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Archaeometric analyses on ceramics from Sicilian Greek colonies: a contribution to the knowledge of Messina, Gela and Agrigento production

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ABSTRACT. — Several samples of the two important archaeological areas of eastern Sicily, Messina in north-eastern Sicily, and Gela and Agrigento in central-southern Sicily, were analysed by optical analysis under a polarized light microscope, XRD, FT-IR, XRF, ICP-MS and ICP-OES.

Petrographic and chemical data processing allowed to characterise pottery fabrics of Greek colonies in Sicily and to identify the principal elements that distinguish the different local productions (Messina, Gela and Agrigento) between them and from those imported (Greece).

RIASSUNTO. — Sono stati analizzati mediante analisi petrografica, XRD, FT-IR, XRF, ICP-MS e ICP-OES, campioni di due importanti aree archeologiche della Sicilia: Messina (Sicilia nordorientale) e Gela ed Agrigento (Sicilia centro meridionale).

I risultati petrografici e chimici ottenuti hanno permesso di caratterizzare le ceramiche delle colonie greche in Sicilia e di indentificare i principali elementi che permettono di distinguere le diverse produzioni locali (Messina, Gela ed Agrigento) tra loro e da quelle importate.

KEY WORDS: Pottery, Messina, Gela, Agrigento,

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Archaic and Classical period, Greek-western, mineralogical petrographic and geochemical characterisation.

INTRODUCTION

The purpose of our research is to contribute to the knowledge of ceramic craft productions in Sicily by archaeometric analyses during the archaic and classic age, by means of the study of the archaeological finds in two sample areas among the most important locations of Sicily: Messina in north-eastern Sicily, Gela and Agrigento in central-southern Sicily.

The study of ancient ceramics is directed towards obtaining a greater detailed knowledge of the physical-chemical characteristics of potteries, cooking temperatures, production centres and the area of provenance of the raw material.

Mineralogical, petrographic and chemical analyses were carried out on some samples of Sicilian Greek colonies. In particular they are classes of ceramics, from the late period of the Classic age (VI-V century B. C.).

Have been analysed principally samples

with prevailing coarse grains because the utilised temper furnish useful information about the geology of the area of the temper provenance.

This research aims at studying some particular problems with specific regard to the Greek-western culture. Until some years ago, many researchers doubted that the Greekwestern colonies possessed their own ceramic production and moreover the material found during digs were considered to be imported from Greece (Dunbabin 1948). However, the existence of flourishing colonial workshops have unequivocally been revealed by several excavations or it was confirmed by a more reliable material classification (Iozzo 1993, Lippolis 1996, Orlandini 1983, Rizza and De Miro 1985, Vallet 1958, Villard 1989). It can not always be achieved on the bases of archaeological data but there is often a need for physical-chemical analyses (Jones 1986. Whitbread 1995). For this reason. archaeometric analysis of the ceramic material is now considered, as never before, to be of great usefulness for an interdisciplinary approach in the study of the archaeological finds.

This need is evident in those cases where the ceramic classes have the same uniform typological characteristics which does not allow an immediate and easy distinction by an autoptic examination.

SAMPLES

The material examined by archaeometric analysis was made up of tiles, ceramics ware (cups, jars, etc) and transport amphorae, with prevailing coarse grains.

In addition to, we have considered samples found in medieval kiln, clay and samples of literature (Alaimo *et al.* 1995, 1997; Barone 2002; Barone *et al.* 2002; Barone *et al.* 2003) in order to better define their provenance and technology.

The samples analysed are:

Pottery found in Messina:

Coarse grained, tile fragments of Greek age (ME18, ME150, ME151, ME152, ME153, ME154, ME155). All of the samples, except ME18, have been found in ancient potters' workshops (Barone *et al.* 2003).

Reference materials: has been considered clay sediment near of Messina area (Barone *et al.* 2003), and clasts of metamorphic rocks (of medium-high grade) outcropping in the Peloritani Mounts (Ioppolo and Battaglia 1983).

Amphorae found in the acropolis of Gela and reference materials:

Coarse, medium and fine grained amphorae samples, used for transport and table purposes, are either *«massaliota»* (VI-V centuries BC) or *«pseudo-chiota»* (V century BC) in shape, or imitations of Corinthian wares (V century BC).

Coarse pottery (23, 24, 37, 38, 39, 40, 44, 48, 75, 76): the colour ranges from pale reddish-yellow in colour (Munsell's index (M.I.) 5 YR 7/6) to red (2.5YR 5/6 o 5/8). Only samples 37 and 38 have a more pinkish colour (7.5YR 6/4). The colour appears as a very pale brown (10Y 8/2) for some samples, and more yellowish for others (2.5 Y 8/3). The surface has a faded appearance, as do most of the samples found at Gela.

Medium grained pottery (26, 30, 41, 42, 27, 34, 35, 36, 77): the colour ranges from pale reddish-yellow (Munsell's index 5 YR 7/6) to red (2.5YR 5/6 o 5/8), and the uniformly faded external surfaces are, for some samples, very pale brown (10 Y 8/2) and for others yellowish (2.5 Y 8/3).

Fine grained pottery (45, 46): the intense red colour is 2.5 YR 5/6 or 5/8. Their external surface is always faded, but was probably only covered with a thin layer of the same yellowish-white colour (10YR 8/2) as in that of previous groups.

Reference materials: the analyses of brick samples from modern kiln in Gela, although of recent manufacture, were carried out for comparison purposes because they represent macroscopic (colour, compactness) and microscopic characteristics similar to the amphorae samples analysed.

Ceramics samples from the VI-V century BC, found in the western area of the Valley of Temples in Agrigento and reference materials:

The samples were coarse potteries (AGR2, AGR3, AGR4, AGR5, and AGR9), a tile (AGR10) and transport amphorae (AGR1, AGR6, AGR7, and AGR8). In particular, the *coarse pottery* group includes an hydria with linear decoration (AGR2), two undecorated jugs (AGR3 and AGR5), an undecorated little cup (AGR4), a basin (AGR9), and a tile (AGR10). The ceramic body show a colour zoning from beige to red, which is often more compact.

The transport amphorae group includes two so-called *«ionico-massaliota»* amphorae (AGR1 and AGR6) and two so-called *«pseudochiota»* amphorae (AGR7 and AGR8). The socalled *«ionico-massaliota»* amphorae (AGR1 and AGR6) show a reddish (M.I.) mixture and in particular, in the sample AGR1, the so-called *«black core»* in the central part; the *«pseudochiota»* amphorae (AGR7and AGR8) show an orange (M.I.) blend.

Reference materials: in order to better define their provenance technology, five samples found in two medieval kilns from paleo-christian necropolis of Agrigento were also examined a scrap (AG4), a support (AG1), a spacer (AG2) and two pottery shreds (AG3 and AG5).

For comparison, some data relative to Hellenistic-roman coarse pottery samples produced in Agrigento, published by Alaimo *et al.* 1995 and 1997 and classified by the authors as group V, were considered.

ANALYTICAL METHODS

The samples have been analysed by chemicalphysical and mineralogical-petrographic techniques: • optical microscopy (OM) for petrographic analysis.

• X-ray diffraction (XRD) to define the mineralogical phases and the new formation minerals after firing. The analyses were performed by SIEMENS D 5000 diffractometer by applying a tension equal to 40kV, an intensity current equal to 30 mA, an entrance slit 1mm open and finally a convergence slit 1mm open as well. For this kind of measurements we used the well known powder method.

• X ray spectrometry analysis (XRF) for major elements. The data were collected by Philips PW 2404. The XRF results were calibrated against several international standards and reproducibility was better than 0.5%. Owing to little quantities of samples, has been possible to carry out the chemical analyses only on a representative samples of each group, selected by petrographical analyses.

• Fourier Transform Infrared absorption (FTIR) spectroscopy (only Gela samples) for trace minerals not detectable by X-ray diffractometric analysis. The FT-IR absorbance data were collected by a BOMEM DA8 spectrometer working under vacuum. The investigated samples were prepared in pellets using 2 mg of bulk sample dispersed in 200 mg of powdered KBr. The investigation range was from 200 cm⁻¹ to 4000 cm⁻¹ so that the FTIR apparatus was equipped with a Globar lamp as source, a KBr beamsplitter and a DTGS/MIR detector. The used spectral resolution was 4 cm⁻¹ and to obtain a good signal-to-noise ratio and spectra reproducibility of high quality as well 32 repetitive scans were automatically added.

• Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for trace elements; analytical uncertainty is given as lower than 5% (only for Messina and Gela samples).

• Optical emission spectroscopy (ICP-OES) for trace elements. The ICP-OES analysis was performed by using an IRIS II Advantage/1000 of Thermo-Jarrel Ash Corp. Analytical uncertainty is given as lower than 5% (Agrigento samples).

EXPERIMENTAL RESULTS

Optical data

Pottery found in Messina

The petrographic analysis revealed that the temper grains (20-30%) about 0.80 mm, are mainly made up of large sometimes chloritised biotite crystals (5 mm), elongated muscovite lamellas, mono and polycrystalline quartz with undulatory extinction, K-feldspar, alterated plagioclase, and numerous iron oxides. Moreover, moulds of foraminifers are also present, together with fragments of metamorphic clasts with rounded edges, fragments of quartz-feldspar rocks with *mirmekitic* texture and *chamotte* (Table 1). The texture appears sometimes compact and sometimes vesicular.

Amphorae found in the Acropolis of Gela

The Gela samples were subdivided into 3 groups according to the grain size of the aggregate: coarse (0.24-0.80 mm), medium (0.08-0.16 mm) and fine-grained (<0.08 mm) (Table 1). It is interesting to note that the oldest ceramics products (VI century B. C.) are made of a mainly coarse mixture, whereas the more recent products (V century B. C.) are made of an increasingly finer, but not cleansed original material.

1. The group with coarse-grained contain the *«ionico-massaliota»* samples (23, 24, 37, 38, 40, 44,39), Corinthian imitation (48), and table amphorae (75 and 76). The clasts (10-20%) are almost exclusively formed by quartz, in shape ranging from rounded to sub-angular, and seldom by feldspars. In the matrix there are iron oxides, rare flakes of muscovite, moulds of microfossils and rare micro-foraminifera. Sometimes the microfossil moulds are filled with recrystallised microcristalline calcite.

2. *The medium-grained aggregate* group contains the *«ionico-massaliota»* (26, 30, 41, 42), and *«pseudo-chiota»* (27, 34, 35, 36), a table amphora (77) samples.

The medium grained group samples differ

from the coarse grained group because of a more homogeneous mixture (temper 10-20%), a more abundant microfossil mould filled with re-crystallised micro-crystalline calcite, and very rare microfossils. Moreover they are a variable contents of muscovite in the matrix from scanty to abundant, particularly in the sample 41 in which the mica is oriented.

3. The fine-grained group consists of samples of Corinthian imitation (45, 46). The clasts (5-10%) are mainly composed of quartz, feldspars, and small quantities of Fe-oxides. In the matrix there are abundant moulds of microfossils.

The various mixtures are not always homogeneous, and sometimes contain a few vesicles varying in shape from rounded to oblong, probably resulting from tiny air bubbles trapped in the clay during modelling of the manufactures and/or organic matter in the clay and later oxidised or decomposed during firing.

Ceramics found in the western area of the Valley of Temples in Agrigento

Coarse pottery. In all the samples, there are traces of muscovite, microfossils and iron oxides. As in sample AGR3, whole microforaminifers and bryozoans were found. The moulds of microfossils are often filled with recrystallised microcrystalline calcite. The temper is heterogranular (20-25%), mainly of quartz, with medium-coarse grains (0.24-0.32 mm) and angular edges.

Tile. The sample AGR10, a tile, appears with heterogeneous texture, coarse grain size and with a very porous mixture. There are also many vesicles left from moulds of microfossils (Table 1).

Transport amphorae. The transport amphoare AGR1, AGR6, («ionico massaliota» and AGR7 and AGR8 («pseudo-chiota») contain traces of muscovite, with a higher quantity in sample AGR7 and traces of microfossils filled with microcrystalline calcite and iron oxide. As in sample AGR8, seaweed and bryozoans were also found.

7 MEI8. MEIS0, MEI51 Messina Messina Fragments of tiles fragments of Ms and Bt and a coarse metamorphic clast MEI55 Qz, Pl. Kf. Ox, Cc, deh dasent in 155), of Greek age a coarse metamorphic clast of metomorphic clast Mei155 Qa, Pl. Kf. Ox, Cc, deh absent in 155), of metomorphic clast of microfossil, Mono-policristalline Qa, Pl. Kf. Ox, Cc, deh absent in 155), of metomorphic clast a coarse metamorphic clast of microfossil, Mono-policristalline Qa, Pl. Kf. Ox, Cc, deh absent in 155), of microfossil, Mono-policristalline Qa, Pl. Kf. Ox, Cc, geh absent in 155), of microfossil, Mono-policristalline Qa, Pl. Kf. Ox, Cc, deh absent in 155), of microfossil, Mono-policristalline Qa, Pl. Kf. Ox, Cc, geh abbi. 900°-950°C 21 Coarse: 23, 24, 37, 38, 39, add 44, 48, 75, 76 South Sicily biolocromasalicta and microforaminifera, trace, sound sciely biolocromasalicta angular-subangular Peeudo-cluicta angular-subangular angular-subangular angular-subangular dat with absent amplorae. Qa, Pl. Kf. Ox, Cc, Min. ± Gh, ± Di, trace, solf, AGR, AGR, AGR, AGR, AGR, AGR, AGR, AGR	N° S	amples	Provenance of samples	Tipology	М.О.	XRD e FTIR	Estimate temperature
21 Coarse: 23, 24, 37, 38, 39, 60 GelaGelaAmphoraeMicaecous minerals in trace, abundant mouldsQ2, Pl, Kf, Ox, Cc, Hm, \pm Geh, \pm Di, medium: 26, 30, 41, 42900°. $\div 950^{\circ}C$ $40, 44, 48, 75, 76South SicilyNot 44, 48, 75, 76Ionico-massaliotaand microforaminifera,migular-subangularMicaecous minerals intrace, abundant mouldsQ2, Pl, Kf, Ox, Cc,Hm, \pm Geh, \pm Di,and microforaminifera,tr Ms900°.\div 950^{\circ}C27, 34, 35, 36, 77South SicilyN BCDNi-V B.C.)and microforaminifera,angular-subangularQ2, tr Pl, Kf, CcWi-Y, BCD27, 34, 35, 36, 77FileSouth SicilyAGR4, 4GR5, AGR9,AGR10AmphoraeSouth SicilyPouth SicilyPouth SicilyPouth SicilyPouth SicilyPouth SicilyPouth SicilyPouth SicilyAGR10Micaecous minerals inAGR4, AGR5, AGR9,Q2, with traces of Ms, Ox of ironAGR10Q2, Kf, Hm,\pm Cc, \pm Di, \pm Geh\pm Co, \pm Di, \pm Geh\pm Co, \pm Di, \pm Geh\pm CoS00°.\div < 900\pm Co15 Coarse: AGR1, AGR5, AGR9,AGR10South SicilyPouth SicilyPout$		ME18, ME150, ME151 ME152, ME153, ME154 ME155	Messina N E Sicily	Fragments of tiles of Greek age	Mica mixture with thick fragments of Ms and Bt and a coarse metamorphic clast of medium-high grade (Peloritani Mountains), moulds of microfossil, Mono-policristalline Qz, Kf, Pl, <i>Mirmekite</i> , Ox	Qz, Pl, Kf, Ox, Cc, Ms, Bt, Hm, Mont, Geh (absent in 155), Wo (present only in 152, 153, 154)	< 900°÷950°C
ISCoarse: AGR2, AGR3,AgrigentoTransport amphorae:Rounded to sub-angularQz, Kf, Hm,>800°÷< 900AGR4, AGR5, AGR9,South SicilyIonic massaliota and pseudo chiota, tilesQz, with traces of Kf, traces of Ms, Ox of iron± Cc, ± Di, ± Geh>800°÷< 900	21 C	Coarse: 23, 24, 37, 38, 39, 40, 44, 48, 75, 76 medium: 26, 30, 41, 42 27, 34, 35, 36, 77 ïne grain: 45, 46	Gela South Sicily (VI-V B.C.)	Amphorae Ionico-masaliota (VI-V B.C.) Amphorae Pseudo-chiota (V B.C.) Corinthian imitation	Micaceous minerals in trace, abundant moulds and microforaminifera, angular-subangular Qz, tr Pl, Kf, Cc microcristalline, Ox	Qz, Pl, Kf, Ox, Cc, Hm, ± Geh, ± Di, tr Ms	900°÷950°C
	15 C + H +	Coarse: AGR2, AGR3, AGR4, AGR5, AGR9, AGR10 Fransport amphorae: AGR1 AGR6, AGR7, AGR8 Xiln: AG1, AG2, AG3, AG4, AG5	Agrigento South Sicily	Transport amphorae: Ionic massaliota and pseudo chiota, tiles and sample medieval kiln	Rounded to sub-angular Qz, with traces of Kf, traces of Ms, Ox of iron and titanium, microfossils and moulds, often filled with recrystallized microcrystalline Cc.	Qz, Kf, Hm, ± Cc, ± Di, ± Geh Dol, Kao, Mont, Ms, Cl, TiOx, FeOx	>800°÷< 900°C

TABLE 1

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The temper (10%), mainly quartz (0.16-0.32 mm), has coarse grain with generally subrounded crystals; only in the sample AGR8 was the plagioclase observed. In general, the transport amphorae fabrics are more compact than the coarse pottery and the tile ones (Table 1).

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In order to discover the provenance of these fragments, five furnace samples produced in Agrigento (AG) were also studied. Macroscopic features, colour and inclusions are revealed to be remarkably similar to those of the previous samples analysed. The Agrigento furnace samples present a coloured mixture ranging from dark yellow to reddish (M.I.). These samples have a fine grain, while all AGR# samples show more coarse and less purified mixture. AG3, AG4 and AG5 fragments are more porous than AG1 and AG2.

Quartz clasts are very abundant in all the samples and their shape varies from subrounded to sub-angular. There are also many iron oxides and calcite microcrystalline. Only in sample AG5 are there rare traces of microfossils and of calcite micro-crystalline.

Diffractometric analysis (XRD) and firing temperature determination

Pottery found in Messina

The diffractometric analysis (Table 1) emphasises the presence of quartz, plagioclase, K-feldspar, montmorillonite, hematite (which is absent in the ME154 and ME155 samples), calcite (absent in ME153), muscovite, biotite, gehlenite (absent in ME155), and wollastonite (present only in ME152, ME153 and ME154). Gehlenite and diopside are criptocrystalline mineralogical phases produced by the reaction between illite, quartz and calcite under high temperature (Capel *et al.* 1985 and Duminuco *et al.* 1996).

It is possible to deduce that the coarse ME18, ME150, ME151 and ME155 was fired at a temperature of < 900°C because of the presence only of gehlenite; whereas it is probable that ME152, ME153 and ME154 pottery's samples were fired at a temperature in the range of $900^{\circ} \div 950^{\circ}$ C because of the presence of wollastonite contents.

Amphorae found in the acropolis of Gela

Diffractometric analysis (Table 1) revealed that the coarse grains group samples have variable quantities of quartz, plagioclase, calcite, hematite, K-feldspar, muscovite, gehlenite and diopside. The presence of new formation minerals (gehlenite and diopside) show for all samples a firing temperature in the range of $900^{\circ} \div 950^{\circ}$ C.

The medium grained samples always have quite high quartz contents, whereas calcite tends to be less abundant than the coarsegrained group, except for sample 30. Gehlenite is absent or only present in traces; diopside is always found (except in sample 30), and is more abundant in sample 35.

The XRD analyses of modern bricks (reference materials) reveal various contents of Qz, Pl, Kf, Hm, Geh, Ms. Calcite is either absent or present in very small quantities, and diopside is abundant, therefore the firing temperature for these bricks is more than 900°C (Barone 2002).

Ceramics found in the western area of the Valley of Temples in Agrigento

The XRD diffractograms have emphasized analyses of the mineralogical phases, as reported in Table 1. In all the samples quartz, feldspars, hematite, dolomite, and calcite, probably in a bigger quantity than the common ceramics, were found; diopside is also present. In some samples of common pottery (AGR5 and AGR9) and amphorae (AGR1 and AGR6), gehlenite was found. Hence, it is possible to deduce that the coarse pottery was fired at a temperature of about 900°C because of the presence of diopside and the low amount of calcite; whereas it is probable that two coarse pottery's samples (AGR #) were fired at a lower temperature because of the presence of higher calcite and gehlenite contents.

The samples coming from a medieval furnace (reference samples) show an abundant amount of quartz and the constant presence of calcite (only in AG2 it is present in trace). Gehlenite, illite and hematite are always present in traces, while there are traces of Diopside only in AG2 and AG3. So, firing temperature must have been lower than 900°C for AG1, AG4 and AG5 and nearer 900°C for AG2 and AG3.

Fourier Transform Infrared analysis, FT-IR

The FT-IR analysis has been carried out only on the samples from Agrigento because for these samples the quantities were bigger than the others (Table 1). This study has confirmed the X-ray results and characterised some minerals present in little quantities or lower than 2 wt%, and therefore not detectable by XRD. Dolomite, montmorillonite, muscovite, chlorite and titanium oxides were found in traces. Dolomite is present mainly in the samples of amphorae and in only one sample of coarse pottery. The FT-IR has revealed also the kaolinite. This mineral becomes amorphous to X-rays at $550^\circ \div 600^\circ$ C and its diffraction pattern disappears, but its structure is destroyed over 800° C (Deer et al. 1998). The presence of kaolinite can mean that the firing temperature, for these samples, is lower than 900° C.

The montmorillonite, found in all the

samples, could be due to the hydrolysis processes during the burial period of the ceramics manufacture (Capel *et al.*, 1985). Lastly, titanium and iron oxides were also identified by FT-IR analysis at the low frequency (200-700 cm⁻¹).

X-ray Fluorescence Spectrometer (XRF) and Plasma Emissions (ICP-MS) analyses.

Pottery found in Messina

The tile samples show high content (in wt%) of Na₂O+K₂O ($3.69 \div 5.34\%$), TiO₂ ($0.77 \div 1.03\%$), Al₂O₃ ($14.92 \div 19.54\%$) and Fe₂O₃ ($5.85 \div 9.74\%$). CaO, except for ME18, is between 7 and 14 % (Table 2). According to the classification by Picon & Olcese (1995), it is a Ca–rich ceramic.

Some trace elements were analysed by ICP-MS. The results, reported in Table 2, emphasise a low concentrations of Cr ($36\div84$ ppm), Ni ($34\div95$ ppm) and Co ($9\div26$ ppm).

Amphorae found in the acropolis of Gela

Table 3 shows the results of the chemical analyses (XRF) of major elements (wt%) of ceramics samples, and the ICP-MS results of trace elements (ppm). We chosen to analyse the samples on the basis of their available amount: for some we analysed major and trace elements and for some others only the major elements or

TABLE 2

sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	V	Cr	Co	Ni
ME18	59.63	1.03	19.54	7.82	0.11	2.86	3.43	1.64	3.70	0.23	n.d.	56	16	34
ME150	61.06	0.67	13.95	5.85	0.12	1.57	12.73	1.10	2.70	0.26	98	47	11	75
ME151	53.43	0.89	17.11	9.74	0.17	1.99	11.65	1.03	3.52	0.47	129	64	18	74
ME152	58.90	0.70	15.96	7.21	0.12	0.00	12.77	1.77	2.24	0.31	132	80	16	92
ME153	57.66	0.68	15.20	6.38	0.12	1.80	13.67	1.26	2.90	0.34	62	36	11	53
ME154	58.58	0.82	17.48	8.46	0.14	2.31	7.30	1.75	2.93	0.23	175	84	26	95
ME155	58.72	0.77	14.92	6.86	0.10	1.29	12.79	0.81	2.88	0.86	98	48	9	63

Messina pottery: Major and trace element chemical analyses.

TABLE 3

Gela pottery: Major and trace element chemical analyses.

TABLE 3a - Major and trace elements

	sar	nple	SiO_2	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K_2O	P_2O_5	V	Cr	Co	Ni
amphorae coarse	ionic massaliota ionic	24	62.04	0.71	13.04	5.41	0.08	2.67	12.83	0.62	2.08	0.51	81	72	9	34
	massaliota	44	59.01	0.74	13.42	6.16	0.09	3.57	14.14	0.63	1.98	0.25	63	50	6	24
medium grained	pseudo- chiota	27	60.21	0.71	13.02	5.76	0.08	3.48	13.70	0.98	1.87	0.19	150	107	12	49
Table 3b -	- Maior elem	ents														
			SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5				

			5102	1102	111203	10203	10mO	1150	CuO	11420	1120	1205	
amphorae coarse	table table	75 e 76 5	50.58 58.36	0.67 0.70	12.69 13.16	5.80 6.23	0.09 0.09	2.60 2.96	14.58 15.09	0.68 0.76	2.06 2.32	0.24 0.34	
medium grained	table amphorae	77 5	59.95	0.73	13.70	6.06	0.09	2.68	13.40	0.69	2.46	0.25	

TABLE 3c – Trace elements

	S	Sample	v	Cr	Co	Ni
amphorae	ionic massaliota	23	135	99	10	45
coarse	ionic massaliota	37	111	84	10	42
	ionic massaliota	38	121	95	9	43
	ionic massaliota	39	125	89	11	44
	ionic massaliota	40	116	77	9	38
	imitations of					
	Corinthian	48	97	73	9	36
medium	ionic massaliota	26	144	102	11	46
grained	ionic massaliota	30	128	98	10	41
	ionic massaliota	41	110	90	11	44
	ionic massaliota	42	69	55	6	26
	pseudo-chiota	34	77	70	9	35
	pseudo-chiota	35	94	73	10	37
	pseudo-chiota	36	76	70	8	33
fine	imitation of					
grained	Corinthian	45	128	112	13	52
	imitation of					
	Corinthian	46	117	91	13	48

trace elements. We liked better to analyse the trace elements because we thought that would be more important to know the content of Co, Cr, Ni believed as discriminant elements to distinguish the Greek from Italian clays (Jones 1986). On the basis of CaO abundances (\approx 14%) they are classified as calcareous ceramics (Picon and Olcese 1995). By examining the composition, the ceramic samples show restricted compositional range of major and trace elements: Na₂O+K₂O (2.62÷3.08%), TiO₂ (0.67÷0.74%), Al₂O₃ (12.69÷13.70%), Fe₂O₃ (5.41÷6.23%), Ni (26÷48 ppm); Co (6÷13 ppm); Cr (55÷112 ppm).

Ceramics found in the western area of the Valley of Temples in Agrigento

The major elements (wt%) (measured by XRF) and the trace elements (ppm), performed by ICP-OES technique, are reported in Table 4.

The amount of CaO of all the Greek samples analysed (Coarse pottery and transport amphorae), ranges from 11.04% to 16.58%, therefore they are classified as calcareous potteries (Picon and Olcese 1995).

Furthermore they present similar composition with Na₂O+K₂O in the range $(2.92\div3.47\%)$, TiO₂ $(0.79\div0.86\%)$, Al₂O₃ $(13.24\div14.97\%)$ and Fe₂O₃ $(5.9\div6.30\%)$, Ni $(32\div124 \text{ ppm})$, Cr $(108\div232)$ and Co $(12\div56 \text{ ppm})$. The sample AGR9 presents amount of Cr (252 ppm), Ni (124 ppm) and Co (176 ppm) higher than the others samples suggesting a different production.

INDIVIDUATION AND CHARACTERISATION OF LOCAL PRODUCTIONS

The individuation of the production centres for the studied samples are based on the petrographic observation and on the chemical comparison with raw materials or well defined local production samples.

On the whole the analysed samples present Ni, Cr, Co abundances lower than the Greek productions and comparable with the south Italy clayey sediments (Jones 1986; Levi *et al.* 1999; Barone *et al.* 2002).

The petrographic analyses of the **Messina** samples suggest that they have been produced with local raw materials being the temper (clasts of medium-high grade) compatible with the metamorphic rocks outcropping in the Peloritani Mounts (Ioppolo and Battaglia 1983). Furthermore, by chemical point of view, the pottery samples of Messina have major and trace elements comparable with the clay sediments outcropping near Gravitelli village (NW of Messina) (Barone *et al.* 2002).

The petrographic analyses of the ancient specimens of **Gela**, do not permit a production definition being observable only quartz grains. However the samples of bricks of Gela taken in the modern kiln showed similar petrographic characteristics suggesting the permanent use of similar resources.

Both the Gela amphorae and the modern bricks have comparable percentages of major and trace elements (Fig. 1 and Fig. 2).

The samples of **Agrigento**, characterised by a skeleton formed principally by quartz, have been compared with some samples found in medieval kilns (AG #) and also with Hellenistic-roman coarse pottery samples produced in Agrigento, published by Alaimo *et al.* 1995 and 1997 and classified by the authors as group V.

On the whole the Agrigento potteries (reported in this paper and in literature Alaimo *et al.* 1995 and 1997) constitute a rather homogeneous petrographic and chemical group (Figure 1). Although the AG(#) present higher SiO₂ and Al₂O₃ and lower CaO abundances, these differences may be related with the use of different temper abundances as function of the uses destination of these potteries.

In agreement with Alaimo *et al.* 1997, it is possible to individuate the clay of Agrigento Formation (Sprovieri, 1968) as the principal raw materials utilised for the production of our samples. These clays are characterised from a notable uniformity of CaCO₃ percentage along the sequence of layers (Sprovieri, 1968). This

			Agrige	nto potte	ry: majo	r and tra	uce elem	ent chem	iical anal	yses.				
	sample	SiO_2	TiO_2	Al_2O_3	$\mathrm{Fe}_{2}\mathrm{O}_{3}$	MnO	MgO	CaO	Na2O	K_2O	P_2O_5	Cr	Co	ï
coarse pottery hydria	AGR2	57.64	0.83	13.63	6.18	0.10	2.83	15.40	0.92	2.24	0.22	160	28	52
undecorated jugs	AGR3	58.61	0.80	13.60	5.91	0.11	2.86	15.00	0.69	2.23	0.20	140	16	4 (
undecorated cup	AGR4 AGR5	59.54 59.09	0.79	13.24 13.89	6.05 6 13	0.10	2.87 2.84	14.21 13.47	1.11	1.89 2.52	0.21	180 224	4 4 1	09 11 q
basin	AGR9	57.26	0.84	14.34	6.37	0.11	3.08	14.75	0.97	2.09	0.19	252	176	124
tile	AGR10	56.28	0.86	14.97	6.77	0.21	3.08	14.79	1.12	1.80	0.11	160	20	56
Transport amphe ionic massalio-	orae													
te amphorae ionic massalio-	AGR1	58.08	0.81	13.67	6.17	0.11	2.23	15.54	1.00	2.18	0.21	108	12	32
te amphorae	AGR6	58.63	0.80	13.47	6.07	0.10	3.07	14.60	0.90	2.18	0.18	232	56	72
pseudo-chiota	AGR7	56.17	0.83	14.08	6.30	0.11	2.42	16.58	0.71	2.59	0.20	140	16	48
pseudo-chiota	AGR8	56.59	0.82	13.87	6.23	0.11	2.37	16.42	0.77	2.63	0.20	140	16	48
reference materi	als													
support	AG1	60.01	0.86	15.63	5.84	0.07	2.98	11.22	0.62	2.57	0.22	n.d.	n.d.	58
spacer	AG2	59.21	0.84	15.64	5.71	0.07	3.08	11.62	1.17	2.47	0.21	n.d.	n.d.	75
pottery	AG3	58.86	0.82	15.13	5.79	0.06	3.27	12.63	0.93	2.30	0.21	n.d.	n.d.	78
scrap	AG4	60.51	0.83	15.39	5.79	0.06	2.71	11.04	1.05	2.42	0.20	n.d.	n.d.	82
pottery	AG5	56.46	0.83	16.09	5.47	0.06	3.13	14.79	0.46	2.50	0.21	n.d.	n.d.	54

TABLE 4

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Fig. 1 – Content of MgO vs Na_2O+K_2O ; MgO vs TiO_2 ; MgO vs Al_2O_3 ; MgO vs Fe_2O_3 ; SiO_2 vs CaO; SiO_2 vs TiO_2 ; SiO_2 vs Co.



Fig. 2 - Content of Cr vs Ni; Cr vs Co.







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explains the fact that the raw material, although extracted in quite different periods, have kept very similar compositional characteristic (Alaimo *et al.*, 1997).

The chemical compositions of the productions of the studied sites have been compared with the aim to discriminate these productions. This is particularly important for Gela and Agrigento pottery which present very similar macroscopic and microscopic characters.

The Gela samples differ from the Agrigento ones on the basis of lower content of Al_2O_3 , TiO₂, Co and Cr (Figure 1 and 2) and this better showed by a dendrogram (Figure 3) which, on the basis of 4 variables (Al_2O_3 , MgO, Ni, Cr), allowed the three ceramics productions to be discriminated. The samples are distributed in 3 main groups (Agrigento, Messina e Gela ceramics), only AGR1 plots with the Gela group, where it is possible to distinguish various subgroups relating to different workshops.

The Messina pottery are clearly distinguishable from the Gela and Agrigento principally on the basis of Na_2O+K_2O , Al_2O_3 , Fe_2O_3 , Ni, Cr, Co (Fig. 1) in agreement with the higher abundances of mica and feldspar.

CONCLUSION

The archaeometric analyses performed on samples found in Messina, Gela and Agrigento have permitted to caracterize the ceramics and individuate the markers of provenance for each production area.

It is possible to easily distinguish, by petrografic and chemical point of view, the Messina potteries from these of Gela and Agrigento. In fact the samples of Messina are characterised by fragments of metamorphic clasts of Peloritani Mounts, but on the contrary the samples produced in Gela, by macroscopic, mineralogical and petrografic point of view, are similar to those produced in Agrigento. This, consequently, allows notable archaeological implications connected with the possibility of distinguishing and characterising the two most important areas of ceramics production in the southern coast of Sicily in the Greek age. Gela and Agrigento samples are distinguishable on the basis chemical composition, the Gela specimens, with respect to the samples of Agrigento and Messina, have a lower amount of Al_2O_3 , TiO_2 , Na_2O+K_2O and much lower concentrations of Fe_2O_3 , Co, Ni and Cr, as are also clearly differentiated in the several sites.

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