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Combination of Physico-Chemical and Lead Isotope Analyses for the Provenance Study of the Archaeological Materials: Example of Saadien Ceramics (16th Century, Marrakech Morocco)

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Abstract: This paper aims to study the provenance of archaeological Saadien ceramics (16th century, Marrakech) based on the chemical, mineralogical and lead isotope composition of clays used as raw materials in the manufacture of ceramics in Morocco and collected in the six major potter sites of Marrakech (Ourika I and II, Saada I and II and Mzouda) and Fez (Benjlikh). The clay chemical, mineralogical and isotopic signatures of these raw materials are compared to the compositions of decorated ceramics from El Badi Palace and Saadien Tombs, the most visited archaeological sites in Marrakech, described as World Heritage by UNESCO. The chemical composition was determined using X-ray fluorescence analysis, while the structural changes of the mineral phases during firing were studied using X-ray diffraction over a temperature range between 500–1000 °C. Pb isotopes, on the other hand, were measured using the Nu Plasma MC-ICP-MS technique. Results show that Saadien ceramics were made using calcareous clay from the Fez region. These clays were imported by the artisans from 400 km away to be used in the manufacturing of ceramics in the Saadien buildings of Marrakech. The firing temperature of these materials ranges between 600 and 700 °C for El Badi Palace, and from 800 to 900 °C for the Saadien Tombs ceramics using traditional ovens. This study reveals the mystery behind the source of Saadien ceramics and provides artisans with information about the origin of the raw materials used in Marrakech's 16th-century buildings, which should be considered for any future restoration of these materials.

Keywords: raw clay materials; provenance; archaeological ceramics; lead isotopes; Marrakech

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1. Introduction

The study of archaeological ceramic provenance has become possible with the integration of multiple analytical techniques [1–8]. Therefore, provenance is more commonly assessed through the comparison of ceramics to reference pottery groups. A number of studies have been conducted to establish the link between pottery and its raw materials (e.g., [9–13] and to explore their manufacturing technology (e.g., [14]). Previous studies show that the elementary composition of ceramics is highly correlated with their raw materials [13,15]. Mineralogical and chemical analyses are then used as tools for provenance studies of archaeological materials. However, several factors can affect ceramics after production, including atmospheric contamination and physico-chemical alteration that can modify the chemical composition of the ceramic product from their raw materials. For this reason, it is common in ceramic provenance studies to combine different analytical techniques [16–18] and to compare archaeological ceramics with a reference material, comprised of ceramic samples with a known or assumed origin [15,19]. Recent studies have demonstrated the effectiveness of lead isotope analyses in pottery provenance studies: they appeared to be an effective tool, not only to discriminate between different materials, but also to link ceramics and their clay sources [8,20,21].

In this study, the mineralogical and the elemental compositions supported by lead isotope analysis are used to link between potential raw materials and Saadien decorated ceramics called zellij. These glazed ceramics are used to decorate walls, floors, and fountains, and are characterized by an array of intricate shapes and vibrant colors. This art form reflects the rich heritage and craftsmanship of terracotta art in Morocco, particularly during its historical zenith. Zellij patterns generally consist of an eight-pointed star called "Khatem", which is often surrounded by a mosaic of over twenty different geometric patterns [22]. These patterns are meticulously hand-cut from glazed tiles and then assembled into complex, interlocking designs. The use of zellij dates back to the Hispano-Moresque period, and its techniques and styles have been passed down through generations. The most common colors used in zellij are cobalt blue, white, green, yellow, and sometimes black, each representing various elements of Moroccan culture and nature [23]. The creation of zellij is a highly skilled craft that requires precision and patience, symbolizing not only artistic beauty but also the cultural and historical essence of Moroccan architecture.

Previous studies were carried out to identify the composition of these ceramics and to understand their manufacturing technology [24,25]. However, the question about provenance remains unanswered: some hypotheses attribute the decorated ceramics of the Marrakech building to Benjlikh raw materials of the Fez region (the first center of manufacturing zellij in Morocco) based on the observation of the glaze/shard interface [23]. On the other hand, the large distance between these two cities "Fez and Marrakech" with the limited transportation means during the 16th century in Morocco suggests that these materials were made in Marrakech using local raw materials.

Saadien historical monuments of Marrakech are listed among UNESCO World Heritage sites for having cultural and historical significance. Despite the efforts made by the inspection of historical buildings in Morocco, the ceramics inside these monuments have reached an advanced state of degradation, which requires conservation–restoration strategies based on scientific and technical studies. Therefore, this study will help to enrich the heritage documentation and will be used as a reference for any restoration attempt in the future.

2. Materials and Methods

The studied ceramics were taken from the El Badi Palace (PBZ) and Saadien Tombs (TSZ), historical buildings established by Ahmed Al-Mansour at the end of the 16th century (Figure 1).

Figure 1. Saadien decorated ceramics (zellij) of El Badi Palace and Saadien Tombs (Marrakech, Morocco).

The sampling technique inside these buildings was conducted under the supervision of the Historical Monument Inspectorate of Marrakech, to ensure team safety and to preserve the vulnerable areas inside each building. A total of 18 original zellij pieces with various shapes and colors were collected (9 samples for each Saadien monument). All were then compared with six samples collected from clay deposits that can be considered as the raw materials of these decorated ceramics (Figure 2):

- The clay–limestone of the Benjlikh site from Fez region (ARF).
- The clay deposits used in the five most important potter villages of the Marrakech region, such as:
    - Quaternary clay deposits collected along rivers of the Marrakech Plain (TEN) and (ZAR);
    - The Pliocene clay deposits of Mzouda "MZD" (located 70 km from Marrakech city);
    - The Triassic clays of Ourika "OUR" and "ARK" (located 35 km from Marrakech city).

The manufacturing technology of traditional ceramics differs from one site to another depending on various factors, including weather, type of ovens and raw material properties (Table 1). These sites were chosen because the studied monuments are located in Marrakech, so the building materials used in them should come from a source close to the city. However, previous studies indicate that decorative materials of Saadian buildings, particularly zellij, were imported from the city of Fez [16–18] based on the manufacturing technology and the geometric pattern of zellij. For this reason, clays from Fez and Marrakech were considered in this study.

The mineralogical composition analysis of raw materials was performed by X-ray diffraction using a Bruker D8-Advance diffractometer with CuKα radiations (scan step size: 0.02°; time/step: 0.6 s; anode: copper with Kα = 1.5418 Å) on powdered bulk sediment. The background noise of the X-ray patterns was removed, and the line position and intensity diffraction peak were calculated with DIFFRACplus EVA 5.1 software (Bruker). High-temperature crystalline phases of fired clay samples were estimated based on the peak area to total diffractograms using DIFFRACplus EVA software. Bulk mineralogical quantification was based on the Rietveld method using TOPAS 2.1.0 software. The evolution of the mineralogical composition of the studied clays during firing was carried out by X-ray diffraction. Each sample was fired in a programmable oven at a temperature ranging from 500 to 1000 °C, with a 4-h time delay. The mineralogical composition diffractograms obtained were then compared with those of the studied ceramics.

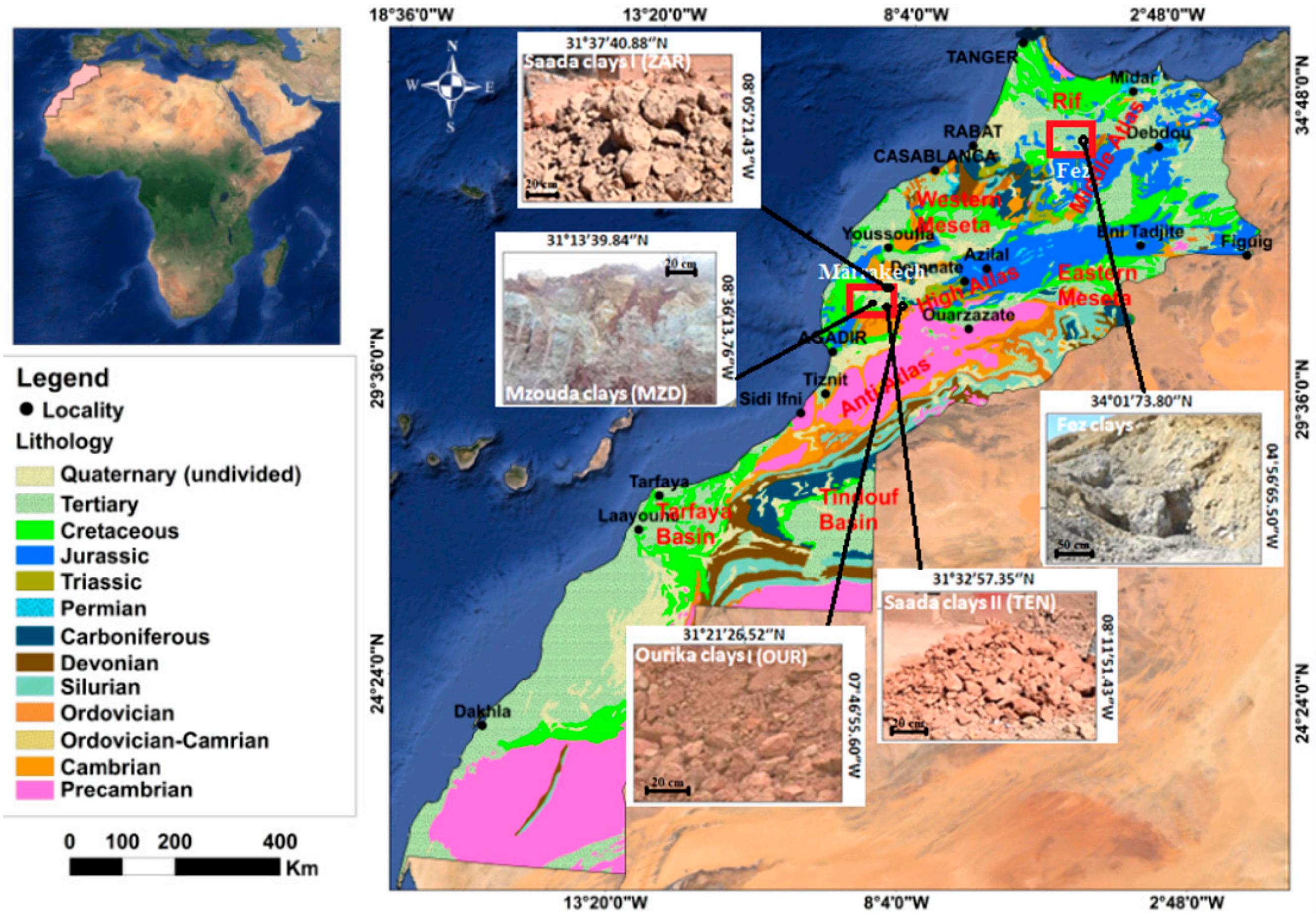

Figure 2. Location of the six potter sites considered as the potential sources of raw materials of Saadien zellij.

Table 1. The main characteristics of the studied clays and their manufacturing parameters.

Site	Sample	Lithology	Color	Type of Kiln	Firing Temperature	Firing Time	References
Fez (Benjlikh)	ARF	Marls	Grey	Traditional	950 °C	4 h (in summer), 8 h (in winter)	[22]
Ourika	OUR	Mudstone	Red	Gas kiln	950 °C	6 h	[26]
	ARK	Mudstone	Red				
Saada	TEN	Silt/Clay Sediment	Red	Traditional and Gas kilns	900 to 950 °C	3 h	
	ZAR	Silt/Clay Sediment	Grey				
Mzouda	MZD	Colluvial clays	Red	Gas kiln	850 to 950 °C	7 h (100°/h) + 4 h (50°/h)	

The chemical composition of major elements was determined by X-ray fluorescence spectroscopy (XRF) on lithium–borate fused glass [27] coupled with a Panalytical Axios spectrometer equipped with Rh-tube, using argon-methane gas. Loss of ignition (LOI) was obtained by heating samples at 1000 °C for 2 h. Data processing was performed with the IQ+ 3.3 software (University of Liège, Belgium).

The Pb purification was achieved on micro-columns of AG1-X8 resin following the chromatographic technique described by [28]. The Pb isotopes (^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb) were measured by static multi-collection in dry mode on Nu Plasma MC-ICP-MS instrument (ULB, G-Time, Belgium). Measurements were corrected for mass bias by using Tl as an internal standard. The sample standard bracketing method was then used to correct instrumental drift. Values were corrected using the NBS 981 standard solution and sample-standard bracketing method (as described by [28,29]), replicates (i.e., a second analysis of the same sample) and duplicates (i.e., the entire procedure was reproduced on the same sample) were measured to test the reproducibility.

It is important to mention that the Saadian zellij was glazed with a lead base glaze [24] and the shard is porous, which implies that the glaze elements can penetrate the upper part of the zellij shard during firing [23]. Taking into account these results the extraction of the analyzed part for Pb isotopes analysis was carried out at the basal section of the shard far from the glaze–shard contact to avoid analyzing lead from the glaze instead of from the shard.

3. Results and Discussion

3.1. Chemical and Mineralogical Composition

In Marrakech, clay samples (OUR, ARK, MZD, TEN, ZAR in Table 2) are rich in SiO_2 (48–64 wt.%) and Al_2O_3 (12–19 wt.%) oxides, related to the clay minerals and quartz particles. These clays show relatively high amounts of iron (6–8 wt.%), which is responsible for the reddish color of the ceramic products after firing [30,31]. The contents of K_2O and MgO range between 1-3 wt.% and can be attributed to the presence of illite in the clay fraction. The clays of the Marrakech region are poor in CaO (0-7 wt.%), while the LOI values range between 6 and 13 wt.%, which is related to the dehydroxylation of the clay minerals, the combustion of organic matter and the decomposition of carbonates [32,33] (Table 2). Marrakech clays are mostly non calcareous raw materials with high amounts of quartz and feldspars [26–34].

The raw clay material from Fez (i.e., ARF in Table 2) shows higher quantities of CaO (>13 wt.%). The LOI and FeO_2 contents were about 10.7 wt.% and 5.2 wt.%, respectively. The mineralogical composition shows high values of calcite and dolomite with relatively low contents of quartz, K-feldspar and plagioclases compared to the Marrakech clays (Figure 3) [13,23].

All the original Saadien zellij (i.e., PBZ and TSZ samples in Table 2) are lime-silica ceramics with 41–57 wt.% of SiO_2 and 11–22 wt.% of CaO. The Al_2O_3 content in these samples varies between 8–11 wt.% for PBZ and 9–14 wt.% for TSZ, being on average lower than the Marrakech clays. The concentration of the iron oxide does not exceed 5 wt.%, while MgO, K_2O, Na_2O and TiO_2 are present as traces (<2wt.%). These zellij samples have similar mineralogical composition [24]: the shards are rich of quartz (26–34 wt.%), plagioclase and alkali feldspar (17–29 wt.%), Ca-silicates (13–19 wt.% of diopside and gehlenite) and calcite (9–25 wt.%) with minor amount of hematite (3 wt.%) (Figure 3).

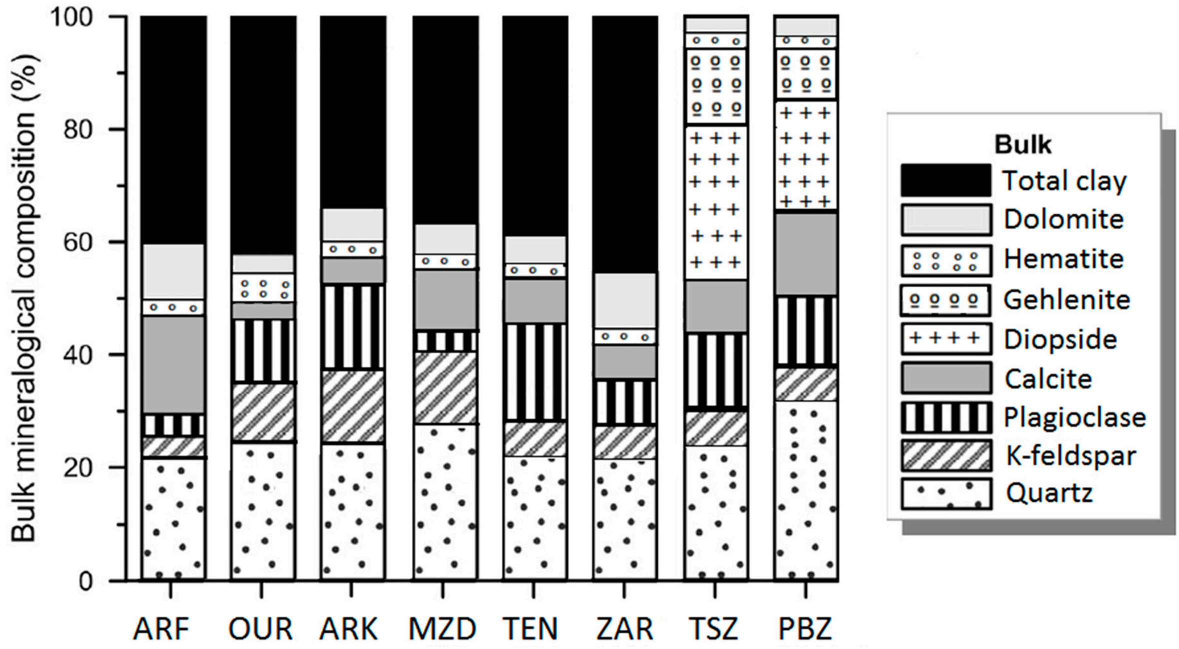

Figure 3. Mineralogical composition of the bulk samples.

Table 2. The chemical composition (wt.%) of the studied materials.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	MnO	P_2O_5	LOI
						Clay minerals					
OUR1	60.05	19.43	7.43	0.45	3.23	1.31	0.21	1.19	0.02	0.1	6.58
OUR2	63.99	13.22	5.6	1.71	3.05	2.08	0.27	0.98	0.04	0.06	8.99
OUR3	59.24	18.16	7.21	0.76	2.73	1.31	0.92	0.98	0.07	0.06	8.55
OUR4	58.71	19.06	7.76	0.62	3.34	1.21	0.6	0.9	0.11	0.03	7.66
ARK	57.35	16.8	7.11	1.99	2.28	1.53	1.31	0.76	0.1	0.02	10.75
MZD	56.38	12.62	5.49	7.84	2.47	2.27	0.76	0.66	0.1	0.18	11.22
TEN	48.88	16.51	6.25	7.27	3.07	3.2	0.99	0.66	0.18	0.19	12.8
ZAR	48.57	17.61	7.22	4.42	3.5	3.58	0.97	0.77	0.28	0.17	12.9
ARF	47.43	10.29	5.26	13.63	1.55	2.55	0.34	0.55	0.04	0.19	10.73
						Archaeological ceramics					
PBZ1	55.92	11.14	4.67	11.55	2.62	1.83	0.87	0.76	0.08	0.18	10.63
PBZ2	55.46	11.72	5.34	14.09	2.09	2.82	0.57	0.62	0.05	0.27	7.09
PBZ3	57.75	11.66	4.78	14	2.23	2.06	0.79	0.79	0.09	0.19	5.59
PBZ4	56.63	12.52	5	12.26	2.76	2.04	0.87	0.82	0.09	0.19	6.27
PBZ5	55.12	11.2	5.13	14.99	3.01	2.1	0.56	0.53	0.05	0.25	7.85
PBZ6	52.6	11.7	4.75	14.64	2.54	1.94	0.92	0.75	0.09	0.28	10.11
PBZ7	56.73	10.99	5.13	13.81	1.89	2.67	0.54	0.58	0.04	0.23	7.12
PBZ8	45.94	8.82	3.65	17.88	1.78	1.78	0.74	0.58	0.06	0.17	18.76
PBZ9	45.79	10.82	4.34	18.57	2.1	1.97	1.07	0.7	0.08	0.17	13.81
TSZ1	49.42	10.96	5.07	16.4	1.84	3.05	0.57	0.58	0.05	0.2	11.11
TSZ2	50.11	11.95	4.84	16.02	2.56	2.3	1.3	0.75	0.09	0.22	9.7
TSZ3	49.72	11.58	4.66	16.21	2.42	2.27	1.1	0.75	0.08	0.16	10.37
TSZ4	46.53	11.56	4.69	22.03	1.99	2.48	1.25	0.72	0.08	0.18	7.67
TSZ5	41.45	9.13	3.67	19.41	1.68	1.84	1.08	0.61	0.06	0.13	20.55
TSZ6	48.91	11.61	4.64	15.87	2.05	2.54	1.33	0.73	0.08	0.21	11.75
TSZ7	57	14.07	5.65	11.7	2.93	2.28	1.16	0.84	0.1	0.29	3.59
TSZ8	48.21	11.11	5.02	16.45	2.4	2.58	1.12	0.75	0.07	0.19	10.89
TSZ9	44.96	11.17	4.52	21.45	2.11	2.19	1.84	0.78	0.09	0.29	7.55

The mineralogical and chemical results can provide information about the provenance of the clays used for the archeological Saadien zellij. The principal component analysis (PCA) reveals two groups of samples (Figure 4). The first group is composed of materials with high amounts of CaO and MgO, while the second one includes samples with high contents of iron silica and aluminum. In the ternary diagram, Fe_2O_3 – CaO + MgO − K_2O + Na_2O, clays of Mzouda and Fez plot closely to the Saadien zellij samples (PBZ and TSZ) (Figure 4), due to their high amount of CaO and MgO. Principal component analysis and similarity diagram show the same results (Figure 5). Based on these diagrams, the clays from Fez region ARF are the more likely source of the Saadien zellij, followed by Mzouda clays (MZD) of Marrakech, while OUR, ARK, ZAR and TEN are excluded.

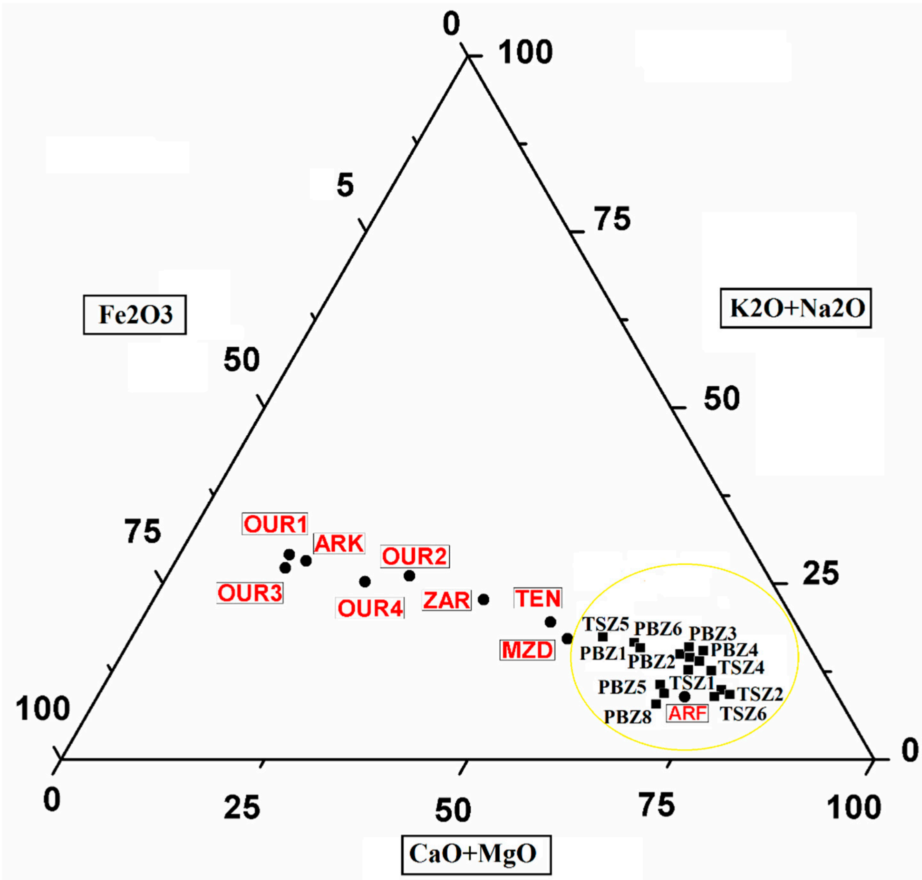

Figure 4. Ternary diagram (Fe_2O_3 – CaO + MgO − K_2O + Na_2O) obtained from the chemical composition of the studied materials.

3.2. Characterization by Lead Isotopes

The measured lead isotope values range between 38.21 and 39.08 for $^{208}Pb/^{204}Pb$, 18.21 and 18.93 for $^{206}Pb/^{204}Pb$, 2.07 and 2.10 for $^{208}Pb/^{206}Pb$ and 0.83 to 0.86 for $^{207}Pb/^{206}Pb$ (Table 3). Most of the archaeological Saadien ceramics present high values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$. However, Marrakech clays display a lead isotopic signature that differs from these materials. The Fez and Mzouda clay isotopic signatures are close to the range of the zellij samples, and they plot in a group with low values of $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ with high values of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ (Figure 6). These results are in good agreement with those obtained above using the chemical and mineralogical analyses indicating that archaeological Saadien ceramics were made using calcareous raw materials brought from Fez (the first site of manufacturing zellij in Morocco) or from clays of Mzouda.

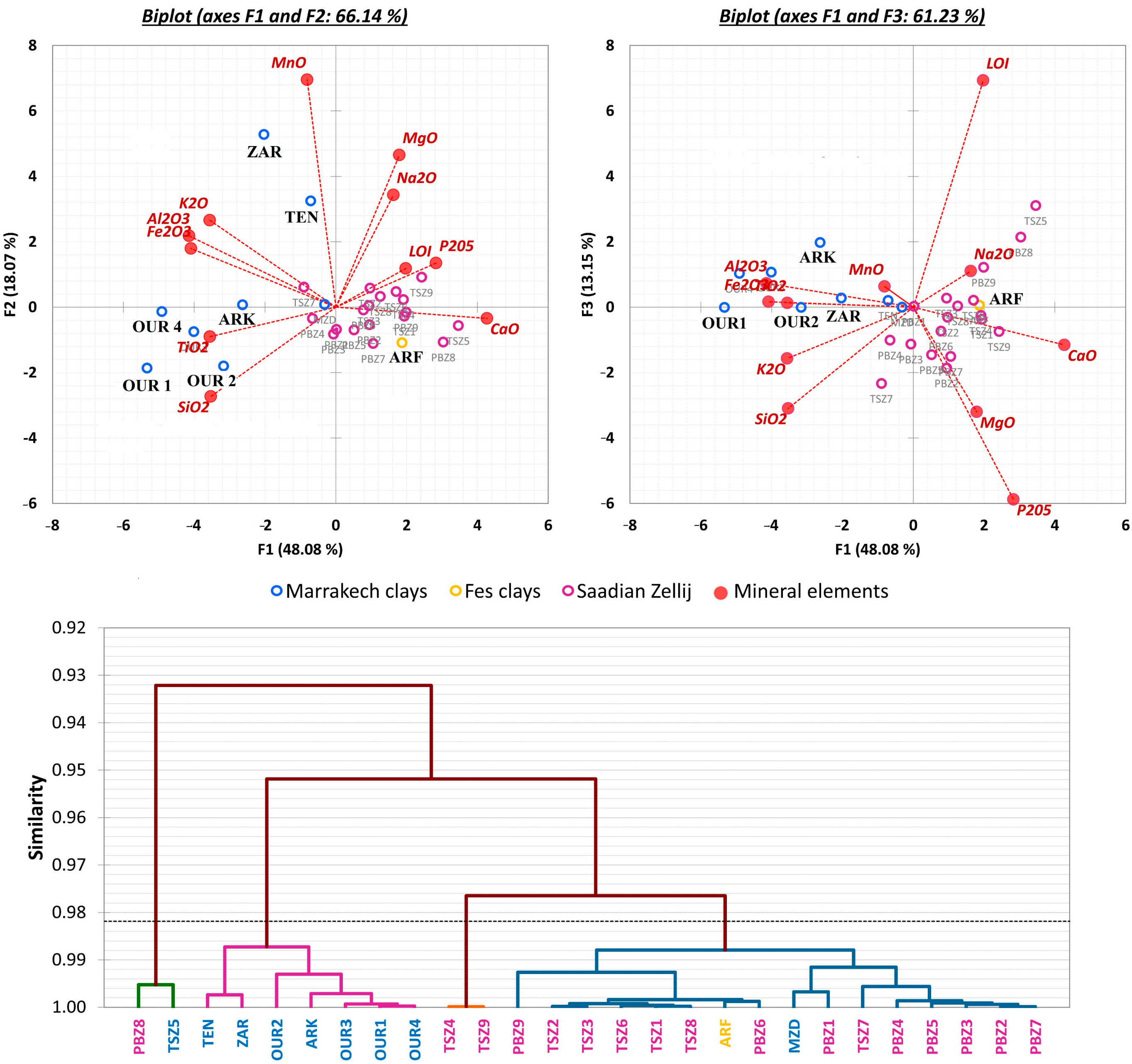

Figure 5. PCA (Biplots: axes F1/F2 and F1/F3) and Similarity diagram.

Table 3. Lead isotopic signature of the Fez and Marrakech clays and archaeological Saadien ceramics.

	Name	Weigth (mg)	208Pb/204Pb	2se	206Pb/204Pb	2se	208Pb/206Pb	2se	207Pb/206Pb	2se
Clays	**MZD**	90.9	38.40	0.0019	18.41	0.00096	2.08	0.000040	0.84	0.000012
Clays	**OUR**	94.9	39.08	0.0020	18.93	0.00085	2.06	0.000037	0.82	0.000011
Clays	**ZAR**	100.5	38.96	0.0021	18.71	0.00083	2.08	0.000035	0.83	0.000012
Clays	**ARK**	105.6	38.64	0.0023	18.50	0.00095	2.08	0.000043	0.84	0.000012

Table 3. *Cont.*

	Name	Weigth (mg)	208Pb/204Pb	2se	206Pb/204Pb	2se	208Pb/206Pb	2se	207Pb/206Pb	2se
Clays	**TEN**	99.5	38.58	0.0020	18.54	0.00077	2.08	0.000041	0.84	0.000013
Clays	**ARF**	106	38.21	0.0017	18.21	0.00070	2.09	0.000044	0.85	0.000011
Zellige El Badi Palace	**PBZ1**	108.3	38.27	0.0022	18.43	0.00096	2.07	0.000038	0.84	0.000011
Zellige El Badi Palace	**PBZ2**	93.7	38.83	0.0020	18.65	0.00088	2.08	0.000039	0.83	0.000011
Zellige El Badi Palace	**PBZ3**	97.8	38.39	0.0022	18.36	0.00065	2.09	0.000043	0.85	0.000014
Zellige El Badi Palace	**PBZ4**	109.6	38.36	0.0018	18.41	0.00074	2.08	0.000039	0.84	0.000011
Zellige Saadien Tombs	**TSZ1**	100.8	38.46	0.0019	18.26	0.00076	2.10	0.000042	0.85	0.000013
Zellige Saadien Tombs	**TSZ2**	95.1	38.31	0.0020	18.42	0.00077	2.07	0.000047	0.84	0.000012
Zellige Saadien Tombs	**TSZ3**	100.2	38.35	0.0017	18.31	0.00080	2.09	0.000041	0.85	0.000013
Zellige Saadien Tombs	**TSZ4**	102.5	38.38	0.0017	18.42	0.00077	2.08	0.000039	0.84	0.000011

Despite the distance separating the two deposits, the Fez and Mzouda clays come from the same geological context, namely the marls of the Mio-Pliocene series, which explains their similarity in terms of chemical and isotopic composition. However, the Mzouda clays are relatively richer in quartz and K-feldspars than the Fez clays.

Lead isotopes are an excellent tool that discriminate efficiently between the various clay sources proposed by petrography and elemental chemistry [35]. The lead isotope ratios reflect the common clay source used for Saadien zellij production and suggest the clays of Fez and Mzouda as potential raw materials.

3.3. Mineralogical Transformation During Firing

After identifying the most likely source of the studied Saadien ceramics, firing tests made on Fez and Mzouda clays between 500 and 1000 °C can provide more information about the origin and the manufacturing technology of these archaeological ceramics. Upon firing, the disappearance of total clay occurs at 550 °C in the calcareous raw clay materials [36], followed by the decomposition of $CaCO_3$ into CaO and CO_2 between 600 and 800 °C. The evolution of carbonates during the firing of this type of material is responsible for the neoformation of Ca-silicates like diopside and gehlenite around 700 °C [37–39]. The formation of Ca-silicates also depends on the amount of free lime, the grain size and the crystalline form of the starting raw materials, as they can co-exist with calcite in high temperature in cases of excess calcite, large calcite grains and well-crystallized form of calcite [40]. Calcite and muscovite disappear completely above 1000 °C. Mineral modifications for non-calcareous clays are characterized by the loss of all phyllosilicates including muscovite from 950 to 1000 °C, and plagioclase at 1100 °C. Quartz and hematite persisted up to 1100 °C. Spinel formed at 950 °C, followed by mullite and cristobalite at 1000 °C in quartz-rich clays [41].

The mineralogical composition obtained between 600 and 700 °C by firing Fez clays using the traditional oven in an oxidizing atmosphere is similar to El Badi Palace zellij's composition (Figure 7). The diopside and gehlenite contents are around 12 wt.% and 11 wt.%, respectively, at this range of temperature, and the calcite amount is about 13 wt.%. At 800 °C, diopside reaches 18 wt.% and gehlenite 13 wt.% with a decrease in calcite amount to 7 wt.%. This composition is close to Saadien Tomb zellij, which suggests that these materials were manufactured at high temperatures compared to the El Badi Palace ceramics.

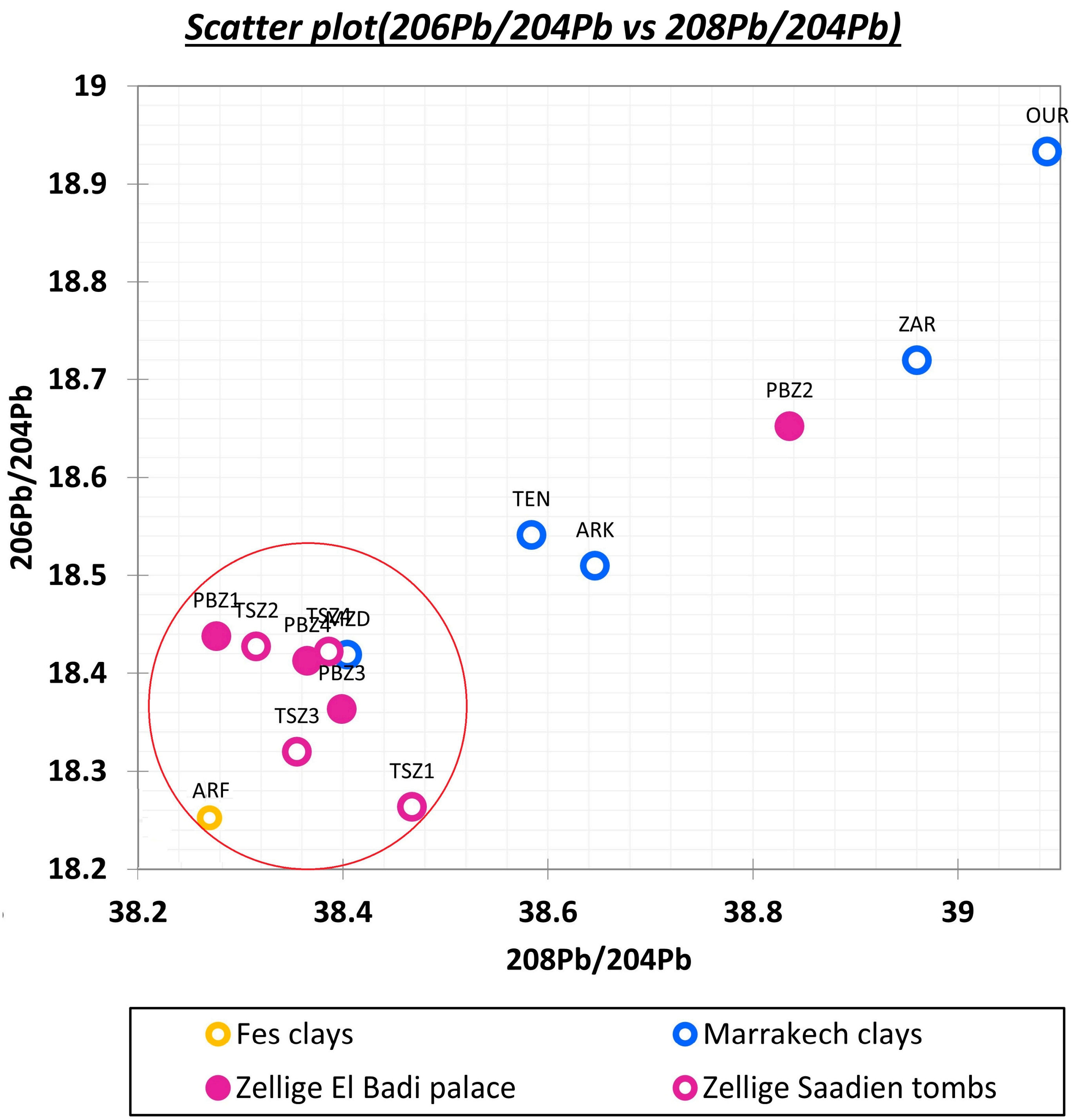

Figure 6. $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{204}Pb$ isotope plot comparing the lead isotope signatures of Marrakech and Fez clays with Saadien zellij.

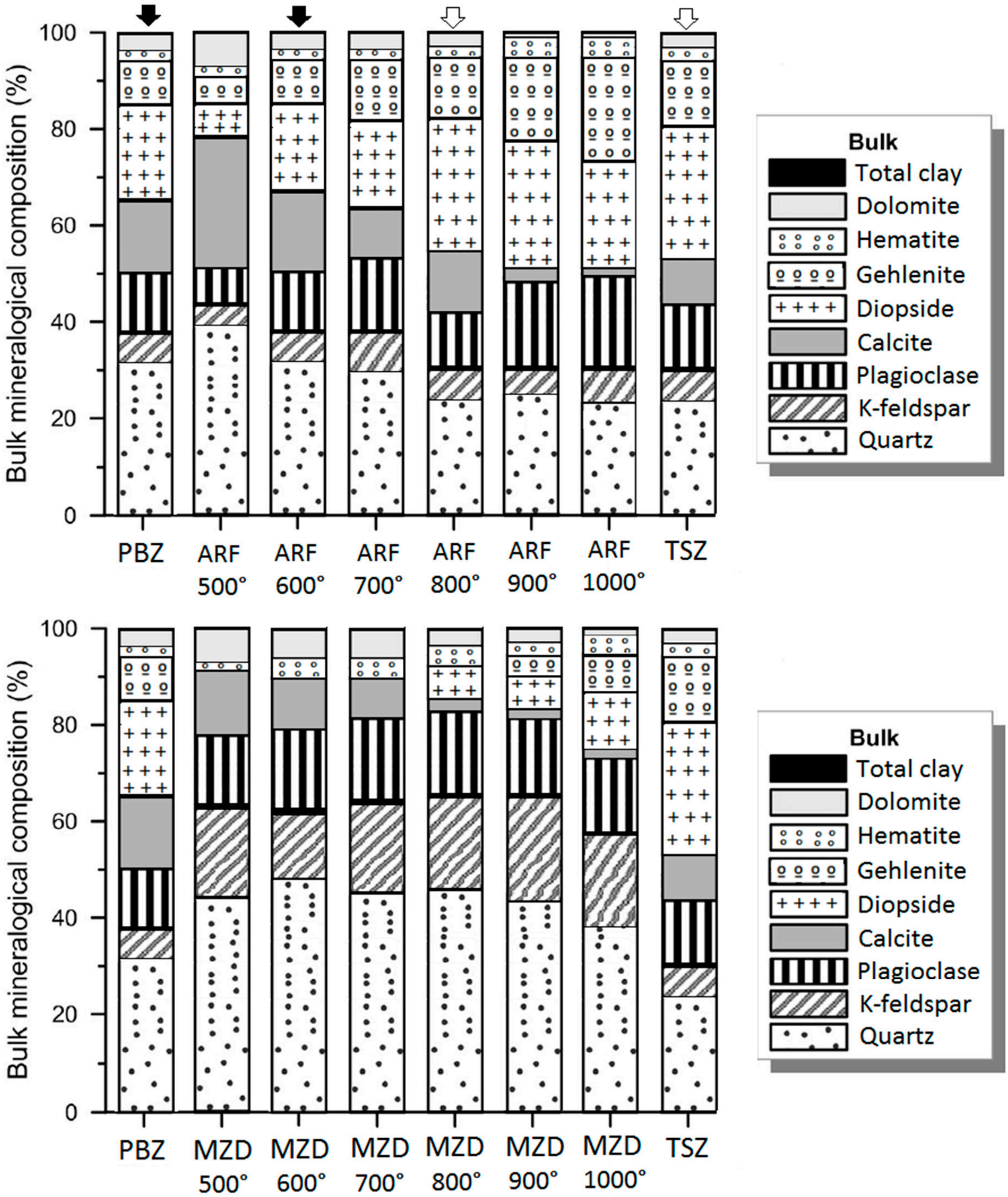

Figure 7. Evolution of the mineralogical composition of Fez and Mzouda clays after firing tests in traditional oven.

4. Conclusions

Chemical, mineralogical and lead isotope compositions were used to trace the provenance of the archaeological decorated ceramics from two historical monuments (El Badi Palace and Saadien Tombs) of Marrakech. The data were compared with six potential regional sources of raw clay materials. This multi-analytic approach yielded three main conclusions:

- The zellij of El Badi Palace and the Saadien Tombs were either imported by Saadien artisans directly from the Benjlikh site of Fez or manufactured in Marrakech using the raw clay materials brought from Fez clay deposits.

- Calcareous clay materials were used to manufacture the Saadien ceramics in traditional ovens with an oxidizing atmosphere.
- The firing temperature of the El Badi Palace ceramics ranges between 600 and 700 °C, while the Saadien Tomb zellij was manufactured at 800–900 °C.

Further investigations coupling lead isotopes, mineralogy and elemental analysis should allow the refinement of hypotheses on the provenance of the other ceramics from other archeological buildings in Marrakech.

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