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MINERALOGICAL-PETROGRAPHIC AND SPECTROSCOPIC INVESTIGATIONS ON COARSE POTTERY AND TRANSPORT AMPHORAE FROM AGRIGENTO

GERMANA BARONE , VINCENZA CRUPI, SERGIO GALLI, DOMENICO MAJOLINO*, PLACIDO MIGLIARDO

*Physics Department and INFM,
Messina Section, Messina University,
P.O. Box 55, 98166 Messina (Italy)*

GRAZIA SPAGNOLO

*Antiquity Science Department, Archaelogical Section,
Messina University, Piazza Pugliatti, 98122 Messina (Italy)*

*e-mail:majolino@unime.it
* to whom all correspondence should be addressed*

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ABSTRACT

In the present work, ten ceramic samples from the VI-V century B.C., found in the west area of the Temples Valley in Agrigento, were analysed by different experimental techniques, such as optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), Inducted Coupled Plasmaa. - Optical Emission Spectroscopy (ICP-OES) and Fourier Transform Infra-Red spectroscopy (FT-IR). The simultaneous use of the above mentioned methods has allowed to unambiguously characterize the provenance of these ceramic findings. In order to verify their provenance, five ceramic samples, found in a medieval kiln in Agrigento (Sicily) and of definite *Agrigentina* production, were used for comparison as well along with some literature data.

Mineralogical analysis has shown mainly quartz with traces of K-feldspar, muscovite, iron and titanium oxides, microfossils even in moulds, often filled with re-crystallized microcrystalline calcite, while presence of gehlenite and diopside, determined by the XRD analysis, indicated the firing temperature of the ceramic.

Oxides content, obtained by XRF measurements, was found quite homogeneous in the analysed ceramic, as in the case of the *Agrigentina* kiln ceramic. Moreover, the values of Ni and Cr, observed by ICP/OES technique, confirmed that all the manufactures were of colonial production, indicating that they were not imported from Greece. Comparing our samples with the *Agrigentina* kiln samples, it was possible to state that the analysed ceramics were made of clayey-sandy materials present in the Agrigento area and one coming from a non-*Agrigentina* quarry.

KEYWORDS: Amphorae, pottery, Agrigento, archaeological, petrographical and geo-chemical characterization.

THE AIM

The present work is part of a complex research essentially addressed to produce a database characterizing the archaic and classical fabrics of coarse pottery and transport amphorae in the most important Greek colonies of the southern coast of Sicily, such as Gela and Agrigento. The aim of this study was twofold, a) we tried to characterize the pottery fabrics of Agrigento and b) at the same time to identify the principal elements that distinguish the *Agrigentina* production from that of Gela. The investigation was carried out on the basis of mineralogical-petrographic and spectroscopic analysis.

SAMPLES

Ten ceramic samples, coming from the west area of the Temples Valley in Agrigento, were analysed, kindly offered by the Superintendence for Cultural Heritage of Agrigento and found in archaeological excavations carried out in 1954-55. The samples have been classified from an archaeological point of view into: coarse potteries (AGR2, AGR3, AGR4, AGR5, AGR9), transport amphorae (AGR1, AGR6, AGR7, AGR8) and tiles (AGR10).

In particular, the coarse pottery group includes an hydria with linear decoration (AGR2), two achromatic jugs (AGR3 and AGR5), an achromatic little cup (AGR4) and an achromatic basin (AGR9).

The transport amphorae group includes two samples, labelled as AGR1 and AGR6, called *ionico-massaliota*, and other two called *pseudo-chiota*, labelled as AGR7 and AGR8. Finally, sample AGR10 is a tile.

Five ceramic samples, certainly produced in Agrigento and found in two medieval kilns in the historical centre of the town, were also investigated in order to be sure of the provenance of our samples by a comparison. They were in particular: a supporting framework (AG1) and a spacer (AG2) for kiln, a kiln reject (AG4) and two pottery sherds (AG3 and AG5).

Finally some literature data by Alaimo *et al.* (1995, 1997), relative to Hellenistic-Roman coarse pottery produced in Agrigento and medieval kiln rejects samples, coming from the paleo-christian necropolis of Agrigento, were also used as a comparison with all the experimental results.

METHODS

Firstly, in order to characterize the mineralogical phases present in the *Agrigentine* ceramic samples, all the findings were analysed by polarized microscopy using thin sections and X-ray diffraction (XRD).

The optical polarized microscopy data were collected by a ZEISS microscope. The crystallographic data, XRD, were performed by a SIEMENS D5000 diffractometer by applying a tension equal to 40kV, an intensity current equal to 30mA, 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.

Furthermore to determine the major and minor elements we performed X-ray fluorescence (XRF) and Inducted Coupled Plasma - Optical Emission Spectroscopy (ICP/OES) measurements respectively.

As far as the XRF measurements are concerned, we used 0.5g of the analysed samples in powder form mixed with boric acid (the latter does not give fluorescence contribution), and then reduced in pellets. The XRF results were calibrated taking into account several international standards and the reproducibility was better than 0.5% after analytical values. Following the standard procedure for Loss On Ignition (LOI), the percentage values of the corresponding oxides present in each sample were obtained. LOI analysis essentially consists in a weight loss, generally expressed as a percent of the original weight of the dried sample. For our samples the initial temperature of burning was 110°, and successively they were burned at 1000°C in order to evaporate the water content and estimate the oxides percentages.

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%.

Moreover for the identification of trace elements, Fourier Transform – Infrared (FT-IR) absorbance measurements were carried out. The FT-IR absorbance data were collected by a BOMEM DA8 spectrometer working under vacuum. The investigated samples were prepared in pellets, about 0.5mm thick, using 2mg of bulk sample dispersed in 200mg of powdered KBr which was transparent in the spectral range of interest. This last varied from 400cm-1 to 4000cm-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 4cm-1 and 32 repetitive scans were automatically added to obtain a good signal-to-noise ratio and a spectra reproducibility of high quality as well.

RESULTS

3.1 Optical polarized microscopy measurements

The coarse potteries presented a generally bicolour mixture, beige in the inner part and red in the outer part (Munsell Index, M.I.), this last being often more compact. The polarized microscopy data of thin sections showed traces of muscovite, microfossils and iron oxides. Only in one sample, namely AGR3, we observed micro-foraminifers which were still intact, seaweeds and bryozoans (see Table. 1). The traces of microfossils were filled with recrystallized microcrystalline calcite and the clast, mainly made of quartz, revealed a medium-coarse grain. Finally the quartz was hetero-granular with generally angular edges.

In the case of the so-called "ionico-massaliota" amphorae (AGR1 and AGR6), the polarized microscopy data revealed a reddish mixture (M.I.). In sample AGR1 a "black core" was present in the central part, due either to the incomplete combustion of carbon substances originally contained in the principal clayey material, or the rapid cooling in an oxidant atmosphere, followed the baking phase in a reducing atmosphere.

Instead, the "pseudo-chiota" amphorae (AGR7 and AGR8), presented an orange blend (M.I.). All the samples had traces of muscovite, this last being particularly abundant in AGR6, traces of micro-fossils, abundance of microcrystalline calcite and iron oxide. Only in sample AGR8, seaweeds and bryozoans were also found. The crystalline phase, mainly quartz, has medium-fine grain with generally sub-rounded crystals. Plagioclase was observed only in AGR8. Generally, the transport amphorae were more compact than the coarse pottery and tiles. All the optical results are summarized in Table1.

The tile labelled AGR10 displayed different characteristics respect to the above described amphorae, since it presented an heterogeneous, more coarse grain, and, hence, very porous mixture (see Table. 1). We observed also many vacuoles left from traces of microfossils, whose calcite shells were burned at temperature higher than 850°C.

In order to determine the provenance of all the analysed fragments, five ceramic samples found in a kiln produced in Agrigento (AG1, AG2, AG3, AG4 and AG5), with macroscopic features, colour and inclusions, remarkably similar to those of the samples analysed, were also studied. These presented a mixture which had a colour ranging from dark yellow to reddish. Furthermore they had a fine granulation, as opposed to the samples AGR# which showed instead a more coarse and less purified mixture. In particular the fragments labelled AG3, AG4 and AG5 were more porous than AG1 and AG2. All these samples were rich in clastic quartz, this last having a shape which varied from rounded to sub-angular. It was also possible to identify a high quantity of iron

Coarse Pottery								
Sample	**Typology**	**Ground-paste**	**Sandy skeleton**					
			Grain size	Quartz	Pl	Cc	Ox	Notes
AGR2	Hydria, linear decoration	Bicoloured mixture: beige-red, microfossils moulds tr of muscovite	Medium coarse	Angular	-	-	xx	The outer part is red and more compact
AGR3	Achromatic jug	Bicoloured mixture: light and dark orange, foraminifers, seaweeds, bryozoans microfossils moulds tr of muscovite	Medium coarse	From sub-rounded to angular	x	x	x	Compact
AGR4	Achromatic cup	Reddish mixture, microfossils moulds	Medium coarse	Angular	-	x	x	The outer part is more compact, the inner part is more porous
AGR9	Achromatic basin	Bicoloured mixture: red-beige	Medium coarse	Sub-rounded	x	tr	x	
Transport Amphorae								
AGR1	Ionico-massaliota amphora	Red mixture, black Ï core ¾ microfossils moulds	Medium fine	Sub-rounded to angular	-	x	x	The amphorae are more compact than common pottery
AGR6	Ionico-massaliota amphora	Reddish mixture microfossils moulds micaceous tr of muscovite	Medium fine	Sub-rounded	-	x	x	The amphorae are more compact than common pottery
AGR7	Pseudo-chiota Amphora	Orange mixture microfossils moulds tr of muscovite	Medium fine, hetero-granular	Angular to sub-rounded	-	xx	x	The amphorae are more compact than common pottery
AGR8	Pseudo-chiota Amphora	Orange mixture microfossils moulds, seaweeds, bryozoans, tr of muscovite	Medium fine	Sub-rounded	x	xx	x	The amphorae are more compact than common pottery
Tile								
AGR10	Tile	Bicoloured mixture: red-beige, microfossils moulds tr of muscovite	Medium coarse	Angular	-	tr	x	The inner part is heterogeneous and porous
Agrigentina kiln ceramic fabric								
AG1	Kiln supporting framework	Brown-yellow mixture	Fine	Abundant, sub-angular	-	x	x	Compact
AG2	Kiln spacer	Brown-red mixture	Fine	Abundant, rounded to sub-angular	-	-	x	Compact
AG3	Ceramic sherd	Red mixture	Fine	Heterogeneous	-	x	x	Porous
AG4	Kiln reject	Reddish mixture	Fine	Abundant, rounded sub-angular	-	x	x	Porous
AG5	Ceramic sherd	Orange mixture, microfossils moulds	Fine	Sub-angular	-	x	x	Porous

Table. 1: Optical polarized microscopy results for the investigated samples (coarse pottery, tile, transport amphorae and Agrigentina kiln ceramic fabric). Pl: plagioclase; Cc : calcite; Ox: oxides.

oxides and micro-crystalline calcite. The sample AG5 showed traces of micro-fossils as well.

Some literature data by Alaimo *et al.* 1995 and 1997, performed on Hellenistic-Roman and Late-Roman coarse potteries of certain *Agrigentina* production were used as reference data to compare our experimental optical results. According to Alaimo, these samples are characterized by a quartz skeleton, the latter having a shape passing from sub-angular to rounded, calcareous lithoclase and micro-fossils in different relative percentage.

X-Ray Fluorescence (XRF) measurements

With X-ray fluorescence (XRF) measurements it was possible to characterize the major elements of the examined ceramic samples. The resulting data of all the analysed specimen are shown as oxides in percentage in Table 2 along with the LOI values.

Coarse pottery and transport amphorae present a content of oxides which is quite homogeneous, although generally in the amphorae the content of SiO_2, TiO_2, $Fe2O_3$ and MgO is lower than in the coarse pottery (see Tab. 2). Figs. 1 A-D plot SiO_2 percentage versus the above mentioned oxides percentage for all the analysed samples including the *Agrigentina* kiln ceramic fabric and the reference samples by Alaimo.

It is worth underlining that the sample AGR9, classified as coarse pottery, presents a slightly higher content of Fe_2O_3, TiO_2, Al_2O_3 than the transport amphorae, as can be seen in Table 2. The amount of CaO (Fig. 1E) for both sets of samples ranges between 12.8% to 15.5%. This implies that they are calcareous ceramics, according to the classification by Picon Olcese (1995), since they have a CaO content higher than 6-8%. Furthermore it is well

Coarse Pottery

Sample	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	P_2O_5 (%)	Fe_2O_3 (%)	MgO (%)	MnO (%)	CaO (%)	Na_2O (%)	K_2O (%)	L.O.I. (%)
AGR2	55.46	0.80	13.11	0.21	5.95	2.72	0.10	14.82	0.89	2.16	3.80
AGR3	53.53	0.73	12.42	0.18	5.40	2.61	0.10	13.70	0.63	2.04	8.66
AGR4	58.07	0.77	12.91	0.20	5.90	2.80	0.10	13.86	1.08	1.84	2.46
AGR5	56.06	0.78	13.18	0.17	5.82	2.69	0.11	12.78	0.90	2.39	5.12
AGR9	55.53	0.81	13.91	0.18	6.18	2.99	0.11	14.30	0.94	2.03	3.02

Transport Amphorae

Sample	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	P_2O_5 (%)	Fe_2O_3 (%)	MgO (%)	MnO (%)	CaO (%)	Na_2O (%)	K_2O (%)	L.O.I. (%)
AGR1	54.97	0.77	12.94	0.20	5.84	2.11	0.10	14.71	0.95	2.06	5.35
AGR6	55.42	0.76	12.73	0.17	5.74	2.90	0.09	13.80	0.85	2.06	5.46
AGR7	52.40	0.77	13.13	0.19	5.88	2.26	0.10	15.47	0.66	2.42	6.72
AGR8	51.95	0.75	12.73	0.18	5.72	2.18	0.10	15.07	0.71	2.41	8.21

Tile

Sample	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	P_2O_5 (%)	Fe_2O_3 (%)	MgO (%)	MnO (%)	CaO (%)	Na_2O (%)	K_2O (%)	L.O.I. (%)
AGR10	55.08	0.84	14.65	0.21	6.63	3.01	0.11	14.47	1.10	1.76	2.14

Table. 2: Percentage of the main oxides found in the investigated samples (coarse pottery, tile and transport amphorae) by XRF measurements. Loss on Ignition (LOI) values are also shown (see text for details).

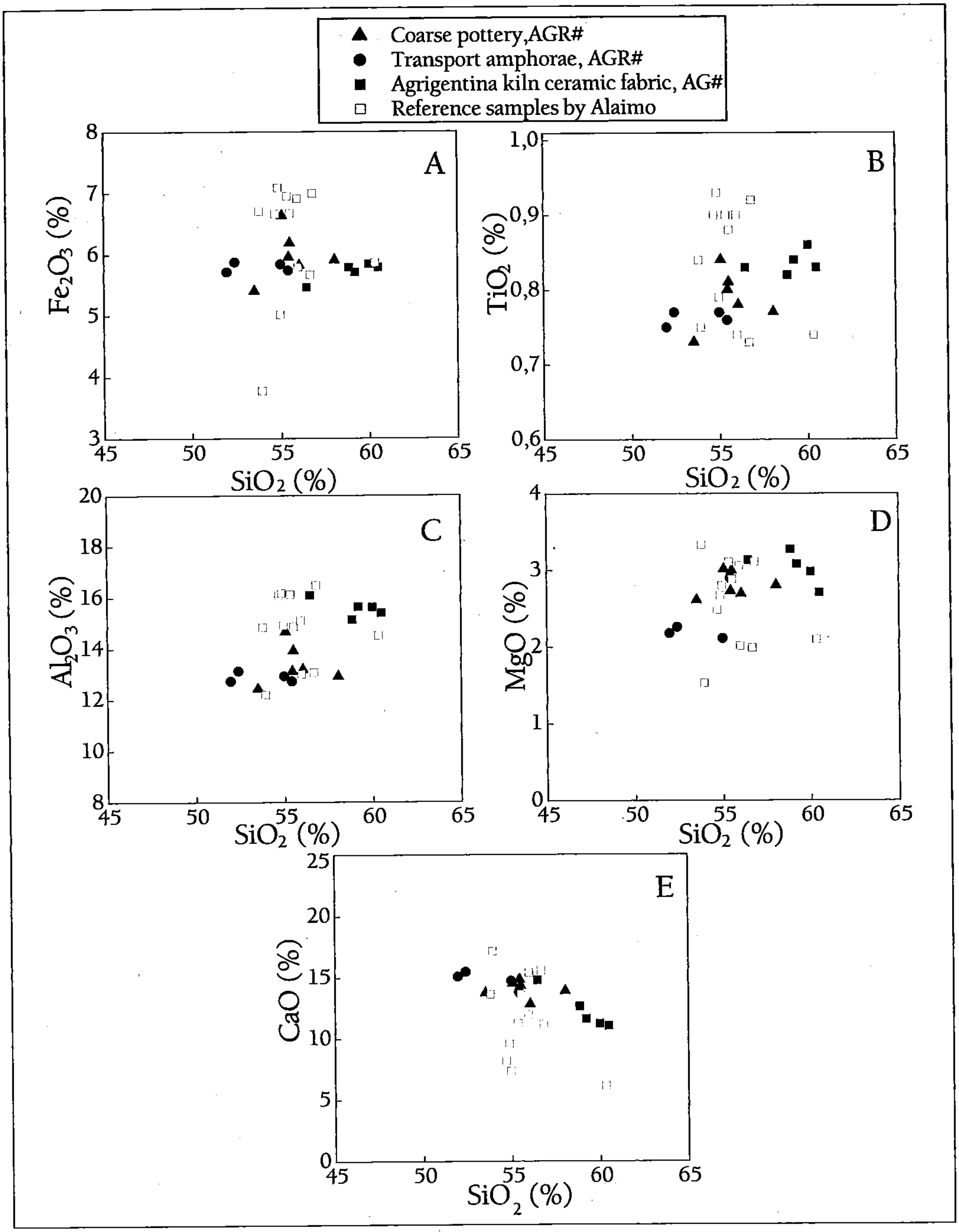

Fig. 1: Plots of oxides percentages present in the investigated samples by XRF measurements together with LOI analysis. ▲ refer to coarse pottery, ● refer to transport amphorae, ■ refer to *Agrigentina* kiln ceramic fabric and _ refer to reference samples by Alaimo.

known that clays which are relatively rich in $CaCO_3$ are most suitable for fabrication of vases for food (e.g. amphorae), albeit not necessarily used for cooking.

In order to unambiguously interpret the obtained results, we also compared the experimental XRF data with those performed on well characterized pottery derived from the *Agrigentina* medieval kilns and with the others taken from literature (Alaimo *et al.* 1995 and 1997), as showed in Figs. 1a-e. We reported all data relevant to the comparison samples within the same plots of the experimental XRF results, i.e. either those of *Agrigentina* fabric (closed squares) and those by Alaimo (open squares), despite that samples used for comparison have a different granulation and as a consequence a different ratio clast/matrix.

From an inspection of Figs. 1a-e, it is evident that the coarse pottery shows a greater chemical affinity with the sherds from the medieval kilns, since they exhibit a similar content of Fe_2O_3, TiO_2, MgO and CaO with a smaller percentage of SiO_2, confirming the results deduced by optical means.

Also the transport amphorae have a content of Fe_2O_3 and CaO comparable to that of *Agrigentine* kiln samples but a slightly lower content of TiO_2, Al_2O_3 and MgO (see Fig. 1a-e).

Furthermore, Fig. 1a-e show a higher content of SiO_2 in the case of the *Agrigentine* medieval kilns samples (closed squares), and confirm the abundance of quartz already found by the optical study. Moreover these plots also show a variation in the composition among the Agrigentina kiln samples and those of reference. This could be attributed to the fact that their mixtures are assigned to different uses, although the same clast constitutes them, while the granulation and the quantitative ratio between the quartz and clayey matrix changes. In fact, the fragments of the *Agrigentina* kiln ceramic fabric require a purer and more compact mixture, so they are homogeneous and characterized by a fine granulation with abundant quartz: this occurrence gives a higher hardness to the ceramic bulk.

The samples of common pottery, tile and amphorae, together with our findings coming from the *Agrigentine* medieval kilns, as well as the pottery studied by Alaimo, constitute a rather homogeneous chemical group. This fact agrees with the composition of raw material (Agrigento Clays Formation), found near the archaeological site which is characterized by a great uniformity in $CaCO_3$ along the stratigraphic sequence (Sprovieri1968). This occurrence explains the fact that the raw material, although extracted in quite different periods, has preserved very similar compositional characteristics (Alaimo *et al.* 1997).

ICP-OES measurements

The determination of the trace elements in part per million (ppm), was performed by ICP-OES technique. From these ICP-OES measurements, our experimental data were compared to those of medieval kilns samples and with those by Alaimo (Alaimo *et al.* 1995 and 1997). From this comparison it was clear that the chemistry of the major and trace elements is nearly comparable.

The results are reported in Table 3. However, the following notes were drawn. In particular:

1) the content of Ba results slightly higher in the coarse pottery than in the amphorae, while the content of Sr is generally higher in the amphorae, as also shown in Fig. 2a. The medieval kilns samples show a nearly coincident content of Ba and Sr with the samples analysed, while the samples of Alaimo show a notable dispersion, probably related to the variable percentage of feldspar.
2) The values of Ni, Cr and Co are quite variable in both groups, coarse pottery and transport amphorae, as can be seen from Figs. 2b and 2c; however, the amount of Ni

Coarse pottery								
Sample	**Sr (ppm)**	**Ba (ppm)**	**Co (ppm)**	**Cr (ppm)**	**Cu (ppm)**	**Mn (ppm)**	**Ni (ppm)**	**Zn (ppm)**
AGR 2	432	340	28	160	88	440	52	72
AGR 3	524	560	16	140	104	400	44	80
AGR 4	480	260	44	180	128	460	60	56
AGR 5	480	188	-	224	108	360	-	44
AGR 9	480	280	176	252	120	500	124	100

Transport amphorae								
Sample	**Sr (ppm)**	**Ba (ppm)**	**Co (ppm)**	**Cr (ppm)**	**Cu (ppm)**	**Mn (ppm)**	**Ni (ppm)**	**Zn (ppm)**
AGR 1	328	200	12	108	48	296	32	40
AGR 6	500	248	56	232	136	452	72	68
AGR 7	524	204	16	140	96	440	48	68
AGR 8	560	200	16	140	100	440	48	68

Tile								
Sample	**Sr (ppm)**	**Ba (ppm)**	**Co (ppm)**	**Cr (ppm)**	**Cu (ppm)**	**Mn (ppm)**	**Ni (ppm)**	**Zn (ppm)**
AGR 10	440	220	20	160	124	528	56	96

Table 3: Trace elements found in the investigated samples (coarse pottery, tile and transport amphorae) by ICP-OES measurements.

and Cr in particular, being always lower than 250 ppm, gives an experimental confirmation that the samples come from a western-Greek site. In literature, in fact, it has been showed that the artefacts produced in the Greek regions usually contain higher than 250 ppm percentages of Ni and Cr (Jones 1986; Levi *et al.* 1999; Barone *et al.* 2002).

3) Only the sample AGR9 presents amount of Cr and Ni higher than the standard, 252 ppm and 124 ppm respectively; moreover it contains the highest values of Zn and Co. This could suggest that the raw material for this sample does not comes from an *Agrigentina* quarry but probably from a western-Greek one, which is in any case Sicilian because it is well known that the contents of Ni and Cr are strictly connected to the provenance of the clays and vary sensibly passing from the Greek regions to Sicily (Jones 1986; Levi *et al.* 1999; Barone *et al.* 2002).

X-Ray Diffraction (XRD) measurements

The characterization of the peaks intensity in the diffractograms has allowed to carry out a semi-quantitative analysis of the mineralogical phases present in the samples, as reported in Table 4.

From the XRD analysis in all the samples, both in coarse pottery and transport amphorae, plenty of quartz, calcite, hematite and feldspars were found. In the coarse pottery samples, the diopside, a mineral of new-formation that develops at a typical temperature of 900°C despite the presence of quartz and dolomite, is also present (Capel *et al.* 1985 and Duminuco *et al.* 1996). In two samples of coarse pottery (AGR5 and AGR9), in the tile (AGR10) and in two fragments of amphorae (AGR1 and AGR6), gehlenite was found. The

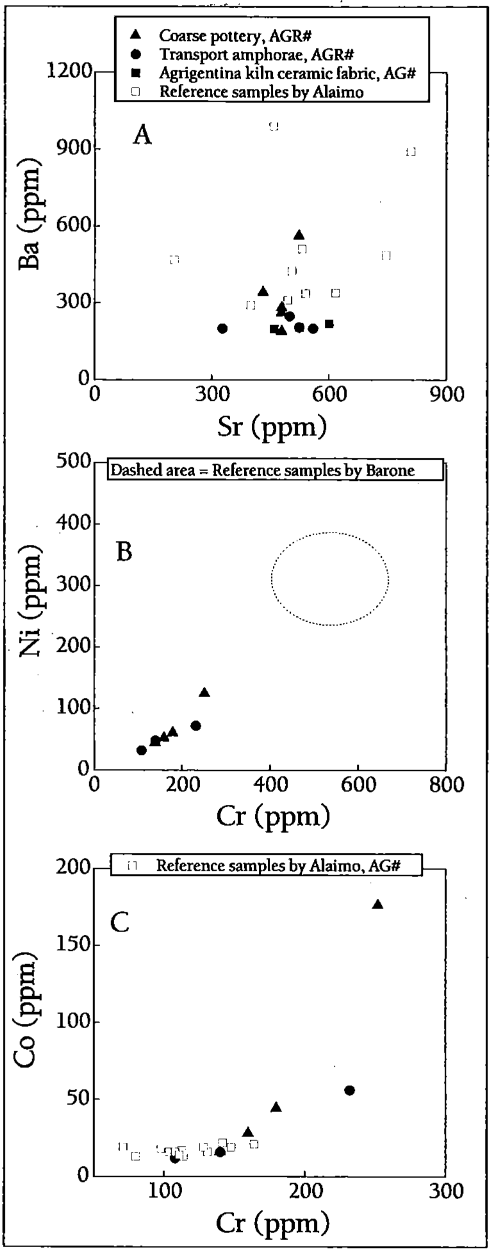

Fig. 2: Plots of trace elements expressed in part per million (ppm) present in the investigated samples by ICP-OES measurements. ▲ refer to coarse pottery, ● refer to transport amphorae, ■ refer to *Agrigentina* kiln ceramic fabric, ❑ refer to reference samples by Alaimo, the dashed area refers to reference samples by Barone.

latter is also a mineral of new formation, whose presence suggests a baking temperature of 650°C, because of the reaction of illite with calcite. Hence, it is possible to deduce that the coarse pottery was baked at a temperature of about 900°C, because of the presence of diopside and the low amount of calcite; instead, it is probable that the two coarse pottery samples, AGR5 and AGR9, were baked at a lower temperature for the presence of higher calcite and gehlenite content. Calcite, in fact, decomposes at about 850°C.

The samples derived from *Agrigentina* kiln ceramic fabric show abundant amount of quartz and calcite is still present; in particular in AG2 calcite is present only in trace (see Table 4). Furthermore, gehlenite and hematite are present in trace, while there are traces of diopside only in AG2 and AG3. This implies that, baking temperature is lower than 900°C for AG1, AG4 and AG5 and closer to 900°C for AG2 and AG3.

Fourier Transform Infrared (FT-IR) absorbance measurements.

The FT-IR absorbance measurements were analysed in the frequency range, 500 cm^{-1} to 2000 cm^{-1}. Table 5 reports the main elements identified in the absorbance spectra. The measurements, which are in full agreement with the X-ray diffraction results, have allowed to characterize also the minerals present in quantity lower than 5%. In fact traces of dolomite (Dol), kaolinite (Kao), montmorillonite (Mont) and muscovite (Ms) were found. Figs. 3a and 3b show the IR absorbance spectra for the samples AGR2 (common pottery) and AGR8 (transport amphorae), as an example. Kaolinite is more abundant in the amphorae but its low content is due to its burning during the baking reactions, as previously mentioned, while montmorillonite, found in all the samples, is due to hydrolysis processes during the burial period of the ceramic manufacture (Capel *et al.* 1985)

Coarse Pottery

Sample	Qz	Cc	Di	Hm	Geh	Kf
AGR 2	xxx	x	xx	tr	-	x
AGR 3	xxxx	xx	tr	-	-	tr
AGR 4	xxxx	x	xx	tr	-	x
AGR 5	xxxx	x	x	x	tr	x
AGR 9	xxx	x	xx	x	tr	xx

Transport Amphorae

Sample	Qz	Cc	Di	Hm	Geh	Kf
AGR 1	xxxx	x	x	-	x	tr
AGR 6	xxxx	x	tr	tr	x	xx
AGR 7	xxxx	xx	-	-	-	tr
AGR 8	xxxx	xx	-	x	-	tr

Tile

Sample	Qz	Cc	Di	Hm	Geh	Kf
AGR 10	xxx	x	xxx	tr	tr	xxx

Agrigentina kiln ceramic fabric

Sample	Qz	Cc	Di	Hm	Geh	Kf
AG1	xxxx	x	-	-	-	tr
AG2	xxxx	tr	tr	Tr	tr	x
AG3	xxxx	x	tr	Tr	tr	x
AG4	xxxx	x	-	Tr	tr	tr
AG5	xxxx	x	-	Tr	tr	tr

Table 4: Main minerals found in the investigated samples (coarse pottery, tile, transport amphorae and kiln clay fabric) by XRD measurements. xxxx: very abundant; xxx: abundant; xx: present; x: present in few amount; tr present in trace; - absent. Qz: quartz; Cc: calcite; Di: diopside; Hm: hematite; Geh: gehlenite; Kf: feldspar.

Coarse Pottery

Sample	Qz	Cc	Di	Hm	Dol	Kf	Ms	Kao	Mont
AGR 2	x	x	x	x	-	x	tr	tr	x
AGR 3	x	xx	x	-	x	x	tr	xx	x
AGR 4	x	x	x	x		- x	x	tr	x
AGR 5	x	x	x	x		- x	x	x	x
AGR 9	x	x	x	x		- x	x	x	x

Transport Amphorae

Sample	Qz	Cc	Di	Hm	Dol	Kf	Ms	Kao	Mont
AGR 1	x	x	x	X	tr	x	-	tr	x
AGR 6	x	x	tr	X	x	x	xx	xx	x
AGR 7	x	xx	-	-	x	x	tr	xx	x
AGR 8	x	xx	-	X	x	x	tr	xx	x

Tile

Sample	Qz	Cc	Di	Hm	Dol	Kf	Ms	Kao	Mont
AGR 10	x	x	x	x	-	x	tr	x	x

Table 5: Main minerals found in the investigated samples (coarse pottery, tile and transport amphorae)
by FT-IR absorbance measurements. xx: present; x: present in few amount; tr present in trace; - absent. Qz: quartz; Cc: calcite; Di: diopside; Hm: hematite; Dol: dolomite; Kf: feldspar; Ms: muscovite; Kao: kaolinite;
Mont: montmorillonite

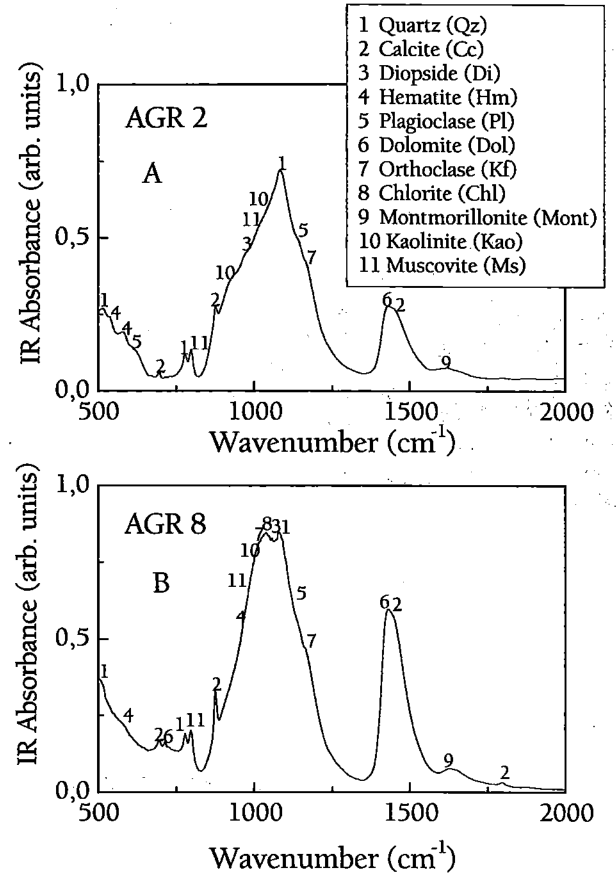

Fig. 3: IR absorbance spectra for AGR 2 (A) (common pottery) and AGR8 (B) (transport amphora). The numbers from 1 to 11 indicate the elements found in the investigated samples.

DISCUSSION

The aim of the presented archaeometric analysis, carried out by different and complementary experimental methods on ceramic findings, was essentially addressed to unambiguously identify the area of production, in order to confirm the hypothesis of the archaeological investigation and to find the compositional characters of the local artefacts. All the results can be discussed according to the following points:

- The clast, characterised by optical microscopy, mainly constituted of quartz, is heterogeneous and coarser in the samples of common pottery and tile than in the transport amphorae fragments;
- The presence of microfossils moulds, shown by optical microscopy, which in some samples were still intact (micro-foraminifers), of seaweeds and bryozoans was observed. The microfossils gave a very useful indication about the provenance of the samples, because their

presence is well known in the ceramic samples from Agrigento by Alaimo (Alaimo *et al.* 1995). From a comparison with these reference ceramic, it was possible to argue that the samples containing microfossils, were baked at a temperature lower than other samples;

- The presence of new-formation minerals such as gehlenite and diopside was observed by XRD measurements, so the baking temperature was approximately determined. This latter seems to be higher for the coarse pottery, except for the sample AGR3, which has abundance of calcite but it is lacking in diopside. Furthermore it must be noticed that the colour of the ceramic mixture is generally bicoloured. This feature is surely connected to the firing conditions used for the artefact. Furthermore, the presence of the so-called "black core" in AGR1 could be attributed to the incomplete combustion of carbon substances originally contained in the raw clayey material, or caused by a rapid cooling in oxidant atmosphere, following a baking phase in reducing atmosphere;
- The clayey matrix, characterised by FT-IR spectroscopy, was composed of traces of kaolinite, besides traces of dolomite, montmorillonite and muscovite;
- It can be reasonably presumed that the clayey raw material of the analysed samples comes from Agrigento, in fact the clayey matrix, the microfossils and the clast are perfectly comparable with the geological formations of this area. This result is further confirmed by the reference data of the ceramic production from Agrigento by Alaimo (Alaimo *et al* 1997). AGR9, belonged to an achromatic basin, is the only exception: for this sample it can be hypothesized that the provisions quarry was western-Greek and non-*Agrigentina*, but surely Sicilian, because it has rather different values of Ni, Co and Cr that are typical elements of *Agrigentina* clay.

5. CONCLUSIONS

Ceramic samples of coarse pottery, transport amphorae and tile, from the VI–V century B.C. and coming from an archaeological excavation in the Agrigento Temples Valley, together with five pottery samples from two medieval kilns found in the historical centre of Agrigento, have been studied by petrographic analysis, X-ray diffraction, X-ray fluorescence and ICP/OES, together with FT-IR spectroscopy.

From the obtained experimental results we can hypothesize that the studied ceramic was made with raw clayey-sandy materials present in the area of Agrigento. In fact the clayey matrix, microfossils and clasts are compatible with the geological formation of the area under investigation, result which is further confirmed by the comparison with the data of the samples produced in the medieval kilns and with some samples from Agrigento published by Alaimo et al. 1995 and 1997. Only in the case of sample AGR9 a different quarry of provisions for the clayey materials could be suggested, since this sample shows many differences in Ni, Co, and Cr, elements strictly connected with the provenance of the clay.

One of the main plans of our future research will be a more detailed comparison of the ceramic manufactures of Agrigento, investigated in the present work, with those contemporary of Gela by Barone (Barone 2002), because of the notable archaeological implications connected with the possibility of unambiguously distinguishing and characterizing the two most important areas of ceramic production in the Greek area of the southern coast of Sicily.

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