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Characterisation of archaeological ceramics from Saadian Tombs (16th century) of Marrakech Morocco

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ABSTRACT

The analysis of archaeological materials can provide information to protect the cultural heritage of civilizations, allowing inferences about their technology and interaction with their surrounding physical and social environments. In this context, the present paper proposes an analytical methodology to characterize samples of ancient ceramic objects (dating to 16th century) from the Saadian Tombs of Marrakech, one of the main Saadian buildings in Morocco. A multi-analytical approach based on optical and scanning electron microscopy, cathodoluminescence, X-ray fluorescence and X-ray diffraction was used to determine the textural, mineralogical and chemical characteristics of these materials. The obtained results allow probing into the past and attempt to re-create prehistory by obtaining information about the provenance and manufacturing proprieties of these archaeological objects. The Saadian artisans have used calcareous clay as raw material to manufacture their decorative ceramics called zellige. These materials are composed of lead glaze applied directly on a silicate shard without ceramic engobe or intermediate layer. The coloring agents are conventional, iron (Fe^{3+}) for the yellow glaze, manganese (Mn^{3+}) for the black glaze, copper (Cu^{2+}) and phosphorus (P) for the green and blue glazes. The estimated firing temperature of these materials ranges between 800 and 900 °C.

Selection and peer-review under responsibility of the scientific committee of the 3rd International Congress on Materials & Structural Stability.

1. Introduction

Ceramic objects are the most common old materials found during archaeological excavations [1]. They were used by civilizations as materials serving for cooking, storage, transport, construction, or pyrotechnical processing [2]. The study of these objects allows to understand their nature, their change in time, their technology and their provenance. Therefore, several analytical methods are currently applied to provide these information for the archaeology and the cultural heritage.

The study of archaeological materials for the investigation of the ancient manufacturing techniques of these objects and the protection of the historical heritage has become indispensable for all communities. In Morocco, despite the efforts made by the Historical Monuments Inspectorate for the conservation-restoration of Moroccan heritage, the archaeological materials inside historical buildings have reached a very advanced state of degradation in lack of a specific scientific approach to the restoration (Fig. 1). Unfortunately, Traditional restoration methods that do not take into account the chemical and mineralogical characteristics of the raw materials are still practiced. In fact, with the exception of some recent studies those concern mainly the El Badi palace [3,4] and Saadian tombs [5,6], very few scientific studies have been undertaken to characterize the materials used in the construction of Saadian monuments of Marrakech, classified as world heritage by UNESCO since 1985. It is in this context where this work fits, which aims to characterize the ceramic materials of the Saadian tombs to provide a scientific database for restorers and

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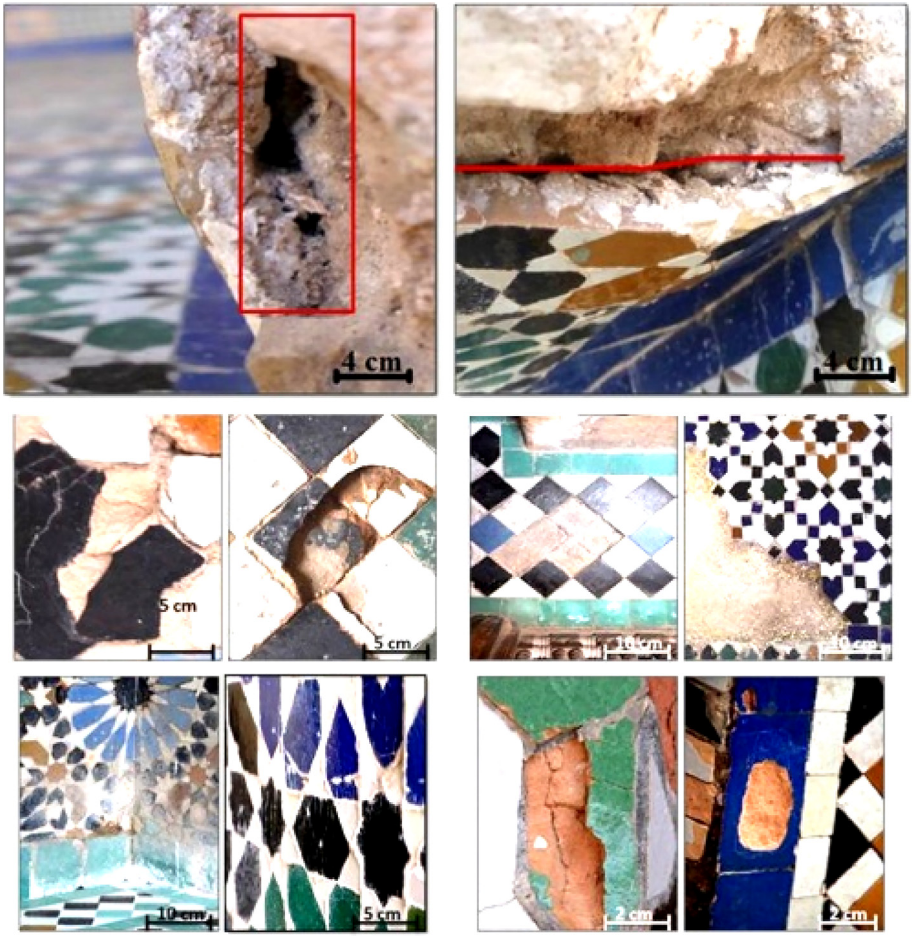
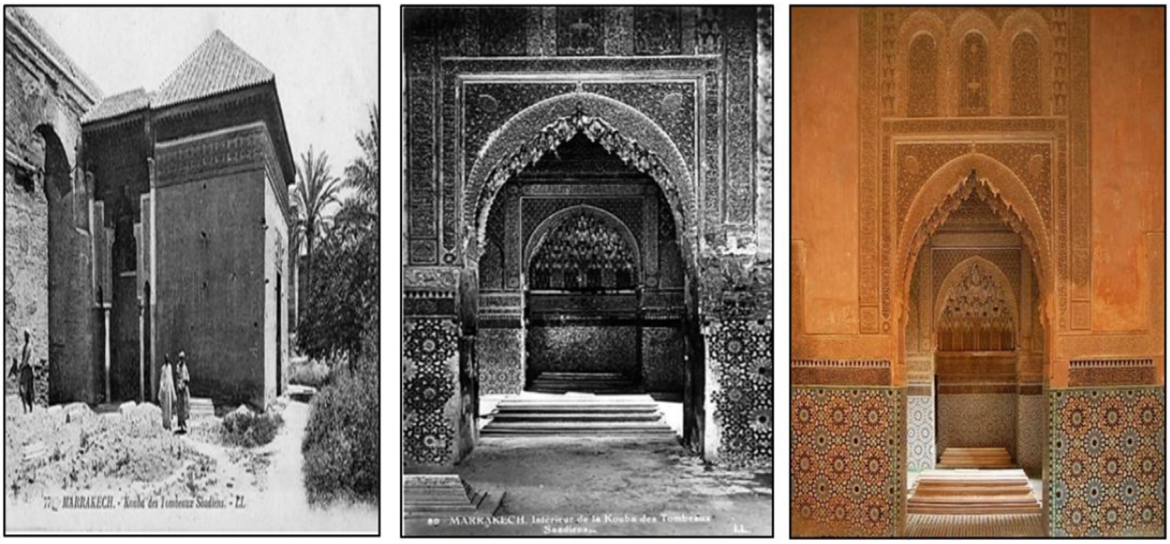


Fig. 1. Examples of degradation of zellige ceramics inside the Saadian buildings of Marrakech.


The Koubba of Lalla Mesouada in 1917

Inside the Koubba in 1917

Inside the Koubba in 2018

Fig. 2. The Koubba of the Saadian Necropolis between 1917 and 2018 holding the tombs of Sultan Moulay Abdallah, his father Mohamed Cheikh and his mother Princess Lalla Mesouada.

archaeologists that will be taken into account in further attempts at conservation restoration of this historical building.

2. Materials and methods

Saadian tombs were built by Ahmed El Mansour Dahbi, one of the most popular Saadian kings, in Marrakech at the end of the 16th century. This building was used as the burial of Saadian caliphs and soldiers (Fig. 2), these tombs were discovered at the beginning of the 20th century and they are now under the preservation of the historical monuments Inspectorate of Marrakech. The building is characterized by a carefully arranged and gorgeous decorative glazed ceramics, also called zellige (Fig. 3). Nine samples of these decorated ceramics were taken from the wall during the restoration of the room called "Koubba of Lalla Mesouada" under the supervision the historic monuments inspectorate and using a sampling technique that preserves the archaeological materials of the building. The collected samples are characterized by different shapes and colors and they are referenced from TSZ11 to TSZ19 (Table 1).

The texture of the samples and their surface characteristics were examined using a binocular loupe. More detailed observations of the textures were made successively by optical microscopy (CETI, Gx1500, Laboratory AGEs, University of Liege), scanning electron microscopy (SEM; XL-FEG-ESEM, University of Liege) and cathodoluminescence (Technosyn Cold cathodoluminescence 8200 Mk3, Laboratory of Sedimentology, University of Liege). For this last technique, samples were placed in a nuclide-type chamber under a vacuum of 0.20–0.01 Torr and bombarded with a beam of electrons accelerated by a voltage varying from 15 to 20 kV. The recording of the emissions from the sample was performed using a 3CCD high-definition camera (Sony DXC-930P).

Subsequently, the materials were carefully ground and homogenized and a portion was crushed in an agate mortar for X-ray diffraction (XRD) analysis. The mineralogical phases present in the terracotta were identified with an XRD powder diffractometer (Bruker Eco D8-Advance using Cu-Kα radiation) at the Laboratory AGEs, University of Liege, in the range of 2–60°2θ. The XRD patterns were handled by the DIFFRACPlus.EVA software to remove the background noise and to calculate line positions and peak intensities. The maximum firing temperature of the ceramics studied was determined by re-firing tests. Aliquots of each sample were ground in agate mortar and were annealed for 4 h in a furnace in the temperature range of 500–1000 °C. The relative abundance of minerals was detected and estimated using TOPAS and DIFFRAC-Plus.EVA software.

Powdered samples were mixed with Spectromelt A12 flux in a sample flux ratio of 1:9 and then analyzed by X-ray fluorescence (XRF) using a Panalytical Axios spectrometer equipped with an Rh tube for major element analysis (Laboratory of Petrology, University of Liege) using argon–methane gas. The data were treated with IQ+ software. The loss on ignition was determined by heating the samples at 1000 °C for 4 h.

The elemental compositions of the glazes were determined by non-destructive XRF analysis applied directly on an area of 108 μm × 88 μm on the surface of each sample (Laboratory of Sedimentology, University of Liege). Quantitative analysis was performed using a hand-held XRF Analyzer (X-MET8000, Oxford Instruments, Fremont, CA, USA) with metal standards, synthetic compounds and natural minerals. The elemental contents represent an average of three to five measurements.

3. Results and discussion

3.1. Mineralogical and chemical composition of the shards

All nine zellige samples are lime/silica sherds (Table 1), with SiO_2 contents of 41–57 wt.%, and 11–22 of CaO. In addition, they

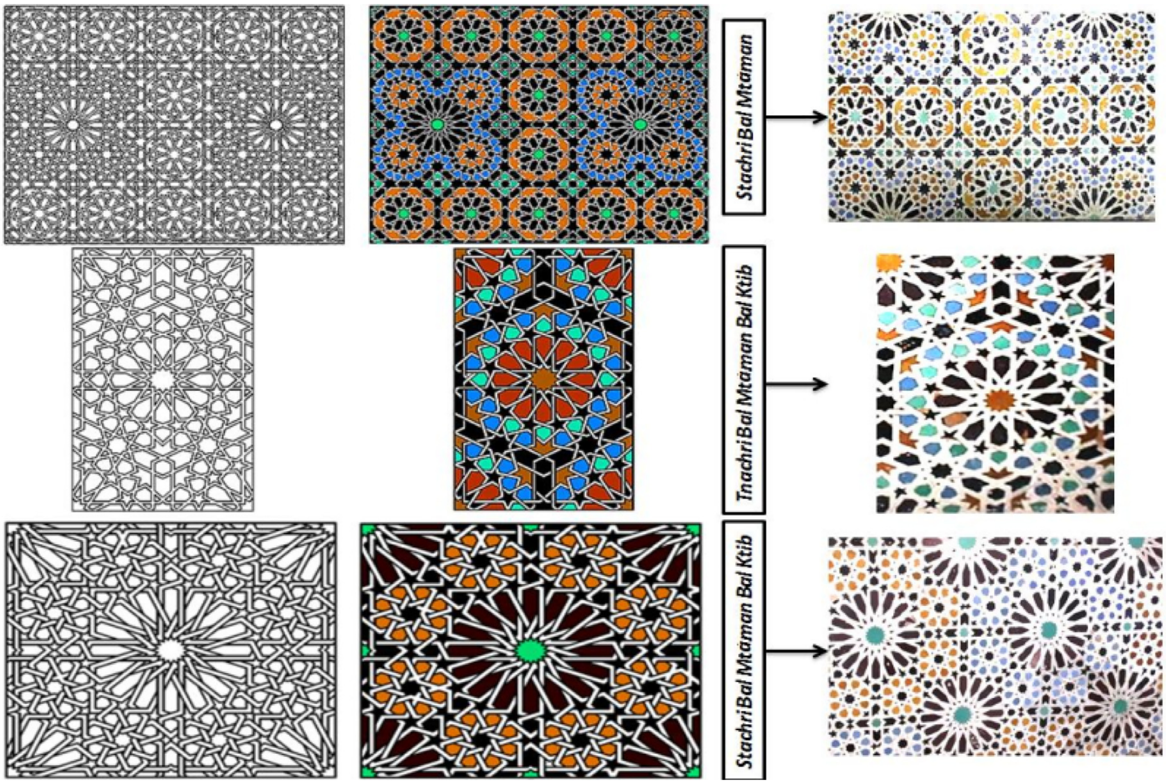


Fig. 3. The main mosaics of zellige inside the Saadian buildings in Marrakech.

Table 1
Shapes, glaze colors and Bulk chemical compositions (wt.%) of the ceramic zellige samples from the Saadian tombs building.

			Chemical composition										
	Name	Color	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI
TSZ11	***Saftthn achri***	**Black**	49	0.6	11	5	0.05	3	16.4	0.57	1.8	0.2	11
TSZ12	***Quandil***	**White**	50	0.7	12	4.8	0.1	2	16	1.3	2.5	0.2	10
TSZ13	***Thelt amel***	**Black**	55	0.8	13	5	0.1	2	11.6	1	2.8	0.2	7
TSZ14	***Saftthn achri***	**Blue**	53	0.8	13	5	0.1	2	13	1	2.8	0.2	6.2
TSZ15	***Kef amel***	**White**	41	0.6	9	3.6	0.06	1.8	19	1	1.7	0.1	20.5
TSZ16	***Thel amel***	**Yellow**	48	0.7	11	4	0.1	2.5	16	1	2	0.2	11.7
TSZ17	***Qtib sarout***	**White**	57	0.8	14	6	0.1	2	11	1.1	3	0.3	3.5
TSZ18	***Saft***	**Blue**	49	0.7	11	4.6	0.1	2	16	1.1	2.4	0.2	10
TSZ19	***Quandil***	**Green**	46	0.7	12	5	0.1	2.5	22	1.25	2	0.2	7.6

contain between 9–14 wt.% of Al_2O_3 and 3–6 wt.% of Fe_2O_3. The alkali content does not exceed 3 wt.% (by mass of Na_2O and K_2O). The organic matter content determined by loss on ignition at 1000 °C (LOI) ranges between 3.5 wt.% and 20.5 wt.%, respectively for samples TSZ17 and TSZ15.

The studied samples have similar mineralogical compositions (Fig. 4). The sherds are rich of quartz (24–27 wt.%), plagioclases and alkali feldspars (9–14 wt.%). The amount of calcite ranges between 3–7 wt.% with moderate content of hematite (~3 wt.%) responsible for the light color (light brown) of the ceramic sherds.

The XRD patterns also revealed the presence of enstatite ($Mg_2Si_2O_6$), which may be attributed to the presence of MgO in the raw clay material [7]. Ca silicates phases (i.e. gehlenite; $Ca_2Al[AlSiO_7]$) and diopside ($CaMgSi_2O_6$) are transitional phases formed at high temperature (≥700 °C) [8,9]. Gehlenite forms by grain boundary reaction between CaO, Al_2O3 and SiO_2 [10–12]. It crystallizes preferentially in comparison with other anhydrous Ca–Al silicates [13]. The presence of Mg in the carbonate–quartz interface also favors the formation of diopside [14].

3.2. Elemental analysis of the glazes

The traditional colors of zellige used in the Saadian tombs building mainly consisted of white, black, green, yellow and blue. These colors are obtained after a mixture of lead and sand with specific chemical agents such as Cu^{2+} for green glaze, Fe^{2+} for yellow and black glazes, and phosphorus for blue glaze (Fig. 5).

The lead and tin oxides constitute the glaze of zellige, tin plays a role of opacifying agent for certain Islamic glazes [15,16]. On the other hand, lead is used as flux in the glaze mixture [17].

All the glazes are rich of lead with Pb contents varying between 32.2 wt.% for the blue color and 56.15 wt.% for the yellow color. The glazes were opacified by tin (6.5 wt.% of Sn for green glaze, 4 wt.% for blue, 2 wt.% for black, 13 wt.% for white and < 1 for yellow). Several studies show that ancient ceramists often use lead mixed with tin as opacified agent [18–21]. Results present fairly consistent compositions for silica and lead, SiO_2 ranges between 35 wt.% and 68 wt.% with an average of 51.5 wt.%, the same results was obtained by Gradmann et al. [22] for some samples collected from the same building. The use of lead as flux in association with alkalis promotes the expansion properties during firing and increases the hardness of the shard and makes the color lighter.

3.3. Glaze/shards interface

Binocular microscope, optical microscope (Gx10) and cathodoluminescence (Gx5) observations, through thin sections taken by sawing on a section perpendicular to the surface of the zellige, show that the glaze was applied directly on the ceramic shard

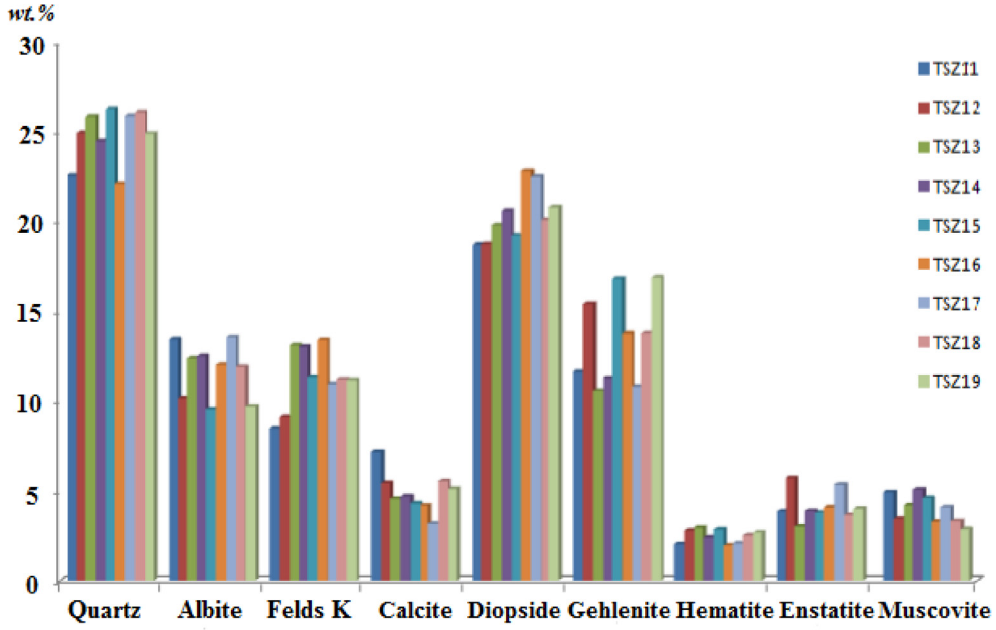


Fig. 4. Mineralogical composition of zellige samples from the Saadian tombs (expressed in wt.%), obtained by X-ray diffraction.

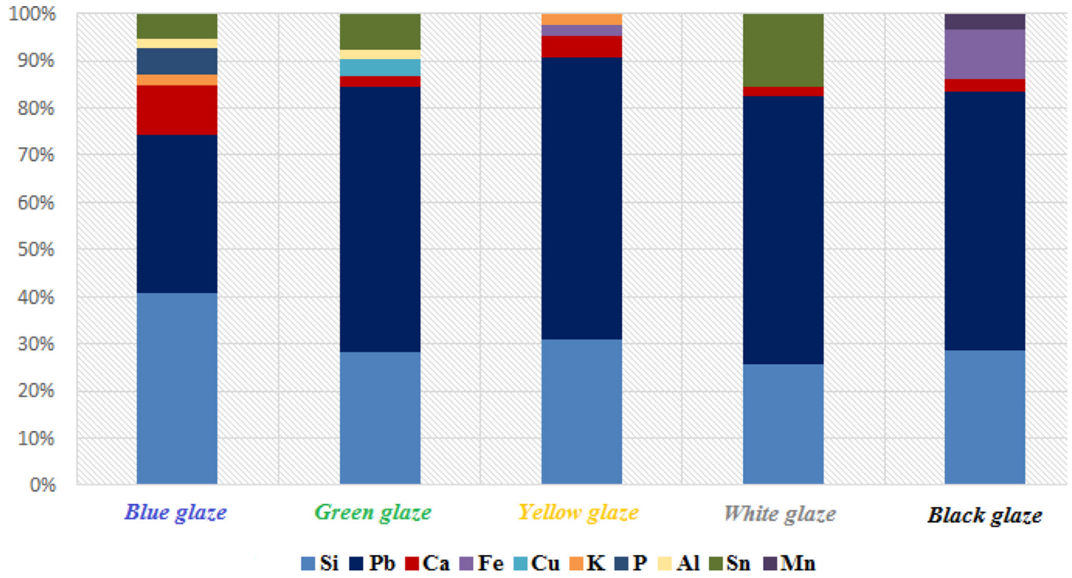


Fig. 5. Elemental composition of Saadian glazes (White, Green, Black, Blue and Yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

without engobe, the shard is porous allowing penetration of glaze elements into the upper part of the ceramic support (Fig. 6).

The light radiation observed by cathodoluminescence at the glaze/shard boundary allows to characterize the minerals present in this area. The luminescence in light blue indicates the presence of tin in cassiterite form (SnO_2) [15]. The Quartz emits a mauve luminescence in shards and blue punctuations in glaze. The heavy minerals that appear in a bright yellow color, are clearly visible on the glaze. The orange color indicates the abundance of calcite while the green areas are related to the presence of plagioclase [23,24].

Natural light observation by optical microscopy allows the examination of the shape and abundance of pores at the glaze-

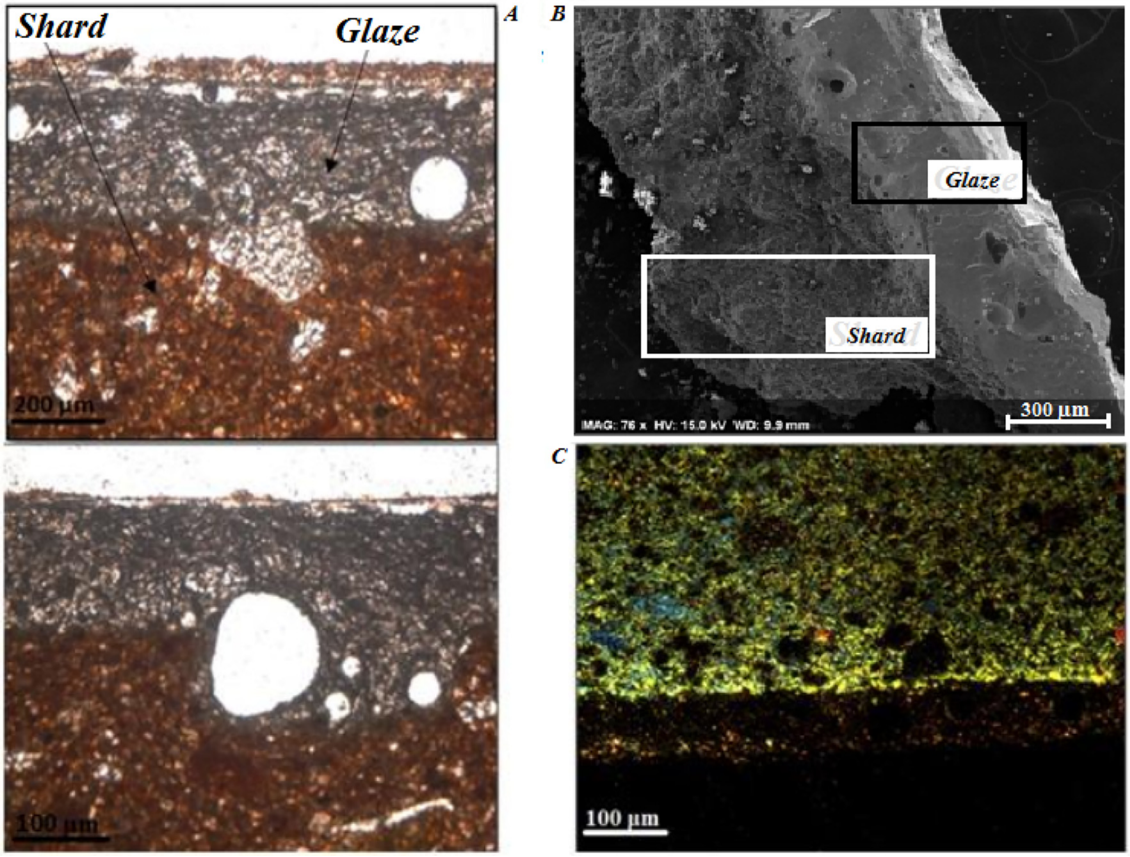


Fig. 6. Observation by optical microscopy (A), scanning electron microscope (B) and cathodoluminescence (C) of the glaze shard interface of Saadian zellige.

shard contact as well as the percentage, the grain size and the distribution of inclusions. The porosity of all samples varies from 10 to 15% of the total volume composed mainly of meso-vesicles and macro-orifices. Pore diameters vary from a few micrometers in the shard to 1 mm in the glaze with an angular to sub-rounded shapes. Secondary calcite grains are dispersed around these pores. No fusion occurred during the firing of the ceramic because no glassy phase appears around the grains.

4. Discussions

Chemical and mineralogical analysis by using X-ray fluorescence (XRF) spectroscopy and X-ray diffraction are well-established techniques for the provenance studies, as they can be used to determine major and minor elements and a selected number of trace elements of ancient Saadian zellige. The determination of these elements is related to the raw material and can be successfully used to determine technical proprieties of the studied materials.

The zellige samples from the Saadian tombs have a similar elemental composition which indicates that the raw material used in the manufacture comes from the same source. It was a clay-limestone soil rich in quartz and feldspar, with moderate iron content which gives the ceramic support a yellow-ocher color after firing in traditional ovens [17,25]. The so-called “high temperature” phases or Ca-silicates, such as gehlenite and diopside, have the power to incorporate Fe^{3+} or Fe^{2+} ions in their crystal matrix [8,26,27]. The calcareous clays used as raw material in ceramic industry give products with high Ca-silicate contents after firing above 700 °C [4,9,27].

The mineralogical composition provides information about firing temperature of the studied ceramics. During the firing process, the disappearance of clays (4.47 Å) occurs at 550 °C in the calcareous raw clay materials [26]. Therefore, the absence of clay minerals in XRD patterns of the Saadian tombs ceramics attests that the firing temperature was above 550 °C. Decomposition of CaCO3 into CaO and CO2 occurs between 600 and 800 °C, depending on the grain size, kiln atmosphere and duration of firing of the system [26,28], calcite can resist longer depending on different factors: coarse granules, automorphic crystalline forms, fast heating rate, and short stage oxidation/reduction conditions of the kiln atmosphere during firing [8,26,27]. As a result of this calcite decomposition, neoformed phases such as diopside and gehlenite begin to appear around 800 °C. The presence of these phases in high concentrations in the studied samples show that these materials were fired at a temperature greater than or equal to 800 °C. Plagioclases, muscovite, hematite and quartz persist until 950 to 1000 °C in these materials.

In order to confirm these firing temperatures, we have experimentally annealed shards of zellige between 500 and 1000 °C in programmable ovens and at each stage X-ray diffraction is performed to determine the changes obtained on the X-ray diffractograms (Fig. 7). The results of the annealing of samples show that no change is observed on the XRD diffractograms until 800 °C. At this stage, gehlenite and diopside start to decompose, with a 25% decrease in quartz and muscovite amounts compared to their initial contents. This result shows that the firing temperature of these materials was between 800 and 900 °C.

5. Conclusion

Overall, the obtained results confirm the homogeneity of the raw material used in the production of the zellige of the Saadian tombs, it was a clayey-calcareous raw material fired at 800 to 900 °C in traditional ovens, then the ceramic support was enamelled using a glaze mixture based on lead and silica, the coloration agents used were: copper for green glaze, iron for black glaze and yellow and phosphorus for blue glaze. Opacification was done with tin. The glaze was applied directly on the ceramic shard without engobe or intermediate layer. This study allows to understand how Saadian artisans were manufactured their decorative ceramics, these information should be taken into consideration for the further restoration attempts to preserve the quality of these objects and to avoid using restoration materials incompatible with the originals.

Declaration of Competing Interest

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

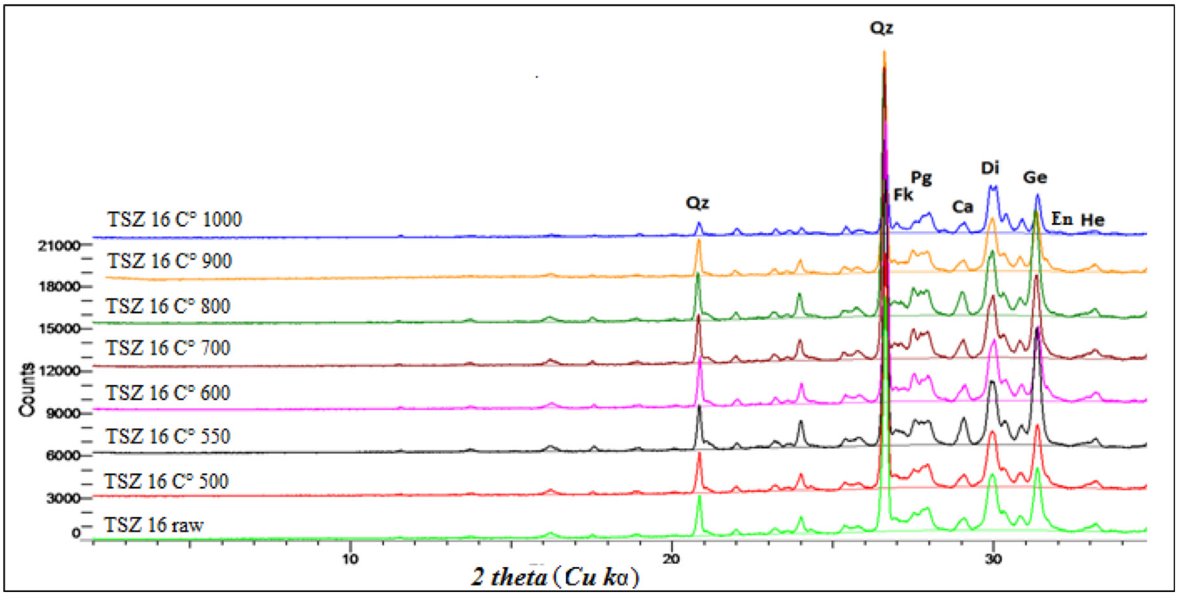


Fig. 7. XRD results of experimental annealing of zellige samples from Saadian tombs. (Qz: Quartz, Ca: Calcite, Di: Diopside, Ge: Gehlenite, Pg: Plagioclases, Fk: Feldspar K, He: Hematite, En: Enstatite).

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