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Archaic and classical ceramic artefacts from Caltagirone (Sicily): a first attempt for distinguishing imports and local imitations through petrography and chemistry

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ABSTRACT. — More than 30 ceramic artefacts of the Archaic and Classical periods ($6^{th}-5^{th}$ centuries BC) found in archaeological sites in the area of Caltagirone (Sicily) and belonging to the collection of the local «Museo Regionale della Ceramica» were analysed in terms of chemistry and petrography (XRD, XRF and optical microscopy). This suite consists of well defined forms (*lekythos*, *pelike*, *kotyliskos*, *oinochoe*), or vascular forms not perfectly identifiable and also cups, *alabastron* and oil lamps, all decorated with red or black varnish. In addition, some undecorated artefacts (two *protomes*, a loom weight and a figurine) and a kiln waster were also analysed.

The main aim of this study was to discriminate the imitations of Attic forms from those actually imported. In fact, the Archaic and Classic local production is strongly suspected by the archaeologists also in the light of the casual discovery in the same urban centre of coeval kiln structures. Moreover, the noteworthy ceramic tradition of Caltagirone, which is largely documented since the Arabian domination puts forward this hypothesis. Analytical results demonstrated what, at present, has been inductively suspected only through pure stylistic considerations. Local manufactures were deeply characterized by their petrographic and chemical features and also compared with the reference raw materials exploited in the same territory. A notable inference in the comprehension of intra-island fine ware circulation of that period is expected.

RIASSUNTO. — Più di 30 manufatti ceramici di età Arcaica e Classica (VI – V sec. a.C.), ritrovati in siti archeologici nell'area di Caltagirone (Sicilia) ed appartenenti alla collezione del locale "Museo Regionale della Ceramica di Caltagirone", sono stati analizzati dal punto di vista chimico e mineralogico – petrografico (XRD, XRF e microscopia ottica). La collezione esaminata consiste di forme ben definite (*lekythos, pelike, kotiliskos, oinochoe*), ovvero forme vascolari non meglio identificabili, ed, inoltre, coppe, *alabastron* e lucerne; tutte decorate con vernice rossa o nera. Inoltre sono stati esaminati alcuni manufatti privi di decorazioni (due *protome*, un peso da telaio e una figurina) e uno scarto di fornace.

L'obiettivo principale di questo studio è consistito nel distinguere i manufatti d'importazione da quelli riconducibili ad imitazioni delle forme Attiche. Infatti, una produzione Arcaica e Classica locale è fortemente sospettata dagli archeologi anche alla luce della casuale scoperta, nello stesso centro urbano, di fornaci coeve. Peraltro, la ben nota tradizione ceramica di Caltagirone, che è largamente documentata sin dalla dominazione Araba, depone a favore di quest'ipotesi. I risultati analitici dimostrano ciò che fino ad oggi è stato supposto soltanto attraverso considerazioni puramente stilistiche. Le manifatture locali sono state caratterizzate approfonditamente, per mezzo delle loro peculiarità chimico-petrografiche e per confronto con le materie prime estratte nello stesso territorio. È possibile in tal modo raggiungere una migliore comprensione dei flussi commerciali e di tecnologia presenti in quel periodo nell'ambito del territorio isolano.

KEY WORDS: Archaeometry, ceramic petrography, red-figure pottery, Sicily, Caltagirone.

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INTRODUCTION

Caltagirone is far famous for its millenary ceramic production, which is, however, well documented only since the early Arabic period. It reached its apogee around the 17th century AD giving *sui generis* majolica artefacts, which are known worldwide. Nevertheless, little is still known about the existence of local ceramic manufacture during the earlier period.

The city is amphitheatrically situated on three calcareous-clayey hills, occupying the southern slopes of Erei Mountains. The lithotypes which characterize the area comprise: the Gessoso-Solfifera series which is mainly represented by gypsum deposits; the Trubi formation of Lower Pliocene age; the Marne argillose (clayey marls) formation of medium-lower Pliocene age; the Argille *marnose e siltose* (marly and silty clays) formation of lower Pleistocene age. Both the later formations were formed due to the emerge of the Apennine chain and its subsequent dismantlement through erosion (Roda, 1965; Frazzetta, 1971; Lentini et al., 1991). The present study is focused on 32 ceramic artefacts dated back to the Archaic and Classical periods $(6^{th} - 5^{th} \text{ century BC})$ which came into light after excavations in the urban centre of Caltagirone and have been only recently conceded for analysis by the local «Museo Regionale della Ceramica». Our main aim was to attempt a first distinction, under an «archaeometric prospective», between imported goods and local imitations of typical Attic forms taking also into consideration the recent findings of ceramic kilns in the area of S.Gregorio (Regione Siciliana, 1999).

The identification of imitating manufacture of Attic forms in the Greek cities (*apoikiai*) in Sicily has since time been considered from the archaeologists (Barresi and Valastro, 2000 and references therein). One of the main problems consists in individuating and differentiating the ceramic productions and exchanges among the various Greek cities, as well as to appraise also their interaction with the indigenous Hellenised centres. In terms of «pure» archaeometric research the major problem which emerges is the low packing and the very fine size of the nonplastic inclusions which could theoretically obstruct the correlation with the reference raw material locally available.

SAMPLES AND METHODS

As above mentioned, this study involved the petrographic thin section analysis of 32 ceramic samples coming from excavations carried out in the urban area of Caltagirone. They include artefacts with easy type attribution and/or clear indications of vessel forms (*lekythos*, *pelike*, *kotyliskos*, *oinochoe*) and also vascular forms not perfectly identifiable, cups, alabastron and oil lamps, all decorated with red and black varnish (Fig. 1). In addition, some uncoloured artefacts (two protomes, a loom weight and a figurine) and a «kiln waster» were also analysed.Data concerning dating, type, form and deposition context of the ceramic artefacts are summarized in Table 1. In addition, 4 raw material samples were carefully selected within a wider set which belongs to a larger scale national project (Sviluppo Tecnologico nel settore delle terrecotte e del restauro, Parco Scientifico e Tecnologico della Sicilia, unpublished report, 2001), in such a way as to better represent the local Plio-Pleistocene clay deposits and in order to provide a «compositional reference group» as well as information concerning possible raw material sources. It has to be underlined that these clay samples came from S. Giorgio Mountain (few kilometres from the city centre) which has been exploited for local ceramic manufacture since several centuries (Ragona, 1949 and 1985).

The thin sections were prepared according to standard procedures and were studied using a ZEISS AXIOMAT polarizing microscope.

X-ray powder diffraction analysis (XRD) was carried out for all the samples included in this study. Measurements were performed using a Rigaku D/max IIIc diffractometer,



Fig. 1 – Photographs of a red-figure *pelike* (sample 105) and a terracotta figurine (sample 102) analysed in this study.

using CuK α radiation (monochomator graphite) at 40kV, 20mA. Spectra were taken from 4° to 70°2 ϑ at 1° 2 ϑ /min of scan speed.

Analytical measurements of a total of 19 elements (Si, Al, Ca, Mg, Fe, Na, K, Ti, Mn, Rb, Sr, Y, Zr, Cr, Ni, Ba, La, Ce, V) were obtained employing X-Ray Fluorescence (XRF), using a Philips PW 1400 wavelength dispersive spectrometer. For both the major and trace elements determinations, a powder pellet (4 cm in diameter) was prepared mixing approximately 1-2 grams of homogenized sample with 0.75 ml of a 4% solution Mowiol N50-98 (a polyvinyl-alcohol binder media. transparent in X-Rays). The mixture was subsequently compressed on a base of boric acid at about 8 tons/cm² by an hydraulic press. A chromium (Cr) target was run for the major elements, while, for the trace elements a Rh and W anode tubes were alternatively used under operating conditions which are reported with great detail elsewhere (Hein et al. 2001, in

press). Machine drift was monitored for, and corrected, by the routine running of a monitor sample using the international standard reference materials G2 for the major elements and BCR1 for trace elements. Quantitative analysis was obtained through the construction of calibration lines made using 52 international standard reference materials (USGS, NBS and IAEA standards). The methods proposed from Franzini *et al.* (1972a, 1972b and 1975) and Leoni and Saitta (1976a and 1976b) were followed in order to correct the raw results for the matrix effects.

RESULTS

Petrographic analysis

The initial grouping of the examined samples based on macroscopic criteria such as decoration, shaping technology and fabric was

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Description of the analysed samples from Caltagirone, according to ceramic cla	ıss,
dating and excavation site.	

#	Form	Period	Excavation site
89	lekythos	6 th -5 th BC	Necropolis of S. Luigi
90	unvarnished cap	6th-5th BC	»
91	black-varnished bowl	6 th -5 th BC	»
93	lekythos	5 th BC	»
95	protome (moulded)	5 th BC	»
96	black-varnished cup	6 th -5 th BC	»
97	black-varnished cup	6 th -5 th BC	»
98	kotyliskos	5 th BC	»
99	black-varnished cup	6 th -5 th BC	»
101	protome (moulded)	6 th BC	unknown
102	figurine (woman with a baby)	6 th BC	»
104	kotyliskos	6 th BC	»
105	pelike	5 th BC	»
111	Alabastron	6 th BC	kiln of S. Gregorio
112	loom weight	6 th BC	»
113	red figure vase	6 th BC	»
114	red figure vase	6 th BC	»
115	red figure vase	6 th BC	»
116	red figure vase	6 th BC	»
117	red figure vase	6 th BC	»
118	red figure vase	6 th BC	»
119	oinochoe	6 th BC	»
120	red-figure cup	6 th BC	»
121	kiln waster	6 th BC	»
122	unvarnished bowl	6 th BC	»
124	red figure vase	6 th BC	»
125	red figure vase	6 th -5 th BC	»
126	red figure vase	6 th -5 th BC	»
127	red figure cup	6 th -5 th BC	»
128	red figure oil lamp	6th-5th BC	»
133	black-varnished vase	6 th BC	»
134	lekythos	5 th -4 th BC	»

further refined and characterized by thin section microscopy. The following features have been considered significative and pointed out for each sample:

- colour and optical activity of the micromass;
- packing, sorting and grain size distribution of the non-plastic inclusions;

• composition of the non-plastic inclusions.

The record of the above attributes has been aimed to form firm *petrographic compositional groups* which could meaningfully yield insights on provenance and technology. As well known, the framework of this approach is dominated not only by the geology (lithology and stratigraphy) of the studied area but also by several «human behavioural factors» concerning the raw material selection and use as well as the forming and the firing techniques (Day, 1999).

The analysed samples can be distributed into 4 petrographic groups:

- Group «A», gathers samples 99, 124, 126, 127, 128 and 133. It deals with a self-tempered (natural tempered, i.e. the clavey raw material was used in as is state, without further addition of temper or purification) low calcareous paste with abundant phyllosilicates minerals occupying the groundmass. The micromass is optical active and ranges in colour from reddish to yellowish brown. The non-plastic inclusions present a packing between 5-15% and their size range between coarse silt and very fine sand (0.04 - 0.12 mm). They consist predominantly of mono and polycrystalline quartz, micas and occasionally feldspars (orthoclase, microcline, plagioclase).Rock fragments of metamorphic origin have also been recognised (Fig. 2a).

- *Group* «*B*» is characterized by a very low packing (1-3%). It comprises samples 89, 90, 91, 93, 96, 97, 98, 104, 105, 111 and 134. The micromass, in most of the cases, appears as optically inactive showing a variation of colour between yellowish brown and brown. The nonplastic inclusions show a coarse silt size and are predominantly represented by monocrystalline quartz. Minor quantities of mica, feldspars and polycrystalline quartz complete the mineralogical association (Fig. 2b).

- Group «C» is composed by samples 113, 114, 115, 116, 117, 118, 119, 120 and 125. They are characterised by non-plastic inclusions falling very fine sand granulometric class (0.06-0.12 mm). Packing is intermediate (5-15%) and colour of the micromass

(moderately active) is orange buff to brown. The main constituents are quartz, decomposed calcareous lithoclasts, bioclasts and feldspars (orthoclase, microcline and plagioclase). Quartzarenite fragments are less abundant while mica flakes have been detected even if in minor quantities (Fig. 2c).

- Group D includes samples 95, 101, 102, 112, 121 and 122, which are all characterized by a slight coarser fabric than the former group. ranging from very fine to fine sand (0.06-0.25 mm). This paste, presumably self-tempered, is moderately sorted and has a relatively high packing (15-30%). The micromass isgenerally, optically active and yellowish brown-brown in colour. The non plastic inclusions comprise predominately monocrystalline quartz, microfossils and calcareous lithoclasts. Feldspars (orthoclase, microcline and plagioclase), quartzarenite fragments and chert are also present in smaller quantities Sporadic mica flakes complete the mineralogical association (Fig. 2d). To be noted that sample 121 (Fig. 2e) was classified by the archaeologists of the MuseoRegionale della ceramica as a «kiln waster». It was found in the furnace of S.Gregorio, which has been quite recently discovered and dated back to the 5th century BC.

To further deal with the possibility of distinguishing locally made artefacts for the defined groups, thin sections were prepared from local raw material sampled from the Plio-Pleistocene clay deposits of S.Giorgio Mountain. Microscope examinations showed a fabric characterized by very fine non plastic inclusions (0.06-0.12 mm) with a medium-high packing. The sand grains are mainly composed of quartz, calcareous microfossils and lithoclasts of different nature. Feldspars (orthoclase, microcline and plagioclase), fragments of quartzarenite and minor quantities of mica have been also recognized (Fig. 2f). It is thus evident a strong similarity, especially from the compositional point of view, between local raw materials and the ceramic fabrics described for the samples belonging to groups 3 and 4.



Fig. 2 – Representative photomicrographs of the various petrographic groups individuated (a= group A, b = group B, c = group C, d = group D), the kiln waster (e) and the local raw material (f) (cross-polarized light; scale bar = 0.25mm).

X-ray diffraction

The result obtained from XRD analysis are summarised in Table 2. The equivalent firing temperatures, estimated by the comparison of the obtained mineralogical associations with those reported in the literature (Maggeti, 1981; Maniatis *et al.*, 1981; Maggetti, 1982), show that samples 95, 98, 101, 102, 105, 112, 117, 121, 122 and 133 were fired without exceeding the 850° C. This is indicated by the absence of gehlenite and pyroxenes and the simultaneous presence of elevated quantities of primary calcite.

On the contrary, in the samples 89, 99, 113,

	Quartz	Calcite	Diopside	Hematite	Feldspar	Gehlenite	Mica/illite
	~		A		L		
A124	+++	tr	++	+	+++	tr	++
A126	+++	+	+	tr	++	+	++
A127	+++	+	+	tr	++	+	++
A128	+++	+	+	tr	++		++
A133	+++	tr	tr	tr	+	tr	
A99	+++		+	tr	++	tr	+
B104	+++		++	tr	++	+	
B105	+++		+	+	++		++
B111	+++	+	++		++	+	
B134	+++	++	++	tr	+++	++	tr
B89	+++	+	+		++	+	+
B90	+++		++	tr	++		
B91	+++		++		++		
B93	+++		++		++		++
B96	***		++	tr	++		
B97	*** +++	+	. ++	tr	++		
B98	+++	++		tr	++		tr
C113	+++	+			++	+	tr
C114	+++	+	+	+	++	+	
C115	+++	+	tr	tr	++	+	
C116	+++	+	+	+	++	+	
C117	+++	++	tr	tr			+
C118	+++	+			+++	++	tr
C119	+++	++	+	tr	+++	++	tr tr
C120	+++	++			++	++	tr
C125	+++	++		+	+++	++	tr
D101	+++	+	tr	+	++	tr	tr
D102	+++	++			+		++
D112	+++	+++			+		+
D121	+++	++			+		++
D122	+++	+	+	tr	+++		+
D95	++	++			+		+

TABLE	2
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Results obtained through X-ray diffraction (+++ = abundant, ++ = common, + = minor quantities, tr = traces).

114, 115, 116, 118, 119, 120, 125, 126, 127, 128 and the occurrence of mineral phases like gehlenite and pyroxenes indicates a higher firing temperature, most probably around 900-

950° C. Few quantities of calcite, in this case, represent a secondary phase precipitated during burialstage, as confirmed by microscope observation.

Finally, samples 90, 91, 93, 96, 97 104, 111, 124, and 134 are characterized by the elevated presence of pyroxenes and Ca-rich feldspar due to the further development of these «firing» mineral phases in parallel with the decrease of illite/muscovite and gehlenite attributed to their decomposition. The equivalent firing temperature in this case is certainly higher than 950°C.

Chemical analysis and statistical treatment of the data set

Raw chemical data of the studied samples, normalised against loss on ignition, are shown in Table 3. In order to minimize the so-called «perturbations problem» due to chemical alteration/contamination which eventually occurred in burial environment, the whole chemical data set, for the grouping procedure, was expressed as log-ratios of each individual element over aluminium. This element was selected because it showed the lowest covariance within the present analytical set (comprehensive of major, minor and trace elements) and therefore the log-ratios based on Al as divisor will not introduce any further variability coming from it. This method has been recently proposed and tested successfully for statistical modelling of ceramic artefacts compositional data (Buxeda, 1999; Baxter, 2001).

In a first step, a *model-based cluster analysis* was performed using as clustering criterion the «centroid» (Fig. 3). Three clear chemical groups were revealed:

□ the first chemical group contains all the samples which were assigned to petrographic group «A» with the exception of sample 133 (chemical *outlier*);

 \Box a second cluster (second chemical group) can be easily distinguished which contains all the samples that are forming petrographic groups «C» and «D»;

□ in the third chemical group all the samples which resulted to form petrographic group «B» are gathered.

From this first point of view, the chemical discrimination observed in the data set seems to

be in a satisfactorily agreement with petrographic observations. In other words, also by means of chemical analysis the studied ceramic artefacts show differences which are sufficient to let them to be classified into different «groups». Therefore, the meaning of these groups in terms of classification is even stronger if the good correspondence with petrographic observation is considered.

In order to investigate the data structure in another way, these initial separations were also treated using the principal component analysis (PCA) by S-plus 2000 package (Mathsoft). Factor scores on the first three components (representing the 83% of the total variance) of the considered samples are plotted on the threedimensional diagram showed in Figure 4. where symbols have been given to the data points to illustrate the groups revealed by the petrographic analysis. Moreover, the elemental loadings on the first two extracted components have been plotted on the binary diagram of Figure 5, to point up the contribution of each single variable on the components. It has to be underlined that no refinement of the data pattern has taken place, by means of outliers removal or group reassignment. Once again, samples belonging to petrographic groups «A» and «B» resulted quite homogeneous and are clearly separated. The samples belonging to petrographic groups «C» and «D» are gathered together forming a single and distinctive chemical group evidently separated from the former ones. It is important to note that local raw materials and the kiln waster (sample 121) cluster in proximity to this last chemical group. The mean concentrations and standard deviations for these chemical groups are given in Table 4, which includes the clay samples as well.

DISCUSSION

Both petrographic and chemical comparisons of the local raw materials and the single kiln waster with the samples described as petrographic groups «C» and «D» put forward

								-				-				-			
#	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	Rb	Sr	Y	Zr	Cr	Ni	Ba	La	Ce	V
89	51.77	20.91	7.09	6.10	10.19	0.56	2.12	0.99	0.13	52	392	26	175	402	468	708	35	84	170
90	51.84	17.50	15.33	3.40	8.13	0.61	1.84	1.00	0.13	40	483	21	194	90	58	382	49	73	143
91	53.15	17.34	9.60	6.15	8.99	0.70	2.94	0.87	0.14	111	295	26	154	338	376	562	33	63	148
93	52.37	19.64	5.40	6.64	9.59	2.62	2.57	0.91	0.13	115	213	24	145	382	427	576	44	58	139
95	56.90	17.13	13.79	2.38	6.64	0.44	1.60	0.86	0.12	71	375	22	255	69	52	382	33	63	102
96	56.37	19.78	12.67	2.19	6.09	0.40	1.47	0.79	0.11	116	219	24	142	340	373	555	34	43	134
97	53.55	18.41	7.88	5.64	9.42	0.78	3.17	0.92	0.13	115	213	24	145	382	427	576	44	58	139
98	47.95	17.21	16.16	5.02	10.11	0.52	1.79	0.92	0.16	62	325	22	123	175	242	354	36	52	140
99	52.10	23.18	6.74	3.26	8.94	1.07	3.62	0.80	0.13	136	285	29	203	96	69	673	55	95	145
101	61.10	16.29	8.99	2.68	7.13	0.65	1.92	0.84	0.15	65	282	24	275	76	46	576	34	65	97
102	60.39	15.76	11.52	2.14	6.54	0.64	1.85	0.84	0.12	67	404	25	292	70	39	911	38	61	97
104	49.90	18.55	13.07	4.17	9.63	0.52	2.84	0.87	0.14	108	288	22	122	168	232	483	42	58	158
105	54.60	20.35	5.60	4.30	10.35	0.73	2.85	0.98	0.14	94	277	27	174	422	463	611	32	48	140
111	50.10	16.41	16.26	4.34	8.68	1.66	1.41	0.83	0.16	71	315	23	139	146	190	450	41	59	144
112	58.04	13.57	17.44	2.12	5.51	0.49	1.76	0.70	0.14	57	369	20	266	53	32	519	30	58	87
113	57.48	15.30	13.58	2.57	6.87	0.70	2.24	0.82	0.13	73	407	24	268	70	37	529	36	65	125
114	59.21	15.55	11.04	3.10	6.95	0.83	2.14	0.82	0.13	74	353	23	250	74	42	516	41	59	114
115	59.08	15.41	11.75	2.66	6.95	0.64	2.29	0.82	0.13	86	387	25	265	67	35	465	41	60	111
116	59.62	15.26	11.12	2.74	7.04	0.86	2.18	0.82	0.12	79	352	25	273	77	40	413	41	77	123
117	59.60	15.42	10.96	2.60	6.91	0.78	2.45	0.82	0.12	81	388	27	268	70	44	378	39	62	94
118	59.28	15.29	11.42	2.42	6.98	0.71	2.59	0.82	0.13	83	1326	25	308	73	45	368	41	67	112
119	58.28	14.85	13.16	2.73	6.81	0.71	2.22	0.82	0.13	71	407	27	318	73	36	382	35	81	121
120	58.11	14.64	14.18	2.50	6.52	0.65	2.14	0.79	0.14	74	390	26	310	64	40	540	32	58	115
121	57.54	14.23	15.24	2.54	6.14	0.70	2.26	0.74	0.13	69	445	23	246	60	37	432	33	62	101
122	59.33	17.48	8.43	2.95	7.48	0.73	2.28	0.93	0.12	71	401	27	277	90	49	624	40	84	140

 TABLE 3

 Elemental concentrations (water-free basis), obtained through X-ray fluorescence analysis

Archaic and classical ceramic artefacts from Caltagirone (Sicily) ...

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TABLE 3: Continued

#	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	Rb	Sr	Y	Zr	Cr	Ni	Ba	La	Ce	V
124	52.47	22.19	7.64	3.11	8.74	1.03	3.72	0.77	0.13	137	283	25	170	93	65	687	54	84	156
125	58.56	14.70	13.73	2.42	6.37	0.94	2.08	0.79	0.13	73	396	24	289	66	34	445	39	74	96
126	53.58	23.58	4.74	2.98	8.95	0.98	4.16	0.73	0.12	147	246	29	209	96	65	779	50	73	162
127	54.82	21.33	6.90	2.75	8.30	1.14	3.59	0.84	0.14	124	266	26	172	80	56	707	52	78	137
128	50.76	21.72	10.01	2.98	8.25	1.02	4.19	0.71	0.14	133	341	29	193	83	52	627	53	80	124
133	61.65	18.08	5.46	2.30	7.46	1.17	2.81	0.89	0.10	131	177	29	262	162	160	452	38	70	131
134	51.47	17.96	10.27	5.71	9.32	0.69	3.41	0.87	0.14	106	315	21	131	120	158	449	38	66	135
m28	58.59	13.88	14.75	3.89	4.9	0.9	2.02	0.74	0.13	73	417	21	272	91	30	250	32	44	105
m29	58.56	14.04	15.96	3.03	4.75	0.62	2.11	0.63	0.13	75	393	17	236	85	31	241	25	74	103
m30	57.91	15.54	13.77	3.46	5.16	0.52	2.11	0.85	0.1	82	454	21	240	94	46	262	39	79	119
m31	57.11	16.03	14.42	3.47	5.09	0.68	2.22	0.86	0.11	89	470	23	204	102	47	287	43	10	120



Fig. 3 – Dendrogram resulting from model based hierarchical cluster analysis using the centroid agglomerative algorithm. Three distinct clusters are separated (letters denote the respective petrographic groups).

to consider them as representing a local production. On the contrary the same evidence let interpret petrographic groups «A» and «B» as imported products. The differences between petrographic group 3 and 4 deal mainly with textural aspects (packing, sorting and grain size distribution) and they might likely attributed to the exploitation of two different stratigraphic levels of the same Plio-Pleistocene clay formation. Further mineralogical investigation on local clavs carried out to characterize the famous Caltagirone's majolica manufacture (Sviluppo Tecnologico nel settore delle terrecotte e del restauro, Parco Scientifico e Tecnologico della Sicilia, unpublished report, 2001) show that, in general, Pliocene stratigraphic levels are characterized by a natural fine sand content which is slightly lower than Pleistocene ones. The application of cluster analysis gave a first confirmation of the existing groups. In the resulted dendrogram, the more extensive group contained all together those samples (petrographic groups «C» and «D»), which petrography indicated as manufactured using a raw material exploited from the proximity of the present urban centre of Caltagirone, being strongly dominated by the Messinian evaporitic serie. Another two groups were recognized which were respectively contained exclusively imported samples.

Principal Components Analysis



Fig. 4 – Projection of the factor scores in the multi-dimensional space of the three first principal components which account for the 83% of the total variance. Samples 93 and 133 represent outliers while individual 90 was probably misled through the petrographic analysis. (1 = group A, 2 = group B, 3 = group C, 4 = group D, m = raw material, 121 = kiln waster).

	normalised subcompositions (oxides in wt %, trace elements in ppm).																		
Group	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	Rb	Sr	Y	Zr	Cr	Ni	Ba	La	Ce	V
mean n=5	C1 52.75 1.54	22.40 0.96	7.21 1.90	3.02 0.19	8.64 0.34	1.05 0.06	3.86 0.29	0.77 0.05	0.13 0.01	135 8	284 35	28 2	189 18	90 8	61 7	695 56	53 2	82 8	145 15
mean n=9	C2 52.09 2.60	18.55 1.52	10.96 3.84	4.85 1.26	9.20 1.29	0.73 0.37	2.44 0.76	0.89 0.07	0.14 0.01	93 25	293 55	24 2	145 20	277 122	325 121	528 105	37 4	59 12	145 12
mean n=16	C3 58.40 2.07	15.52 1.11	12.61 2.39	2.62 0.33	6.81 0.57	0.69 0.13	2.12 0.26	0.83 0.07	0.13 0.01	71 11	448 238	24 2	272 30	71 9	42 7	491 137	38 5	67 8	111 16
mean n=4	R.M. 58.04 0.70	14.87 1.07	14.73 0.92	3.46 0.35	4.98 0.19	0.68 0.16	2.12 0.08	0.77 0.11	0.12 0.02	80 7	434 35	21 3	238 28	93 7	39 9	260 20	35 8	72 20	112 9

TABLE 4

Elemental concentration means and standard deviations for the three defined chemical groups and the raw materials, for normalised subcompositions (oxides in wt %, trace elements in ppm).

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Subsequently, the projection of the three first components of a principal component analysis in the three dimensional space gave a clearer image of the three separated groups, permitting also the individuation of possible outliers such as samples 93 and 133 and eventual petrographic misclassifications (sample 90). The larger group contains altogether the samples representing the petrographically established local artefacts. The aggregation of samples in this group was also subjected to a second PCA, omitting chemical groups «A» and «B», but no others evident structure in the data was revealed. This is a further confirm of the similar origin for the raw material utilized in the manufacture of these samples.

It is intriguing to underline that all the samples that gather in petrographic group «D» (with the exception of sample 122) are noncontainers and all undecorated items, such as moulded protomes, figurine and loom weight, including also the kiln waster. This, from a first viewpoint could satisfactorily account for the coarseness of the relevant petrographic fabric which may be attributed to a selection of a different, coarser, stratigraphic level within the same clay outcrop. On the other hand, the presence of utilitarian items in this group (loom weight) as well as the lack of decoration could give to them the property, although not unequivocally, of an additional monitor parameter for controlling the local character for the samples of petrographic group «C». The latter is composed exclusively from samples attributed to red varnished vessel forms.

The samples gathered in petrographic group «A» represent red varnished artifacts with the exception of sample 133 which is a black varnished vase and was identified as an outlier through the statistical treatment of the chemical data set. According with archaeological stylistic considerations, the mineralogical attributes of this group and in particular the abundance of mica's and fragments of metamorphic rocks (phyllites) pronounce the incompatibility of the raw

material utilized for the manufacture of this artefacts with the locally available sources and in the same time give subtle indications for an extra-island provenance, which might be circumscribed to the well established Attic production from the homonymous region in central Greece (Higgins et al, 1996; Barresi and Valastro, 2000). Similar consideration was difficult to be assumed for the samples contained in petrographic group «B» as a result of the fineness of the relative fabric and the variety of ceramic forms included. Nevertheless, chemistry helped to obtain a specific chemical pattern for these samples and to roughly assign a non local character to them. Moreover, sample 90 was individuated as probably misclassified through the petrographic analysis and was grouped together with the local manufactures (petrographic groups «C» and «D») which is an easily accepted output, considering also its lack of decoration, whilst sample 93 resulted an outlier.

The tendency shown for the chemical separation of the group «B» from the rest reflects the influence of the clay fraction of the ceramic paste, as elements like Fe, Ti, Ni, V, Cr and Mg show their major expression in this fraction and are those by which component one is mainly loaded (Fig. 5). The elevated abundance of feldspars and micas in the samples of group «A» seems to afford for the influence of the elements Na, K, Al, Ba, and Rb, whilst Ce, La and Y may attribute to the elevated presence of accessory minerals rich in rare earth elements (e.g. monazite) in the metamorphic fragments present. Petrographic groups «C» and «D» are influenced from the elements Ca and Sr which can easily be correlated with the specific attributes of the local raw material which includes abundant fragments of limestone and microfossils. Moreover, the satisfactory concordance between the local raw material and the samples from groups «C» and «D» may lie in the fact of the use of a single self-tempered clay for the manufacture of the artefacts.



Fig. 5 – Elemental loadings regarding the two first components extracted through the principal components analysis.

CONCLUSIVE REMARKS

The archaeometric research undertaken in this case study, both in terms of petrography and chemistry, lead to a strong pronouncement of the archaeological hypothesis based only on stylistic aspects. Caltagirone has been demonstrated to be a manufacture centre in Sicily where classic Greek fine pottery, decorated with red and black varnishes, was imitated. The used analytical techniques have therefore pointed out the exploitation of local raw material (Plio-Pleistocene marly clay) as the source for a consistent part of the studied manufactures and traced up those parameters, compositional and textural, which strongly help to individuate extra-island imports.

This study also established the usefulness of the combined approach using petrography and chemistry for the characterization (provenance) of ceramic artefacts with «fine fabric» (low packing and very fine size of the non-plastic inclusions) such as those examined, specially when a correlation with the potential local raw material locally is obtainable.

Finally, it becomes evident that a wider upcoming research could, on this basis, shed more light on the interaction between the incoming colonial Greek elements and the indigenous inhabitants, in terms of intra-island goods circulation (trade) as well as technology transmission.

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REFERENCES

- BARRESI S. and VALASTRO S. (2000) Vasi attici figurati, vasi sicelioti. Maimone Eds., Catania, 192 p.
- BAXTER M. J. (2001) Statistical Modelling of Artefact Compositional Data. Archaeometry **43**(1), 131-147.
- BUXEDA I. and GARRIGOS J. (1999) Alteration and contamination of archaeological ceramics: the perturbation problem. J. Archaeol. Sci. 26, 295-313.
- DAY P.M., TSOLAKIDOU A., KIRIATZI E. and KILIKOGLOU V. (1999) — Group therapy in Crete: A comparison between analyses by INAA and petrographic thin sections of Early Bronze Age pottery from Knosos. J. Archaeol. Sci. 26(8), 1025-1036,
- FRAZZETTA G. (1971) La sezione stratigrafica plio-pleistocenica di Monte della Scala presso Caltagirone (Catania). Atti Acc. Gioenia Scienze Nat., 3(7a), Catania, 193-240.
- FRANZINI M. and LEONI L. (1972) A simple method to evaluate the matrix effects in X-ray fluorescence analysis. X-Ray Spectrometry, 1, 151-154.
- FRANZINI M. and LEONI L. (1972) A full matrix correction in X-ray fluorescence analysis. Atti Soc. Tosc. Sc. Nat. Mem., **79**, 7-22.
- FRANZINI M., LEONI L. and SAITTA M. (1975) Revisione di una metodologia analitica per fluorescenza-X, basata sulla correzione completa degli effetti di matrice. Rend, Soc. It. Mineral. Petrol., **31** (2), 365-378.
- HEIN A., TSOLAKIDOU A., ILIOPOULOS I., MOMMSEN H., BUXEDA I., GARRIGOS J., MONTANA G. and KILIKOGLOU V. (2001) — Standardisation of elemental analytical techniques applied to provenance studies of archaeological ceramics – an inter laboratory calibration study. Analyst (in press).
- HIGGINS M.D. and HIGGINS R. (1996) A geological companion to Greece and the Aegean. Cornell University Press, Ithaca (NY), p. 240.
- LENTINI F., CARBONE S., CATALANO S., GRASSO M.

and MONACO C., (1991) — Presentazione della carta geologica della Sicilia centro-orientale. Mem. Soc. Geol. It., 47, 145-156.

- LEONI L. and SAITTA M. (1976a) Determination of Yttrium and Niobium on standard silicate rocks by X-Ray fluorescence analyses. X-Ray Spectrometry, 5, 29-30.
- LEONI L. and SAITTA M. (1976b) X-ray fluorescence analysis of 29 trace elements in rock and mineral standards. Rend, Soc. It. Mineral. Petrol., **32** (2), 497-510.
- REGIONE SICILIANA, ASSESSORATO BENI CULTURALI, AMBIENTALI and PUBBLICA ISTRUZIONE (1999) — Linee guida del Piano Territoriale Paesistico Regionale, Palermo, p.434.
- MAGGETTI M. 1981 Composition of Roman pottery from Lousonna (Switzerland). In: «Scientific studies in ancient ceramics», British Museum Occasional Paper, M.J. Hughes (Ed.), London, **19**, 33-49.

- MAGGETTI, M. 1982 Phase Analysis and Its Significance for Technology and Origin. In: «Archaeological Ceramics», Smithsonian Institution Press, J.S. Olin & A.D. Franklin (Eds.),Washington DC., 121-133.
- MANIATIS Y., SIMOPOULOS A. and KOSTIKAS A. (1981) — Moessbauer study of the effect of calcium content on iron oxide transformations in fired clays. J. Am. Ceram. Soc., 64, 263–269.
- ORSI P. (1904) Sicilia. VI. Caltagirone- Siculi e Greci a Caltagirone, in «Notizie degli Scavi di Antichità», 132-141
- RAGONA A. (1949) La ceramica caltagironese alla luce dei documenti. Faenza, 2, 40-49.
- RAGONA A. (1985) La maiolica siciliana dall'origine all'ottocento. Ed. Sellerio, Palermo.
- RODA C. (1965) I sedimenti plio-pleistocenici della Sicilia centro-meridionale. Atti Acc. Gioenia Sc. Nat., 17, 37-62.