MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF

ARCHAEOLOGICAL CERAMICS FROM EL BADI PALACE (XVITH CENTURY),

MOROCCO

Mouhssin El Halim^{1,2*}, Lahcen Daoudi¹, Meriam El Ouahabi², Valérie Rousseau³,

Catherine Cools³ and Nathalie Fagel²

¹Laboratoire de Géosciences et Environnement (LGSE), Département de Géologie, Faculté

des Sciences et Techniques, Université Cadi Ayyad, BP 549 Marrakech, Morocco

²UR Argile, Géochimie et Environnement sédimentaires (AGEs), Département de Géologie,

Université de Liège, Quartier Agora, Bâtiment B18, Allée du six Août, 14, Sart-Tilman, B-

4000, Belgium

³Ecole Supérieure des Arts, Saint Luc de Liège (ESA), Boulevard de la constitution, 4020

Liège, Belguim

E-mail: Elhalim.mouhsin@gmail.com

[Received: 16 November 2017; revised: 16 June 2018. Guest Associate Editor: Michele

Dondi]

DOI: 10.1180/clm.2018.33

Footnote: This paper was originally presented during the session: 'CZ-01- Clays for ceramics' of

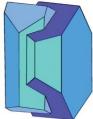
the International Clay Conference 2017.

ABSTRACT: Textural, mineralogical and chemical characterization of archaeological

ceramics (zellige) of the El Badi Palace (Marrakech, Morocco), the main islamic monument

from the Saadian period (XVIth century), has been performed, to enhance restoration issues

and to determine technology of manufacturing. A multi-analytical approach based on optical



Mineralogical Society

This is a 'preproof' accepted article for Clay Minerals. This version may be subject to change during the production process.

DOI: 10.1180/clm.2018.33.

and Scanning Electron Microscopy (SEM), cathodoluminescence, X-ray fluorescence (XRF) and X-ray diffraction (XRD) was used. Re-firing tests on ceramic supports were also performed to determine the firing temperatures used by the Saadian artisans. A calcareous clay raw material was used to manufacture these decorative ceramics. The sherds were fired at a maximum temperature of 800°C in oxidizing atmosphere. The low firing temperature for zellige facilitates cutting of the pieces but also causes fragility to these materials due to the absence of vitreous phases.

Keywords: zellige, technological properties, manufacturing process, El Badi Palace, Morocco.

INTRODUCTION

Historical monuments are tangible witnesses to the evolution of civilizations over time. In Morocco, several cities are renowned for their historical sites, because the Amazigh, Arab and Andalusian cultures, which have succeeded each other over time, blend perfectly to enrich the Moroccan heritage. Today, eight sites have been classified as world heritage by UNESCO, the main sites located in the imperial cities Fez and Marrakech which played the role of the kingdom's capital for nearly 900 years (Paccard, 1981).

Among the most fascinating historical sites, the El Badi Palace in Marrakech reflects the glory of the Saadian dynasty that governed Morocco from 1554 to 1659 (Touri, 1999). The construction of this magnificent palace lasted 16 years (1578 to 1594). The general layout (Fig. 1) and decoration show the beauty and perfection of Moroccan architecture at that time. The mosaic and ceramics used to decorate the building constitute key elements of this exciting architecture. The palace was partially demolished at the time of the Ismaili dynasty a century after its construction, and a large part of its materials was transferred to Meknes city

for reuse in the construction of the royal town of Moulay Ismail (Terrace, 1949; Deverdum, 1957). The remains of this building have now reached an advanced deterioration phase and ceramic materials have been increasingly weakened due to human impact over time. Restoration attempts coordinated by the inspection of historical monuments of Marrakech have not been successful because the new materials used in the restoration have deteriorated faster than the old ones. Traditional restoration methods that do not take into account the chemical and mineralogical characteristics of the raw materials are still practiced. Therefore, studies on the old building materials must be conducted as a first step before taking any conservation or restoration decision (Barluenga et al., 2013). Actually, with the exception of some recent studies that concern mainly Saadian tombs (Casas et al., 2008, Ben Daoud et al., 2013, Gradmann et al., 2015) and the Saadian sugar factory of Chichaoua (Gamrani et al., 2012, 2014), very few scientific studies have been undertaken to characterize the materials used in the construction and restoration of these Saadian monuments.

This study aims at characterizing the zellige ceramics used in the construction of the El Badi palace to understand the technical practices adopted by the Saadian dynasty in the 16th century. The physical and chemical properties, and the texture of the ancient ceramics are mainly influenced by raw material composition (Tschegg et al., 2009; De Vito et al., 2014), amounts of inclusions in the ceramic fabric and firing conditions (Riccardi et al., 1999; Rathossi & Pontikes, 2010; İssi et al., 2011). The purpose of the present study is to determine how these parameters control the formation of these handmade materials and the choice of the raw material used in the manufacture of various Saadian ceramics. This study will permit the selection of the appropriate materials and the development of a specific approach to the restoration, maintenance and enhancement of El Badi Palace decorative ceramics.

MATERIALS AND METHODS

Materials

The mosaic ceramics, also called zellige, constitute fundamental and characteristic elements of the Saadian monuments (Fig. 2). More than twenty different patterns have been identified in the walls of the El Badi Palace, the main pattern being composed by a basic element with eight-pointed star called *Kahtem* (Benamara, et al., 2003). This technique simultaneously appeared in different regions under the control of the Almohads (1130 - 1269) and the Merinides (1244 - 1465) in Fes (Morocco), the Zayanids (1236-1554) in Tlemcen (Algeria), the Nasrids (1232-1492) in Granada (Spain) and the Hafsides (1229-1574) in Tunis (Tunisia) (Erzini, 1993; Hattstein & Delius, 2000).

The studied samples include nine decorative ceramics with different shapes and colors (Fig. 3). The samples were either taken directly from the wall, using a micro-sampling procedure adopted by the General Inspectorate of Historic Monuments of Marrakech, or were provided directly from the palace reserve (Table 1).

Methods

The texture of the samples and their surface characteristics were described with a binocular loupe. More detailed observations of the texture were made successively by optical microscopy (CETI, Gx1500, Laboratory AGEs, Univ. Liege), Scanning Electron Microscopy (XL-FEG-ESEM, Univ. Liege) and by cathodoluminescence (Technosyn Cold cathodoluminescence 8200 Mk3, Laboratory of Sedimentology, Univ. Liege). For this last technique, samples were placed in a Nuclide type chamber, under a vacuum of 0.2 to 0.01 Torr and bombarded by a beam of electrons accelerated by a voltage varied from 15 to 20 kV.

The recording of the rays emitted by the sample was performed by 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 analysis (XRD). The mineralogical phases present in the terracotta were identified with an XRD powder diffractometer (Bruker Eco D8-Advance using $CuK\alpha$ radiation) at the Laboratory AGEs, Univ. Liege, in the range 2 - 60° 20. 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 studied ceramics was determined by re-firing tests. Aliquots of each sample were ground in agate mortar and were annealed for 4 hours in a furnace in the temperature range 500-1000°C. The relative abundance of minerals was detected and estimated using TOPAS and DIFFRACPlus.EVA software.

Powdered samples were mixed with Spectromelt A12 flux in 1:9 ratio, and then analyzed by X-Ray Fluorescence (XRF) using a PanalyticalAxios spectrometer equipped with Rh-tube for major elements analysis (Laboratory of Petrology, Univ. Liege), using argon-methane gas. The data were treated with IQ+ software. The loss on ignition (LOI) was determined by heating the samples at 1000°C for 2h.

The elemental composition of glazes was determined by non-destructive XRF analysis applied directly on an area of $108 \mu m \times 88 \mu m$ on the surface of each sample (Laboratory of Sedimentology, Univ. Liege). Quantitative analysis was performed with Oxford Instruments (Fremont, USA) using standards of metals, synthetic compounds and natural minerals. The elemental contents represent the average of three to five measurements.

RESULTS

Petrographic analysis of ceramic body

Observation in natural light by optical microscopy allows examination of pore shape and abundance in the edge and on the ceramic shards as well as the percentage, grain size and distribution of inclusions (Fig. 4). The main features in terms of microstructure, groundmass and inclusions were described according to the criteria of Whitbread (1986, 1995). The porosity of all samples varies from 10% to 15% of the total volume, which consists mainly of meso-vescicles and rare macro-vughs. The pore diameter varies from a few micrometers in the shard to 1mm in the glaze and their shape is angular to sub-rounded. The absence of vitreous phase surrounding the grains indicates that no melting occurred during firing. The glaze-shard interface of the zellige samples is poorly defined due to the penetration of the glaze mixture into the open-pores of ceramics. The glaze was applied directly to the ceramic support without intermediate layer. The thickness of the glaze is 250 - 350 µm. The groundmass is generally homogeneous, optically inactive with beige to light brown color. The inclusions are mainly represented by equidimensional grains of quartz, iron oxides and rare mica.

Cathodoluminescence indicates the chemical elements of the boundary glaze /shard according to their natures and their distributions (Piponnier, 1990) (Fig. 4). Under the effect of electronic bombardment, the white (PBZ15, PBZ17 and PBZ19) and yellow (PBZ18) glazes luminescent slightly in blue, indicate the presence of tin in the form of cassiterite (El Marraki, 1998). Heavy minerals appear in bright yellow color, they are clearly visible on the glaze intruded deeply into the ceramic shard, and this one is generally purple, reflecting the high amount of quartz inclusions (Bechtel & Schvoerer, 1984). The orange color reflects the

abundance of calcite, whereas the associated green areas are indicative of plagioclase (Duttine, 2008; Muller et al., 2010).

Mineralogical and chemical composition of shards

The Zellige samples have similar mineralogical composition (Fig. 5). The sherds are rich in quartz (26-34 wt.%), plagioclase and alkali feldspar (17-29 wt.%) and calcite (10-12 wt.%). The low amount of hematite (\sim 3 wt.%) is responsible for the light color (light brown) of the ceramic sherds. The XRD patterns also reveal the presence of enstatite ($Mg_2Si_2O_6$) which may be attributed to the presence of MgO in the raw clay material (Hernandez et al., 2005). Ca-silicates phases, i.e. gehlenite (Ca_2Al [$AlSiO_7$]) and diopside ($CaMgSi_2O_6$), are transitional phases formed at high temperature ($\geq 700^{\circ}C$) (Maniatis et al., 1983; El Ouahabi et al., 2015). Gehlenite forms by grain-boundary reaction between CaO, Al_2O_3 and SiO_2 (De Vito et al. 2014, 2016; Rathossi et al. 2010). It crystallizes preferentially in comparison with other anhydrous Ca-Al silicates (Goldsmith, 1953). The presence of Mg in the carbonate-quartz interface also favors the formation of diopside (Jordan et al., 2001).

All nine zellige studied samples are lime-silica sherds (Table 2), with SiO_2 contents from 38.9 - 57.7 wt.%, being on average lower than the other studied materials. In addition they contain 8.8 - 12.8 wt.% Al_2O_3 , 4.7 wt.% Fe_2O_3 and 15 wt.% CaO on average.

The studied sherds display limited variation in the total amorphous phase content (18 - 22%, Table 4). The absence of any broad hump between 4.03 and 3.00Å, confirms the absence of amorphous hydrous silicate of aluminum, derived from weathering of volcanic materials.

Elemental Analysis Study of Glazes

Glaze plays a decorative and protective role for the shard surface, being responsible for a smooth and tight appearance. There is evidence for decrease in lead, copper, tin and iron oxide contents from the glaze exterior to the shard (Table 3). All glaze samples display enrichment of Pb and Sn in accord with previous reports that ancient ceramists often used lead oxide mixed with tin as opacified agent (Hochuli-Gysel, 1977; Hatcher et al. 1994; El Marraki, 1998; Gliozzo et al., 2015). The Pb and Sn oxides define two contrasting areas, as evidenced by SEM in backscattered electron (BSE) mode. The dark area is rich in Pb (45.2 wt.%) with relatively less amount of Sn (10.7 wt.%). The light area is richer in Sn (12.6 wt.%) and poorer in Pb (36 wt.%) (Fig. 6, Table 3).

The chemical composition of the various colors of glazes suggests the use of conventional dyes (Table 3). Hence:

- Copper (Cu²⁺) was used for the green glaze (2.95 wt.% of CuO);
- Iron (Fe³⁺) and manganese (Mn²⁺) for the black glaze (9.61 wt.% Fe₂O₃ and 2.99 wt.% MnO);
- Lead (Pb) and tin (Sn) associated with trace of iron (2.05 wt.%) and lime (4.15 wt.%) are responsible for the yellow-brown (honey) color;
- Phosphorus (P₂O₅) is responsible for the blue glaze opalescence.

The higher lime contents observed in the P-rich glaze (8.4 wt.% of CaO) could be due to efflorescence of the shard surface made from calcareous clays (Walton *et al.*, 2010).

All glazes except for the yellow-brown ones are opacified with tin, with glaze beign rich in SnO₂ (13.4 wt.%). A glaze becomes opaque with just 5 wt.% of SnO₂ (Rhodes 1999). The

high proportion of SiO_2 (39.4 - 50.4 wt.%) favors the formation of vitreous phases during firing.

The Fe₂O₃ gives the black, manganese-coloured glaze a brown hue. In the black samples, the MnO₂ is present as idiomorphic Mn-rich crystals (Fig.7). About 3.0 wt.% MnO₂ is present in the upper part of the ceramic-glaze interface beside the major components SiO₂ (39.5 wt.%), Fe₂O₃ (9.6 wt.%), PbO (38.2 wt.%), and CaO (2.16 wt.%).

Yellow-brown and blue glazes have higher CaO contents (4.15 and 8.4 wt.%), whereas the K₂O content does not exceed 2 wt.% in all glazes. The low amount of Cl found in the yellow-brown glaze (1.23 wt.%) may be attributed to the calcium fluoride used as a flocculating agent in glazes.

DISCUSSION

Mineral phases and firing conditions

Clayey raw materials undergo a complex set of thermal modifications during firing; thus it is often difficult to predict the phase changes in fired ceramic clays (Jordan et al., 2001; Pardo et al., 2011). However, the disappearance of certain mineral phases and neoformation of other may constitute a good indicator of the firing temperature (Cultrone, 2001; Maritan *et al.*, 2006; Trindade *et al.*, 2009; Rathossi & Pontikes, 2010). Decomposition of clay minerals begins at 300°C, and of carbonates from 700°C (Périnet, 1983; Chen, 2000; Toledo, 2004). The decomposed elements produce new mineral phases whose nature and abundance depend on the chemical and mineralogical composition of the raw materials, the maximum heating temperature, heating rate, duration of firing, and the kiln redox atmosphere (Brown & Bailey, 1963; Khalfaoui & Hajjaji, 2009; Pardo *et al.*, 2011).

The studied zellige sherds display similar chemical and mineralogical composition (Fig. 8), reflecting the homogeneity of the raw clay material used for the El Badi Palace decoration. The absence of vitreous phases and the presence of Ca-silicates confirm that calcareous clays were used as raw materials in the manufacturing of zellige (Riccardi et al., 1999; Cultrone et al., 2001). The samples show a good linear correlation between CaO-Al₂O₃ (r^2 = 0.878) and CaO-SiO₂ (r^2 = 0.921). Only the zellige sample PBZ14 plots separately in all binary diagrams. This sample is characterized by very high CaO contents and relatively low amounts of Fe₂O₃ and SiO₂. The firing time and the placement of the articles in the traditional Saadian kilns were likely responsible for minor differences in the mineral constituents of each zellige. Upon firing, the disappearance of the total clay peak at 4.47 Å occurs at 550°C in the calcareous raw clay materials (Cultrone et al., 2004). The absence of this peak in the XRD

calcareous raw clay materials (Cultrone et al., 2004). The absence of this peak in the XRD diffractograms of the El Badi Palace ceramics (Fig. 5) attests that the firing temperature was higher than 550°C. Otherwise, the zellige sherds have moderate calcite content. 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 (Riccardi et al., 1999; Cultrone et al., 2001). Calcite resists longer in well crystallized coarse granules, in very fast heating rates, short soaking time in the critical temperature interval, and in conditions of reducing atmosphere during firing (Maritan *et al.*, 2006). SEM observations show that primary calcite identified in the studied zellige shards presents well crystalline form (Fig. 9), suggesting that firing temperature was likely ~ 800°C.

On the other hand, the evolution of carbonates during firing, in this type of calcareous raw material, is responsible for the neoformation of gehlenite and diopside at ~ 700°C (Maggetti, 1981; Perinet *et al.*, 1983; Echallier, 1989; Dondi *et al.*, 1999). The formation of Ca-silicates reduces the amount of free-lime, and consequently the possibility for re-carbonation. The formation of Ca-silicates depends also on the grain size and the crystalline form of the starting

raw material (Maggetti et al., 1981; Jordán et al., 1999; Nagy et al., 2000; Maritan et al., 2006; Nodari et al., 2007; Tschegg et al., 2009). Thermal reactions between the decomposed calcite and the relics of clay minerals to produce Ca-silicates may be incomplete. New Ca-silicates may be observed together with calcite in the case of excess calcite, large calcite grains and the well crystallized form of calcite (Fabri et al., 2014). Accordingly, the coexistence of primary calcite and the Ca-silicates in the studied zellige samples indicates that the firing temperature was between 700 and 800°C.

The firing temperatures thus determined are checked by "experimental firing test". Firing below 600°C yielded similar mineralogical composition. At 700°C, the calcite peaks (d = 3.04-3.01 Å) decreased in intensity and disappeared completely at 800°C, with an increase in gehlenite, diopside and hematite contents (Fig. 5B).

Glaze characterization

The visual appearance of the zellige samples indicates that the glaze does not flow to the edges of the sherds pointing out that the glaze mixture has been previously applied to the fired clay sherds as 15cm×15cm tablets, and then a second firing was applied. Subsequently, the pieces were carved into small pieces like puzzles. This technique is still used by the artisans in Fez, i.e. the main production center of zellige in Morocco, since the XIV century (Erzini, 1993), with the difference that the shelves currently used have dimensions 10cm×10cm. The zellige pieces used in the construction of the El Badi Palace were therefore either imported from Fez or manufactured locally in Marrakech according to the current standards and procedures in Fez. The glaze technique used by the Saadian seems to be similar to that used currently in Fez; it consists of immersing the upper face of the ceramic articles directly in the glaze mixture and then let them to dry in air. The glaze is therefore applied to the ceramic sherd without slip or intermediate coating. The glazes are very rich in PbO (41.5-20.9 wt.%

PbO) with a SiO_2 content in the range 50.4-37.1 wt.%. The mixtures of PbO and SiO_2 react to form the glaze that then interacts with the clay body. Although the SiO_2 amounts in the glazes are slightly lower than that in the sherds, this feature suggests that siliceous sand was used as a source of silica in the glaze mixture. The PbO/SnO₂ ratio of the glaze samples was very high, ranging from 3.1 to 41.3, indicating high viscosity of the glaze (high PbO) and firing at temperature < 700° (Tite et al., 2008; Gliozzo, 2015).

CONCLUSION

The application of multi-analytic approach on archeological ceramics (zellige) of El Badi Palace (Morocco) yielded 3 main conclusions:

- The similar mineralogical and chemical composition of the studied zellige samples from the El Badi Palace evidence that all ceramics were made from the same calcareous raw clay material.
- All ceramics were fired in traditional furnaces under similar temperature and kiln oxidizing atmosphere. The maximum firing temperature ranged between 700 and 800°C.
- The lead-type glazes were directly applied to the ceramic pieces without any intermediate layer according to the technique used since ages in Fez. The zellige pieces are therefore either transported from Fez or manufactured locally in Marrakech according to the standard procedures in Fez.

ACKNOWLEDGEMENTS

- The financial support was provided by a bilateral cooperation project Wallonie Bruxelles-Maroc (WBI 2015-2017 project 2.7) and by the PPR-CNRST (Centre

National de Recherches Scientifiques et Techniques) program (grant PPR1/2015/63) that are gratefully acknowledged. The first author acknowledges the EU financial support through a 12 month grant at the University of Liege through the Erasmus plus program for the foreigner PhD Student. Mr. Féréderic Boulevain from University of Liege is immensely acknowledged for comments that greatly improved the manuscript.

REFERENCES

André P. (1981). Morocco and traditional Islamic craftsmanship in architecture. Editions workshop 74. V1, 371-381.

Aras A. (2004). The change of phase composition in kaolinite- and illite-rich clay-based ceramic bodies. *Applied clay science*, 24, 257–269.

Barluenga G., Estirado F., Raimundo U., Conde J., Agua F., Villegas M. & García-Heras M. (2013). Brick masonry identification in a complex historic building, the Main College of the University of Alcalá, Madrid (Spain). *Construction and Building Materials*. 54, 39–46.

Bechtel F. & Schvoerer M. (1984). Cathodoluminescence: Application to the study of the texture of ceramic pastes, PACT 10 - Dating-characterization of ancient ceramics, *European Intensive Course*, ed. Council of Europe - CNRS, 247–260.

Benamara A., Schvoerer M., Haddad M. & Akerraz A. (2003). Search for clues on techniques of zelliges production from the 14th century (Chellah, Morocco). *Review of Archeometry*, 27, 103–113.

Bendaoud R., Guilherme A., Zegzouti A., Elaatmani M., Coroado J., Carvalho M.L. & Queralt I. (2013). Elemental mapping of Moroccan enameled terracotta tile works (Zellij) based on X-ray micro-analyses. *Applied Radiation and Isotopes*, 82, 60–66.

Brown G.E. and Bailey S.W. (1963). Chlorite polytypism: II. Crystal structure of a one-layer Cr-chlorite. *American Mineralogist*, 48, 42–61.

Casas L., Briansó J.L., Álvarez A., Benzzi K. & Shaw J. (2008). Archaeomagnetic intensity data from the Saadian Tombs (Marrakech, Morocco), late 16th century. *Physics and Chemistry of the Earth*, 33, 474–480.

Chen C.Y., Lan C.S. & Tuan W.H. (2000). Microstructural evolution of mullite during the sintering of kaolin powder compacts. *Ceramics International*. 26, 715–720.

Cultrone G., Rodriguez-Navarro C., Sebastian E., Cazalla O. & De la Torre M.J. (2001). Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy*, 13, 621–634.

Cultrone G., Eduardo S., Kerstin E., Maria José T., Olga C. & Carlos R.N. (2004). Influence of mineralogy and firing temperature on the porosity of bricks. *Journal of the European Ceramic Society*, 24, 547–564.

De Vito C., Medeghini L., Mignardi S., Orlandi D., Nigro L., Spagnoli F., Lottici P. & Bersani D. (2014). Technological fingerprints of Black-Gloss Ware from Motya (Western Sicily, Italy). *Applied clay science*, 88–89, 202–213.

De Vito C., Medeghinia L., Mignardia S., Coletti F. & Contino A. (2016). Roman glazed inkwells from the "Nuovo Mercato di Testaccio" (Rome, Italy): Production technology. *Journal of the European Ceramic Society*, 37, 1779–1788.

Deverdum G. (1957). Marrakech from the origins to 1912. North African technical editions, Rabat, 2thédition, 610–611.

Dondi M., Ercolani G., Fabbri B, Marsigli M. (1999). Chemical composition of melilite formed during the firing of carbonate-rich and iron-containing ceramic bodies, J Am Ceram Soc, 82, pp. 465-468.

Duttine M. (1998). Laser cleaning of historical limestone buildings in Bordeaux appraisal using cathodoluminescence and electron paramagnetic resonance. *Environmental Science and Pollution Research*, 15(3) 237–243.

Echallier J.C. & Mery S. (1989). Experimental laboratory approach of the mineralogical and physico-chemical evolution of ceramics during cooking. *Document* n°74, 1.GAL. Paris.

EL Marraki A. (1998). Point defects and luminescence of devitrification crystals: Detection and study in glazes. *Physics Thesis Applied to Archeology*, Michel de Montaigne University - Bordeaux 3, 129.

EL Ouahabi M., Daoudi L., Hatert F. & Fagel N. (2015). Modified mineral phases during clay ceramic firing. *Clays and Clay Minerals*. V. 63 (5), 404–413.

Erzini N. (1993). Zillig: A historical context, Zellig: the art of Moroccan ceramics, Hedgecoe J. et Damluji S.S. éds., *édition Garnet*, 156–170.

Fabri B., Gualtieri S., Shoval S. (2014). The presence of calcite in archeological ceramics. *Journal of European Ceramic Society*, 31, 1899–1911.

Gamrani N., R'khaChaham K., Ibnoussina M., Fratini F., Rovero L., Tonietti U., Mansori M., Daoudi L., Favotto C. & Youbi N. (2012). The particular "rammed earth" of the Saadian

sugar refinery of Chichaoua (XVIth century, Morocco): mineralogical, chemical and mechanical characteristics. *Environmental Earth Sciences*, 66, 129–140.

Gamrani N. (2014). Etude de quelques monuments historiques Saadians (XVI-XVII siècle) de la ville de Marrakech (Maroc): caractérisation et pathologie. *Thèse de l'Université de Marrakech*, 174 p.

Gliozzo E., Lepri B, Saguì L. & Memmi L. (2015). Glass ingots, raw glass chunks, glass wastes and vessels from fifth century AD Palatine Hill (Rome, Italy). *Archaeological and Anthropological Science*, *9*, 709–725.

Goldsmith J.R. (1953). A "simplexity principle" and its relation to "ease" of crystallization. Bull. *Geological society of America*, 64, 439–451.

Gradmann R., Bertlhold C., Schussler U., (2015). Composition and colouring agents of historical Islamic glazes measured with EPMA and μ -XRD. *European journal of mineralogy*, 27, 325–335.

Hatcher H., Kaczmarczyk A., Scherer A. & Symonds R. P. (1994). Chemical classification and provenance of some Roman glazed ceramics, *American Journal of Archaeology*, 98, 431–56.

Hattstein M., Delius P., 2000, Arts et civilisations de l'Islam, ed. Könemann, 408–419.

Hernandez M. S., Romero M. & Rincon J. M., (2005). Nucleation and crystal growth of glasses producted by a generic plasma Arc-Process, *Journal of the European Ceramic Society*, 9, 1–10.

Hochuli-Gysel A. (1977). Kleina siatische Glasierte Reliefkeramik, (50 v. Chr Bis 50 n.Chr.) Und IhreOberitalienischen Nachahmungen (Acta Bernensia), Stampfli, Bern. İssi A., Kara A. & Oğuz Alp A. (2011). An investigation of Hellenistic period pottery production technology from Harabebezikan/Turkey. *Ceramics International*. 37, 2575–2582.

Jordán, M., Boix A., Sanfeliu T. & de la Fuente C. (1999). Firing transformations of retaceous clays used in the manufacturing of ceramic tiles. *Applied clay science*, 14, 225–234.

Jordán M., Sanfeliu T. & de la Fuente C. (2001). Firing transformations of cretaceous clays used in the manufacturing of ceramic tiles. *Applied clay science*, 20, 87.

Khalfaoui, A. and Hajjaji, M. (2009). A chloritic-illitic clay from Morocco: Temperature-time transformation and neoformation. *Applied Clay Science*, 45, 83–89.

Maggetti M., Galetti G., Schwander H., Picon M. & Wessicken R. (1981). Campanian pottery: the nature of the black coating. *Archaeometry*, 23, 199–207.

Maggetti M. (1982). Phase analysis and its significance for technology and origin, *in* "Archaeological Ceramics", *Olin, J.S.*, ed. Smithsonian Institution Press, Boston, 121–133.

Maniatis Y., Simopoulos A., Kistikas A. & Perdikatsis V. (1983). Effect of reducing atmosphere on minerals and iron oxides developed in fired clays: the role of Ca. *Journal of the American Ceramic Society*, 66, 11, 773–781.

Maritan L., Nodari L., Mazzoli C., Milano A. & Russo U. (2006). Influence of firing conditions on ceramic products: experimental study on clay rich in organic matter. *Applied clay science*, 31, 1–15.

Müller A., Herrington R., Armstrong R. Reimar S., Douglas J.K., Nina G.S. & Kronz A. (2010). Trace elements and cathodoluminescence of quartz in stock work veins of Mongolian porphyry-style deposits. *Miner Deposita*, 45, 707.

Nagy S., Kuzmann E., Weiszburg T., Gyökeres-Tóth M. & Riedel M. (2000). Oxide transformation during preparation of black pottery in Hungary. *Journal of Radioanaytical and Nuclear Chemistry*, 246, 91–96.

Nodari L., Marcuz E., Maritan L., Mazzoli C. & Russo U. (2007). Hematite nucleation and growth in the firing of carbonate-rich clay for pottery production. *Journal of the European Ceramic Society*, 27, 4665–4673.

Pardo, F., Meseguer, S., Jorda´n, M.M., Sanfeliu, T., and Gonza´lez, I. (2011). Firing transformations of Chilean clays for the manufacture of ceramic tile bodies. *Applied Clay Science*, 51, 147–150.

Périnet G. & Courtois L. (1983). Evaluation of the firing temperatures of Syria's ceramics and white Neolithic dishes. *Bulletin of the Prehistoric French Society*, vol. 80, n°5, 157–160.

Piponnier D. (1990). Cathodoluminescence of archaeological ceramics: development of a new method for the typology of pastes. 65–66.

Rathossi C. & Pontikes Y. (2010). Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part I: reaction paths, crystalline phases, microstructure and colour. *Journal of the European Ceramic Society*, 30, 1841–1851.

Rhodes D. (1978). Lands and glazes - Enamelling techniques, éd. Dessain et Tolra, Paris.

Riccardi M.P., Messiga B. & Duminuco P. (1999). An approach to the dynamics of clay firing. *Applied clay science*, 15, 399–409.

Terrasse H. (1949). The Almoravid monuments of Marrakech, in acts of the XXIst international congress of Orientalists. Asian Company, impr. National, Paris.

Tite M., Pradell T. & Shortland A. (2008). Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the late Iron Age onwards: a reassessment. *Archaeometry*, 50, 67–84.

Toledo, R., dos Santos D.R., Faria J., Carrió J.G., Auler L.T. & Vargas H. (2004). Gas release during clay firing and evolution of ceramic properties. *Applied clay science*, 27, 151–157.

Touri A. (1999). Maroc, les trésors du royaume. Dynasties islamiques, Edition Plume, Paris.

Trindade M.J., Dias M.I., Coroado J. & Rocha F. (2009). Mineralogical transformations of calcareous rich clays with firing: A comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Applied Clay Science*, 42, 345–355.

Tschegg C., Ntaflos T. & Hein I. (2009). Thermally triggered two-stage reaction of carbonates and clay during ceramic firing — A case study on Bronze Age Cypriot ceramics. *Applied clay science*, 43, 69–78.

Walton M. & Tite M. (2010). Production technology of Roman lead-glazed pottery andits continuance into late antiquity, *Archaeometry*, 52, 733–759.

Whitbread, I.K. (1986). The characterization of argillaceous inclusions in ceramic thin sections. *Archaeometry*, 28, 79–88.

Whitbread, I.K. (1995). Greek transport amphorae. A Petrological and Archaeological Study. Fitch Laboratory Occasional Papers, 4. British School at Athens, Athens.

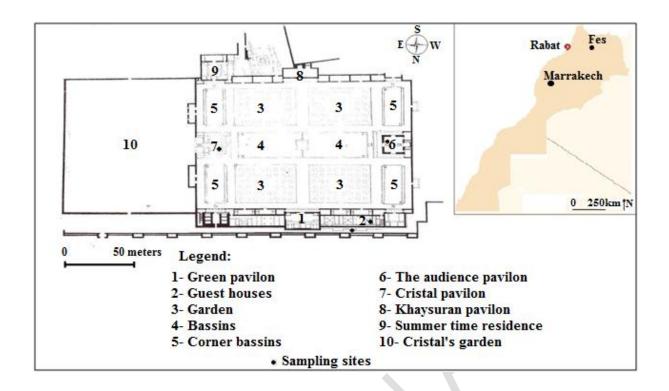


Fig. 1. Geographical location and plan of El Badi Palace.

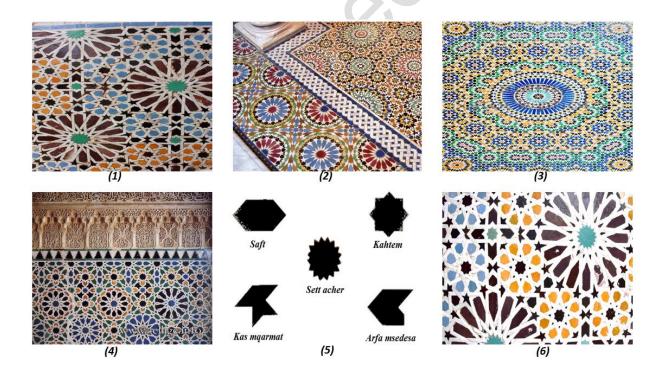


Fig. 2. Main islamic forms of zellige; (1) El Badi Palace, Marrakech. (2) Royal Palace, Fes. (3) El Glaoui Kasbah, Fès. (4) Alhambra Palace, Grenade. (5) Names of the main forms of zellige found in El Badi Palace. (6) Saadian Tombs, Marrakech.

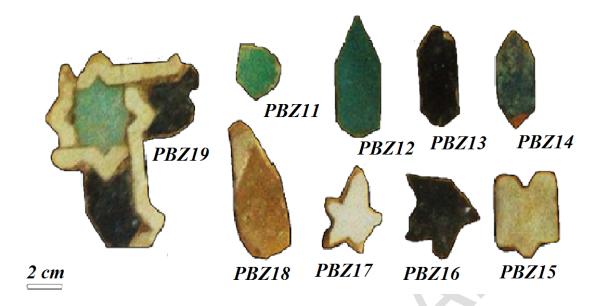


Fig. 3. The studied ceramic samples from the El Badi Palace.

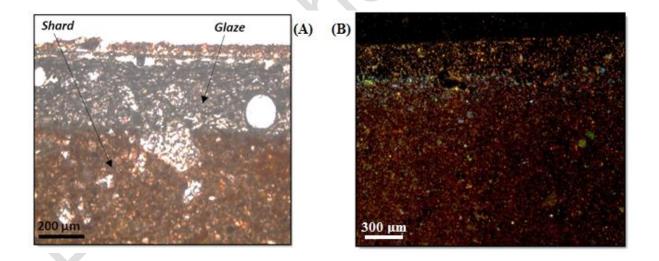


Fig. 4. Observation by light microscopy (A) and cathodoluminescence (B) of the Glaze-shard interface.

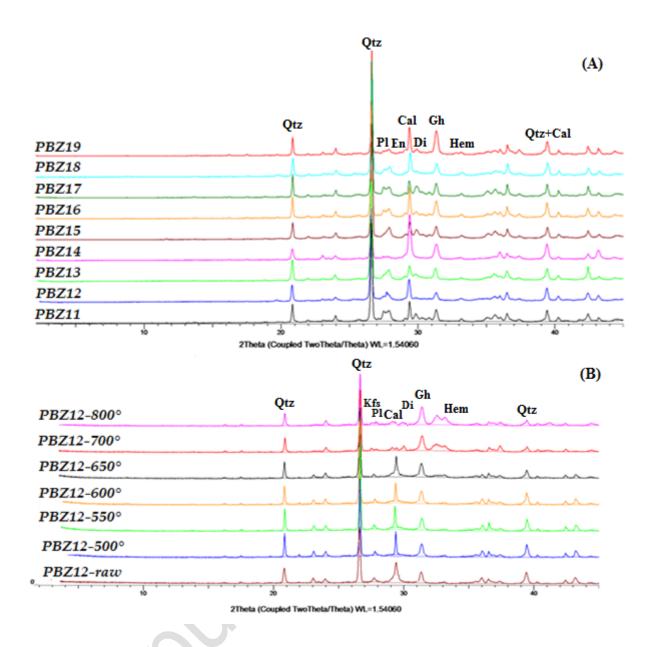


Fig. 5. (A) XRD traces showing the uniformity of mineral compositions of zellige samples (B) Firing test of zellige sample (PBZ12). (Qtz: Quartz, Kfs: Potassium Feldspar, Pl: Plagioclase, Cal: Calcite, Di: Diopside, Gh: Gehlenite, Hem: Hematite, Sd: Siderite, En: Enstatite, Ms: Muscovite).

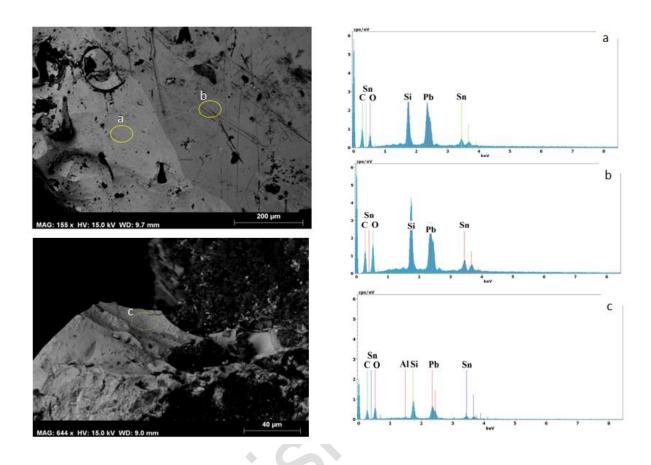


Fig. 6. SEM micrographs of the surface of the lead glaze (a, b) and the shard / glaze interface (c) with the EDS analysis.

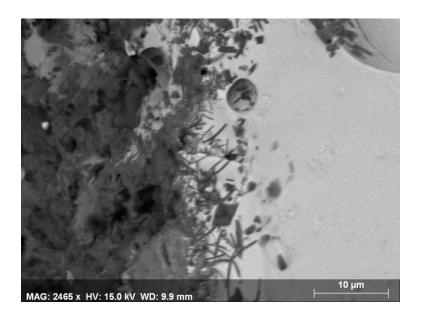


Fig. 7. SEM-BSE-image of a black glaze from the El Badi palace. The long prismatic precipitates are manganese-rich crystals.

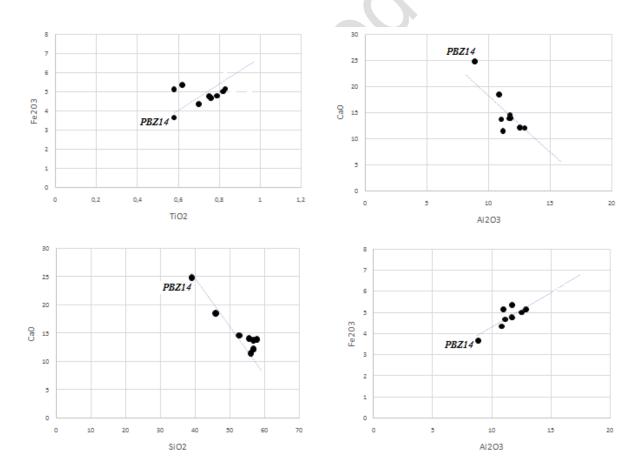


Fig. 8. Binary diagrams Al₂O₃-Fe₂O₃, Fe₂O₃-TiO₂, CaO-Al₂O₃ and CaO-SiO₂, showing compositional differences among the zellige samples.

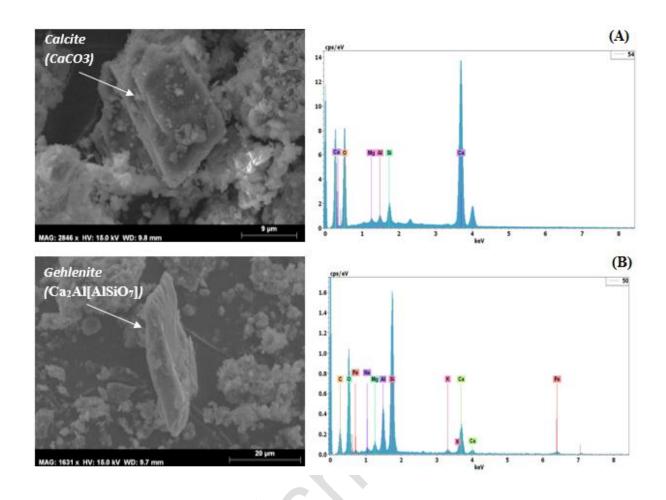


Fig. 9. SEM image showing the former presence of calcite crystal in ceramic shard (A), and neoformed melilite (gehlenite) crystals formed during firing (B).

Table 1. Characteristics and location of the analyzed samples.

Studied samples	Nature	Sample location
PBZ11	Light green zellige on shape Thelt'amel	
PBZ12	Bleu zellige on shape Saftthn'achri	
PBZ13	Black zellige on shape Saft	
PBZ14	Blue zellige on shape Saft	
PBZ15	White zellige on shape <i>Qfa</i>	stockpile
PBZ16	Black zellige on shape Kasmqermat	stockpiic
PBZ17	White zellige on shape Quandil	. (7)
PBZ18	Honey zellige on shape Saftthn'achri	
PBZ19	Piece composed of <i>Qtib sarout</i> , <i>Khatem</i> and <i>Arfa medsea</i>	

Table 2. The bulk chemical composition of the ceramic shard samples from the El Badi Palace (%).

Samples	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O5	LOI
PBZ11	56.7	0.8	12.8	5.1	0.1	2.1	12.1	0.9	2.9	0.2	6.1
PBZ12	55.9	0.7	11.1	4.7	0.1	1.8	11.5	0.9	2.6	0.2	10.6
PBZ13	56.7	0.6	10.9	5.1	0.0	2.6	13.8	0.6	1.8	0.2	7.1
PBZ14	38.9	0.6	8.8	3.6	0.1	1.7	24.8	0.7	1.7	0.2	18.7
PBZ15	55.4	0.6	11.7	5.3	0.1	2.8	14.1	0.6	2.09	0.3	7.1
PBZ16	52.6	0.7	11.7	4.7	0.1	1.9	14.6	0.9	2.5	0.3	10.1
PBZ17	57.7	0.8	11.6	4.7	0.1	2.1	14	0.8	2.2	0.2	5.5
PBZ18	56.6	0.8	12.5	5	0.1	2.1	12.2	0.9	2.7	0.2	6.2
PBZ19	45.7	0.7	10.8	4.3	0.1	1.9	18.5	1.1	2.1	0.2	13.8

Table 3. Elemental composition of glazes expressed as percent by weight of oxides (nd: not detected; <1: element detected but less than 1%).

Oxides	PBZ18 (Honey)	PBZ11 (Green)	PBZ16 (Black)	PBZ15 (White)	PBZ14 (Blue)
SiO2	42.64	40.01	39.46	37.11	50.47
PbO	41.29	39.98	38.2	41.51	20.93
CaO	4.15	2.31	2.16	1.73	8.40
Fe2O3	2.05	<1	9.61	<1	<1
K2O	1.94	<1	<1	<1	1.55
SO3	1.77	nd	<1	<1	<1
P2O5	1.67	<1	<1	1.63	7.48
Al2O3	1.55	2.44	1.35	<1	2.35
SnO2	<1	6.53	1.55	13.40	3.89
CuO	<1	2.95	<1	<1	<1
Cl	1.23	<1	<1	<1	<1
MgO	<1	<1	<1	<1	1.17
MnO	<1	<1	2.99	<1	<1
Na2O	<1	<1	<1	<1	1.24

Table 4. XRD analysis of El Badi palace ceramics (%).

Samples	PBZ11	PBZ12	PBZ13	PBZ14	PBZ15	PBZ16	PBZ17	PBZ18	PBZ19
Quartz	30	33	34	30	32	29	32	31	30
Plagioclase	15	13	16	9	15	13	14	13	9
Feldspath K	13	13	9	8	9	12	14	13	13
Calcite	10	12	9	25	10	11	9	11	12
Diospide	7	6	8	4	10	8	9	5	8
Gehlenite	10	7	8	10	9	11	8	9	10
Hematite	3	2	2	3	3	2	2	3	3
Enstatite	5	6	7	5	5	5	4	3	5
Muscovite	4	6	4	5	4	5	5	8	8
Anhydrite	1	2	2	1	2	2	2	2	2
Total amorphous	19	22	18	18	19	19	18	20	20