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Provenance and technology of bricks from the Greek colony of Kaulon (Calabria, Italy)

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ABSTRACT - This paper presents the first results from a study of 26 bricks used in two buildings (called Casa Matta and San Marco) of the ancient city of Kaulon of Magna Graecia, in Calabria, Southern Italy. Archaeological research dates the beginning of Greek occupation of the area around the end of the VII century B.C.. Several methods were used to study the bricks of ancient Kaulon: petrographical analyses by optical microscopy, mineralogical analysis by XRD, and chemical analysis by XRF. Petrographical analysis distinguished the bricks into two groups: the first composed of some of the bricks of Casa Matta, in which non-plastic inclusions are mainly represented by granitic rocks, and the second, which includes all the San Marco bricks and the remaining ones of Casa Matta, in which non-plastic inclusions contain metamorphic and granitic rocks. XRF chemical analyses of all brick samples confirmed optical microscopy observations. Clay and silty clay, potential raw materials for producing bricks, were taken from Pliocene deposits near the present-day town of Monasterace Marina, and subjected to XRF analyses for major and trace elements, in order to compare them with the chemical composition of the bricks. Results show that the raw materials for all bricks were probably quarried locally. Clay samples were also experimentally fired in an oxidising atmosphere, in order to compare the developed mineral phases of the

studied bricks. On the basis of these results, a furnace temperature of at least 900°C is inferred for most of the bricks.

RIASSUNTO - Nel presente lavoro sono illustrati i risultati ottenuti dalle analisi mineralogiche, petrografiche e chimiche su 26 laterizi utilizzati in due costruzioni (Casa Matta e San Marco) dell'antica Kaulon, importante città della Magna Grecia, situata sulla costa ionica della Calabria, in Italia Meridionale (attuale Monasterace Marina). Le ricerche archeologiche fanno risalire l'occupazione di tale area da parte dei greci, alla fine del VII secolo a.C. Lo scopo del lavoro è la caratterizzazione dei laterizi e delle potenziali materie prime della zona, per ottenere informazioni sulla loro possibile produzione locale e sulla tecnologia impiegata. Lo studio dei laterizi al microscopio ottico ha permesso la distinzione di due gruppi, il primo in cui la frazione non plastica è formata in prevalenza da granuli di minerali e di rocce granitiche, e un secondo gruppo in cui la frazione non plastica è invece costituita in prevalenza da granuli di rocce metamorfiche e granitiche. Le differenze riscontrate nella composizione chimica in fluorescenza a raggi X (elementi maggiori ed elementi in tracce), hanno confermato i risultati dell'analisi petrografica. Le potenziali materie prime per la produzione dei laterizi, prelevate nella zona di Monasterace Marina (depositi argillosi pliocenici e sabbie), sono state analizzate in XRF e confrontate con i laterizi. I risultati ottenuti indicano che le argille e le

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sabbie locali sono state utilizzate con molta probabilità per la produzione dei laterizi. Le fasi mineralogiche formate nelle argille cotte sperimentalmente in condizioni ossidanti, sono simili a quelle riscontrate nei laterizi, per cui si ipotizza una temperatura di cottura di almeno 900 °C, per la maggior parte dei laterizi studiati.

KEY WORDS: Kaulon, Bricks, Petrographic analysis, XRD, XRF, Raw Materials.

INTRODUCTION

The object of this study are 26 bricks used in two buildings called *Casa Matta* and *San Marco* (Fig.1) of the ancient city of Kaulon of Magna Graecia, in Calabria - Italy. The aim is the characterization of the bricks throughout several methods in order to compare their composition with clay and silty clay, potential raw materials collected near the present-day town of Monasterace Marina, in order to infer if production was performed in loci or not. Further aim is to investigate the technology of the bricks production throughout experimental firing of the local raw materials.

Located on the Ionian coast of Calabria, Kaulonia (Fig. 2), the present-day Monasterace Marina, occupied an area between the two *poleis* of Locri and Crotone, near the present-day Punta Stilo (once Cocyntum promontorium). Scholars now agree in considering Kaulonia as an Acaian colony founded in the early VII century B.C., later recolonised by Crotone, with the aim of limiting the northward expansion of the inhabitants of Locri. In the 1990s, studies in the village of San Marco revealed one of the largest and very well conserved sectors of the Greek city. Excavations are still under way, and some dwellings going back to several chronological phases have been found: the Hellenistic phase (IV-III centuries B.C.) and the archaic and classic phases (V century B.C.), with later urban building work undertaken in Roman times. The building excavated near Casa Matta, south of San Marco, is very complex, and several of its rooms are still being studied. Excavation data indicate that the building was constructed on a pre-existing house in the second half of the IV century B.C., and that it was inhabited until later than the second half of the II century B.C.. It was abandoned at the end of that century, probably coinciding with the abandon of the entire quarter of the city. The bricks examined here, from the Archaeological Museum of Monasterace Marina, were chosen according to their provenance. Among many available materials,



Fig. 1 - Kaulon archaeological site. a) Casa Matta; b) San Marco.



Fig. 2 - Simplified geological map of the Monasterace Marina area. 1 =Quaternary continental conglomerates and reddish sands; 2 = Pliocene sandstones and sands; 3 = Pliocene clays. silty clays and silts with local sand intercalations; 4 = Pliocene conglomerates and gravels with intercalations of coarse sand. Location of archaeological site is also indicated.

we chose to study some fragments, found in the above two areas of the ancient city, which is already known the stratigraphic position of the findings and their chronology. It should be noted that these materials are artefacts used to construct load-bearing structures (bricks) and roofs (tiles), i.e., commonly used objects and presumably produced on the spot, or in any case with materials from areas not far from those in which they were found. In ancient Greek cities, there were always workshops producing building materials nearby, and the sign, or mark, of each workshop was stamped on their products. It is often difficult to date these materials, since they have remained almost unchanged in the course of time. Although products from the various workshop were for sale, it has been ascertained that the actual workshops were not widespread, but more often located on a regional scale. One part of Kaulon, situated immediately outside the city walls, in the present-day village of Lupa, was devoted to working clay. Studies have documented the existence of a furnace of probable Hellenistic age and other structures, still awaiting excavation (Iannelli, 2001). In this work, 26 fragments, mainly of bricks and tiles, were studied (Fig. 3). Eighteen were found during excavations of the house near Casa Matta and eight in the San Marco site. Their texture is mainly coarse, with a homogeneous matrix, and



Fig. 3 - Brick samples representative of Casa Matta (a) and San Marco (b) respectively.

thicknesses varying from 2 to 5 cm. As regards dates, the material collected from the building near Casa Matta is almost exclusively due to collapse of walls and/or roofs, suggesting an approximate date between the construction of the house, i.e., the second half of the IV century B.C., and when it was abandoned, at the end of the II century B.C. It is more difficult to date the findings from San Marco, because there are a greater number of fragments and because it is difficult to establish stratigraphic relationships, since the ceramic material is still being studied. This problem will have to be postponed until excavation data can be published. Raw materials from the surrounding area were sampled in order to establish the provenance of the clay and sand used to make the bricks (Fig. 2). The area of Monasterace lies on Pliocene sandstone and clay sediments of the Monte Narbone Formation (Cavazza et al., 1997). The continental terraces, composed of conglomerate and reddish sand, belong to the Upper Pleistocene. The ancient city of Kaulon rose on fluvial-coastal Holocene deposits, while quarries may have been exploited in the Pliocene sediments. The raw material to

be compared with the finished bricks is Pliocene clay, ranging from pale grey to brown in colour, containing local sandy intercalations and rich foraminiferous microfauna. Six samples of clay came from an old quarry and nine from various points, all close to the archaeological site. Three clay samples were taken from the sandy intercalations of the same Pliocene deposit and three others from the Quaternary continental deposit of reddish sand (Fig. 2).

ANALYTICAL METHODS

The bricks were examined macroscopically, and also characterised by several mineropetrographic and geochemical methods. Analytical techniques included petrographic analysis by optical microscopy, XRD mineralogical analysis and XRF chemical analyses. The clay samples from areas around the excavations were subjected to grain-size analysis by the fractionated sedimentation method according to Stockes' law, and to XRD mineralogical and XRF chemical analyses. The sand samples were examined by XRF chemical analysis and studied in thin sections on the fraction between 0.5 to 2 mm. Furthermore, some clay samples were specially prepared and experimentally fired in an electric furnace at temperatures of 650 °C and 900 °C, in order to take information on brick firing temperature. Mineralogical compositions were determined by XRD on a Philips PW 1710 diffractometer with vertical goniometer, Cu-K α radiation, operating at 40 kV and 20 mA. The investigated areas ranged between 5° and 60° of 20. A Philips PW 1480 spectrometer was used for XRF analysis of all samples, correction of matrix effects was made through computer processing (Franzini *et al.*, 1975).

RESULTS AND DISCUSSION

Petrographic analysis

For petrographic analysis, the bricks were subdivided into two groups. Group 1 containing some bricks from Casa Matta and group 2, which includes the remaining Casa Matta bricks and all those of San Marco. The first group is mainly characterized by fragments of minerals and rocks of granitic origin in the non-plastic fraction (Fig. 4a) set in a reddish birefringent matrix and weakly oriented. Non plastic fraction is composed mainly by sub-angular to rounded



Fig. 4 - Optical microphotographs of: a) first group of bricks – Dashed line indicate the granitoid clasts; b) reddish sand containing granitoid rock fragments similar to the first group of bricks; c) second group of bricks - Dashed line indicate phillites and micaschists; d) Sand intercalations containing the phillites and micaschists fragments similar to the second group of bricks.

grains of quartz, orthoclase with pertitic growths, zoned plagioclase and biotite. The average size of the non-plastic fraction is around 1 mm, up to 2 mm for the granitic rock inclusions, without sorting. The scarce and small voids have an elongated shape parallel to the matrix orientation and may be considered a primary porosity (Eramo et al., 2004). The matrix of group 2 samples is very similar to the group 1, but is much finer. The non-plastic fraction is composed by grains of quartz, microcline, pertitic orthoclase, plagioclase twinned according to the laws Albite and highly oxidized biotite. The more abundant rock fragments are micaschists and minor phyllites with subordinate granitic rock fragments (Fig. 4c). The average size of the non-plastic fraction is about 0.8 mm, but the schist fragments have not angular, elongated shape and size up to 2.5 mm. Only tree bricks contain small amount of microfossils mould (foraminifera) and secondary calcite. The voids are more abundant than the group 1 and their shape is both rounded and elongated with the same orientation of the matrix. Comparisons between the non-plastic fraction of the bricks and thin sections of sandy intercalations showed that the latter are compatible with group 2 bricks, since they contain fragments of granitic and metamorphic rocks (Fig. 4d). Instead, the thin sections of the sand of the overlying continental deposit is mainly composed of fragments of granitic rocks (Fig. 4b). The association of granitic and low-grade metamorphic rocks is typical of the Stilo unit exposed in this area of the Calabria region (Bonardi et al., 1984; Pezzino et al., 1990; Barra Bagnasco et al., 2001).

Grain-size analysis of clay

Nine representative samples of Pliocene clay were subjected to grain-size analysis (Dell'Anna and Laviano, 1987), to establish the percentages of sand, silt and clay. According to Shepard's classification (Shepard, 1954), seven of the clay samples are silty clay and the others clayey silt (Fig. 5), showing that the local clay may have been potentially used to produce bricks, with or without the addition of the non-plastic fraction.

XRD analysis of bricks and clays

Diffractometric results showed the constant occurrence of quartz, K-feldspar and plagioclase in great quantities in almost all the brick samples. Diopside and micas are present in variable amount in quite all the bricks. Chlorite were rarely found in subordinate quantities, and calcite occur in only three bricks. Ghelenite is clearly present in few bricks, while traces of it are evident in some other samples. The mineral content of all the bricks are shown in TABLE 1. Instead, clay, although coming from different outcrops, showed great homogeneity in mineralogical composition, all samples containing variable quantities of quartz, calcite, feldspar and clay minerals. The mineral content of the clayey materials are shown in TABLE 2.

XRF chemical analyses

TABLE 3 and TABLE 4 show results of XRF chemical analyses on bricks and on the potential



Fig. 5 - Grain size classification (Shepard, 1954) of the sampled clayey materials.

TABLE 1 Results of XRD analysis of the bricks. Qtz: Quartz; Pl: Plagioclase Kfs: K-feldspar; Cal: Calcite; Chl: Chlorite; Micas; Di: Diopside; Gh: Gehlenite. **** = very abundant; *** = abundant; ** = average presence; * = present; tr = traces.

Bricks	Qtz	Pl	Kfs	Cal	Chl	Micas	Di	Gh
CM1	****	**	***			**		
CM2	****	***			*		**	
CM3	****	**	***	*	*	**	*	tr
CM4	****	***	**				**	
CM6	****	**	***				**	tr
CM7	****		***				**	*
CM8	****	**	***			**	**	*
CM9	****	**	***				*	
CM10	****	***				***	*	
CM11	****	**	***				**	tr
CM12	****	***	**				**	tr
CM13	****	***	**			*	**	*
CM14	****	***	**			**	*	
CM15	****	***	**			*	**	
CM16	****	***	**			**	**	tr
CM17	****	***	**			**	*	
CM18	****	***	**			*	**	tr
CM19	****	***				**	*	tr
SM1	****	***	**	**	*	**		
SM2	****	***	**			**	tr	
SM3	****		***			***	tr	
SM4	****	***	**			**	tr	
SM5	****	**	***			**	**	tr
SM6	****	***	**	*			*	tr
SM7	****	***				**	*	**
SM8	****	**	***			**	*	tr

raw materials (clay and sand), respectively. Major elements are expressed in weight % and trace elements in ppm. Water content (Loss On Ignition) was obtained as loss by calcination and FeO by wet titration. For better understanding the relations between the bricks and the raw materials, results of XRF chemical analysis were processed graphically and compared with chemical data of the clay and sand sampled near the ancient city of Kaulon. The differences between the two groups, already shown by petrographic study, were confirmed by their

TABLE 2 Results of XRD analysis of the clayey materials. Qtz: Quartz; Fs: Feldspars; Cal: Calcite; Chl: Chlorite; Micas; Di: Diopside; Gh: Gehlenite. **** = very abundant; *** = abundant; ** = average presence; * = present; tr = traces.

Clays	Qtz	Fs	Cal	Chl	Micas
GV1A	***		****	**	**
GV1B	****	**	***	**	**
GV1C	****	**	**	**	*
GV2A	***	**	****	**	*
GV2B	****	*	**	*	**
GV2C	***	**	****	**	**
GV3	***	**	****	**	**
GV9	****	*	**	**	**
AM	****	**	***	**	*

chemical composition, as shown in the Co vs. Cr diagram (Fig. 6a). Bricks with lower Cr are indeed the same ones which contain granitic fragments in the non-plastic fraction. Multivariate statistical analysis of the XRF data on all brick samples produced the dendrogram of Fig. 7, using all variables, in which the separation between the two main sample groups is confirmed. The first group is formed by the bricks CM1, CM6, CM8, CM9, CM11, CM13, CM17 and CM18 and represent all the bricks of the first petrographic group. The second group is composed by the bricks CM2, CM3, CM4, CM7, CM10, CM12, CM14, CM15, CM16, CM19, SM1, SM2, SM3, SM4, SM5, SM6, SM7 and SM8 and include all the samples of the second petrographic group. This last group show further subdivisions into several subgroups, related to compositional variations. The SiO₂ vs. CaO diagram (Fig. 6b) shows that all the bricks fall in the compositional range from Pliocene clay to the local sand. It is hypothesized that the bricks were produced by natural mixing of these raw materials. The variability in SiO2 also indicates that various proportions of sand were used, mainly in the bricks from San Marco, which were further divided into subgroups. The SiO₂

TABLE 3

Major elements (weight %) and trace elements (ppm) of brick samples from Casa Matta and San Marco determined by XRF.

Bricks of Casa Matta

sample	CM1	CM2	СМЗ	СМ4	СМ6	СМ7	CM8	СМ9	СМ10	CM11	CM12	СМ13	CM14	CM15
SiO ₂	59.47	58.81	58.59	57.66	58.42	59.05	58.96	60.47	60.02	57.73	57.94	60.48	59.69	60.20
TiO ₂	0.75	0.76	0.71	0.71	0.67	0.68	0.63	0.62	0.72	0.67	0.71	0.65	0.71	0.68
Al_2O_3	17.55	17.56	16.86	17.19	17.51	16.56	16.36	17.30	18.06	16.91	16.84	18.23	17.74	16.88
Fe ₂ O ₃	5.99	6.84	5.95	6.36	5.57	5.99	5.14	4.91	6.63	5.54	6.51	5.17	6.45	6.25
FeO	0.10	0.10	0.10	0.20	0.19	0.20	0.10	0.25	0.15	0.10	0.20	0.40	0.20	0.40
MnO	0.08	0.10	0.09	0.10	0.07	0.09	0.07	0.07	0.10	0.07	0.10	0.07	0.10	0.09
MgO	3.83	3.75	3.33	4.13	3.71	3.80	3.48	3.36	3.84	3.62	4.13	3.95	3.80	3.61
CaO	7.00	8.41	10.33	9.62	9.13	9.86	10.54	8.05	6.33	10.46	9.55	6.06	7.21	8.01
Na ₂ O	1.71	1.20	1.22	1.43	1.67	1.18	1.55	1.73	1.11	1.72	1.29	1.76	1.23	1.35
K ₂ O	3.43	2.36	2.69	2.64	2.64	2.61	3.11	3.31	3.00	3.11	2.57	3.43	2.87	2.76
P_2O_5	0.19	0.21	0.23	0.20	0.19	0.17	0.17	0.18	0.18	0.18	0.35	0.18	0.18	0.17
LOI	2.51	4.00	5.16	19.24	2.06	2.54	2.54	2.93	5.97	2.60	2.81	3.10	4.78	2.50
Nb	17	18	15	14	18	15	15	14	15	15	15	17	17	15
Zr	186	175	187	164	182	177	179	171	168	178	172	178	177	162
Y	33	29	29	22	32	26	31	31	29	31	31	32	30	26
Sr	369	416	439	799	405	433	428	401	308	430	426	375	388	403
Rb	124	74	103	104	97	97	107	108	116	107	79	107	111	109
Ni	30	71	45	48	33	49	33	28	69	35	75	34	64	65
Cr	58	122	89	61	60	101	52	51	100	61	121	55	93	112
V	79	107	89	66	59	99	67	60	104	63	103	71	104	105
La	51	48	50	44	53	54	46	48	46	50	49	46	43	47
Ce	86	87	84	85	103	83	78	81	91	92	82	98	66	80
Со	15	20	14	16	15	17	14	12	20	14	20	12	19	20
Ba	585	554	633	796	555	527	625	801	731	618	581	1131	669	571

vs. Fe_2O_{3tot} diagram (Fig. 6c) confirms the intermediate position of all the bricks between the Pliocene clay and both the sands and the sandy intercalations, and also shows variable contents of Fe_2O_{3tot} . In particular, the highest values (>6 %) are those of the second group of bricks, already distinguished on petrographic bases and containing more phyllites and oxidised schists in the non-plastic fraction. The local origin is confirmed by similarities with the low values of Ni an Cr (TABLE 3) in southern Italian ceramics (Levi, 1999; Barone *et al.*, 2002;

Barilaro *et al.*, 2006). It is well-known that a district in Kaulon was devoted to working clay, and studies have documented the existence of a probable Hellenistic kiln (Iannelli, 2001).

XRD results of experimental firing of the clayey materials

To establish brick firing temperatures, firing tests were carried out on clay samples from the Monasterace Marina area. Each sample, as it was, was mixed with the quantity of water

Table 3
Continued

Bricks of Casa Matta							Bricks of S. Marco					
sample	CM16	CM17	CM18	CM19	SM1	SM2	SM3	SM4	SM5	SM6	SM7	SM8
SiO_2	55.39	59.92	58.72	57.88	58.59	62.89	61.93	59.74	58.48	55.74	55.46	58.79
TiO ₂	0.79	0.72	0.66	0.77	0.67	0.67	0.75	0.70	0.68	0.71	0.71	0.75
Al_2O_3	18.03	18.52	16.95	18.28	15.77	17.80	18.19	17.07	16.44	16.09	15.86	17.82
Fe_2O_3	7.09	5.82	5.39	7.07	5.75	5.79	6.28	6.37	6.36	6.46	6.28	6.77
FeO	0.60	0.15	0.12	0.15	0.30	0.30	0.25	0.35	0.35	0.25	0.20	0.35
MnO	0.11	0.07	0.07	0.11	0.09	0.09	0.09	0.10	0.09	0.11	0.09	0.12
MgO	4.62	3.56	3.46	3.96	3.08	2.96	2.79	3.44	3.95	3.59	3.83	3.7
CaO	10.12	6.21	9.70	7.99	11.60	5.23	5.47	7.90	9.60	12.90	13.66	7.8
Na ₂ O	1.22	1.64	1.57	1.09	1.32	1.34	1.17	1.30	1.35	1.24	1.24	1.12
K_2O	2.45	3.32	3.30	2.65	2.93	3.03	3.10	3.15	2.84	2.85	2.60	2.88
P_2O_5	0.18	0.22	0.19	0.21	0.22	0.20	0.24	0.23	0.20	0.30	0.26	0.24
LOI	3.24	3.70	3.70	5.04	6.22	3.90	6.97	3.95	2.33	5.66	4.91	4.8
Nb	19	18	17	18	17	15	18	17	15	15	15	17
Zr	193	178	182	183	182	170	197	169	165	172	192	180
Y	31	37	33	30	27	27	31	27	26	26	30	29
Sr	455	363	427	389	417	335	347	414	438	486	490	391
Rb	81	113	115	90	131	114	123	134	123	129	127	111
Ni	84	35	31	73	43	44	48	67	75	65	63	69
Cr	135	55	46	114	84	84	83	105	117	99	92	113
V	121	71	72	102	82	95	93	111	109	99	88	101
La	40	50	45	39	37	41	45	35	45	48	48	43
Ce	97	85	84	87	86	76	83	74	90	88	74	80
Со	22	15	14	20	15	16	18	18	17	19	18	19
Ba	535	604	604	571	576	775	763	605	519	540	752	671

necessary to produce a plastic, homogeneous paste. This was then used to make hand made square test samples measuring 3.2 x 3.2 x 0.5 cm (Cairo *et al.*, 1997). Two test samples were prepared for each sample: one was taken to 650 °C and the other to 900 °C, in a electric kiln (Pavia, 2006), in order to verify the potential of the sampled clayey materials to develop the high temperature minerals found through XRD analysis of the bricks and to infer the possible firing conditions. The firing cycle involved temperature increases of 100 °C/hour (Buxeda I

Garrigòs *et al.*, 2003), after which the test samples were exposed to the maximum temperature for almost 3 hours and then left to cool slowly. They were then pulverised and subjected to diffractometric analysis. XRD analysis (TABLE 5) showed that calcite was no longer present in the test samples fired at 900 °C, whereas it was in those fired at 650 °C. However, the most important aspect was the increasing of An-rich plagioclase peak intensity (Riccardi *et al.*, 1999; Cultrone *et al.*, 2001) and the appearance of diopside and gehlenite in all

 TABLE 4

 Major elements. (weight %) and trace elements (ppm) of sampled potential raw materials, determined by XRF.

Clays									Sandy intercalations Sands						
Sample	e GVIA	GV1B	GV1C	GV2A	GV2B	GV2C	GV3	GV9	AM	GV12	GV13	<i>GV14</i>	S1	<i>S2</i>	<i>S3</i>
SiO_2	49.89	50.76	49.06	50.35	50.45	48.53	48.66	50.76	49.60	64.88	65.71	65.02	69.20	69.46	70.50
TiO ₂	0.81	0.81	0.77	0.81	0.80	0.77	0.82	0.81	0.77	0.73	0.70	0.74	0.46	0.42	0.42
Al_2O_3	15.60	15.90	15.36	15.70	15.90	15.33	15.84	15.80	14.70	19.22	18.94	19.10	16.88	17.66	16.35
Fe ₂ O ₃	3.64	3.49	4.29	5.17	5.99	4.81	5.15	5.38	6.27	4.76	3.28	3.75	2.85	2.79	2.59
FeO	3.04	3.07	2.50	1.94	1.74	2.15	1.74	1.76	0.15	0.63	1.80	1.47	0.48	0.26	0.39
MnO	0.14	0.14	0.14	0.15	0.15	0.16	0.12	0.16	1.15	0.07	0.07	0.08	0.06	0.06	0.06
MgO	3.54	3.52	4.27	3.44	3.38	4.23	4.70	4.57	3.61	2.47	2.18	2.32	1.69	1.48	1.64
CaO	19.00	17.40	16.88	17.50	16.60	17.35	17.46	16.40	20.19	1.04	1.00	0.93	2.03	1.32	1.72
Na_2O	1.02	1.46	3.43	1.75	2.49	3.40	2.12	0.97	0.67	2.22	2.18	2.43	2.37	2.56	2.47
K_2O	2.89	2.95	2.84	2.88	2.91	2.83	3.03	3.03	2.73	3.79	3.81	3.87	0.17	3.68	3.57
P_2O_5	0.12	0.13	0.18	0.14	0.14	0.19	0.17	0.16	0.15	0.12	0.13	0.13	0.17	0.12	0.13
LOI	24.70	25.00	19.79	25.10	24.70	20.62	20.08	19.60	18.07	2.37	3.39	3.04	3.90	3.10	2.65
Nb	15	14	17	16	15	15	17	16	15	16	15	16	11	8	7
Zr	142	132	151	139	137	147	165	179	175	202	190	184	135	112	108
Y	22	23	26	22	23	24	23	26	28	24	22	28	19	20	13
Sr	518	523	476	505	514	503	571	515	566	169	169	165	200	190	195
Rb	140	138	135	136	140	133	138	140	121	131	127	132	111	112	109
Ni	50	50	64	46	46	65	83	82	54	21	18	19	10	10	9
Cr	97	98	122	96	97	116	132	130	115	48	41	42	24	20	21
V	115	119	144	117	116	143	142	146	129	90	83	91	50	44	46
La	32	34	31	31	34	41	47	40	38	37	41	52	37	44	33
Ce	55	60	70	60	71	79	72	96	76	85	74	79	71	82	71
Со	14	13	19	14	14	17	20	20	17	15	14	14	7	8	7
Ва	244	221	293	242	234	288	360	380	403	637	599	657	696	801	728

samples of fired clays at 900 °C according to Tschegg *et al.* (2009), while Jordan *et al.* (2009) reported gehlenite formation at temperature of 950 °C, in fired Ca rich Tertiary clays. Comparison of the mineralogy of the test samples with that of the bricks - as diopside was present in 21 brick samples - shows that they were fired at temperatures of at least 900 °C (Peters and Iberg, 1978; Maggetti, 1982; Gliozzo *et al.*, 2005). The other samples were probably fired at lower temperature, testifying a non standard firing process.

CONCLUSIONS

Results from the studied bricks show that production was local and exploited raw materials quarried in the area. Petrographic analysis distinguished the samples into two groups: the first containing bricks from Casa Matta, in which the non-plastic fraction contain granitoid rock fragments, and the second which includes all bricks from San Marco and the remaining ones from Casa Matta, in which the aggregate contains low-grade metamorphic and granitic rocks. XRF chemical analysis of both bricks and local raw



Fig. 6 - Comparisons between chemical composition of bricks (CM - SM) and clay (A). sandy intercalations (IS) and reddish sand (S). (a, b, c: see text).

materials (clay and sand) indicate that the bricks of group 1 were probably the result of natural mixing of Pliocene clay with the local overlying reddish sand in careless variable proportions.



Fig. 7 - Dendrogram obtained using XRF analysis data of all the bricks from the ancient Kaulon.

Those of group 2 were the result of mixing of the same Pliocene clay of the area with variable quantities of the sandy intercalations in it contained. The occurrence of reddish sands or sandy intercalations in the bricks may be unintentional or due to different periods of construction or different workers, or else to the re-use of bricks for restoration operations to dwellings in Kaulon. As already mentioned, studies have documented the existence of a furnace of probable Hellenistic age situated immediately outside the city walls. Experimental firing of clay samples showed that 21 out of 26 studied bricks reached firing temperatures of around 900 °C. The others were probably fired minor temperature, indicating firing in furnaces which, although technologically adequate, were not sufficiently evolved to guarantee perfectly reproducible conditions.

	Qtz	Pl	Cal	Micas	Di	Gh
650°C						
GV1A	****	**	***			
GV1B	****	**	***	*		
GV1C	****	**	***	*		
GV2A	****	**	***	*		
GV2B	****	***	**	**		
GV2C	****	*	***	**		
GV3	****	**	**	**		
GV9	****	**	***	**		
AM	****	*	***			
900°C						
GV1A	****	***			***	*
GV1B	****	***			***	*
GV1C	****	***			***	*
GV2A	****	***			***	**
GV2B	****	***			***	*
GV2C	****	**			***	*
GV3	****	***			***	*
GV9	****	***		tr	***	*
AM	****	***		tr	***	*

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REFERENCES

- BARILARO D., BARONE G., CRUPI V., MAJOLINO D., MAZZOLENI P., TRISCARI M. and VENUTI V. (2006) -Characterization of ancient amphorae by spectroscopic techniques. Vib. Spectrosc., 42, 381-386.
- BARONE G., IOPPOLO S., MAJOLINO D., MIGLIARDO P. and TIGANO G. (2002) - A multidisciplinary

investigation on archaeological excavation in Messina (Sicily). Part I: a comparison of pottery findings in "the Strait of Messina area". J. Cult. Herit., **3**, 145-153.

- BARRA BAGNASCO M., CASOLI A., CHIARI G., COMPAGNONI R., DAVIT P. and MIRTI P. (2001) -Mineralogical and chemical composition of transport amphorae excavated at Locri Epizephiri (southern Italy). J. Cult. Herit., 2, 229-239.
- BONARDI G., MESSINA A., PERRONE V., RUSSO S. and ZUPPETTA A. (1984) - L'Unità di Stilo nel settore meridionale dell'Arco Calabro- Peloritano. Boll. Soc. Geol. It., 103, 279-309.
- BUXEDA I GARRIGÓS J., JONES R.E., KILIKOGLOU V., LEVI S.T., MANIATIS Y., MITCHELL J., VAGNETTI L., WARDLE K.A. and ANDREOU S. (2003) - Technology transfer at the periphery of the Mycenaean world: the cases of Mycenaean pottery found in central Macedonia (Greece) and the Plain Of Sybaris (Italy). Archaeometry, **45** (2), 263-284.
- CAIRO A., MUGGIA A. and RICCARDI M.P. (1997) Le temperature di cottura dei laterizi di epoca romana: i manufatti dello scavo di Pomello (PV), in: Atti della prima giornata di archeometria della ceramica. 1th annual Meeting, Febrary 28, University press Bologna, Bologna, 162-168.
- CAVAZZA W., BLENKINSOP J., DE CELLES P.G., PATTERSON R.T. and REINHARDT E.G. (1997) -Stratigrafia e sedimentologia della sequenza sedimentaria oligocenico-quaternaria del bacino calabro-ionico. Boll. Soc. Geol. It., **116** (1), 51-77.
- CULTRONE G., RODRIGUEZ-NAVARRO C., SEBASTIAN E., CAZALLA O. and DE LA TORRE M.J. (2001) -Carbonate and silicate phase reactions during ceramic firing. Eur. J. Miner., **13**, 621-634.
- DELL'ANNA L. and LAVIANO R. (1987) Analisi granulometrica di argille: esame dei principali metodi, Atti workshop "Procedure di analisi di minerali argillosi". ENEA, La Spezia, 215-234.
- ERAMO G., LAVIANO R., MUNTONI I.M. and VOLPE G. (2004) - Late Roman cooking pottery from the Tavoliere area (Southern Italy): raw materials and technological aspects. J. Cult. Herit., 5, 157-165.
- 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. Miner. Petrol., 31, 356-378.
- GLIOZZO E., FORTINA C., MEMMI TURBANTI I.,

TURCHIANO M. and VOLPE G. (2005) - Cooking and painted ware from San Giusto (Lucera, Foggia): the production cycle, from the supply of raw material site the commercialization of products. Archaeometry, **47** (1), 13-29

- IANNELLI M.T. (2001) Nuove acquisizioni a proposito della presenza dei Brettii a Caulonia. In: Parra MC (Eds.), Kaulonia, Caulonia, Stilida (e oltre) -Contributi storici, archeologici e topografici, I. Quaderni Annali Scuola Normale Superiore di Pisa, Pisa, 117-158.
- JORDÁN M.M., MARTÍN-MARTÍN J.D., SANFELIU T., GÓMEZ-GRAS D. and DE LA FUENTE C. (2009) -Mineralogy and firing transformations of Permo-Triassic clays used in the manufacturing of ceramic tile bodies. Appl. Clay Sci., 44, 173-177
- LEVI S.T. (1999) Produzione e circolazione della ceramica nella Sibaritide protostorica. All'insegna del Giglio, Firenze.
- MAGGETTI M. (1982) Phase analysis and its significance for technology and origin. Archaeological ceramics (eds. J.S. Olin and A. Franklin), Smithsonian Institution Press, Washigton, 121-133.

- PAVIA S. (2006) The determination of brick provenance and technology using analytical techniques from physical sciences. Archaeometry, 48 (2), 201-218.
- PEZZINO A., PANNUCCI S., PUGLISI G., ATZORI P., IOPPOLO S. and LO GIUDICE A. (1990) - Geometry and metamorphic environment of the contact between the Aspromonte-Peloritani Unit (Upper Unit) and Madonna dei Polsi Unit (Lower Unit) in the central Aspromonte area (Calabria). Boll. Soc. Geol. It., **109**, 455-469.
- PETERS T. and IBERG R. (1978) Mineralogical changes during firing of calcium-rich brick clays. Ceram. Bull., 57 (5), 503-509.
- RICCARDI M.P., MESSIGA B. and DUMINUCO P., (1999) - *An approach to the dynamics of clay firing*. Appl. Clay Sci., **15**, 393-409.
- SHEPARD F.P. (1954) Nomenclature based on sandsilty-clay ratios. J. Sediment. Petrol., 24, 151-158.
- TSCHEGG C., NTAFLOS T. and HEIN I. (2009) -Thermally triggered two-stage reaction of carbonates and clay during ceramic firing- A case study on Bronze Age Cypriot ceramics. Appl. Clay Sci., **43**, 69-78.