

Archaeometric study of roman pottery from Caudium area (Southern Italy)

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Abstract - Aim of this work is the mineralogical characterization of late antique painted common wares from the ancient roman settlement of Caudium (today Montesarchio, Campania region, italy).

Twenty-two samples (4th to 6th century AD) collected during the archaeological survey of the area, were studied to investigate their manufacturing technology and to attest a possible local production. Ceramics shards are represented by 16 painted common ware samples; furthermore, 2 bricks, 2 kiln rejects and 2 fragments of cooking ware were investigated for comparison.

Polarized light microscopy (PLM) observations and X-ray fluorescence chemical analyses (XRF) allowed to characterize the Caudium pottery production. Two main groups of fragments were distinguished: the first one composed by painted common wares, bricks and kiln rejects, the other one by cooking ware only. Two textural typologies were recorded within the first group (composed by calcareous clay pastes: average CaO ~ 11.0%), one characterized by fine pastes containing tiny clasts of quartz, feldspars and few volcanic inclusions, the other by coarser pastes with predominant volcanic temper. Cooking wares (composed by non-calcareous clay: average CaO ~ 1.6%) show a large amount of temper of both volcanic and detrital origin, the latter mainly constituted by

quartzarenite clasts. Multivariate statistical analysis (Hierarchical Clustering and Principal Component Analysis) confirms the already identified groups. Mineralogical analyses and scanning electron microscope observations of the sintering degree of clayey paste enabled to evaluate the firing temperatures of the most representative samples (from 800 to 1200°C).

The whole data set, along with geological features of the investigated area (wide availability of raw materials) and archaeological evidences (kiln refuses, large number of fragments of the same ceramic class), allowed to hypothesize a local production of the painted common wares and thus to define the respective reference group.

Riassunto - Lo scopo di questo lavoro è la caratterizzazione mineralogica di frammenti di ceramica comune dipinta d'età tardo antica provenienti dall'antico insediamento romano di Caudium (attuale Montesarchio, Campania, italia). Ventidue campioni (datati dal IV al VI secolo d.C.), ritrovati durante la ricognizione archeologica della zona, sono stati analizzati per ricostruire le tecnologie produttive e definire una possibile produzione locale. I reperti ceramici sono rappresentati da 16 frammenti di ceramica comune dipinta; inoltre sono stati investigati per confronto 2 laterizi, 2 scarti di fornace

e 2 frammenti di ceramica da cucina. Al fine di caratterizzare i vari reperti sono state eseguite osservazioni in microscopia ottica a luce polarizzata e analisi chimiche in fluorescenza per raggi X. in questo modo è stato possibile individuare due raggruppamenti principali: il primo composto dalla ceramica comune dipinta, dai laterizi e dagli scarti di fornace, l'altro esclusivamente dalla ceramica da cucina. fra i campioni del primo gruppo (composti da argilla calcarea: media $CaO \sim 11,0\%$) è possibile distinguere due tipologie tessiturali, una caratterizzata da impasti fini contenenti piccoli clasti di quarzo, feldspati e poche inclusioni vulcaniche, l'altra da impasti grossolani costituiti prevalentemente da degrassante vulcanico.

i frammenti di ceramica da cucina (composti da impasti non-calcarei: media $CaO \sim 1,6\%$) sono costituiti da abbondante degrassante, sia vulcanico che sedimentario, quest'ultimo formato prevalentemente da clasti quarzarenitici. l'analisi statistica multivariata ha confermato i raggruppamenti già individuati.

tramite l'analisi mineralogica diffrattometrica su polveri e l'osservazione in microscopia elettronica del grado di sinterizzazione degli impasti sono state valutate anche le temperature di cottura di alcuni campioni rappresentativi (comprese fra 800 e 1200°C). Questi risultati, insieme con le caratteristiche geologiche (ampia disponibilità di materie prime) e archeologiche (presenza di scarti di fornace, gran numero di frammenti della stessa classe di ceramica) della zona in esame, hanno permesso di identificare una produzione locale limitata alla ceramica comune dipinta e di definirne il relativo gruppo di riferimento.

Key words: *Caudium; reference group; painted common ware; Avellino Pumice; Ariano Unit.*

INTRODUCTION

the archaeological area of Caudium is sited in a valley (*Valle Caudina*) located in the middle of the southern Apennine chain of Campania region (Italy). Caudium (today Montesarchio) can be considered the ancient capital of the *Caudini*, a samnite tribe that peopled the area before the roman conquest in the third century B.C. in the roman period the city kept good trade exchanges especially with Naples and the

tyrrhenian area thanks to its favorable position along the *Via Appia*, the ancient roman road connecting Rome and *Brundisium* (Salmon, 1985). the occurrence of large clay outcrops and many kiln refuses in the same area, as well as a ceramic tradition so far preserved strongly suggest a local production of painted common ware.

the studied ceramic samples, the first investigated in the Caudium area, were all dated by comparison with some known shapes in late antique (4th to 6th century AD; Perrone, 2005).

the aim of this study is the archaeometrical characterization of a set of painted common ware fragments, in order to attest a local crafting of this typical ceramic production widespread in southern Italy during late roman period. the archaeometrical data on this set of fragments were compared with a couple of kiln refuses attributed to the same painted common ware. Moreover two bricks and two cooking ware samples were also analyzed in order to verify differences or similarities of the technological features among local ceramic productions.

All the specimens come from three of the 151 sites forming the Caudium archaeological area (sites 111, 118, 121), discovered during an archaeological reconnaissance survey. this preliminary survey represents a very important step of an archaeological investigation necessary to reconstruct the ancient settlements arrangement, and to estimate a site frequentation on the basis of the surface distribution of the findings, especially ceramics shards.

GEOLOGICAL BACKGROUND

the *Valle Caudina* (fig. 1) is a tectonic depression delimited by the Mesozoic carbonate massifs of the Taburno-Camposauro northwards, s. Agata de' Goti mountains westwards and Avella-Partenio chain southwards, the east side is characterized by the smoother morphologies of Miocene formations characterized by

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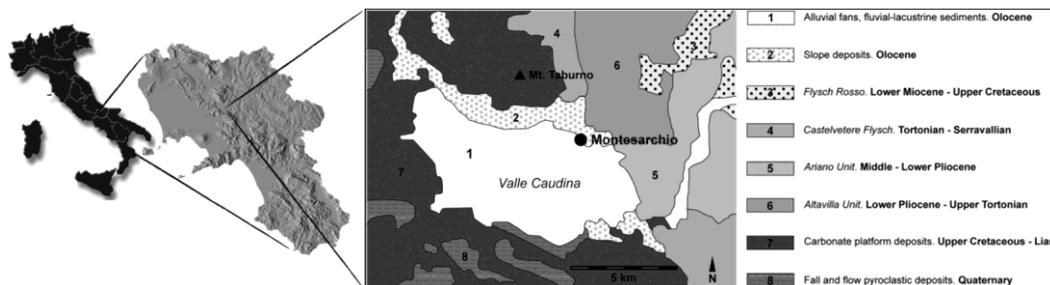


fig. 1 - sketch map (1:250000) showing the main lithologies of the Valle Caudina area (modified after “Carta Geologica dell’Appennino Meridionale”. bonardi *et al.*, 1988).

silicoclastic sedimentary successions.

The field geology relieved some of the most representative southern Apennine tectono-stratigraphic units including the *Lagonegro Unit*, outcropping in the northwestern area of Montesarchio with the *Flysch Rosso* formation, a Late Cretaceous to Oligocene red marls and shales with interbedded coarse detrital limestone (Pescatore *et al.*, 1999).

In unconformity with the *Lagonegro Unit*, the *Altavilla Unit* (Messinian to Pliocene) crops out. Deposited in a *piggy-back* basin along the active border of the Apennine chain (Ori and Friend, 1984), this unit is formed by sandstones with silty clay layers; Messinian evaporites are also present in the lower portion.

The succession continues with the *Ariano Unit* (early to Middle Pliocene) represented by gray-blue, well stratified marly and sandy clays. This unit was deposited in a *piggy-back* basin in open or shallow waters as showed by micropalaeontological evidence (De Castro Coppa *et al.*, 1969).

Silicoclastic turbiditic successions can be also recognized, such as the *Castelvetero flysch*, (Serravallian to Tortonian) formed by sandstones and conglomerates with plutonic-metamorphic and carbonate clasts (Critelli and Le Pera, 1995), also including mountain-block carbonate olistholiths of south Apennine carbonate platform edge (Ciarcia *et al.*, 2006).

Olistostromes of *Argille Varicolori* along with pelitic intercalations are also present in the

Fortore Unit formation (Chiocchini, 2001), which outcrop principally on the Avella-Partenio slopes, not far from the southern side of the Valle Caudina.

In the Quaternary age the valley was covered by slope deposits, alluvial fans, fluvial-lacustrine sediments and volcanic products coming from Tyrrhenian margin eruptive vents: Campanian ignimbrite (39 ka BP; De Vivo *et al.*, 2001; Fedele *et al.*, 2008) from Phlegraean fields and Avellino Pumice of Somma-Vesuvius (4.3 ka BP; Santacroce *et al.*, 2008). Furthermore, the presence of other products of the Somma-Vesuvius activity cannot be excluded (e.g., AD 472 eruption).

MATERIALS AND METHODS

The 22 investigated shards (Table 1/A, 1/B), collected during the archaeological survey of the Caudium area, consist of 16 fragments of painted common ware (PCW) composed principally by basin rims (fig. 2a, b) and amphora fragments (fig. 2c), two shards of cooking ware (CW; fig. 2d), two bricks (IAt 1, IAt 2) and two kiln rejects (sCf 1, sCf 2), these latter to be assumed as PCW wastes.

Macroscopic observations gave preliminary information about color, hardness, weight and fabric of the ceramic objects (Williams, 1990).

Polarized light microscopy (PIM) analysis of thin sections, using a “Leitz Laborlux 12 Pol”,

Table 1/A

Main macroscopic characteristics and petrographical features of ceramic fragments, the modal analysis data are shown as percentage in bold fonts.

Abbreviations (siivola and schmid, 2007): Qtz=Quartz, Afs=Alkalifeldspar, Cpx=Clinopyroxene, Ms=Muscovite, bt=biotite, Pl=Plagioclase, Am=Amphibole, Cal (sec)=Calcite (secondary), Ict=Ieucite, Grt=Garnet, Mc=Microcline, op=opaque min., Drf=Detrital rock fragments, Arf=Argillaceous rock fragments, tr=traces.

Sample	Ceramic class	Inner color	Outer color	Hardness	Feel	Surface treatment	Thickness (mm)	Weight (g)	Optical properties	Packing	Grain sorting	Porosity
9-27	PCW	grayish green	grayish green	hard	rough	smoothed	10	22.9	isotropic	10-20 %	seriate	medium-low
9-30	PCW	dark red	light red	hard	rough	coated	10	18.5	isotropic	5-15 %	seriate	low
9-32	PCW	orange-red	orange-red	hard	rough	coated	20	38.0	isotropic	20-30 %	seriate	low
9-33	PCW	gray	red	hard	rough	smoothed, coated	25	32.7	isotropic	5-15 %	seriate	low
9-34	PCW	grayish green	grayish green	hard	rough	smoothed, coated	28	35.0	isotropic	18.0%	bimodal	5.5%
9-35	PCW	gray	gray	hard	rough	-	17	17.2	isotropic	10-20 %	seriate	medium low
9-51	PCW	light red	light red	hard	rough	coated	20	9.9	isotropic	15-25 %	bimodal	low
9-52	PCW	gray	gray	hard	smooth	smoothed, coated	7	17.0	isotropic	5-15 %	bimodal	very high
9-184	PCW	gray	gray	hard	rough	rough	10	30.5	isotropic	5-15 %	seriate	high
9-300	PCW	grayish green	grayish green	hard	rough	smoothed	20	94.7	isotropic	10-20 %	seriate	high
9-301	PCW	grayish green	grayish green	hard	rough	smoothed, coated	7	19.5	isotropic	5-15 %	bimodal	medium
9-308	PCW	grayish green	gray	hard	rough	smoothed, coated	9	11.3	isotropic	10-20 %	seriate	very high
84-1	PCW	dark red	light red	hard	rough	smoothed, coated	13	79.5	isotropic	10-20 %	bimodal	low
84-6	PCW	red	yellow-brown	hard	rough	smoothed, coated	40	74.1	isotropic	23.1%	bimodal	4.0%
84-10	PCW	greenish yellow	yellow	hard	rough	smoothed	10	43.3	isotropic	10-20 %	seriate	medium
89-2	PCW	red	light red	hard	rough	smoothed, coated	15	86.3	isotropic	15-25 %	bimodal	low
84-3	CW	dark red	dark red	hard	rough	smoothed, coated	45	34.6	isotropic	37.3%	bimodal	5.4%
9-38	CW	dark red	light red	hard	rough	coated	15	17.4	isotropic	36.4%	bimodal	1.9%
LAT 1	brick	light gray	light gray	hard	rough	-	18	13.9	isotropic	17.5%	bimodal	3.7%
LAT 2	brick	light red	light red	soft	rough	-	5	16.5	isotropic	31.2%	bimodal	4.4%
SCF 1	kiln waste	grayish green	dark gray	hard	rough	coated	45	42.4	isotropic	12.0%	bimodal	15.6%
SCF 2	kiln waste	grayish green	grayish green	hard	rough	coated	20	20.1	isotropic	17.8%	bimodal	10.7%

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Table 1/b

Sample	Qtz, Afs, DRF	Cpx	Ms	Bt	Other minerals	Scoriae	Pumices	Volcanic lithics	ARF	Grog
9-27	XX	X	Tr.	Tr.	Pl, Op	X	X	X		
9-30	XX	X	X		Op	X	X	X		
9-32	XXX	Tr.	X	X	Pl	X	X	X	X	X
9-33	X	X	X	Tr.		X	X	X	X	
9-34	12.1%	2.1%	0.8%	0.2%	Am (0.1%), Pl, Grt, Op (1.5%)	0.8%	0.3%	0.1%		
9-35	XX	X	Tr.							
9-51	XXX	tr.	X	X	Pl, Op				X	
9-52	X	Tr.	Tr.	Tr.	Pl, Op			X		
9-184	X				Op					
9-300	X				Op, Cal (sec)					
9-301	X	X	Tr.	Tr.	Pl, Op, Cal (sec)	X	X	X		
9-308	X	Tr.	X			Tr.				
84-1	XXX	X	X	X	Pl	X	X	X	X	
84-6	16.3%	2.5%	0.8%	Tr.	Am (Tr.), Pl, Op (0.9%)	0.5%	1.3%	0.1%	0.7%	
84-10	XX	X	X	Tr.	Pl, Cal (sec), Op	Tr.			X	
89-2	XX	X	Tr.	Tr.	Pl, Op	Tr.	X	X	X	
84-3	31.7%	1.0%		Tr.	Pl, Am (Tr.), Mc, Op (0.6%)	1.6%	2.0%	0.2%	0.2%	
9-38	34.0%	0.3%	Tr.	Tr.	Pl, Mc, Op (0.4%)	0.6%	0.6%	Tr.	0.5%	
LAT 1	10.6%	1.6%	0.3%	0.1%	Lct, Pl, Op (1.0%)	1.0%	1.5%	Tr.	1.4%	XX
LAT 2	11.8%	4.8%	1.5%	0.5%	Lct, Op (1.1%)	2.1%	4.5%	1.4%	3.5%	XX
SCF 1	0.4%	1.1%	1.5%	Tr.	Pl, Grt, Am (Tr.), Op (1.8%)	2.9%	3.6%	0.7%		
SCF 2	9.7%	1.1%			Pl, Op (2.0%)	1.3%	1.4%	2.3%		

allowed to describe the texture, the matrix and the type of temper of the ceramic shards; a modal analysis (based on 4500 points) was also carried

out (3.2.1 version of the “Leica Qwin” software equipped with a “Leica DFC 280” camera), to determine the relative abundance of inclusions,

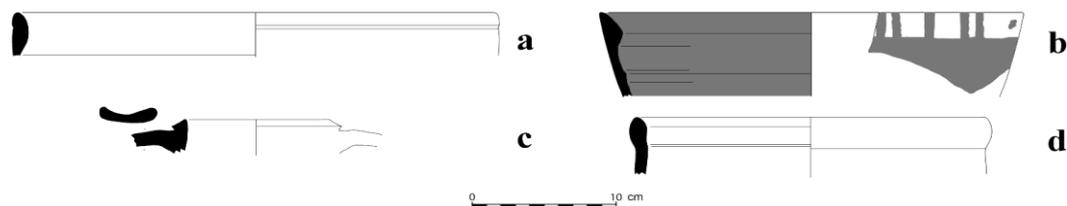


fig. 2 - representative shapes of pottery finds from Caudium area. a) sample 89-2. Painted common ware, basin rim fragment, 5th - 6th century AD (site 111). b) sample 84-1. Painted common ware, basin rim fragment, 4th - 5th century AD (site 118). c) sample 9-32. Painted common ware, amphora shards, 5th - 6th century AD (site 121). d) sample 84-3. Cooking ware, pot fragment, 5th century AD (site 118).

matrix and pores.

Chemical analysis of major and trace elements was performed by X-ray fluorescence (Xrf) with a “Philips Pw1400” spectrometer (procedures and detection limits according to Melluso *et al.*, 2005). *lo*i (weight loss on ignition) was measured gravimetrically. statistical treatment of chemical data (*Hierarchical Clustering and Principal Component Analysis*) was carried out with the 2.2.1 version of the “*r* Development Core team” software.

X-ray powder diffraction (XrPD) was carried out with a “Philips Pw 1730/3710” diffractometer (CuK α radiation 40 kV, 30 mA, curved graphite monochromator, scanning interval 3-80°, step size = 0.020° 2 θ , counting time 5s per step). scanning electron Microscopy (seM), performed with a “Jeol 5310” instrument, allowed to evaluate the sintering degree and the microtextural features of the clay matrix (tite and Maniatis, 1975).

Results

Macroscopic analysis

the majority of PCW samples show a green grayish colour; other samples of this class are red coloured with frequent zonings characterized by dark red or gray cores. A few fragments show red cores and creamy external surfaces. CW fragments are formed by red pastes with abundant temper grains. the brick **IA**t 1 shows

a hard paste of light gray colour whereas **IA**t 2 sample is characterized by a red paste and a coarser texture. Hard gray greenish pastes typify kiln rejects with black edges in sample sCf 2.

Polarized light microscopy (PLM)

All analyzed samples have an isotropic matrix. PCW shards show two different textural characteristics. A group of fragments (84-10, 9-27, 9-30, 9-35, 9-52, 9-184, 9-300, 9-301, 9-308) show finer pastes with an average packing of about 10-15% and by seriate distribution (mean size range 15-150 μ m) of the inclusions (fig. 3a) constituted by tiny quartz grains, alkali feldspar and subordinated volcanics. the other group (84-1, 84-6, 89-2, 9-32, 9-33, 9-34, 9-51) is formed by samples showing a packing of about 15-25% and a bimodal distribution. the finer fraction (10-50 μ m) is constituted by quartz and alkali feldspar whereas the coarser one (100-200 μ m) mainly by volcanics (clinopyroxene, pumices, scoriae; fig. 3b). Many samples of both groups also show minor mineral phases such as muscovite, biotite, plagioclase and opaque oxides. Amphibole and garnet only occur in samples 84-6 and 9-34. two shards (84-1, 84-6) also contain few arenaceous rock fragments. Calcite was found as post-depositional pore-filling phases of samples 84-10, 9-300 and 9-301.

CW specimens are characterized by elongated fractures of the matrix and by a large amount of temper (packing 35-40%) with a bimodal grain

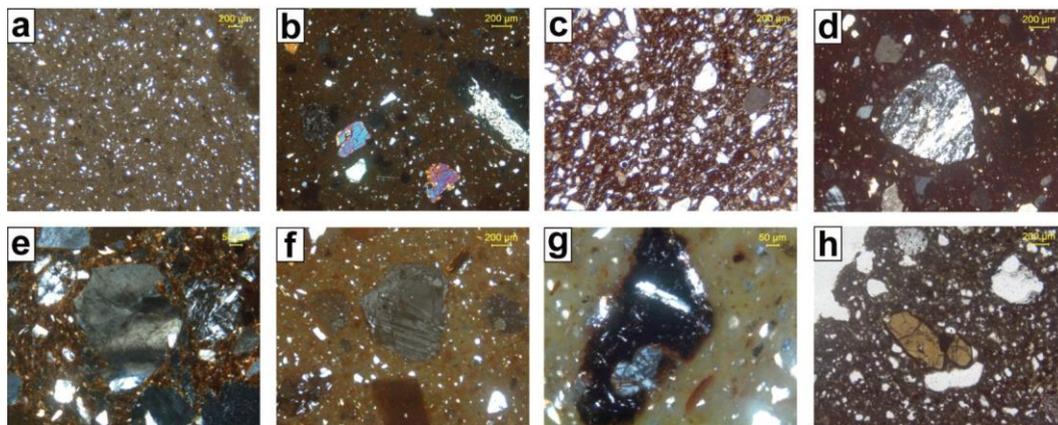


fig. 3 - thin sections images of some representative fragments. a) PCW sample 9-184. b) PCW sample 84-6. c) CW sample 9-38. d) CW sample 84-3. e) CW sample 84-3. f) brick sample IAt 2. g) brick sample IAt 1. h) Kiln reject sample sCf 1.

size distribution (fig. 3c). Quartz and alkali feldspar occurs either in fine (10-50 μm) or coarse fraction (100-200 μm). the coarse fraction also shows fragments of arenitic rocks (fig. 3d), quartz crystals (fig. 3e) with undulating extinction, microcline, clinopyroxene, volcanic scoriae, pumices and ArF (*Argillaceous Rock Fragments*; whitbread, 1986).

the bricks show a bimodal distribution of the grains and a packing of 15-20% in IAt 1 and of 30-35% in IAt 2. Quartz and alkali feldspar mainly occur in the fine fraction (10-50 μm) whereas the coarse fraction (150-350 μm) is composed by clinopyroxenes (diopside, feldspar), leucite (fig. 3f), pumices and scoriae of trachytic and leucitic composition. Leucite in scoriae shows faint polysynthetic twinning traces because of leucite-analcime transformation (fig. 3g).

Kiln rejects are characterized by large rounded pores and dark green matrix in plane polarized light. both samples present a bimodal distribution with a 10-20% packing with just few coarser grains. Alkali feldspar and quartz are mainly present in the fine fraction (10-50 μm); coarser grains (150-250 μm) are constituted by clinopyroxene, clinopyroxene-feldspar bearing

lava fragments, scoriae, pumices and rare plagioclase crystals. Amphibole, biotite and garnet (fig. 3h) are present in sCf 1 sample, while in sCf 2 analcimized leucite occurs in scoriae.

Modal analysis

Modal analysis (data shown in bold in table 1/A and 1/b) was performed on eight representative samples to evaluate the relative abundances of grains, matrix and pores visible in thin section (fig. 4). the two analyzed PCW samples (84-6, 9-34) show an average content of temper of 20.6%, mostly represented by a quartz-feldspathic detrital fraction (14.2%); the porosity is 4.7%. CW fragments (84-3, 9-38) are characterized by abundant temper (36.9%) with a quartz-feldspathic component of 32.8%; the porosity do not exceed 5.4%. brick samples show a quite different content of temper (17.5% in IAt 1 and 31.2% in IAt 2). both show an average porosity of about 4.0%. temper in kiln rejects sCf 1 and sCf 2 is of 12.0% and 17.8%, respectively. their mean porosity is 13.1%.

Chemical analysis (XRF)

As far as major and trace elements are

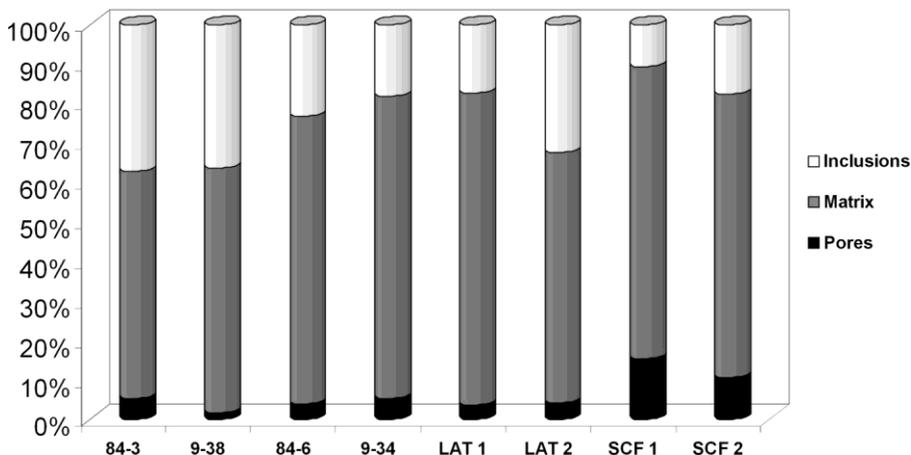


fig. 4 - relative abundances of inclusions, matrix and pores visible in some representative thin sections. CW sample 84-3, CW sample 9-38, PCW sample 84-6, PCW sample 9-34, brick sample LAT 1, brick sample LAT 2, Kiln reject sample sCf1, Kiln reject sample sCf2.

considered (Table 2), all PCW samples can be distinguished in two different groups. the Cao content ranging between 7.90 and 16.4% (average 10.9%), is always above 6% therefore proving the calcareous character of all samples attributed to this ceramic class (Maniatis and Tite, 1981). only the sample 9-32, is slightly below this limit (Cao = 5.72%). two groups can be distinguished: a first one (84-10, 9-27, 9-34, 9-35, 9-184, 9-300, 9-301, 9-308) characterized by higher values of Cao (on average 13.1%) and another one (84-1, 84-6, 89-2, 9-30, 9-32, 9-33, 9-51, 9-52) with a mean value of 8.62% (fig. 5a). the first group also shows a lower average content of Al₂O₃ (14.2%) if compared with the remaining PCW specimens (16.2%) and a lower average values of Fe₂O₃ (5.65%) and TiO₂ (0.62%) if compared with the other samples of this ceramic class (Fe₂O₃ = 6.56%, TiO₂ = 0.73%; fig. 5b).

the sample 9-52 shows highest K₂O (4.22%) and Na₂O (2.15%) values among all the PCW fragments, while the sample 9-51 reaches the highest P₂O₅ value (1.96%).

Concerning trace elements all the PCW samples show a quite homogeneous compositions making difficult to distinguish any grouping. to note the

high Ba content (794 ppm) in sample 9-33.

As can be easily noticed in diagrams of figures 5a, b, c, the chemical composition of kiln rejects is similar to that of PCW, with the only exception of a slight higher Sr value (fig. 5d).

Also the bricks have a chemical composition very similar to PCW samples; only strontium is on average higher in the bricks (439 ppm). Moreover the LAT 2 sample shows the highest Ba content (982 ppm).

CW samples can be distinguished from all the other analyzed fragments for the low Cao content (on average 1.54%). other chemical features characterizing these two specimens are the average values of SiO₂ (68.0%) and MgO (1.99%), respectively the highest and the lowest among all studied samples. CW samples also show the lowest average contents of some trace elements (fig. 5c, d), such as Zn (63 ppm), Ni (47 ppm) and Sr (196 ppm), whereas Zr (265 ppm) attains the highest value.

Statistical analysis

statistical treatment of chemical data (Hierarchical Clustering and Principal Component Analysis) was performed depriving

Table 2

Chemical analysis. Average and standard deviation (σ) are reported for each chemical group.

PCW group 1	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Sum	LOI	Zn	Ni	Rb	Sr	Y	Zr	Nb	Sc	V	Cr	Cu	Ba
84-10	54.81	0.61	13.99	5.46	0.10	4.93	16.43	0.83	2.51	0.32	100	5.58	99	61	113	385	31	144	21	21	134	149	30	422
9-27	58.02	0.64	14.75	5.86	0.12	3.88	12.18	1.18	2.77	0.61	100	1.30	103	62	150	401	33	143	14	17	143	148	22	458
9-34	57.47	0.63	14.51	5.75	0.11	3.99	13.55	1.07	2.75	0.18	100	1.23	88	67	135	390	34	147	18	19	145	153	20	461
9-35	59.28	0.63	14.38	5.75	0.11	3.72	11.96	0.98	2.90	0.29	100	2.30	93	59	141	363	16	149	25	19	129	130	19	516
9-184	59.96	0.60	13.59	5.53	0.14	3.66	12.48	1.08	2.70	0.26	100	1.14	91	54	116	345	40	167	11	18	117	120	21	343
9-300	59.70	0.60	13.58	5.42	0.10	3.76	12.60	1.20	2.72	0.32	100	1.48	90	56	116	340	28	162	15	20	126	117	25	361
9-301	57.96	0.62	14.36	5.63	0.13	3.97	13.26	0.87	2.75	0.44	100	1.79	98	63	138	381	37	146	14	20	143	146	17	406
9-308	59.05	0.63	14.27	5.84	0.14	3.62	12.37	0.96	2.77	0.34	100	0.90	95	62	122	359	20	146	20	21	130	135	26	404
average	58.28	0.62	14.18	5.65	0.12	3.94	13.11	1.02	2.73	0.35		1.96	94.67	60.58	128.91	370.34	29.75	150.43	17.07	19.37	133.34	137.22	22.41	421.28
σ	1.66	0.01	0.42	0.17	0.01	0.42	1.45	0.13	0.11	0.13		1.52	5.06	4.23	13.82	22.12	8.23	8.81	4.56	1.41	9.73	13.94	4.33	56.39
<i>PCW group 2</i>																								
84-1	59.21	0.80	16.79	6.99	0.14	4.00	7.90	0.80	2.99	0.39	100	3.62	114	62	144	311	17	157	27	23	138	157	28	588
84-6	58.34	0.71	15.74	6.33	0.12	4.22	10.14	1.09	2.86	0.45	100	1.90	103	60	132	386	31	172	18	23	135	146	33	568
89-2	59.50	0.77	16.27	6.83	0.13	4.17	7.94	0.94	2.97	0.47	100	3.68	116	62	135	335	26	165	23	20	131	145	33	587
9-30	58.52	0.74	16.14	6.75	0.14	3.94	9.31	0.90	2.97	0.59	100	3.50	122	65	138	353	37	167	19	19	146	160	24	505
9-32	61.26	0.78	16.68	6.83	0.16	4.06	5.72	0.77	3.33	0.41	100	4.93	132	60	163	291	27	214	24	16	124	122	26	562
9-33	58.96	0.75	15.93	6.66	0.14	4.23	9.00	0.83	2.88	0.61	100	4.66	112	67	128	303	35	181	15	20	146	148	21	794
9-51	58.09	0.74	15.94	6.63	0.17	3.89	8.70	0.88	3.00	1.96	100	3.48	112	59	136	337	49	181	12	16	125	150	23	611
9-52	57.82	0.59	16.05	5.46	0.15	3.10	10.25	2.15	4.22	0.22	100	0.14	93	61	180	323	33	233	30	15	119	99	12	325
average	58.96	0.73	16.19	6.56	0.14	3.95	8.62	1.05	3.15	0.64		3.24	112.98	62.16	144.49	329.75	32.02	183.72	20.99	19.02	132.85	140.86	24.97	567.58
σ	1.09	0.07	0.37	0.49	0.02	0.37	1.46	0.46	0.45	0.55		1.55	11.82	2.60	17.70	30.30	9.47	26.41	6.09	3.07	10.32	20.33	6.59	129.16
<i>CW</i>																								
84-3	67.01	0.79	17.03	6.92	0.14	2.05	1.86	1.14	2.99	0.08	100	0.72	66	50	175	219	40	260	26	14	138	112	30	940
9-38	68.94	0.70	16.63	6.07	0.06	1.94	1.22	1.27	3.15	0.01	100	0.96	61	44	221	172	28	271	31	12	112	84	9	545
average	67.98	0.74	16.83	6.50	0.10	1.99	1.54	1.21	3.07	0.04		0.84	63	47	198	196	34	265	28	13	125	98	20	742
σ	1.37	0.06	0.28	0.60	0.06	0.07	0.45	0.09	0.12	0.05		0.17	3.65	4.53	32.43	33.08	8.32	7.93	3.16	1.00	17.95	20.06	15.30	279.11
<i>Bricks</i>																								
LAT1	56.74	0.66	15.58	6.10	0.12	4.59	11.42	1.73	2.67	0.39	100	2.00	100	68	168	420	27	171	21	16	139	146	28	619
LAT2	57.17	0.71	17.57	6.52	0.17	3.97	8.99	1.42	3.16	0.31	100	2.10	103	61	161	458	28	208	28	18	138	126	44	982
average	56.96	0.69	16.58	6.31	0.15	4.28	10.20	1.57	2.92	0.35		2.05	101	64	164	439	27	190	24	17	139	136	36	800
σ	0.31	0.04	1.41	0.30	0.03	0.44	1.71	0.22	0.35	0.05		0.07	2.39	5.03	4.84	26.75	0.64	26.35	4.71	1.45	0.53	14.38	11.48	256.62
<i>Kiln Rejects</i>																								
SCF1	57.66	0.65	15.69	5.74	0.12	3.59	11.49	1.32	3.34	0.39	100	0.99	101	62	143	422	29	168	25	21	140	129	30	584
SCF2	57.74	0.64	15.34	5.78	0.12	3.93	11.82	1.39	2.96	0.28	100	1.04	97	62	142	411	35	163	22	20	143	138	30	514
average	57.70	0.64	15.52	5.76	0.12	3.76	11.66	1.36	3.15	0.34		1.01	99	62	142	417	32	166	23	21	141	133	30	549
σ	0.05	0.01	0.24	0.03	0.00	0.24	0.24	0.04	0.27	0.08		0.04	2.40	0.26	1.09	7.85	4.15	3.18	1.73	1.30	2.34	6.21	0.09	49.38

Archaeometric study of roman pottery from Caudium area (Southern Italy)

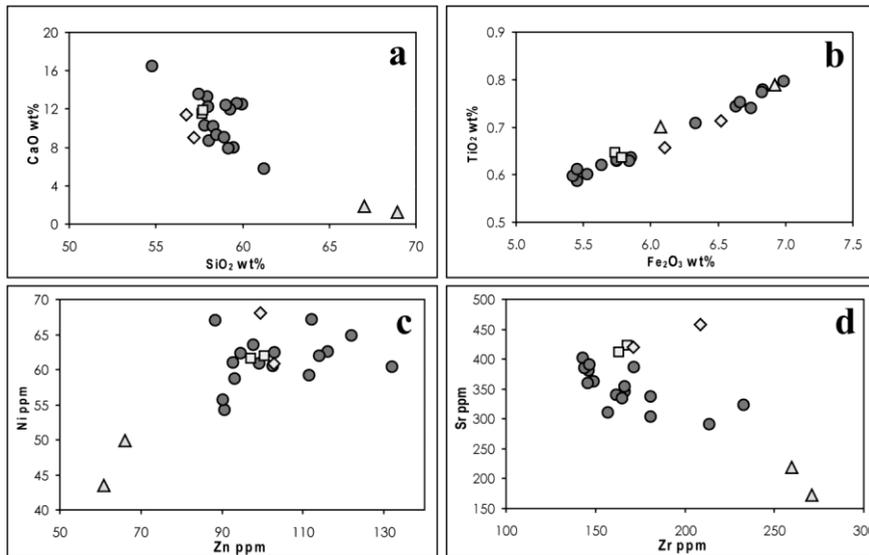


fig. 5 - XRF binary diagrams of major (wt.%) and traces elements (ppm). Dots indicate PCW, triangles indicate CW, rhombs indicate bricks, squares indicate kiln rejects.

starting data set of some chemical components, in particular CaO, MnO, P₂O₅ and Ba, as they could have been affected by post burial contamination processes (fabbri *et al.*, 1994; Maggetti, 2001). Afterwards, data were log₁₀ transformed in order to avoid deleterious effects of scale effects of clustering results (e.g., V-shaped chemical data; Aruga, 2003; Hall, 2004). in order to further simplify statistical procedures Principal Components Analysis (PCA) was carried out.

the cumulative proportion of variance, which explained the 96% of the problem, is at the 7th component (table 3). thus, the seven variables that mostly affect the problem were chosen (Hall, 2004): Fe₂O₃, MgO, Na₂O, Y, Sr, V and Cu. the dendrogram (fig. 6) resulting from the Hierarchical Clustering Analyses (average method, euclidean distance) enabled to distinguish two groups. the first one (group 1) is further subdivided in three subgroups: 1a, including PCW and kiln rejects; 1b, formed by bricks; 1c, formed by the three samples of PCW which showed the lowest values of Y. the group 2 is characterized by the CW samples and a PCW

fragment (84-3).

Mineralogical analysis (XRPD)

X-ray diffraction data (table 4) confirmed the prevailing quartz-feldspathic composition of all samples as evidenced by PIM. Quartz prevails in CW (84-3, 9-38) while is less abundant in the kiln rejects (sCf1, sCf2). feldspar was recorded in trace in the 9-52 PCW sample. Calcite only occurs in 84-10; illite was clearly observed in 9-32 and is only in trace in 84-1, 9-30, 9-51 and 9-33. Pyroxene is ubiquitous except for samples 84-1, 84-3, 89-2, 9-32, 9-33, 9-38. A low amount of gehlenite was observed in 84-1, 9-30, 9-33, 9-51, IAt 1, whereas occurs only in traces in samples 84-6, 84-10, 89-2, and 9-27. Leucite was found in the two bricks (IAt 1, IAt 2) and in the kiln refuses (sCf 1, sCf 2). Analcime was recorded in IAt 1, sCf 2 and only in trace in IAt 2.

Scanning electron microscopy (SEM)

the observation of ceramic paste by scanning electron microscope (SEM) provided information

Table 3

Principal component analysis. The table shows the weight of the variables of each principal component. Standard deviation (σ), variance and cumulative proportion are also reported.

Component	1	2	3	4	5	6	7
SiO ₂	-0.303	-	0.290	-0.108	0.104	-	-
TiO ₂	-	0.487	0.200	-	-	-	-
Al ₂ O ₃	-0.172	0.429	-0.171	-	-	-	-
Fe ₂ O ₃	-	0.497	0.157	-	-	-	-0.127
MgO	0.325	-	-0.107	-	-0.211	-	-0.317
Na ₂ O	-0.128	-0.181	-0.498	0.185	0.246	0.141	-0.168
K ₂ O	-0.192	0.106	-0.412	-	-0.407	-	0.497
Zn	0.240	0.255	-0.102	-	-0.487	-	-
Ni	0.287	0.123	-0.249	0.128	-	-0.320	-
Rb	-0.291	0.117	-0.23	-	0.104	-0.325	-0.314
Sr	0.295	-	-0.307	-	0.104	0.158	-0.117
Y	-	-	0.152	0.768	-	0.150	0.267
Zr	-0.320	0.127	-	0.167	-	0.214	-
Nb	-0.183	0.176	-0.36	-0.397	0.155		0.122
Sc	0.292	-	-	-0.312	-	0.143	0.518
V	0.210	0.192	-	0.154	0.544	-0.378	0.340
Cr	0.311	0.180	-	-	-	-0.232	-
Cu	0.191	0.256	-	-	0.349	0.676	-
σ	2.82	1.90	1.47	1.21	1.01	0.84	0.64
Variance	0.44	0.20	0.12	0.08	0.06	0.04	0.02
Cumulative proportion	0.44	0.64	0.76	0.85	0.90	0.94	0.96

on the sintering degree and the pore structure developed in the clay matrix after the firing process. This allowed to evaluate the firing temperatures as suggested by the thermal stability of the mineral phases detected by XRPD analysis (Tite and Maniatis, 1975; Maniatis and Tite, 1981). The estimation of the firing temperatures was carried out on 11 representative samples chosen on the basis of their mineralogical composition. Table 5 reports some technological features of the samples (firing atmosphere and firing temperatures) hypothesized according to the vitrification stages of the clay matrix (fig. 7).

Discussion

A group of PCW samples (84-10, 9-27, 9-34, 9-35, 9-52, 9-184, 9-300, 9-301, 9-308) show very hard pastes of green grayish colour, likely due to high firing temperatures of calcium-rich clays (Picon, 2002), as confirmed by XRPD and seM analyses. Hard and coarser red coloured pastes, sometimes showing sandwich zoning with dark red or gray cores, characterize the other samples of this ceramic class. Some specimens (84-6, 84-10) show red or yellow-red cores and creamy edges. This shading red hues of the outer layers of the ceramic walls is the

A. De bonis, C. Grifa, A. IAnGe11A, M. MerCurio, M.I. Perrone and V. Morra

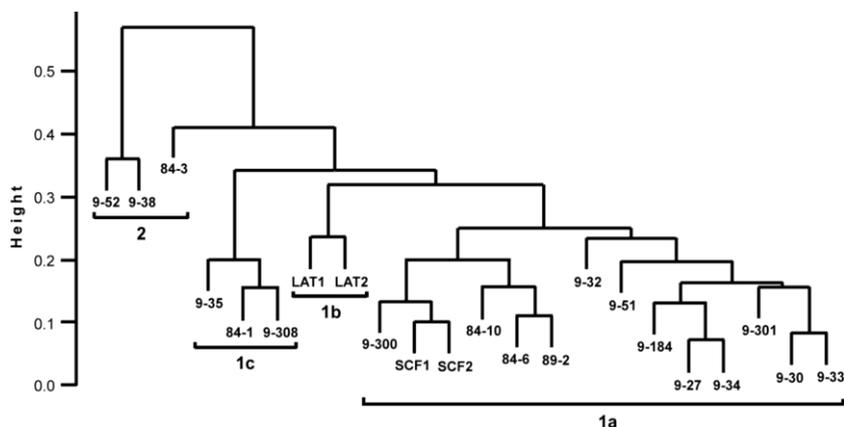


fig. 6 - Hierarchical clustering dendrogram representation (average method, euclidean distance).

Table 4

Semiquantitative mineralogical evaluation (XRPD) of investigated samples.
 xxx = predominant, xx = abundant, x = frequent, - = sporadic, tr = traces.

Sample	Quartz	Feldspar	Calcite	Hematite	Illite	Gehlenite	Clinopyroxene	Analcime	Leucite
9-27	XX	XXX	-	-	-	traces	XX	-	-
9-30	XX	XXX	-	traces	traces	X	traces	-	-
9-32	XXX	XXX	-	traces	X	-	-	-	-
9-33	XXX	XXX	traces	X	traces	X	-	-	-
9-34	XX	X	-	XX	-	-	XX	-	-
9-35	XXX	X	-	XX	-	-	XX	-	-
9-51	XXX	XX	-	X	traces	X	traces	-	-
9-52	XXX	traces	-	XX	-	-	XX	-	-
9-184	XX	X	traces	-	-	-	XX	-	-
9-300	XX	XX	-	XX	-	-	XX	-	-
9-301	XX	X	-	XX	-	-	XX	-	-
9-308	XX	X	-	XX	-	-	XX	-	-
84-1	XXX	XXX	-	X	traces	X	-	-	-
84-6	XX	XXX	-	X	-	traces	XX	-	-
84-10	XXX	XX	XX	-	-	traces	XX	-	-
89-2	XX	XXX	-	traces	-	traces	-	-	-
84-3	XXXX	XX	-	X	-	-	-	-	-
9-38	XXXX	XX	-	traces	-	-	-	-	-
LAT 1	XX	XXX	-	traces	-	X	XX	X	X
LAT 2	XX	XXX	-	X	-	traces	XX	traces	X
SCF 1	X	XXX	-	X	-	-	XX	-	X
SCF 2	X	XX	-	X	-	-	XX	X	X

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Table 5

Firing temperature ranges of some representative samples. Type of clay: nC = Non calcareous, C = Calcareous; firing atmosphere: ox = oxidizing, red = reducing; vitrification stages: iV = initial vitrification, V =extensive vitrification, CV = continuous vitrification, (Mb) = medium bloating pores, (Cb) = coarse bloating pores; abbreviations according to Tite and Maniatis, (1975).

Sample	Type of clay	Firing atmosphere	Vitrification stage	Firing temperatures (°C)
9-32	NC	ox	IV	800 – 850
84-1	C	ox	V	850 – 950
84-6	C	ox	V	850 – 1050
9-33	C	ox	V	850 – 950
LAT 1	C	ox	V	850 – 1050
LAT 2	C	ox	V	850 – 1050
84-3	NC	ox	CV	950 – 1000
84-10	C	ox	CV(MB)	1050 – 1200
9-52	C	ox	CV(CB)	1050 – 1200
SCF 1	C	ox - red	CV(CB)	1050 – 1200
SCF 2	C	ox - red	CV(CB)	1050 – 1200

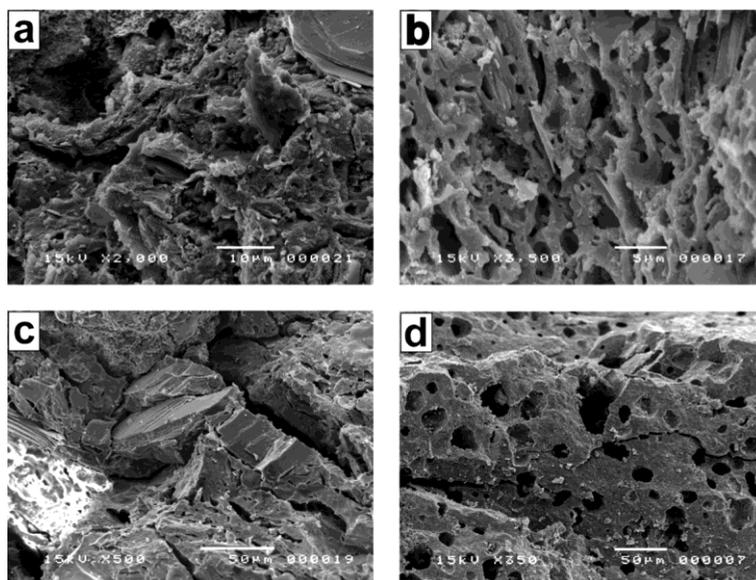


fig. 7 - seM images of ceramic pastes. a) PCW sample 9-32, vitrification stage iV; b) PCW sample 84-1, vitrification stage V. c) CW sample 84-3, vitrification stage CV. d) Kiln reject sample sCf 2, vitrification stage CV(Cb). Abbreviations according to Tite and Maniatis (1975).

results of the Fe^{3+} incorporation in the structures of new forming calcium silicates (e.g., clinopyroxene as revealed by XRPD) in the calcium-rich pastes fired at high temperatures (Molera *et al.*, 1998).

The optically isotropic matrix observed in optical microscopy may also account for the quite high firing temperatures of all the investigated samples. Most of the PCW fragments (84-10, 9-27, 9-30, 9-35, 9-52, 9-184, 9-300, 9-301, 9-308) are characterized by fine pastes with serial distribution of grains mainly represented by quartz, feldspar and mica with few volcanics. The other PCW samples (84-1, 84-6, 89-2, 9-32, 9-33, 9-34, 9-51) show a bimodal distribution with a relatively abundant coarse fraction mostly constituted by volcanic inclusions (clinopyroxene, pumices, lithics, scoriae). PCW samples display a chemical composition reflecting in many cases the textural grouping observed in PIM. A group formed by all the finer pastes PCW samples (84-10, 9-27, 9-34, 9-35, 9-184, 9-300, 9-301, 9-308) but also including the fragment 9-34 of coarser texture, is characterized by higher values of CaO and lower contents of Al_2O_3 , Fe_2O_3 and TiO_2 in comparison with the group of PCW fragments (84-1, 84-6, 89-2, 9-30, 9-32, 9-33, 9-51, 9-52), mainly composed by coarser paste samples (the finer ones being 9-30 and 9-52). The anomalous P_2O_5 content (1.96%) of sample 9-51 may be due to post-burial contamination phenomena (Fabbri *et al.*, 1994; Maggetti, 2001).

CW specimens also showing optically isotropic matrix, are characterized by abundant temper mainly constituted by detrital quartz-arenitic rock fragments, which account for the higher SiO_2 values observed (68 wt%); some metamorphic rock fragments and frequent volcanics are present as well. They are marked by a strong non-calcareous character (average CaO = 1.54%) due to the use of a different clay raw material.

The bricks are characterized by a chemical

composition similar to that of PCW samples. The highest values of Al_2O_3 (17.6%) and some trace elements (Ba, Sr) recorded in IAt 2 are likely due to the larger abundance of temper (31.2%) if compared to that of IAt 1 (17.5%) and all PCW samples. Among the volcanic products observed in these specimens leucite stands out either as individual crystals or analcimized in scoriae.

Kiln rejects, as expected, show marked evidences of high firing temperatures, as testified by their very hard pastes and by the large rounded pores as evidenced by SEM observations. Also, the dark gray colour is another effect of high temperatures. In particular, the dark green core fading in black edges of sCf 2 could be due to reducing conditions of the furnace atmosphere as a result of oxygen deficiency caused by the combustion of large quantities of wood (Picon, 2002). Kiln refuses show a chemical-petrographical composition very similar to that of PCW, with the only exception of higher Sr value. The occurrence of amphibole, garnet (sCf 1), and scoriae with analcimized leucite crystals typical of high potassium silica undersaturated rocks (HKs; Conticelli and Peccerillo, 1992) allows to correlate them to the Somma-Vesuvius volcanic complex, whose products are widespread in the valley (Zanchetta *et al.*, 2004).

The statistical treatment of chemical data confirms the existence of a large group of PCW samples including the kiln rejects and the bricks; the two CW fragments are well separated from the other specimens.

The evaluation of the firing temperatures according to Tite and Maniatis (1975) points out for most samples temperatures above 850°C. Only for one PCW sample (9-32), the presence of illite and the initial vitrification stage (iV), indicate a firing temperature ranging between 800 and 850°C.

Five samples (84-1, 84-6, 9-33, IAt 1, IAt 2) show an extensive vitrification stage (V),

typical of firing temperatures between 850 and 1050°C. The presence of traces of gehlenite, starting to form at around 800°C (Cultrone *et al.*, 2001) along with the persistence of illite, generally destroyed at around 950°C (Jordán *et al.*, 1999) leads to hypothesize a range of 850-950°C for the 84-1 sample. The same considerations can be done also for the PCW sample 9-33. A firing temperature of 950-1000°C was assumed for the non calcareous CW sample 84-3 due to a continuous vitrification stage (CV). The persistence of gehlenite in traces along with neoformed clinopyroxene and a continuous vitrification stage with medium bloating pores CV(Mb) in the PCW sample 84-10 account for temperatures next to 1050°C.

The continuous vitrification stage with coarse bloating pores CV(Cb) observed in the kiln rejects (sCf 1, sCf 2) points out temperatures at least higher than 1050°C. The same firing temperatures were evaluated for the 9-52 PCW sample where a CV(Cb) vitrification stage and the presence of neoformed diopside were recorded. The occurrence of analcime in the bricks (IAt 1, IAAt 2) and in the kiln rejects (sCf 1, sCf 2) is likely due to leucite alteration or even related to the alteration of the glassy phase (buxeda i Garrigós *et al.*, 2002); nevertheless, analcime cannot be formed during the firing of the ceramics because of its high content of crystal water (Schwedt *et al.*, 2006).

CONCLUSIONS

The specimens of the present research represent the first ceramic findings of the Caudium area carefully analyzed. This site is particularly important for its strategic position along the *Via Appia*, the consular road connecting the west and the east coast of Italic Paeninsula since Roman period.

Furthermore, the discovery of many late antique findings witnesses the intense occupation of the *Valle Caudina* despite the scarce

documentation available for that period.

This archaeometric investigation was focused on a large set of ceramic fragments, namely painted common ware, widespread in southern Italy during late Roman and Byzantine period (Grifa *et al.*, 2008), discovered during the archaeological reconnaissance survey of the site. Other samples of different type and function (cooking ware, bricks and kiln rejects) were also studied as comparison.

Painted common ware (PCW), bricks and kiln rejects are all characterized by calcareous pastes, presumably crafted with the same clayey raw material, mixed with different proportions of temper and fired between 850 and 1200°C.

CW samples show different chemical (e.g. low Cao) and petrographical features if compared to the PCW group so that the use of a different clayey raw material and temper is hypothesized. A possible exploitation area of the raw material should be one of the several non calcareous clay outcrops (*Argille Varicolori*) falling within the surrounding area of Caudium. Firing temperatures of about 950-1000°C were estimated for these samples.

The whole dataset, along with the archaeological (large number of fragments in the same site and the presence of kiln rejects) and geological (outcrop referred to blue-gray common clays of Ariano unit, extensively used for ceramic production; Grifa *et al.*, 2009) evidences indicate a local production of painted common ware (PCW) and allow to identify its reference group (Maggetti, 2001).

The volcanic temper observed in the samples has been ascribed to the Avellino Pumice, a Somma-Vesuvius related deposit, widespread in the *Valle Caudina*, whose products were used for other pottery productions of the neighbour Benevento area (e.g., Protomajolica; Grifa *et al.*, 2006, 2009). Nevertheless, leucite found in kiln rejects and bricks, is a mineral whose occurrence is not attested in this deposit and has to be related to other Somma-Vesuvius products. It would be

possibly associated to the Pollena eruption (AD 472), a leucite-bearing product, whose dispersal area overlaps the *Valle Caudina* (zanchetta *et al.*, 2004). in this case, the use of volcanic temper related to Pollena eruption could likely indicate the AD 472 as the lower limit of manufacturing for bricks and kiln rejects, these latter closely correlated with painted common ware (PCW).

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