - sécs. XVII. (2. Ed.). Fundação Calouste Gulbenkian, 1997.
- TRINDADE, M. J., et al. Mineralogical transformations of calcareous rich clays with firing: a comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Appl. Clay Sci.*, v. 42, n. 3-4, p. 345-355, 2009.
- TRINDADE, R.A.A. Revestimentos cerâmicos portugueses. Meados do século XIV à primeira metade do século XVI. Lisboa: Edições Colibri, Faculdade de Ciências Sociais e Humanas da Universidade Nova de Lisboa, 2007.
- VAZ, M. F. et al. Effect of the impregnation treatment with Paraloid B-72 on the properties of old Portuguese ceramic tiles. *Journal of Cultural Heritage*, v. 9, n. 3, p. 269-276, 2008.

---

Artigo recebido em 11 de setembro de 2012. Aprovado em 18 de janeiro de 2013.