Mineralogical and geochemical characterization of archaeological ceramics from the 16th century El Badi Palace, Morocco

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ABSTRACT: Textural, mineralogical and chemical characterization of archaeological ceramics (zellige) from El Badi Palace (Marrakech, Morocco), the main Islamic monument from the Saadian period (sixteenth century), has been performed to enhance restoration and to determine the technology of manufacturing. A multi-analytical approach based on optical and scanning electron microscopy, cathodoluminescence, X-ray fluorescence and X-ray diffraction 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 in these materials due to the absence of vitreous phases.

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

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 succeeded each other over time, blend perfectly to enrich the Moroccan heritage. Today, eight sites have been classified as 'world heritage' by UNESCO,

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with the main sites located in the imperial cities of Fez and Marrakech, which have been 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 took 16 years (1578–1594). The general layout (Fig. 1) and decoration show the beauty and perfection of Moroccan architecture at that time. The mosaics 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 proportion of



FIG. 1. Geographical location and plan of the El Badi Palace, Marrakech.

the construction material was transferred to Meknes 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 its ceramic materials have been increasingly weakened due to human impacts over time. Restoration attempts following inspection of the 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 decisions (Barluenga et al., 2013). In fact, with the exception of some recent studies that concern mainly Saadian tombs (Casas et al., 2008; Bendaoud 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 aimed to characterize the 'zellige' ceramics used in the construction of the El Badi Palace in order to understand the technical practices adopted by the Saadian dynasty in the sixteenth century. The physical and chemical properties and the texture of the ancient ceramics are mainly influenced by the composition of the raw material (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 was 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 selection of 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 referred to as 'zellige', constitute fundamental and characteristic elements of the Saadian monuments (Fig. 2). More than 20 different patterns have been identified in the walls of the El Badi Palace, the main pattern being composed of a basic element with an 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 (1229–1574) in Tunis (Tunisia) (Erzini, 1993; Hattstein & Delius, 2000).

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



FIG. 2. Main Islamic forms of 'zellige'. (1) El Badi Palace, Marrakech; (2) Royal Palace, Fes; (3) El Glaoui Kasbah, Fes;
 (4) Alhambra Palace, Granada; (5) names of the main forms of 'zellige' found in the El Badi Palace; and (6) Saadian Tombs, Marrakech.

Methods

The textures 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



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

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- $K\alpha$ radiation) at the Laboratory AGEs, University of Liege, in the range

 TABLE 1. Characteristics of samples analysed from the palace reserve.

Sample studied	Nature
PBZ11	Light green 'zellige' of shape Thelt'amel
PBZ12	Blue 'zellige' of shape Saftthn'achri
PBZ13	Black 'zellige' of shape Saft
PBZ14	Blue 'zellige' of shape Saft
PBZ15	White 'zellige' of shape Ofa
PBZ16	Black 'zellige' of shape Kasmgermat
PBZ17	White 'zellige' of shape Quandil
PBZ18	Honey-coloured 'zellige' of shape Saftthn'achri
PBZ19	Fragment composed of shapes <i>Qtib sarout</i> , <i>Khatem</i> and <i>Arfa medsea</i>

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 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 *DIFFRACPlus.EVA* software.

Powdered samples were mixed with Spectromelt A12 flux in a sample: flux ratio of 1:9 and then analysed by X-ray fluorescence (XRF) using a PanalyticalAxios 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 2 h.

The elemental compositions of the glazes were determined by non-destructive XRF analysis applied directly on an area of 108 μ m × 88 μ m on the surface of each sample (Laboratory of Sedimentology, University of Liege). Quantitative analysis was performed using a hand-held XRF Analyser (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.

RESULTS

Petrographic analysis of the ceramic body

Observation in natural light by optical microscopy allowed examination of pore shape and abundance at the edges 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 varied 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 micrometres in the shard to 1 mm in the glaze, and their shape is angular to sub-rounded. The absence of a 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 an intermediate layer. The thickness of the glaze is 250-350 µm. The groundmass is generally homogeneous and optically inactive with a beige to light brown colour. The inclusions are mainly represented by equidimensional grains of quartz, iron oxides and rare mica.

Cathodoluminescence can provide general information about the distribution and nature of the chemical elements in the glaze/shard boundary (Piponnier, 1990) (Fig. 4). Under the effect of electronic bombardment, the white (PBZ15, PBZ17 and PBZ19) and yellow (BPZ18) glazes luminesce slightly in blue, indicating the presence of tin in the form of cassiterite (El Marraki, 1998). Heavy minerals appear bright yellow in colour; they are clearly visible in the glaze, intruding deeply into the ceramic shard that is generally purple in colour because of the large number of quartz inclusions (Bechtel & Schvoerer, 1984). The orange colour reflects the abundance of calcite, whereas the associated green areas are indicative of plagioclase (Duttine, 2008; Müller *et al.*, 2010).



FIG. 4. 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 = haematite; Sd = siderite; En = enstatite; Ms = muscovite.

Mineralogical and chemical composition of the shards

The 'zellige' samples have similar mineralogical compositions (Fig. 5). The sherds are rich in quartz

(26–34 wt.%), plagioclase and alkali feldspar (17–29 wt.%) and calcite (10–12 wt.%). The small amount of hematite (\sim 3 wt.%) is responsible for the light colour (light brown) of the ceramic sherds. The XRD

TABLE 2. Bulk chemical compositions (%) of the ceramic shard samples from the El Badi Palace.

Samples	SiO_2	TiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O5	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	2.1	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	0.8	2.2	0.2	5.5
PBZ18	56.6	0.8	12.5	5.0	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

LOI = loss on ignition.

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 (Hernandez *et al.*, 2005). Ca silicates phases (*i.e.* gehlenite; Ca₂Al [AlSiO₇]) and diopside (CaMgSi₂O₆) are transitional phases formed at high temperature (\geq 700°C) (Maniatis *et al.*, 1983; El-Ouahabi *et al.*, 2015). Gehlenite forms by grain boundary reaction between CaO, Al₂O₃ and SiO₂ (Rathossi *et al.* 2010; De Vito *et al.*, 2014, 2016). It crystallizes preferentially in comparison with other anhydrous Ca–Al silicates (Goldsmith, 1953). The presence of Mg in the carbonate–quartz interface also favours the formation of diopside (Jordán *et al.*, 2001).

All nine 'zellige' samples studied are lime (CaO)– silica sherds (Table 2), with SiO₂ contents of 38.9-57.7 wt.%, being less, on average, than the other materials studied. In addition, they contain 8.8-12.8 wt.% Al₂O₃, 4.7 wt.% Fe₂O₃ and 15 wt.% CaO, on average.

The sherds studied display limited variation in terms of the total amorphous phase content (18–22%) (Table 3).

Elemental analysis of the glazes

Glaze plays decorative and protective roles for the shard surface, being responsible for its smooth and tight appearance. There is evidence for decreases in lead, copper, tin and iron oxide contents from the glaze exterior to the shard (Table 4). 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 an opacification 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 mode. The dark area is rich in Pb (45.2 wt.%) with relatively less Sn (10.7 wt.%). The light area is richer in Sn (12.6 wt.%) and poorer in Pb (36 wt.%) (Fig. 6; Table 4).

The chemical composition of the various colours of glazes suggests the use of conventional dyes (Table 4). Hence:

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

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

All glazes except for the yellow-brown ones were opacified with tin, with the glaze being rich in SnO_2 (13.4 wt.%). A glaze becomes opaque with just 5 wt.% SnO_2 (Rhodes, 1978). The high proportion of SiO_2 (39.4–50.4 wt.%) favours the formation of vitreous phases during firing.

The Fe_2O_3 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

TABLE 3. Quantitative XRD analysis (%) of the El Badi Palace ceramics.

Mineral	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
K-feldspar	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 minerals content	19	22	18	18	19	19	18	20	20

Oxides	PBZ18 (honey-coloured)	PBZ11 (green)	PBZ16 (black)	PBZ15 (white)	PBZ14 (blue) 50.47	
SiO ₂	42.64	40.01	39.46	37.11		
PbŐ	41.29	39.98	38.20	41.51	20.93	
CaO	4.15	2.31	2.16	1.73	8.40	
Fe ₂ O ₃	2.05	<1	9.61	<1	<1	
K ₂ 0	1.94	<1	<1	<1	1.55	
SO ₃	1.77	nd	<1	<1	<1	
P_2O_5	1.67	<1	<1	1.63	7.48	
Al ₂ O ₃	1.55	2.44	1.35	<1	2.35	
SnO ₂	<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	
Na ₂ O	<1	<1	<1	<1	1.24	

TABLE 4. Elemental composition of glazes expressed as oxide wt.%.

nd = not detected; <1 = element detected but at <1%.



FIG. 6. SEM images of the surface of the lead glaze (a, b) and the shard–glaze interface (c), with respective energydispersive X-ray analysis (EDS).



FIG. 7. SEM-BSE image of a black glaze from the El Badi Palace. The long prismatic precipitates are Mn-rich crystals.

3.0 wt.% MnO_2 is present in the upper part of the ceramic–glaze interface beside the major components SiO_2 (39.5 wt.%), Fe_2O_3 (9.6 wt.%), PbO (38.2 wt.%) and CaO (2.16 wt.%).

Yellow-brown and blue glazes have greater CaO contents (4.15 and 8.4 wt.%), whereas the K_2O content does not exceed 2 wt.% in all glazes. The small amount of Cl found in the yellow-brown glaze (1.23 wt.%) may be attributed to the calcium chloride used as a flocculating agent in the glazes.

DISCUSSION

Mineral phases and firing conditions

Clavey 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 (Jordán et al., 2001; Pardo et al., 2011). However, the disappearance of certain mineral phases and the neoformation of others 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, the nature and abundance of which depend on the chemical and mineralogical composition of the raw materials, the maximum heating temperature, the heating rate, the duration of firing and the kiln redox atmosphere (Brown & Bailey, 1963; Khalfaoui & Hajjaji, 2009; Pardo et al., 2011).

The 'zellige' shards studied display similar chemical and mineralogical compositions (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 manufacture of 'zellige' (Riccardi *et al.*, 1999; Cultrone *et al.*, 2001). The samples show a good linear correlation between



FIG. 8. Binary diagrams of Al₂O₃–Fe₂O₃, Fe₂O₃–TiO₂, CaO–Al₂O₃ and CaO–SiO₂, showing compositional differences among the 'zellige' samples.

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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 small amounts of Fe₂O₃ and SiO₂. The firing time and the placement of the articles in the traditional Saadian kilns were probably 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 traces of the El Badi Palace ceramics (Fig. 5) attests that the firing temperature was >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, at very fast heating rates, at short soaking times in the critical temperature interval and in conditions of a reducing atmosphere during firing (Maritan *et al.*, 2006). SEM observations show that the primary calcite identified in the 'zellige' shards studied is well crystallized (Fig. 9), suggesting that the firing temperature was probably ~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, 1982; Périnet 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 also depends 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



FIG. 9. SEM images showing the presence of a calcite crystal in a ceramic shard (a) and neoformed melilite (gehlenite) crystals formed during firing (b) with accompanying EDS analyses.

of calcite (Fabri *et al.*, 2014). Accordingly, the coexistence of primary calcite and the Ca silicates in the 'zellige' samples studied indicates that the firing temperature was between 700 and 800°C.

The firing temperatures thus determined were checked by an 'experimental firing test'. Firing below 600°C yielded a 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, highlighting that the glaze mixture had been applied previously to the fired clay sherds as 15 cm \times 15 cm tablets, and then a second firing was applied. Subsequently, the pieces were carved into smaller pieces like puzzles. This technique is still used by artisans in Fez (i.e. the main production centre of 'zellige' in Morocco since the fourteenth century) (Erzini, 1993), with the difference being that the shelves currently used have dimensions of 10 cm \times 10 cm. 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 Saadians 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 letting them 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 SiO₂ content in the range 50.4-37.1 wt.%. The mixtures of PbO and SiO₂ react to form the glaze that then interacts with the clay body. Although the amounts of SiO₂ in the glazes are slightly smaller than those 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 a firing of temperature <700°C (Tite et al., 2008; Gliozzo, 2015).

CONCLUSION

The application of a multi-analytical approach to archaeological ceramics (zellige) of the El Badi Palace (Morocco) yielded three main conclusions:

- The similar mineralogical and chemical compositions of the studied 'zellige' samples from the El Badi Palace demonstrate that all of these ceramics were made from the same raw calcareous clay material.
- All of the ceramics were fired in traditional furnaces under similar temperatures and kiln oxidizing atmospheres. The maximum firing temperature ranged between 700 and 800°C.
- The lead-type glazes were applied directly to the ceramic pieces without any intermediate layers according to the technique that has been used for a long time in Fez. The 'zellige' pieces were therefore either transported from Fez or manufactured locally in Marrakech according to the standard procedures in Fez.

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