



Ceramic replicas of archaeological artefacts in Benevento area (Italy): Petrophysical changes induced by different proportions of clays and temper

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ABSTRACT

The Gran Potenza clay and the Pomici di Avellino pyroclastics, respectively the clay sediments and temper of the typical ceramic manufacture in Benevento area (Italy), were mixed in different proportion and fired at 850°, 900° and 950 °C. These experimental replicas were compared with historical ceramic products of Benevento. The similarities and/or differences between archaeological materials and replicas (in terms of amount of temper, firing temperature, pore system, etc.) have been discussed. The whole data confirm the wide utilization of the local available clayey raw material and the Pomici di Avellino, and give a new contribution on the petrophysical modifications of volcanic-rich ceramic pastes that occur in the firing temperature range comprised between 850° and 950 °C. Some peculiar features in the historical manufacturing are also reported.

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1. Introduction

Exploitation and utilization of abundant clayey materials to produce ceramic artefacts was an ancient activity in the Benevento area (Italy) where, from Samnite (2nd century BC) to modern period, an extensive ceramic production is testified by important archaeological findings and large utilization in architectural heritage (Grifa et al., 2006, 2007a).

A large outcrop of clay-rich sediments, known as Gran Potenza hill, located near the Calore and Sabato river confluence and close to the medieval city wall, has been utilized until recent time for the production of pottery and bricks. This common clay deposit can be ascribed to the Grigio-Azzurre clay formation widespread on Apennine chain and extensively exploited for industrial ceramic production (Dondi et al., 1999). The same clayey raw materials were likely used to handcraft two different ceramic productions from the city of Benevento a fine-grained common ware (Protomajolica) and a coarse-grained brick production (Grifa et al., 2006, 2007a).

The so-called Protomajolica ceramic, widespread in Southern Italy during Middle Age, followed some technical peculiarities of Islamic tradition such as the glazed cover and the colourful decorations. The petrographical analyses carried out on a set of fragments from two different medieval sites in Benevento allowed to determine the technological features of the local Protomajolica production. Based on textural features (matrix/temper proportion) two different groups were distinguished: without (Group 1) or with a very low content of

volcanic temper (ca. 1%, Group 2). The estimated firing temperature of this ceramic class was 950 °C (Grifa et al., 2006).

The coarse-grained brick samples come from different buildings and archaeological sites in Benevento dated from Samnite to medieval ages. Microscopic observations showed a variable amount of volcanic temper (from 10 up to 15 mass%, measured by OM-modal analyses) as a function of the production age. The bricks were fired at temperatures lower than the Protomajolica ware, estimated between 850° and 900 °C (Grifa et al., 2007a).

The temper utilized, identified with the Pomici di Avellino, were formed by a well sorted volcanic deposit with crystals (sanidine, clinopyroxene, plagioclase and biotite) and juveniles (pumices and scoriae).

The present research aims at reproducing at laboratory scale ancient potteries by mixing in different proportions (0–1–10 mass%) and firing at different temperatures (850°, 900° and 950 °C) the two raw materials likely used in the above reported archaeological findings (the Gran Potenza clay and a temper belonging to the Pomici di Avellino formation) to attain products as much as possible similar to these archaeological artefacts.

Mineralogical and textural changes induced by firing and temper addition were then evaluated on the fired replicas and compared with those measured on the ancient manufactures. Moreover pore size distribution and wetting behaviour were also determined to highlight physical changes induced by reaction dynamics.

Several papers described mineralogical and textural changes of clay materials subjected to firing. Pyrometamorphic reactions and dynamics of new and prograde phases were well defined considering

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both CaO-rich and CaO-poor clays (Duminuco et al., 1996; Riccardi et al., 1999; Cultrone et al., 2001; Aras, 2004; Maritan et al., 2006; Nodari et al., 2007). Microtextural changes due to the increase of firing temperature in terms of melting and vitrification development of ceramic paste were described by Tite and Maniatis (1975). Other authors pointed out that textural changes influence porosity, water adsorption, linear shrinkage and mechanical resistance of ceramics (Mallidi, 1996; Dondi et al., 1998; Cultrone et al., 2004).

Regarding additional components commonly mixed to clay to improve technical properties of ceramics, other papers highlighted how vitrification, wetting behaviour, porosity and mechanical properties can be influenced by the type of temper used such as feldspar- and feldspathoid-bearing rocks, quartz-feldspar sands or calcite, dolomite and salts when available clays do not satisfy quality criteria (Fabbri and Fiori, 1985; Parras et al., 1996; Cultrone et al., 2005).

However, no data are so far available about the interaction between clayey particles and volcanic sands during firing and how these tempers influence the ceramic properties, despite the large use of volcanic products in ceramic artefacts since pre-historic age as commonly found in the Benevento area. On this account, the Campania region (Southern Italy, Fig. 1) offers a wide range of examples due to the large availability of pyroclastics and volcanics, mainly deriving from the activity of the Somma–Vesuvius, Campi Flegrei and Ischia volcanic districts (Grifa et al., 2007b, 2009).

2. Geological setting

Benevento is located in a Plio-Pleistocene tectonic depression bordered by N–NE faults, with pre-Quaternary rocks widely deformed, and upper monoclinic undeformed continental deposits, deriving from the modelling and depositional action of Calore and Sabato rivers (Fig. 1). The town is entirely built on ancient terraced alluvial deposits (Middle Pleistocene) made up of stratified conglomerates with sand, silt and clay interlayers (Pescatore et al., 1996).

Younger terraced alluvial deposits are also recognized, in SE area of the town and along the Sabato river (Fig. 1); recent alluvial and colluvial deposits overlay the terraces. Volcano-clastic deposits are often encountered belonging to the Campanian Ignimbrite and Pomici di Avellino fall-out deposits. Campanian Ignimbrite deposit is the product

of the most powerful eruption of Campi Flegrei occurred 39,000 yBP (e.g. Fedele et al., 2008). Pomici di Avellino formation (3700 ca. yBP) is related to the Somma–Vesuvius activity (e.g. Santacroce, 1987).

Middle Pliocene marine deposits are mainly constituted by sandy and clayey materials belonging to the Ariano Unit. The oldest deposits cropping out in the area are represented by the Lagonegro Units (Cretaceous–Lower Miocene; Coppa de Castro et al., 1969).

3. Materials and methods

Raw materials used for the present investigation and replicas are listed in Table 1. Both the clay raw material (GP) and the volcanic temper (AV) were sampled at the Gran Potenza hill site (Fig. 1). The raw material consists of a clay-rich deposit that belongs to the sedimentary cycle of the Ariano Unit to which defined proportions of pyroclastic products belonging to the Pomici di Avellino formation were added. The GP and AV materials were mixed to form ceramic pastes, trying to reproduce as much as possible historical samples of Protomajolica and bricks, in the following proportions:

- BN0 sample: 100 mass% GP;
- BN1 sample: 99 mass% GP + 1 mass% AV;
- BN10 sample: 90 mass% GP + 10 mass% AV.

The pastes were fashioned in a wooden mould (11.5×7×4 cm) and dried at a temperature of 20 °C and 50% RH. After 72 h the dried samples were fired in an air-ventilated electric oven (Herotec CR-35) at the following temperatures: 850°, 900° and 950 °C.

The oven heating rate was 3 °C per minute, with a soaking time of 1 h to 100° and 3 h at maximum temperature (i.e., 850°, 900° or 950°C). The entire firing-cooling cycle lasted 24 h.

Grain-size distribution of clay raw materials was determined following ASTM D1 140–92 (1992). Water content at limit liquid (W_L), plasticity index (PI) and activity of the clay fraction were determined according to ASTM D3017–88 (1993).

The mineralogical composition of the unfired samples and the evolution of mineralogy after firing were determined by X-ray diffraction (XRD) using a Philips PW-1710 diffractometer with automatic slit, CuK α radiation, 40 kV, 40 mA, 3° to 60° 2 θ explored area and 0.02° 2 θ ⁻¹

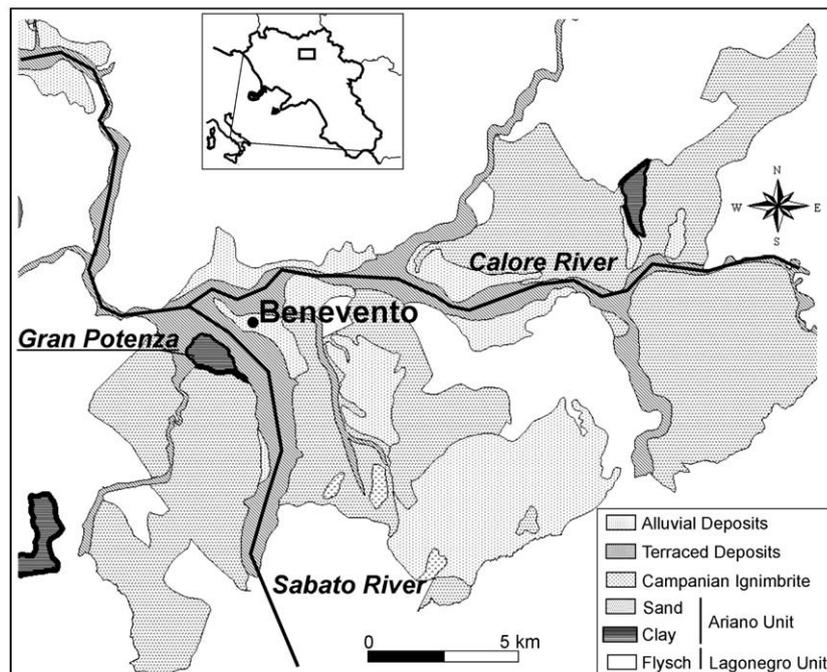


Fig. 1. Geological simplified sketch map of Benevento area (after Pescatore et al., 1996, modified).

Table 1
Description of the analyzed samples.

Sample	Type	Location	Description
GP	Clay-silt	Gran Potenza	Blue-greyish clay-silt sediment. Ariano Unit
AV	Pyroclastic fall	Gran Potenza	Pomici di Avellino. Unwelded pyroclastic deposit composed of pumice, scoriae and crystals. 20–40 cm thick.
BN0-dry	Replica		GP dried at 100 °C
BN0-850	Replica		GP fired at 850 °C
BN0-900	Replica		GP fired at 900 °C
BN0-950	Replica		GP fired at 950 °C
BN1-dry	Replica		GP + AV (1%) dried at 100 °C
BN1-850	Replica		GP + AV (1%) fired at 850 °C
BN1-900	Replica		GP + AV (1%) fired at 900 °C
BN1-950	Replica		GP + AV (1%) fired at 950 °C
BN10-dry	Replica		GP + AV (10%) dried at 100 °C
BN10-850	Replica		GP + AV (10%) fired at 850 °C
BN10-900	Replica		GP + AV (10%) fired at 900 °C
BN10-950	Replica		GP + AV (10%) fired at 950 °C

goniometer speed. Semi-quantitative analyses were performed using experimentally determined reflectance power of each phase, according to the method proposed by Culliti (1956) and Rodríguez Gallego et al. (1968). To determine the mineralogical composition of the clay fraction, a dilute acetic acid was used to remove the carbonates. The < 2 µm fraction was separated from the whole sample by centrifugation. The clay fraction was smeared on glass slides and air dried. The slides were then saturated with ethylene glycol at 80 °C for 24 h (Brunton, 1955) to ensure maximum saturation, reacted with dimethyl sulphoxide to differentiate

kaolinite from chlorite (Gonzales Garcia and Sanchez Camazano, 1968), and heated at 550 °C for 1 h (Moore and Reynolds, 1997).

Bulk chemical analyses of the raw materials (clay and temper) and fired bricks were carried out by X-ray fluorescence (XRF, Philips PW-1480); ZAF correction was performed (Scott and Love, 1983) and international standards were used (Govindaraju, 1989). Detection limit for major elements was 0.01 mass% and for trace elements 1–5 ppm.

Thin sections were prepared for each sample and observed under polarized optical microscope (OM, Leitz Laborlux-F) to determine mineral phases and texture of the paste.

Microtextures and vitrification stage of ceramic samples were detected on small fragments using a scanning electron microscope (SEM) JEOL 5310.

The parameters associated to fluid uptake and transport inside the pores were determined by wetting tests. Water absorption (UNI EN 13755, 2008) and drying (NORMAL 29/88, 1988) were determined by weighing the samples at regular intervals. Absorption and saturation coefficients, drying index and open porosity were calculated (Cultrone et al., 2003).

Mercury intrusion porosimetry (MIP) was carried out on 2 cm³ specimens dried for 24 h at 110 °C using a Micrometrics Autopore III 9410 porosimeter with a maximum injection pressure of 414 MPa.

4. Results

4.1. Raw material and temper characterization

The main grain-size fraction of GP (Fig. 2a; 55 mass%) ranged between 0.002 and 0.06 mm (silt fraction); 37 mass% was clay, while

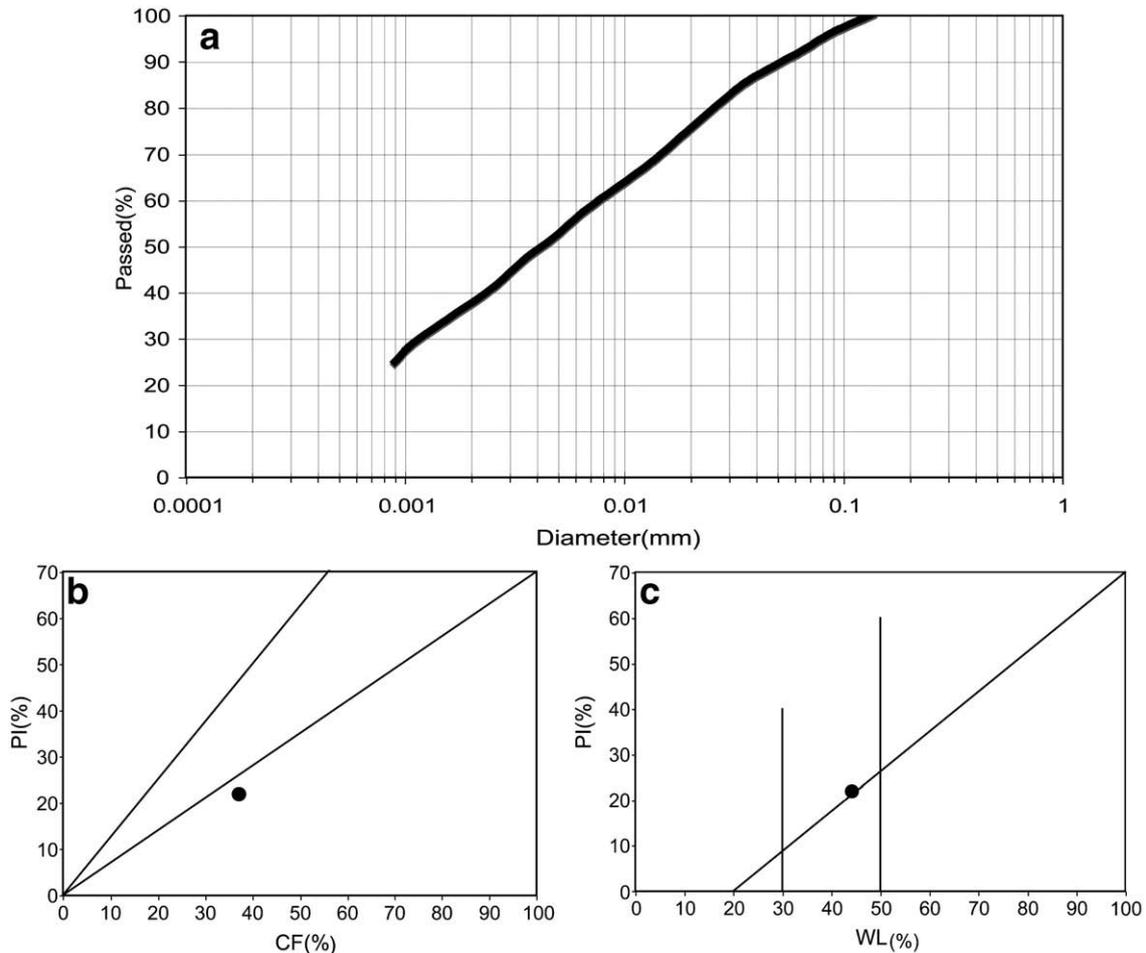


Fig. 2. Diagrams refer to the Gran Potenza (GP) clay, showing: a) cumulative grain-size distribution curve; b) clay fraction (CF) vs. plasticity index (PI); c) liquidity limit (W_L) vs. plasticity index (PI).

Table 2
Chemical (XRF) and mineralogical (XRD) composition of Gran Potenza clay (GP) and Pomici di Avellino (AV).

	XRF		XRD	
	GP	AV	GP	AV
SiO ₂	57.67	53.24	Quartz	xxxx
TiO ₂	0.69	0.45	Feldspars	x
Al ₂ O ₃	14.96	19.24	Calcite	xxx
Fe ₂ O ₃	5.51	4.32	I/S	xx
MnO	0.07	0.14	Kaolinite	x
MgO	3.36	3.00	Clinopyroxene	xxxx
CaO	14.15	7.54	Biotite	xx
Na ₂ O	1.02	5.17	Chlorite	x
K ₂ O	2.43	6.61	GP index parameters	
P ₂ O ₅	0.14	0.30	W _L	43.7
LOI	14.13	8.7	W _P	21.6
Sc	7	12	CF	37.0
V	113		PI	22.0
Cr	95	59	A	0.6
Cu	23	30		
Ba	232	850		
Zn	93	98		
Ni	42	21		
Y	16	22		
Zr	140	360		

Major (mass%) and trace elements (ppm) are reported; XRD results are expressed as semi-quantitative abundance (legend: xxxx = very abundant, xxx = abundant, xx = frequent, x = scarce, tr = traces); GP index parameters: W_L and W_P represent the liquid and plasticity limits (expressed in mass%); CF is the clay fraction (mass%); PI is the plastic index; A is the activity.

the remaining 8 mass% was sand. The clayey deposit can be classified as “clay with medium plasticity” according to ASTM D2487-93 (1993) standard. The low activity of the clay is expressed by the A index which measured 0.6 (Table 2) and by PI vs. W_L diagram (Fig. 2c). Plasticity index (PI=22.0) and plastic limit (W_P=21.6) of GP clay make them suitable for ceramic productions (Table 2).

As far as the detrital phases are considered, XRD analyses of bulk clay-rich samples (GP, Fig. 3a) showed quartz and calcite as major components and lower amounts of feldspars (Table 2). Oriented aggregates (inset in Fig. 3a) evidenced the presence of kaolinite, chlorite and illite/smectite mixed-layers (I/S; R = 0 ill = 20–30%, Moore and Reynolds, 1997).

The chemical composition of Gran Potenza raw material (Table 2) showed a high silica content (~58 mass%) as well as relevant CaO and Fe₂O₃ contents (14.1 mass% and 5.51 mass%, respectively). Among trace elements, Ba and V showed quite high values (232 and 113 ppm) whereas Sc and Y were definitely low (7 and 16 ppm, respectively).

XRD pattern of Pomici di Avellino (Fig. 3b), accounts for the prevailing amorphous character of this product; feldspars and clinopyroxene were recognized. From a chemical point of view sampled AV can be classified as a tephri-phonolite according to T.A.S. classification (Fig. 3b, inset; Le Bas et al., 1986). To be noted is the high content of Ba and Zr (850 ppm and 360 ppm, respectively; Table 2).

4.2. Optical microscopy

BNO samples showed a seriate texture with no-plastic inclusions ranging from 0.04 to 0.10 mm and an estimated packing of about 10% (Terry and Chilingar, 1955). Quartz, feldspar and rare carbonatic

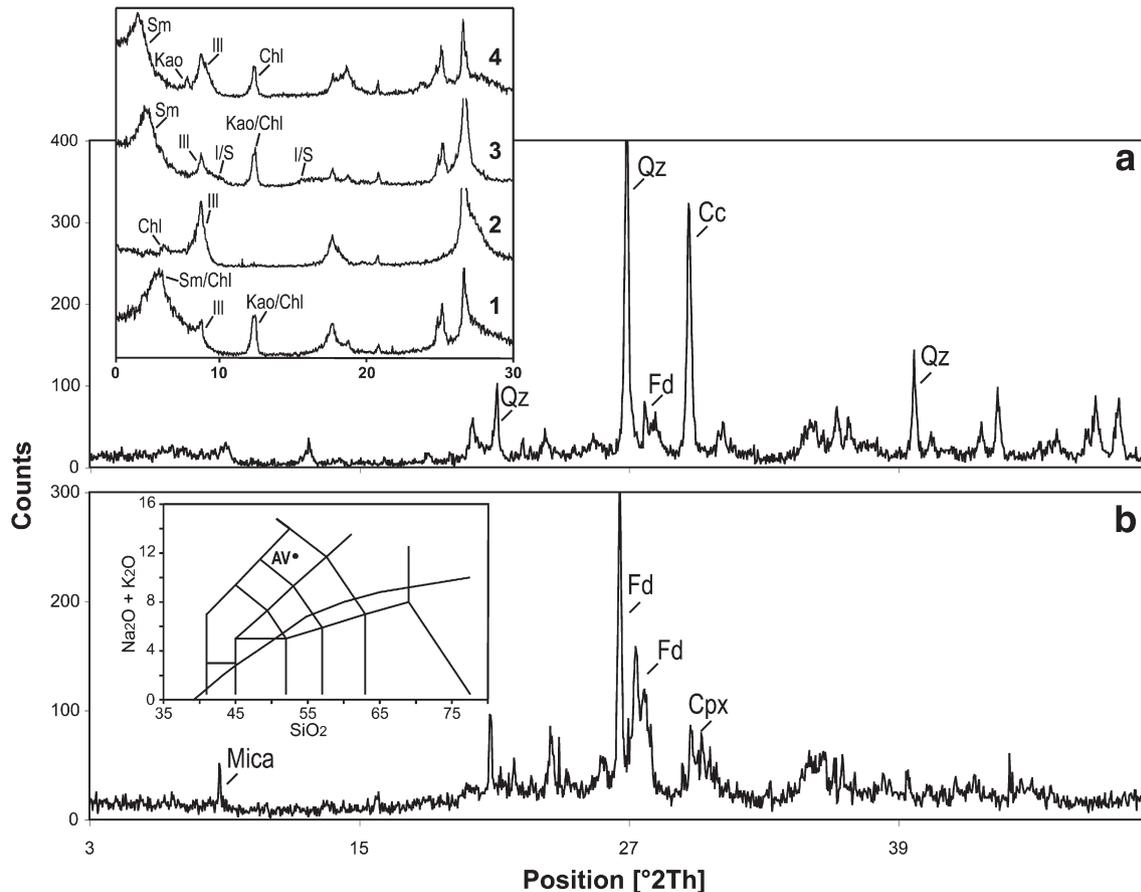


Fig. 3. XRD patterns of raw materials and temper. a) Gran Potenza clay (GP); in the inset, oriented aggregates: 1) air dried, 2) heated 550 °C, 3) ethylene glycol saturated, 4) DMSO; b) Pomici di Avellino (AV) volcanic deposit; in the inset T.A.S. diagram showing chemical classification (Le Bas et al., 1986). Main peaks of quartz (Qz), calcite (Cc), feldspar (Fd), clinopyroxene (Cpx), smectite (Sm), kaolinite (Kao), illite (Ill), chlorite (Chl) and I/S mixed layer minerals (I/S) are indicated.

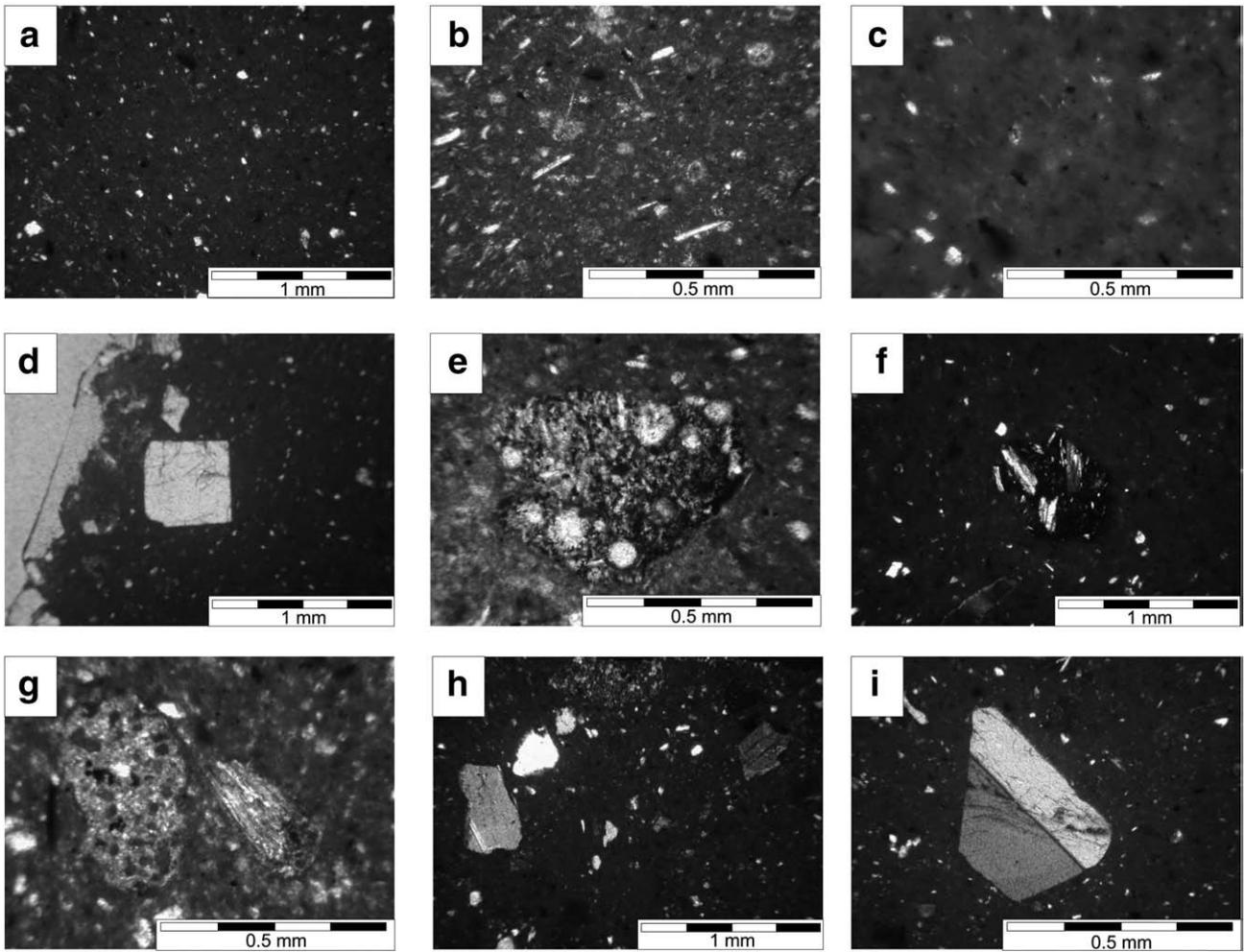


Fig. 4. Optical features of the fired specimens. a) matrix and no-plastic inclusions, BN0-850 sample, PPL; b) muscovite lamellae, quartz and feldspars in the clay matrix, BN0-900 sample, XPL; c) matrix and no-plastic inclusions, BN0-950 sample, PPL; d) sanidine crystal from volcanic temper, BN1-850 sample, PPL; e) leucite-bearing volcanic scoria, BN1-900 sample, PPL; f) trachytic scoria, BN1-950 sample, PPL; g) pumices, BN10-950 sample, PPL; h) Ca-rich pyroxene, BN10-900 sample XPL; i) sanidine, BN10-950 sample, XPL.

grains are the main detrital constituents although muscovite and biotite flakes have also been identified (Fig. 4a, b, and c).

BN1 samples showed a bimodal grain-size distribution due to the addition of a volcanic component (from 0.5 to 2.00 mm ca.) which increases the packing up to 15%. Sanidine (Fig. 4d), Ca-rich pyroxene, plagioclase, biotite, trachytic and leucitic scoriae (Fig. 4e and f) pumices and rare obsidian fragments were also observed, together with residual inclusions similar to those found in BN0 samples.

BN10 samples differ from samples BN1 for a higher content of volcanic grains (Fig. 4g, h and i) which leads to a higher packing (up to 25%).

Samples fired at the highest temperature (950 °C) showed an isotropic brown-orange matrix. Increasing temperature caused a progressive loss of the optical features of biotite (i.e. pleochroism and birefringence) due to its dehydroxylation; at 950 °C only pseudomorphs of former micas were observed (e.g. Rodríguez Navarro et al., 2003).

4.3. XRD

Unfired samples (BN0-dry, BN1-dry, BN10-dry; Table 3), as expected, showed similar mineralogical compositions: quartz, calcite, feldspars, I/S mixed layer minerals, chlorite and kaolinite (in the order of abundance). The XRD patterns did not record significant changes due to the addition of temper, except for a slight increase in the content of feldspars.

After firing, significant mineralogical changes were recorded for the three types of ceramic paste. As an example, Fig. 5 reports XRD patterns of sample BN0 at the different temperatures. A pronounced illite reflec-

tion corresponding to a dehydrated illite-like phase (Cultrone et al., 2001) was observed at 850 °C and was still present at 900 °C. The breakdown of this phase only occurred when samples were fired at 950 °C (Fig. 5a). At 850 °C calcite was almost totally dissociated (Fig. 5b). According to Boynton (1980), the calcite breakdown process occurs at 830–870 °C leading to the crystallization of a new calcium silicate phases such as gehlenite. As temperature increases (from 900° to 950 °C),

Table 3

XRD semi-quantitative results of the replicas (legend: xxxx = very abundant, xxx = abundant, xx = frequent, x = scarce, tr = traces).

Sample	Quartz	Feldspars	Calcite	Illite	Kaolinite	I/S	Chlorite	Cpx	Gehlenite
BN0-dry	xxxx	x	xxx	xx	x	x	x		
BN0-850	xxxx	xx	tr	tr				x	x
BN0-900	xxxx	xx						xx	x
BN0-950	xxxx	xx						xx	tr
BN1-dry	xxxx	x	xxx	xx	x	x	x		
BN1-850	xxxx	xx	tr	tr				xx	x
BN1-900	xxxx	xx						xx	tr
BN1-950	xxxx	xx						xx	tr
BN10dry	xxxx	xx	xxx	xx	x	x	x		
BN10-850	xxxx	xx	tr	x				x	x
BN10-900	xxxx	xx		tr				xx	tr
BN10-950	xxxx	xx						xx	tr
Protomajolica	xxxx	x						x	xx
Brick	xxxx	xx	tr	x					x

Representative values of historical Protomajolica ware and bricks from Benevento area are also reported (Grifa et al., 2006, 2007a).

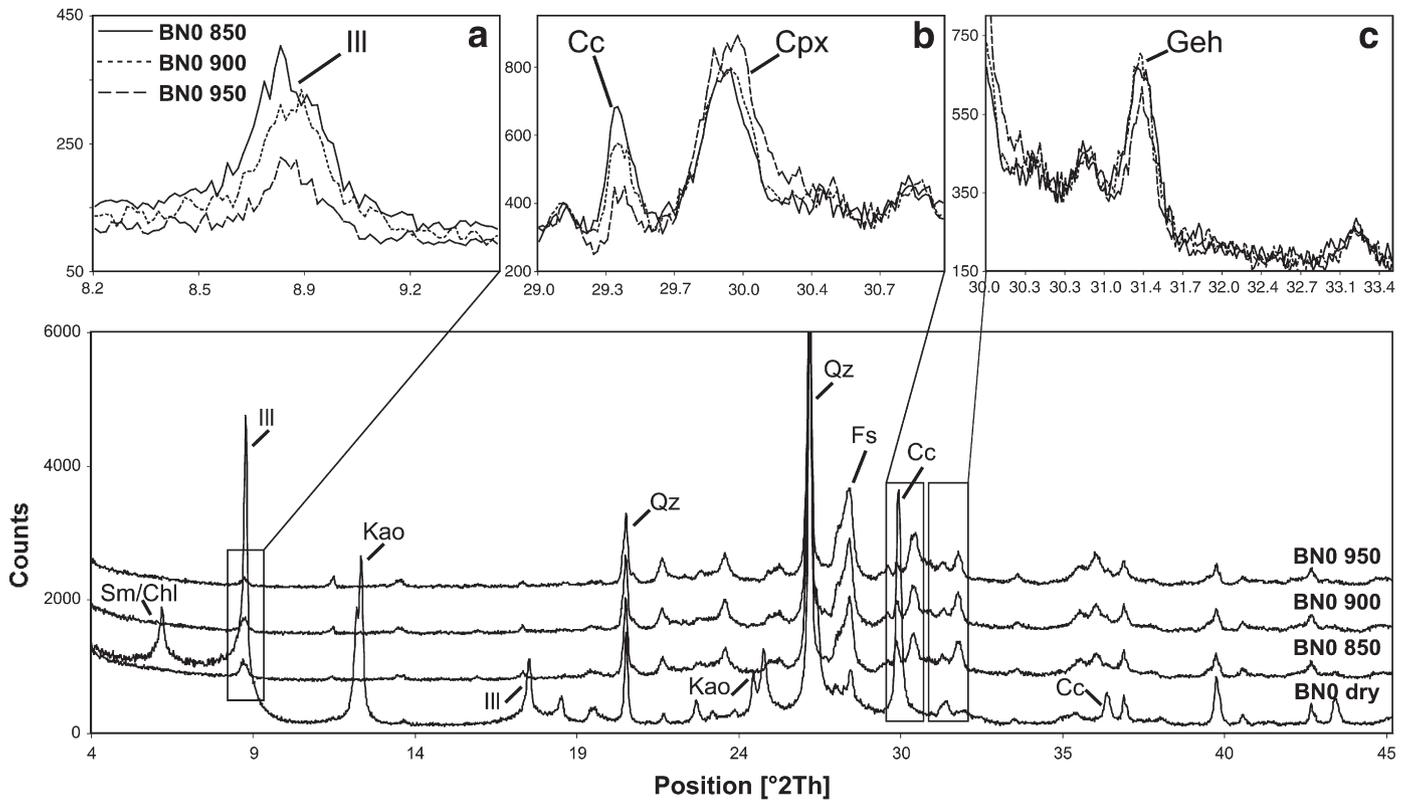


Fig. 5. XRD diagrams showing main mineralogical changes during firing of BNO pastes; the insets shows: a) illite peaks; b) calcite and Ca-rich pyroxene reflection; c) gehlenite reflection at the different temperatures. Main reflection of quartz (Qz), calcite (Cc), feldspar (Fs), Ca-rich pyroxene (Cpx), kaolinite (Kao), smectite/chlorite (Sm/Chl) and illite (Ill) are indicated.

gehlenite progressively disappeared, thus promoting the formation of a Ca-rich pyroxene (Fig. 5b, c). The same behaviour was recorded for samples BN1 and BN10 (Table 3).

4.4. XRF

Assuming an isochemical firing process, chemical analyses have been carried out only on specimens fired at the highest temperature (BNO-950, BN1-950, BN10-950, in Table 4). The isochemical process was confirmed by the almost similar composition of the raw material (GP, Table 2) and of replica without temper (BNO-950). As expected, only the LOI value shows a strong decrease from 14.1 to ~ 1%.

Table 4
Major (mass%) and trace elements (ppm) composition of the replicas fired at 950 °C.

	BNO-950	BN1-950	BN10-950
SiO ₂	57.60	57.39	58.01
TiO ₂	0.64	0.65	0.64
Al ₂ O ₃	15.80	15.71	15.86
Fe ₂ O ₃	5.57	5.55	5.59
MnO	0.06	0.06	0.07
MgO	3.31	3.31	3.24
CaO	13.31	13.62	12.68
Na ₂ O	1.09	1.06	1.15
K ₂ O	2.48	2.51	2.61
P ₂ O ₅	0.14	0.14	0.15
LOI	1.11	0.90	0.94
Sc	10	11	11
V	142	140	139
Cr	117	112	111
Cu	34	31	32
Ba	266	294	345
Zn	130	120	120
Ni	48	46	46
Y	16	16	17
Zr	148	147	155

As far as BN1-950 and BN10-950 are considered, the addition of the volcanic component slightly increased the content of Na₂O (1.06% in BNO and 1.15% in BN10) and K₂O (2.48% in BNO and 2.61% in BN10) and, more pronounced of Ba (from 266 to 345 ppm).

4.5. SEM

Microtextural changes occurring in ceramic pastes after firing can be observed in SEM micrographs of Fig. 6. The morphology of unfired clay particles revealed a well-developed but irregular sheet-like texture (Fig. 6a), which completely disappeared already at the lowest firing temperature considered (850 °C). The cellular structure (Tite and Maniatis, 1975) of the sintered clay matrix was detected in samples fired at higher temperatures (900° and 950 °C) with progressive development of larger pores with increasing temperature (Fig. 6b, c and d). Quite common is the occurrence of cavities and discontinuities at the matrix/temper interface (Fig. 6e and f).

4.6. Mercury intrusion porosimetry

All porosimetric curves (Fig. 7) showed a unimodal distribution, but some differences were observed depending on the firing temperatures and temper content. Increasing amount of temper caused a shift of the main pore radii towards larger values in the unfired samples (from 0.08 μm in BNO-dry to 0.13 μm in BN10-dry). A well marked shifting towards larger pore radii was also detected for all the samples at increasing firing temperature, reaching about 1 μm at 950 °C. This behaviour is consistent with sintering phenomena (see SEM analysis) which imply textural changes (Cultrone et al., 2001, 2004).

4.7. Wetting test

Fig. 8 reports for the three investigated group of samples the wetting behaviour as a function of temperature. Only sample BNO accounts for

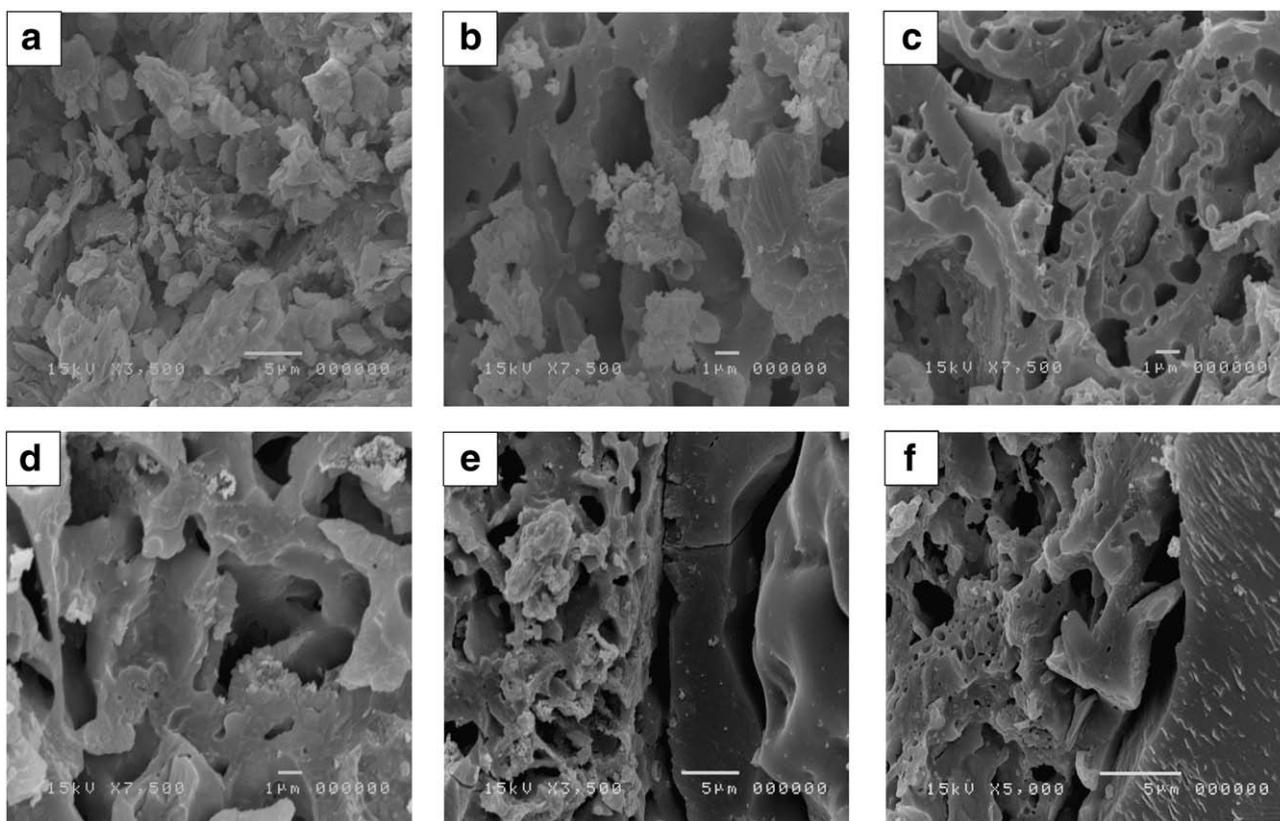


Fig. 6. SEM microphotographs. a) clay matrix in unfired BN0-dry sample; b) “cellular-like” structure in BN0-950; c) and d) sintered matrix in BN0-900 and BN0-950; e) and f) matrix/temper boundary in BN1-950 and BN10-950, respectively.

an increase of water absorption with temperature. The addition of temper (BN1 and BN10) definitely hinder this phenomenon with curves almost perfectly overlapping regardless the temperature (Fig. 8). Drying curves (Fig. 8) evidence how the presence of temper promotes a slightly faster loss of water from the samples, as also confirmed by higher drying index values (Di, Table 5).

The other parameters reported in Table 5 show significant changes only for samples without addition of temper (BN0). This is clearly expressed by the open porosity (O_p) and free water adsorption (A_f) values which increase as a function of temperature only in BN0 whereas remain almost constant at any firing temperature for all the other group of samples (BN1 and BN10). The adsorption coefficient (C_a) as well as saturation coefficient (S) values turned to be quite homogeneous throughout the entire set of samples. Slight differences do not seem to indicate a preferential trend as a function of temperature and/or temper amount.

5. Discussion

Data collected on replica samples allowed to point out the effects of different temperatures and temper on the features of the fired specimens.

As expected, the increasing amount of volcanics added to the clayey material modified the texture and the bulk mineralogy of the ceramic pastes as evidenced by optical observations. Specifically, grain-size changed from seriate to bimodal; the added volcanic phases, even though scattered in the clay matrix, were clearly distinguishable by optical observations whereas XRD and XRF analyses did not show any significant difference, with the only exception in the latter for a slight increase of feldspar and Ba consistent with the abundance of sanidine in the volcanic deposit.

On the other hand, SEM observations evidenced how the occurrence of temper brought about discontinuities at the clay matrix-temper grain

interface, thus causing the opening of a secondary pore system. However, the microtextural changes occurring during the firing operations, in terms of sintering and pores development, were strongly related to pyrometamorphic reactions, mainly ruled by the chemical and mineralogical composition of the clay raw material. The most important mineralogical changes evidenced in the specimens were strongly controlled by the high calcium oxide content in the raw materials ($\approx \text{CaO} = 14 \text{ mass\%}$) which promoted the formation of Ca-bearing mineral phases, such as gehlenite and Ca-rich pyroxene. As a consequence, the ceramic paste showed a lower attitude at developing a vitreous phase thus inhibiting the sintering phenomena (Cultrone et al., 2001). The lack of an extensive vitrification, as also testified by microtextural and porosimetric analyses, accounted for the wetting behaviour of the investigated samples mainly conditioned by the high pore interconnection up to highest firing temperatures (950 °C). This was well evident in the BN0 group of samples which showed a clear direct dependence of wetting parameters such as porosity (O_p) and free water adsorption (A_f) with the firing temperature (Table 5). It was hypothesized that the lack of temper in BN0 favoured the formation of Ca-bearing phases which inhibit a sintering of the ceramic paste, so that pores persisted interconnected thus allowing the paste to absorb a higher amount of water.

This linear dependence between wetting parameters and firing temperatures was almost annealed in BN1 and BN10 ceramics with values of open porosity and free water adsorption roughly similar throughout the whole set of temperatures. The attitude at forming Ca-bearing phases was partly hindered in BN1 and BN10 samples due to the indirect lower content of clay fraction whereas temper likely inhibited sintering as a consequence of its different plasticity and higher melting temperatures with respect to the clay matrix.

Petrophysical data of replicas were compared with those of two historical ceramic productions from Benevento; in particular, the replica groups BN0 and BN1 were compared with a fine-grained

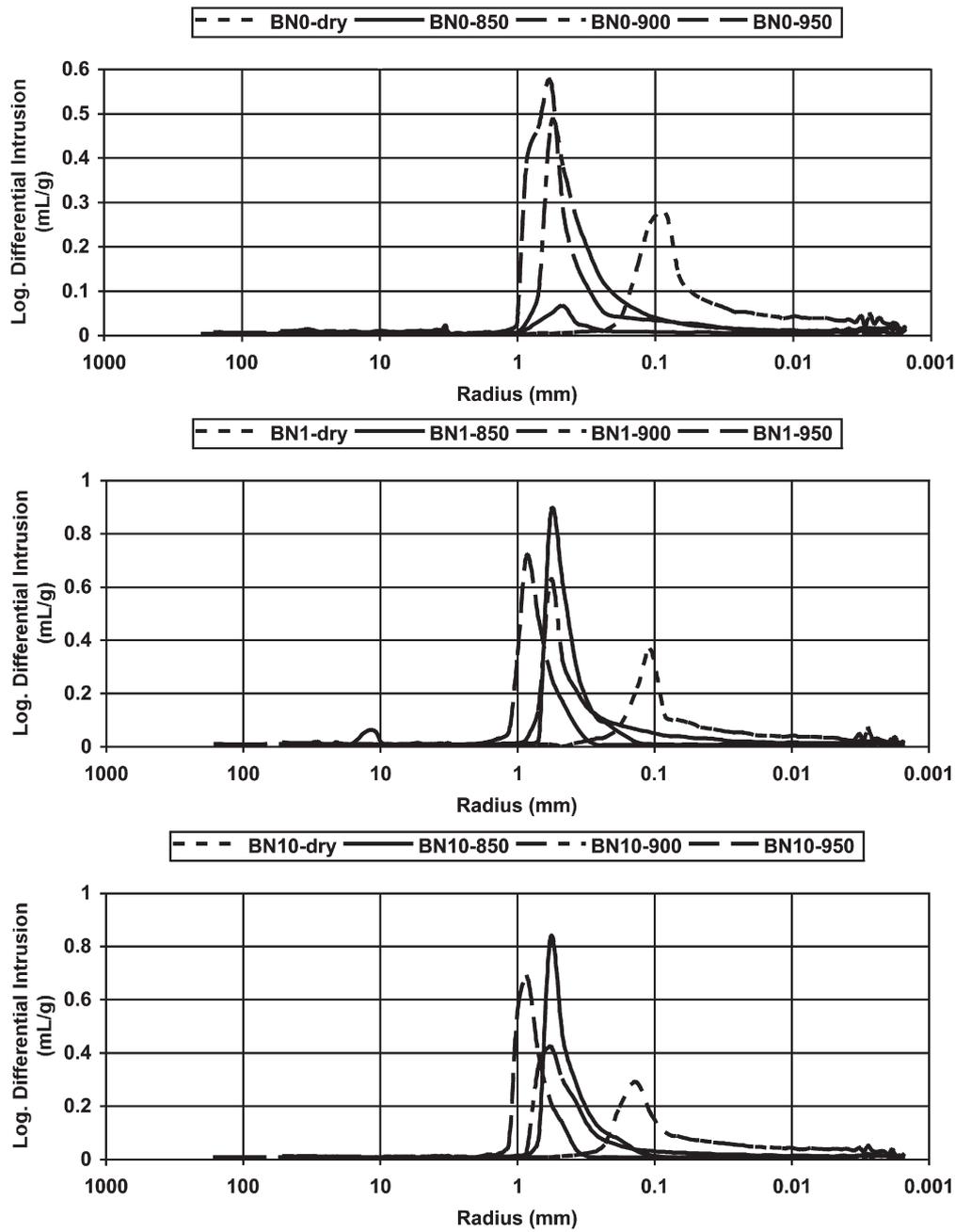


Fig. 7. Porosimetric curves of the investigated samples. Radius (in μm) vs. Log. Differential Mercury Intrusion volume (in mL/g).

domestic-use ceramic (Protomajolica Ware), while BN10 with coarse-grained bricks (Grifa et al., 2006, 2007a).

Previous studies on the above mentioned historical shards hypothesized a local manufacture for these productions, based on the large availability of workable clay materials in Benevento surrounding areas and archaeological evidences (presence of kiln wastes and furnaces; Grifa et al., 2006).

The use of local clay raw materials and temper was definitely proved by comparing the chemical composition of historical samples with replica specimens. This resulted evident in the two diagrams of Fig. 9 which report the variation of oxides or elements (K_2O vs TiO_2 ; Zr vs Ba) within the raw materials (GP clay and Pomici di Avellino AV), the replicas and the historical ceramics. Replica specimens and historical ceramics always lie close to the line held by the GP and AV compositions, with a trend toward AV depending on the temper content (Fig. 9).

These evidences along with mineralogical and textural data allowed to emphasize a significant similarity between historical findings and replica specimens.

Some other considerations can be drawn in terms of firing temperatures used to manufacture the historical ceramics and replicas taking into account XRD data and SEM observations. The Protomajolica samples showed sintered pastes (CV FB – continuous vitrification with fine bloating pores; Tite and Maniatis, 1975) along with extensive occurrence of gehlenite and Ca-rich pyroxene thus suggesting estimated temperatures of ca. 950 °C. The persistence of dehydroxylated illite along with a lower amount of calcite and gehlenite in the bricks samples accounted for lower firing temperatures (ca. 850 °C).

Mineralogical analyses on replica samples are in a quite good agreement with the above reported data. Samples fired at 950 °C released the occurrence of gehlenite and Ca-rich pyroxene as verified in the Protomajolica ceramic class (Table 3); by contrast, the illite +

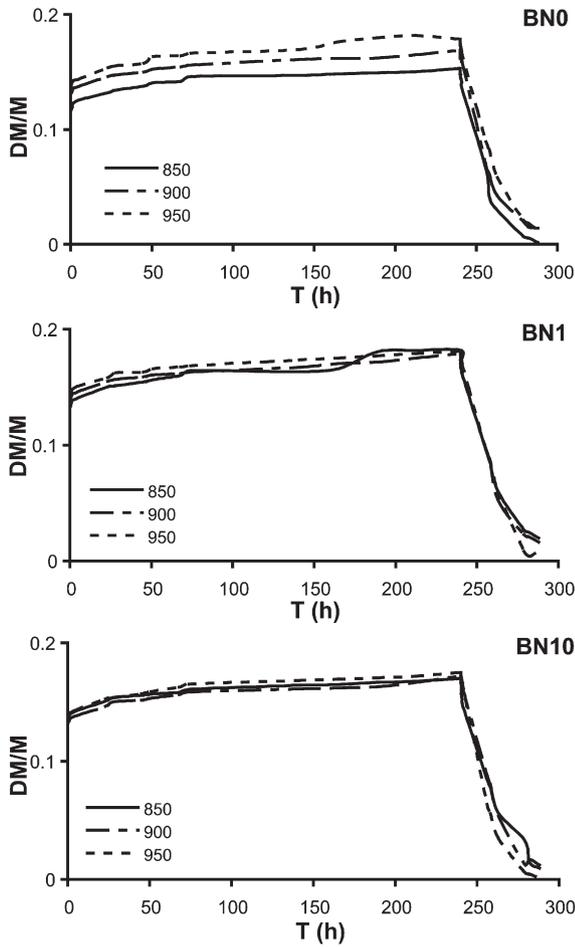


Fig. 8. Adsorption and drying curves of the replica samples.

calcite + gehlenite paragenesis observed at 850 °C is comparable with brick mineralogy. These data confirmed the previously proposed firing temperatures on historical samples (Grifa et al., 2006, 2007a) using mineralogical (XRD) and microtextural (SEM) methods.

Firing temperature, along with the type and content of temper, was a crucial parameter strictly related to the use of the ceramic artefacts. The direct relationship occurring between the rigidity coefficient (α , Tite et al., 2001) and the firing conditions makes the choice of correct firing temperatures essential to achieve the best efficiency of the ceramic paste, in term of strength resistance and thermal dilation.

These technical parameters, deeply affecting the physical behaviour of the productions, were kept in rigorous consideration by craftsmen, especially as concerned the final use destination of ceramics.

Table 5
Wetting properties of the fired replicas.

		A_f	C_a	D_i	O_p	S
BN0	850	19.71	15.14	15.86	33.85	81.16
	900	19.76	15.06	15.89	34.80	85.49
	950	22.19	15.35	17.89	38.52	80.54
BN1	850	22.23	15.32	17.06	36.74	79.67
	900	21.23	16.03	16.54	36.34	86.80
	950	21.82	16.41	17.65	36.93	86.83
BN10	850	20.14	15.65	16.38	34.89	88.95
	900	19.99	15.25	16.35	35.44	84.90
	950	20.77	15.78	17.64	35.81	86.34

A_f , free water absorption; C_a , absorption coefficient; D_i , drying index; O_p , open porosity (%); S, saturation coefficient (%).

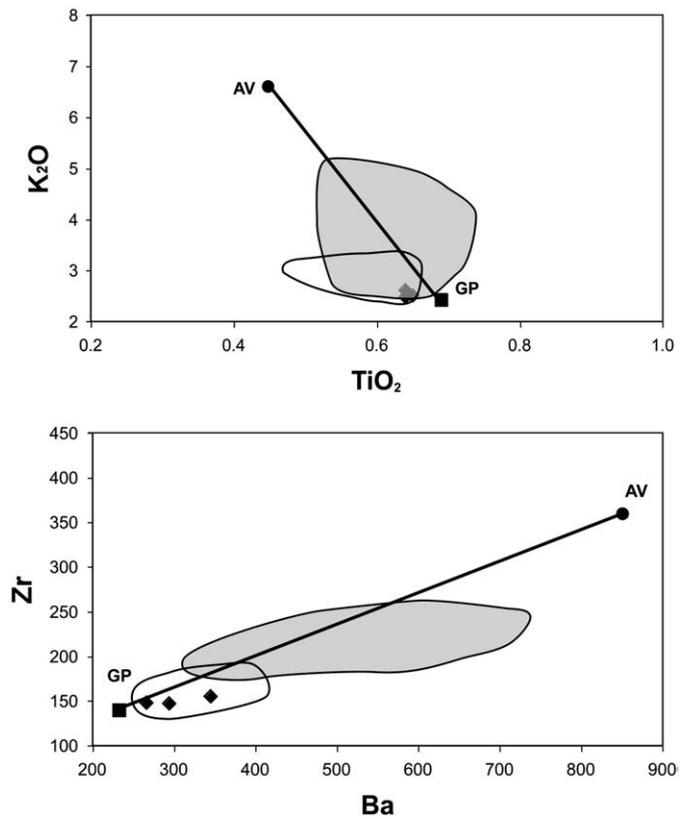


Fig. 9. Chemical diagrams of K_2O vs. TiO_2 and Zr vs. Ba within GP clay (square), volcanic temper (circle) and replicas (diamonds). Blank field represents the Protomajolica ware composition whereas shaded field refers to historical bricks.

As far as the table ware production was considered, such as the Protomajolica ware, the high firing temperatures as well as the low temper content were necessary to achieve a good shock resistance of the ceramic products (Tite et al., 2001). However, as pointed out by the replica experiments, this allowed the ceramic body to absorb much water with respect to the specimens with higher temper content (BN10-850). The replica samples reproducing the Protomajolica ware (BN0-950 and BN1-950) showed the highest open porosity and water adsorption values ($A_f = 22.2\%$ and $O_p = 38.5\%$ in BN0-950; $A_f = 21.8\%$ and $O_p = 36.9\%$ in BN1-950, Table 5).

In order to avoid excessive water absorption by the ceramic manufactures the ancient craftsmen applied on the ceramic body a fine glazed slip by subsequent immersion in different silica-based solutions (Grifa et al., 2006).

The low porosity values ($O_p = 34.9\%$) and free water adsorption coefficient ($A_f = 20.1\%$) of replica specimens characterized by the highest amount of temper and fired at the lowest temperature (BN10-850) were also in good agreement with the features of the bricks widely used in historical masonry. Such technological properties enhanced the wetting parameters, in terms of lower water absorptions and faster water release, thus assuring a long-term durability of the manufactured ceramics (Grifa et al., 2007a).

6. Conclusions

The Gran Potenza raw materials (GP) and the Pomici di Avellino volcanic fall-out deposit (AV) cropping out in the Benevento area have been largely exploited since ancient times for ceramic manufacturing. These materials, mixed in different proportions, were used to craft replica specimens and then fired at 850°, 900° and 950 °C in order to reproduce the technological properties of two historical ceramic productions. From mineralogical and textural points of view, the

increasing temperature promoted pyrometamorphic reactions with the development of new silicate phases (gehlenite and Ca-rich pyroxene) and the sintering of pastes, especially at highest firing temperature.

The increasing amount of temper did not change the wetting properties of the manufacts. The volcanic sand probably acted as a barrier to sintering due to its different plasticity and melting temperatures with respect to the clay matrix.

The comparison between the replicas and the ceramic production of the Benevento area allowed to understand how parameters such as temper amount and firing temperature could have addressed some important technological choices aimed at optimizing the use of the different manufacts. In particular, it was shown how the use of a glazed slip of the Protomajolica ware was not only an aesthetic choice but mainly dictated by technological requirements, i.e. decreasing of water absorption.

This study demonstrates that a fine domestic ware and coarse paste bricks were produced using the same clayey raw materials from the Gran Potenza hill. Their features such as medium plasticity and a good clay fraction assure a good workability to the paste whereas the addition of different proportion of volcanic sand enables to achieve the technological properties required by their destination use.

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