

ARCHAEOMETRIC CHARACTERIZATION OF LATE ARCHAIC CERAMIC FROM ERICE (SICILY) AIMED TO PROVENANCE DETERMINATION

Giuseppe MONTANA^{1*}, Luciana RANDAZZO², Chiara BLASETTI FANTAUZZI³

¹ Dipartimento di Scienze della Terra e del Mare (DiSTeM), Università degli Studi di Palermo (Italy)

² Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Università della Calabria (Italy)

³ Archäologisches Institut, Georg-August-Universität Göttingen (Germany)

Abstract

A set of 20 ceramic samples was autoptically selected from the numerous findings recovered from the stratigraphic excavations of the late Archaic city walls of Erice (western Sicily), in order to be analyzed with archaeometric techniques for provenance determination. The excavations were recently carried out as part of a research project funded by the Freie Universität Berlin and the Fritz Thyssen Foundation. Specifically, the ceramic material consists of tableware with a painted geometric decoration of presumed local/regional production, as well as apparently imported black-glazed pottery. Both the categories can be traced back to a chronological period between the second half/last quarter of the 6th and the beginning of the 5th century BC. The methodological approach was aimed to the characterization of the ceramic pastes in terms of relative abundance, size distribution and mineralogical composition of the aplastic inclusions by the observation of thin sections with the polarizing microscope. The objective of the microscopic observations consisted in verifying the existence of textural and/or mineralogical analogies to be ascribed to the same clayey raw material and, consequently, to the same production centre. The chemical analyses of the same set of ceramic samples were carried out using the ICP-OES and ICP-MS techniques (55 elements in total). The aim of chemical analyses was to verify the adequacy of the petrographic classification and identify any chemical marker useful for provenance determination. All the analyzed samples of painted ceramic with geometric decoration have consistent compositional and textural characteristics, to the point of considering their assignment to a single 'paste group'. Specifically, it was found the use of very peculiar clay rich in calcareous bioclasts among the included aplastic and relatively poor in quartz and mica. The production, well distinguishable from those to date already attested in western Sicily, could be local. Concerning samples taken from the ceramic fragments decorated with black glaze, the evidence derived from mineralogical-petrographic observations and chemical analyses help confirm their importation from extra-insular production centres, specifically from the Attic region. The Ca-poor paste and the peculiar concentration of many trace elements such as Cr, Ni, Co, As, Pb, Zn, Cu, Sc, Be, V, Ga, Ge, Sn, Tl in the ceramic body strongly support this hypothesis.

Keywords: Erice; Sicily; Ceramic archaeometry; Archaic painted pottery with geometric decoration; Attic black-glazed pottery.

Introduction

The Elymian settlement of Erice is located in the western side of Sicily (Fig. 1) on the top of Mount San Giuliano (Trapani) at an altitude of approximately 750m above sea level. Thanks to its strategic location Erice controlled a wide territory in close proximity to the

* Corresponding author: giuseppe.montana@unipa.it

Phoenician settlement of Mozia. Since early archaic times onwards its importance gained by the connection to the cult of Aphrodite Ericina.

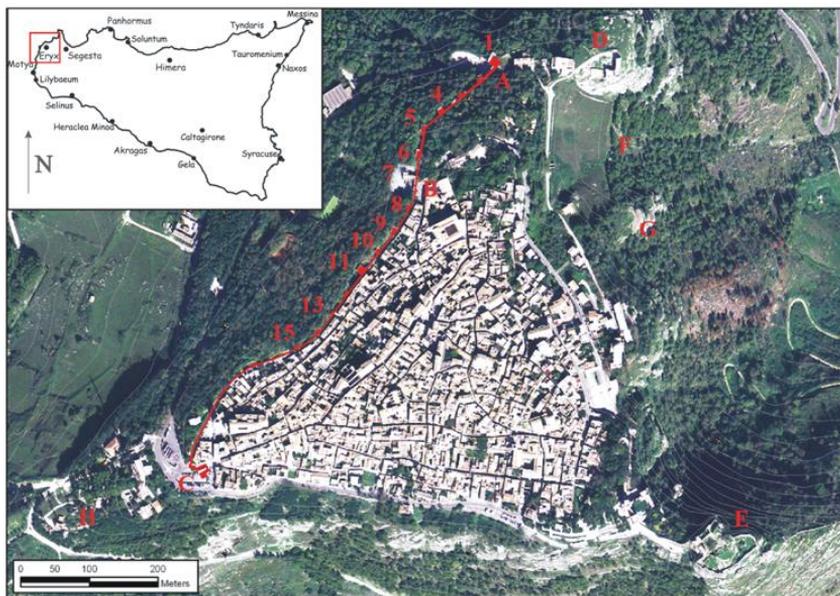


Fig. 1. Erice. Orthophoto, city wall (red) along the western ridge of the city. 1-15: Examined towers. Legend: A. Porta Spada; B. Porta Carmine; C. Porta Trapani; D. Quartiere Spagnolo; E. Castello normanno; F. Porta Castellammare; G. Ridge with southern city limit; H. Necropolis, analysed by A.M. Bisi [1]

The excavation project along the city walls of Erice, directed by S. De Vincenzo, which was initially carried out by the Freie Universität Berlin and then by the Università degli Studi della Tuscia, began in summer 2009 and lasted in summer 2016 thanks to a grant from the Fritz Thyssen Foundation. The first aim of the investigations was to analyse the structure of the walls and determine their chronological phases in order to make visible the extension of the urban area in a diachronic perspective. The archaeological excavations have revealed two ancient construction phases and three later phases (Middle Ages - Early Modern Period). The first construction phase was dated to the first half of the 5th century BC. This dating was mainly confirmed by the excavations of the towers 8 and 9 where Archaic pottery fragments have been recovered from layers under the foundations. The new chronological data concerning the city walls and topographic observations allowed the reconstruction of the boundaries of the ancient city at the beginning of the 5th century BC on the northern summit of the mountain [1, 2].

The studies concerning the ceramic materials started more recently as integral part of the research project. The majority of the ceramic fragments brought to light during the excavations of the late Archaic layers belong to the so called 'Elymian' or 'indigenous' pottery, typically characterized by painted geometric decoration, which is known to have been diffused between the 7th and the beginning of the 5th century BC [3]. Bowls, cups, basins, and jugs are the forms that occur most frequently. Furthermore, numerous fragments of late Archaic black-glazed and black-figured 'Attic' pottery, dated between the end of the 6th and the beginning of 5th century BC, have been collected from the foundation layers of the Archaic walls. Cups and skyphoi are definitely the most attested forms within this ceramic class (Fig. 2).

The archaeometric study of both these classes of pottery, being the first petrographic and chemical analyses carried out on the materials from Erice should facilitate the reconstruction of the cultural and commercial contacts of this Elymian settlement between the end of the 7th and the beginning of the 5th century BC. In particular, for what concerns the samples representative

of the pottery with painted geometric decoration the analysis should allow to verify if they are local products or, on the contrary, imports from production centres already attested in western Sicily. Instead, in the case of the black-glazed pottery the analysis should confirm the exclusive import from Attica and, at the same time, produce new data about the mineralogical and chemical composition of the ceramic body that has been relatively much less studied from this point of view than the black glaze.

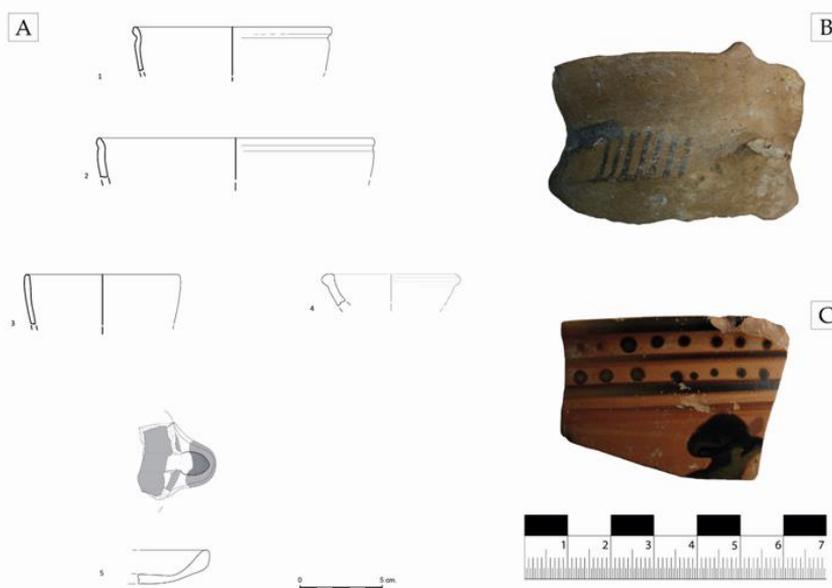


Fig. 2. (A) Drawings of the most attested forms from the foundation layers of the Archaic walls in Erice (B) Archaic painted pottery with geometric decoration, Bowl; (C) Attic black-figure skyphos

Materials and methods

A total of 20 samples were autoptically selected, respectively 10 for the painted pottery with geometric decoration and 10 for the black-glazed pottery (Fig. 2).

Thin-section microscopy was carried out on all the ceramic samples with a Leica DC 200 polarizing microscope equipped with a digital camera. The relative abundance of non-plastic inclusions (modal mineralogy expressed as area %) was determined by conventional point-counting procedures [4].

Bulk chemical data were determined by the Activation Laboratories Ltd (Ontario, Canada), using the fusion inductively coupled plasma optical emission spectrometry (ICP-OES) technique for major oxides and inductively coupled plasma mass spectrometry (ICP-MS) for trace elements. Samples were first air-dried, ground and homogenized in a planetary agate ball-mill (Retsch PM100) after the mechanical abrasion of the black coating. Samples were prepared and analysed in a batch system. Each batch contains a method reagent blank, certified reference materials and some replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt is immediately poured into a solution of 5% nitric acid containing an internal standard until completely dissolved. The samples were run for major oxides and selected trace elements on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP or a Varian Vista 735 ICP. Calibration is performed using 7 prepared USGS and CANMET certified reference materials. One of the 7 standards is used during the analysis for every group of ten samples. Twenty-four elements were considered: Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe (given as oxides, weight %)

and Cr, V, Cu, Zn, Rb, Sr, Y, Zr, Ba, Pb, Ce, Nb, La and Ni (ppm). The results were then normalized on a dry-weight basis.

Results

Petrography

Painted ceramic with geometric decoration

After the observation of thin sections by polarized light microscopy, the 10 samples classified as Archaic ceramics with painted geometric decoration showed reasonably comparable microfabrics. Some slight differences noticed between them, only in terms of textural characteristics (packing and granulometric distribution of aplastic grains), have been deliberately considered as an expression of the natural variability of the exploited raw material and accordingly not sufficient to justify their further subdivisions into subgroups. Therefore, it is possible to consider these samples as preliminarily belonging to a single 'paste group' which is mineralogically characterized by the rarity (almost absence) of sandy inclusions of siliceous composition (i.e. quartz, chert, sandstone, K-feldspar, etc.) and, on the contrary, by a marked predominance of calcareous bioclasts and fragments of carbonate rocks (biocalcarene and subordinate fine grained limestone). Consequently, this class of findings was made by employing a 'calcareous clay' (content of CaO > 6% by weight, in accordance with the classic definition given by [5]) characterized by abundant macrofossils and microfossils (Fig. 3A and 3B).

When the calcareous bioclasts reach dimensions greater than 0.1 mm they can be considered 'inclusions', although forming an integral part of the original clay deposit (marine clay), as they perform the function of rigid skeleton in the ceramic paste that constitutes the body of the ceramic object. As expected, inclusions of this compositional nature are destined to undergo to important structural changes as a result of the firing phase, strongly dependent, specifically, from the size of the calcareous grain and the maximum temperature reached in the kiln and also by the duration of the whole process. In fact, at temperatures close to or above 750 °C the decomposition of CaCO₃ into CaO and CO₂ (volatile) begins and it will complete at around 900 °C. Already during the cooling phase, the calcium oxide reacting with atmospheric CO₂ will re-form calcium carbonate (calcite) in the form of aggregates of very small crystals (micrometric). Substantially, lumps of irregular or sub regular form (defined micritic clots from [6]) will be formed, being roughly equivalent to the size of the original calcareous clasts. In the set of ceramic samples under study, a non-negligible part of the calcareous aplastic inclusions, originally present in the ceramic mixture could be in some extent altered, depending on the intensity of the transformation after the firing process. Since any single calcareous grains could fade into the groundmass it could probably be achieved an underestimation of the abundance (area % packing) of the inclusions, which is an important diagnostic parameter of any ceramic production. In the specific case, to avoid this potential estimation error, given that there are no inclusions of a different nature from the calcareous ones, if not a small amount of tiny quartz grains (mostly relegated to the finest fraction: 0.04-0.1 mm), the packing estimations were made taking into consideration not only the inclusions still preserved after the firing process but also the 'micritic clots' and the pore casts, which are without doubt trace of their original presence and function.

The textural and compositional description concerning all the samples classified as painted ceramic with geometric decoration is reported in Table 1. As regards the textural aspects all the examined samples are characterized by an irregular distribution of aplastic grains with abundances ranging from a minimum of 25% (area estimate by comparative tables, after [4]) to almost 50%. Their distribution is thus serial and variable between the classes of coarse silt (0.04-0.06 mm) and very coarse sand (1-2 mm). However, most of aplastic grains have size between 0.1 and 0.25 mm (fine sand). Grains with dimensions greater than 0.25 mm are

sporadic and the ones with dimensions greater than 1 mm (coarse sand) are rare. Most of the calcareous bioclasts and limestone fragments appear to be deeply altered by the firing process, no longer showing traces of the original internal structure, and appearing as masses (sometimes sub-rounded) composed of microcrystalline calcite.

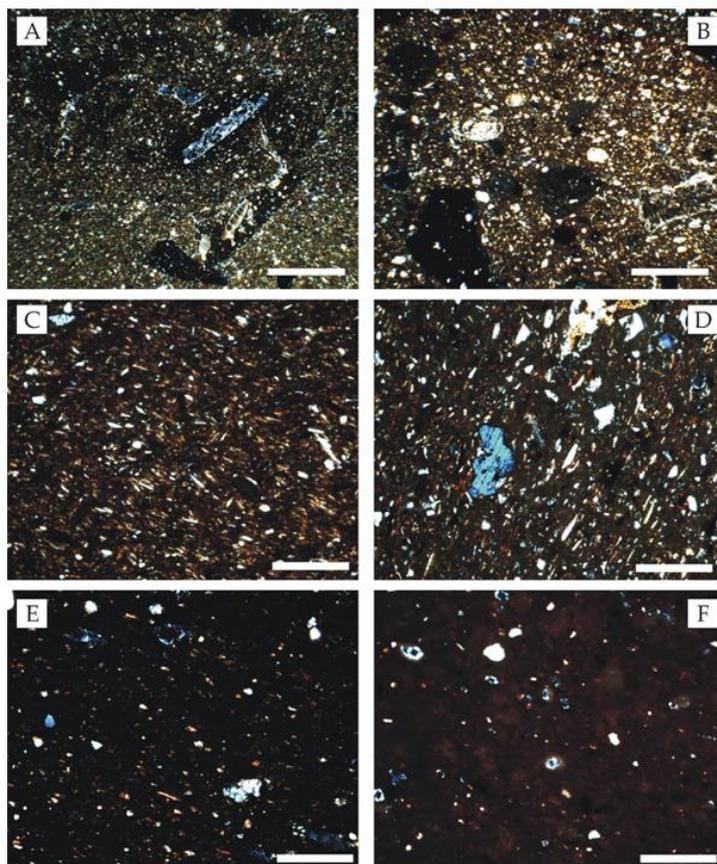


Fig. 3. (A, B) Thin section microphotographs of some representative samples of indigenous matt painted pottery with geometric decoration (crossed nicols; scale bar = 0.5 mm); (C, D, E) thin section microphotographs of some representative samples of black-glazed Attic ceramic (crossed nicols; scale bar = 0.2 mm); (F) thin section microphotograph of the sample ER-20 (crossed nicols; scale bar = 0.2 mm)

In the samples ER-3 and ER-6, the calcareous inclusions (significantly transformed by the firing process) are relatively less represented than the other samples of the group. The finest granulometric fraction is composed of monocrystalline quartz and even rarer tiny mica flakes. The groundmass is generally optically isotropic and shows reddish-brown color when observed under plane polarised light. Sometimes it shows a weak aggregate birefringence (i.e. samples ER-4 and ER-5). The structure is visibly not homogeneous due to the presence of brownish black lumps made of poorly tempered clay rich in iron oxides. The macropores (15-20% areal estimate) have sizes ranging from 0.01 to 1.0mm. Their shape is mainly irregular (casts) and subordinately elongated (sub-parallel contraction cracks to the external surface of the fragment). Small quantities of secondary calcite (precipitated during burial) fill the pore space and cover as encrustations the surface of the ceramic fragments.

Table 1. Schematic description of the compositional and textural features of the Archaic painted pottery with geometric decoration

Sample code	Sandy Aggregate				Groundmass					
	Distribution	Sorting	Prevalent Grain size (mm)	MGS (mm)	Packing (%)	Inclusion	Texture	Optical activity	Porosity	Note
ER-1	Not homogeneous	Serial	Coarse silt – coarse sand	1.5 mm	30%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 15% Irregular or channel (0.01-2 mm)	Secondary Calcite (+)
ER-2	Fairly homogenous	Serial	Coarse silt – very coarse sand	1.8 mm	40-50%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 15-20% Irregular or channel (0.01-1 mm)	Secondary Calcite (+)
ER-3	Not homogeneous (black core)	Serial	Coarse silt – very coarse sand	1 mm	30-35%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 15-20% Irregular or contraction fissures sub parallel to external surface (0.01-1 mm)	Secondary Calcite (f)
ER-4	Not homogeneous	Serial	Coarse silt – coarse sand	1.5 mm	30%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Slightly active	Porosity 15-20% Irregular or contraction fissures sub parallel to external surface (0.01-1 mm)	Secondary Calcite (+)
ER-5	Not homogeneous (black core)	Serial	Coarse silt – very coarse sand	1.2 mm	25-30%	Bioclasts and calcareous lithic fragments recarbonated. Quartz (f)	Lumpy (++)	Slightly active	Porosity 15-20% Irregular, sub rounded or pore cast, contraction fissures sub parallel to external surface (0.01-1 mm)	Secondary Calcite (+)
ER-6	Not homogeneous (black core)	Serial	Coarse silt – very coarse sand	1 mm	30-35%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 15-20% Irregular or contraction fissures sub parallel to external surface (0.01-1 mm)	Secondary Calcite (f)
ER-7	Fairly homogenous	Serial	Coarse silt – very coarse sand	1.8 mm	30-35%	Bioclasts and calcareous lithic fragments recarbonated. Quartz (f)	Lumpy (++)	Inactive	Porosity 15-20% Irregular or rare channel (0.01-1 mm)	Secondary Calcite (f)
ER-8	Not homogeneous	Serial	Coarse silt – coarse sand	1.6 mm	25%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 15-20% Irregular (0.01-0.8 mm)	Secondary Calcite (+)
ER-9	Not homogeneous	Bimodal	Coarse silt (1 st moda) Very coarse sand (2 nd moda)	2 mm	30-35%	Bioclasts and calcareous lithic fragments recarbonated. Quartz (f)	Lumpy (++)	Inactive	Porosity 20% Contraction fissures sub parallel to external surface (2 mm)	Secondary Calcite (+)
ER-10	Not homogeneous	Serial	Coarse silt – coarse sand	1 mm	25%	Recarbonated bioclasts. Quartz (f)	Lumpy (++)	Inactive	Porosity 10-15% Irregular or channel (0.01-1.6 mm)	Secondary Calcite (+)

Legend: +++ = abundant; ++ = common; + = sporadic; f = rare

Table 2. Schematic description of the compositional and textural features of the black-glazed Attic ceramic

Sample code	Sandy Aggregate					Groundmass					
	Distribution	Sorting	Prevalent Grain size (mm)	MGS (mm)	Packing (%)	Mineralogical phases	Lithic fragments/bioclasts	Texture	Optical activity	Porosity	Note
ER-11	Homogeneous	Good	Coarse silt	0.3 mm	< 5%	Qtz (++), Kfs (+), Pl (r), Ms (+++)	Mica schists (r)	Homogeneous	Slightly active	Porosity 5-10%	Secondary calcite (+)
ER-12	Homogeneous	Good	Coarse silt	0.15 mm	< 5%	Qtz (++), Kfs (+), Qtz poly (r), Ms (+)	Mica schists (r)	Lumpy (r)	Inactive	Porosity 5-10% Irregular and pore cast	Secondary calcite (+)
ER-13	Homogeneous	Good	Coarse silt	0.9 mm	< 5%	Qtz (++), Kfs (+), Pl (r), Ms (+++)	Mica schists (+r)	Homogeneous	Slightly active	Porosity 5-10% Pore cast	Secondary calcite (+)
ER-14	Homogeneous	Good	Coarse silt	0.2 mm	< 5%	Qtz (++), Kfs (+), Pl (r), Ms (+++)	-	Homogeneous	Slightly active	Porosity 5-10%	Secondary calcite (+)
ER-15	Homogeneous	Good	Coarse silt	0.15 mm	< 5%	Qtz (++), Kfs (+), Qtz poly (r), Ms (+)	Mica schists (r)	Lumpy (r)	Inactive	Porosity 5-10% Irregular and pore cast	Secondary calcite (+)
ER-16	Homogeneous	Senal	Coarse silt-fine sand	0.25 mm	5-10%	Qtz (++), Kfs (+), Pl (r), Ms (+++)	Mica schists (+), Phyllite (r)	Lumpy (r)	Slightly active	Porosity 5-10% Irregular and channels	Secondary calcite (+)
ER-17	Homogeneous	Senal	Coarse silt-medium sand	0.6 mm	5-10%	Qtz (++), Kfs (+), Pl (r), Ms (+++), Cpx (r), Bt (r)	-	Lumpy (r)	Slightly active	Porosity 5% Irregular and channels	Secondary calcite (+)
ER-18	Homogeneous	Good	Coarse silt-fine sand	0.1 mm	< 5%	Qtz (++), Kfs (+), Ms (+)	Mica schists (r)	Lumpy (r)	Inactive	Porosity 5%	Secondary calcite (+)
ER-19	Homogeneous	Good	Coarse silt	0.4 mm	< 5%	Qtz (++), Kfs (+), Pl (r), Ms (+++)	Mica schists (+r)	Homogeneous	Slightly active	Porosity 5-10%	Secondary calcite (r)
ER-20	Faily homogeneous	Good	Coarse silt-very fine sand-fine sand	0.2 mm	< 5%	Qtz (++), Kfs (+), Qtz poly (r), Ms (r) Glt (r)	Micritic clots (+) Microfossils (+)	Not micaceous	Inactive	Porosity 10% Pore cast and channels	-

Legend: +++ = abundant; ++ = common; + = sporadic; r = rare

Black-glazed pottery

Samples taken from fragments of cups/skyphoi decorated with black glaze, although they are all represented by extremely purified and very fine pastes can be divided into two paste subgroups and a loner. Table 2 reports the textural and compositional description regarding all the samples selected for the archaeometric analyses concerning this ceramic class.

The first 'paste subgroup' is represented by samples ER-11, ER-13, ER-14, ER-17, ER-19. It is characterized by a scarce presence of sandy aggregate (packing around 5%, areal estimation by comparative table after [4]), homogeneously distributed in the groundmass. It falls mostly in the coarse silt class (0.04-0.06mm) and, subordinately, in the very fine sand class (0.06-0.125mm). From the compositional point of view, tiny flakes of muscovite predominate homogeneously dispersed in the groundmass, followed by angular grains of monocristalline quartz (Fig. 3C). K-feldspar (orthoclase) and plagioclase are from sporadic to rare as well as small lithic fragments deriving from metamorphites of low-medium grade (i.e. metapelites and micascists). Sporadically (for example in the ER-17 sample) clinopyroxene crystals (Fig. 3D) are also present together with biotite and fragments of metabasites. The groundmass is homogeneous with very rare lumps (testifying a very good manufacturing technique) and it has slight optical activity. Distinguishable macropores are relatively infrequent (at around 5% area by visual estimation) and irregular in shape; no preferential orientation is evident. The black glaze has a fairly homogeneous thickness, between 0.01 and 0.02mm, with a good adherence to the ceramic body.

The second 'paste subgroup' (samples ER-12, ER-15, ER-16, ER-18) is similarly characterized by scarce sandy aggregate (mostly less than 5% area, visual estimation by comparative table). Aplastic inclusions are homogeneously distributed falling in the coarse silt class (0.04-0.06mm) and in the very fine sand class (0.06-0.125mm). Compared to the previously described paste, the muscovite flakes are rather less represented in the groundmass. Angular grains of monocristalline quartz are the most common constituents followed by K-feldspar (orthoclase), rare plagioclase and rare fragments of micaceous schists (Fig. 3E). The groundmass has a homogeneous structure with rare lumps, and it is optically inactive. Porosity is relatively low (at around 5%). Pores are irregular in shape without preferential orientation. The black glaze adheres very well to the ceramic body showing uniform thickness (between 0.01 and 0.02mm).

The sample ER-20 has different petrographic characteristics with respect to the groups previously described. In fact, despite having textural characteristics quite similar to those of the other samples (similar packing and grain size distribution), it has peculiarly different compositional characteristics. In fact, mica flakes are no longer present in the groundmass. Inclusions consist of angular grains of monocristalline quartz, K-feldspar (orthoclase), polycristalline quartz, glauconite, bioclasts and micritic clots (Fig. 3F). Porosity is around 10%, mainly as pore casts. The glaze adheres quite well to the ceramic body and it has an average thickness of 0.01mm.

Chemistry*Painted ceramic with geometric decoration*

The raw data concerning the chemical composition of matt painted ceramic are shown in table 3. The concentrations of major elements were normalized against weight loss by calcination and expressed as weight percentage (wt%), while abundance of trace elements was reported in parts per million (ppm).

All the analyzed samples are characterized by high concentrations of CaO, although very variable, from a minimum of 15.12% to a maximum of 30.02% by weight (average value 22.98%). Due to the dilution effect, the concentrations of SiO₂ are comparatively lower, mostly less than 50% by weight, and represented by an average value of 48.77%. It should be emphasized that only the sample coded ER-3 and ER-6 samples show CaO values lower than 20% by weight and are thus characterized by fairly higher silicon dioxide content. The content

in Al_2O_3 appears to be relatively low (between 12.70% and 16.94%; average value = 14.56% by weight), reflecting also the dilution effect caused by the peculiar abundance of calcium oxide. Among the remaining major oxides, the average content of Fe_2O_3 (equal to 6.31wt%) and MgO (equal to 2.35wt%) are both in line with most of the clays outcropping in western Sicily and traditionally used as ceramic raw materials [7, 8]. Concerning the alkali metals, while for Na_2O concentrations equal to or less than 0.80% by weight were measured, the K_2O content was on the contrary relatively high with an average value equal to 2.96% by weight. This latter concentration value, in light of the petrographic observations that did not show any particular abundances of mica or feldspar among the aplastic inclusions (sand and coarse silt grains), appears at the moment explicable only considering the prevail of the illite among the phyllosilicates (clay minerals) composing the groundmass. The concentration of TiO_2 is similarly slightly higher (on average equal to 1.03wt%). In figure 4A the dispersion intervals between the 95th and 5th percentile is shown in a comparative manner together with the average values of concentrations of the corresponding oxides of the more significant major elements. The average values are acceptably symmetrical within the corresponding range of variation, thus highlighting the absence of particularly significant outliers, with the sole exception of Al_2O_3 . Furthermore, it is possible to appreciate a more than acceptable compositional homogeneity of the whole set of samples. Exceptions are the variations in the CaO/SiO_2 and $\text{CaO}/\text{Al}_2\text{O}_3$ ratios that, in this case study, respectively, express in the individual samples the diversifications in the abundances of calcareous and siliceous inclusions and the aplastic/groundmass ratio (packing). These rations in chemistry is called the caustic ratio and represents a chemometric feature, with an archaeometric function, used in authenticating ancient ceramic artifacts [9, 10].

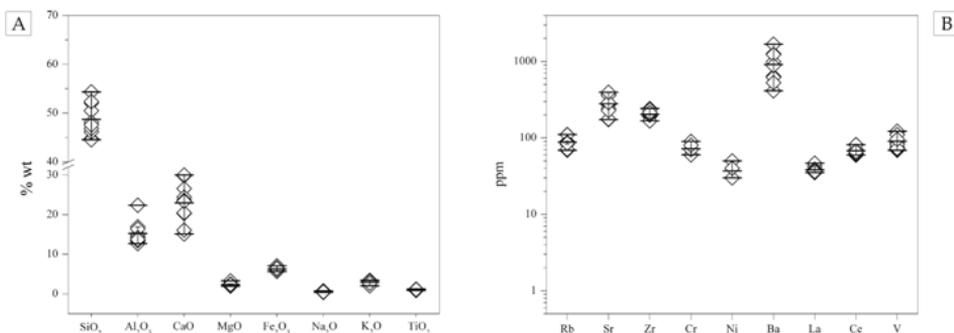


Fig. 4. Box plots showing compositional ranges for Archaic painted pottery with geometric decoration: (A) major oxides and (B) trace elements

Also, for what concerns the trace elements, the 10 samples classified as painted Archaic ceramics with geometric decoration are characterized by fairly similar values, characterized by relatively modest variation intervals. This corroborates the congruity of the ‘paste group’ established according to the corresponding mineralogical and textural characteristics. In table 3 are shown the raw concentration data measured on 45 trace elements. For a certain number of elements (in total 13: Be, Cu, Ge, Mo, Ag, In, Sn, Sb, Hf, Ta, W, Tl, Bi) the concentrations are below the instrumental detection limit or very close to it. The whole series of rare earths (REE, 17 elements including lanthanides and Sc and Y) shows concentration values in line with what was previously found in Sicilian marine clays without highlight specific markers [7]. In Figure 4B are represented (by logarithmic scale) the dispersion intervals between the maximum and minimum values and the average values of the concentrations of the trace elements that are usually valuable in the differentiation of clay-based raw materials for ceramic use. In good agreement with the mineralogical compositions and the textural characteristics, only Ba and Sr

(to a lesser extent) show relatively larger variation intervals and particularly high concentration values.

Table 3. LOI normalized chemical composition of the Archaic painted pottery with geometric decoration

Oxides (wt%) Elements (ppm)	ER-1	ER-2	ER-3	ER-4	ER-5	ER-6	ER-7	ER-8	ER-9	ER-10
SiO ₂	44.76	44.56	54.36	52.06	50.49	52.36	46.17	46.84	48.14	47.59
Al ₂ O ₃	13.28	12.70	16.94	14.43	15.04	16.40	13.49	14.20	13.72	15.44
Fe ₂ O ₃ (T)	5.70	5.81	6.43	5.83	6.52	7.10	6.46	6.57	6.30	6.42
MnO	0.06	0.07	0.04	0.05	0.06	0.06	0.07	0.06	0.08	0.05
MgO	1.97	2.03	2.02	2.17	2.32	2.48	2.30	3.30	2.52	2.39
CaO	29.79	30.02	15.12	20.31	20.47	16.09	26.59	24.42	23.63	23.39
Na ₂ O	0.80	0.64	0.40	0.40	0.51	0.60	0.48	0.51	0.58	0.53
K ₂ O	2.07	2.72	3.08	3.46	3.23	3.26	3.09	2.77	3.22	2.70
TiO ₂	0.96	0.90	1.22	0.94	1.09	1.19	0.86	1.04	1.03	1.12
P ₂ O ₅	0.62	0.54	0.38	0.35	0.27	0.46	0.49	0.29	0.77	0.37
Total	100	100	100	100	100	100	100	100	100	100
Sc	13	12	17	13	14	17	13	13	13	14
Be	2	2	3	2	2	3	2	2	2	2
V	69	71	120	122	86	110	75	82	73	96
Ba	640	621	884	1261	1681	990	414	1227	883	528
Sr	272	283	174	176	242	228	372	360	289	396
Y	27	26	30	27	27	33	29	27	28	28
Zr	190	191	242	193	195	234	167	198	206	215
Cr	60	60	90	70	70	90	60	70	70	80
Co	7	6	13	10	9	15	10	9	9	10
Ni	30	30	40	40	30	50	40	40	30	40
Cu	20	10	< 10	20	20	< 10	20	< 10	20	20
Zn	60	80	60	80	80	100	70	60	90	60
Ga	15	14	21	16	16	20	15	15	15	17
Ge	< 1	< 1	1	< 1	1	1	1	1	< 1	1
As	9	9	13	9	9	13	9	9	8	10
Rb	83	69	111	89	90	110	87	71	85	85
Nb	18	16	24	18	19	22	16	19	19	20
Mo	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	2	< 2
Ag	0.9	0.8	1.1	0.8	0.9	1.2	0.8	0.9	1	0.9
In	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Sn	2	2	3	2	3	4	2	2	2	3
Sb	< 0.5	< 0.5	0.5	< 0.5	< 0.5	0.5	< 0.5	< 0.5	0.6	< 0.5
Cs	3.4	3	5.5	3.8	3.3	4.7	4.2	2.8	3.3	4.4
La	35.1	35.4	42.7	37.1	36.2	46.7	38.9	37.3	37.7	36.3
Ce	59.5	60.6	81.7	70.7	62.9	81.5	67.3	62.1	63.4	66.3
Pr	8.12	8.02	9.96	8.69	8.34	10.4	8.75	8.61	8.63	8.53
Nd	30.2	30.8	37.3	32.7	32.2	39.2	32.2	32.4	32.7	31.2
Sm	6.1	5.9	7.3	6.7	6.3	7.6	6.5	6.5	6.4	6.3
Eu	1.27	1.29	1.58	1.39	1.37	1.66	1.42	1.37	1.38	1.33
Gd	5.4	5.3	6.3	5.8	5.7	7	5.7	5.8	5.9	5.7
Tb	0.9	0.8	1	0.9	0.9	1.1	0.9	0.9	0.9	0.9
Dy	5.1	4.8	6.1	5.4	5.2	6.6	5.3	5.3	5.5	5.4
Ho	1	1	1.2	1	1	1.3	1	1	1	1.1
Er	2.9	2.7	3.2	2.9	2.9	3.6	2.9	2.9	3	3.1
Tm	0.43	0.41	0.48	0.45	0.45	0.54	0.43	0.43	0.44	0.47
Yb	2.9	2.6	3.5	2.8	2.9	3.7	3	2.8	2.9	3.1
Lu	0.47	0.42	0.5	0.42	0.44	0.57	0.42	0.42	0.44	0.48
Hf	5.4	5.7	6.8	5.4	5.3	7.1	4.7	5.8	6	5.9
Ta	1.2	1.2	1.6	1.3	1.3	1.6	1.2	1.3	1.3	1.3
W	< 1	1	2	< 1	1	3	< 1	1	1	1
Tl	0.2	0.2	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.3
Pb	15	15	21	17	17	24	21	16	16	17
Bi	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Th	9.7	9.1	13.4	10.2	10.3	13.1	9.4	10.2	10.2	11.2
U	2.2	2.9	2.7	2.4	3.3	3	2.7	2.4	2.2	2.4

Both these elements (to a greater extent the Sr) are in fact geochemically linked to calcium, especially in the aragonite whose structure can accommodate ions with a radius greater than 1.0 Angstrom (ionic radius Ca^{2+}). Most of the mollusks tend to form the aragonite shell and this could explain the anomalous concentrations in some samples of the above-mentioned trace elements. In fact, it could be the abundance of calcareous microfossils in the ceramic paste to cause the higher average values of Ba (especially) and Sr. Alternatively, it could be hypothesized that the clayey deposits exploited as raw material are in stratigraphic proximity with the gypsum of the Upper Miocene (Messinian) evaporitic succession. Both barium and strontium form, in fact, sulphates (i.e. Barite and Celestine) quite common in the Evaporite Sicilian outcrops. However, it is indicative that, in this regard, no significant correlation was found between the concentration of Ca on one side and that of Ba or Sr on the other. The same applies to the correlation between the concentration of K (as already said exceptionally high) and those of Rb and Ba (vicariant with potassium), also in light of the relative scarcity of mica and feldspars detected in the groundmass by observations with the polarizing microscope.

Black-glazed pottery

Compositional data of black-glazed pottery are shown in Table 4, both for the major elements (expressed as wt % normalized on a dry-weight basis) and trace elements (expressed as ppm). Optical microscopic observations, based on the comparative evaluation of the compositional and textural characteristics, just allowed identifying two subgroups and a loner. Chemical analyses, in general, fully confirmed what highlighted by petrographic observations.

With regard to the concentrations of the major elements, samples ER-11, ER-13, ER-14, ER-17, ER-19 (first paste subgroup on petrographic basis) clearly differ from samples ER-12, ER-15, ER-16, ER-18 (second paste subgroup) for a relatively higher concentration of Na_2O (respectively, 1.10 wt% and 0.62%) and, on the contrary, for lower concentrations of MgO (2.93% and 4.54% respectively) and TiO_2 (0.79% and 0.94%, respectively). Also, the Fe_2O_3 content is slightly lower in the first subgroup (7.75% against 8.73%), while, on the contrary, Al_2O_3 is slightly higher (20.61% compared to 18.72%). The concentrations of the oxides of the other major elements, which commonly are diagnostic towards the determinations of provenance, are roughly equivalent. In fact, the concentration of SiO_2 in both groups differs little from 55% (54.65% for the first group and 55.81% for the second one). The same applies to the average CaO content (7.86% versus 6.38%) and K_2O (3.95% versus 3.84%). The loner (ER-20) is clearly different from both the two subgroups, for the relatively higher concentration of CaO (11.77%) and the lower levels of MgO (2.33%) and K_2O (2.73%).

The scatterplots shown in Figure 5 provide a graphical representation of the chemical differences between the two identified paste subgroups and the loner. For what concerns the concentrations of the trace elements, the distinctions between the samples ER-11, ER-13, ER-14, ER-17, ER-19 (first paste subgroup) and samples ER-12, ER-15, ER-16, ER-18 (second paste subgroup) become even more evident.

In fact, while for some elements such as Ba, V, Zr, Zn and Rb the values were rather overlapping, in the case of Sr and REE, the samples belonging to the first subgroup show relatively higher average values compared to those of the second one (for the Sr, respectively: 359ppm against 229ppm, for the La, as an example of the REE, respectively: 49 ppm against 38ppm). In contrast, almost double or considerably higher Co, Cu and Cs concentrations characterize samples pertaining to the second subgroup. An extraordinarily difference in concentration was determined for what concerns Cr, which, in the samples of the second paste subgroup shows concentrations four to six times higher, undoubtedly attesting these two elements as chemical markers of the corresponding production. In fact, in samples ER-12, ER-15, ER-16, ER-18 the average Cr content is equal to 420ppm (dispersed between 230 and 490ppm) against an average value of 102 ppm of the samples belonging to the first paste subgroup; likewise, the average Ni content is 303ppm for the samples of the second paste subgroup against 52ppm of those of the first subgroup.

Table 4. LOI normalized chemical composition of the black-glazed Attic ceramic.

Oxides (wt%) Elements (ppm)	ER-11	ER-12	ER-13	ER-14	ER-15	ER-16	ER-17	ER-18	ER-19	ER-20
SiO ₂	52.86	56.73	54.11	55.05	56.17	56.86	57.49	53.49	53.77	56.11
Al ₂ O ₃	22.40	19.14	21.00	19.64	20.13	18.17	18.47	17.45	21.55	18.30
Fe ₂ O ₃ (T)	8.30	8.92	7.73	7.44	8.37	8.98	6.82	8.68	8.47	7.00
MnO	0.10	0.10	0.11	0.11	0.11	0.10	0.09	0.12	0.10	0.04
MgO	3.00	4.72	2.91	3.01	3.05	4.88	2.78	5.53	2.95	2.33
CaO	7.23	4.76	8.30	8.78	6.27	5.61	8.31	9.20	6.67	11.77
Na ₂ O	0.96	0.71	1.02	1.11	0.51	0.69	1.33	0.59	1.11	0.49
K ₂ O	4.22	3.82	3.80	3.69	4.24	3.58	3.58	3.72	4.46	2.73
TiO ₂	0.75	0.95	0.83	0.82	0.99	0.93	0.86	0.89	0.72	0.93
P ₂ O ₅	0.20	0.16	0.19	0.36	0.16	0.21	0.29	0.32	0.19	0.29
Total	100	100	100	100	100	100	100	100	100	100
Sc	22	24	20	19	21	23	17	23	22	17
Be	4	3	4	4	4	3	3	3	4	3
V	144	153	137	118	159	130	121	135	146	148
Ba	702	698	606	654	648	552	620	613	708	300
Sr	355	219	359	381	201	233	403	265	299	397
Y	30	27	27	30	27	28	27	27	32	25
Zr	161	141	146	164	192	140	165	128	183	176
Cr	110	480	100	100	230	480	90	490	110	120
Co	20	36	18	17	24	36	14	34	21	13
Ni	70	340	50	50	170	350	40	350	50	60
Cu	30	40	30	30	30	70	20	30	30	10
Zn	180	160	150	140	120	160	130	130	160	120
Ga	31	24	30	27	25	24	26	22	31	25
Ge	2	2	2	2	3	2	1	2	2	2
As	17	23	14	10	24	36	< 5	41	27	< 5
Rb	184	167	171	155	235	159	157	154	190	123
Nb	18	12	18	17	21	12	19	12	17	19
Mo	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Ag	0.7	0.6	0.6	0.6	0.9	0.6	0.7	0.6	0.7	0.8
In	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Sn	5	3	5	5	4	3	5	4	5	3
Sb	0.6	1.3	0.5	< 0.5	1.7	1.4	< 0.5	1.3	0.5	< 0.5
Cs	9.9	13.4	9.5	7.9	87.8	12.2	7.5	12.8	10.2	7.5
La	50.4	38.1	45.4	49	38.7	37.8	45.6	37	52.8	47.8
Ce	102	80.2	90.8	99.2	77.5	79.2	92.7	75.7	108	94.4
Pr	11.3	9.11	10.2	10.9	8.39	9.02	10.1	8.76	12.3	10.3
Nd	42.1	34.9	37.3	41	30.8	33.8	38.1	33.1	45.7	38.1
Sm	8.4	7.2	7.2	7.8	6.1	7.2	7.5	6.9	8.8	7
Eu	1.63	1.57	1.47	1.62	1.34	1.54	1.51	1.43	1.69	1.57
Gd	6.8	6.3	6	6.5	5.6	6.4	6.4	6	7.6	5.8
Tb	1.1	1	0.9	1	0.9	1	1	1	1.2	0.9
Dy	6.2	5.8	5.4	5.8	5.4	5.7	5.5	5.4	6.5	5.2
Ho	1.1	1.1	1	1.1	1	1.1	1	1	1.2	1
Er	3	3.2	2.8	3.1	3.1	3.1	3	3	3.6	2.9
Tm	0.45	0.47	0.42	0.45	0.49	0.46	0.43	0.46	0.54	0.38
Yb	3.2	3.2	2.8	3	3.3	3.2	2.8	3	3.5	2.7
Lu	0.46	0.47	0.45	0.45	0.5	0.48	0.47	0.48	0.53	0.43
Hf	4.8	4.1	4.3	4.6	5.6	4	4.7	3.6	5.2	4.7
Ta	1.2	1	1.4	1.4	1.5	1	1.5	1	1.3	1.4
W	2	1	2	2	2	2	2	1	2	1
Tl	0.5	0.5	0.5	0.6	0.5	0.6	0.4	0.5	0.5	0.4
Pb	83	34	34	34	32	35	24	31	38	26
Bi	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Th	16	12.8	15.5	16.1	18.1	12.3	15.9	12	17	12.4
U	3.6	2.6	3.2	3.2	2.8	2.6	3.4	2.8	3.7	3.5

Bar charts shown in Figure 5D display the significant chemical differences existing between the contents in some trace elements in the two subgroups and in the loner, definitively confirming the subdivision derived from the petrographic observations. The concentrations of the trace elements allow further considerations. In fact, in addition to the anomalies already

discussed, all the samples belonging to the second subgroup have anomalous values (i.e. higher than the average values known for the clayey deposits) of the following elements: As, Pb, Zn, Cu. Moreover, for several other trace elements the values found are close to the known upper limits for soils and clayey deposits (Be, V, Ga, Ge, Sn, Tl).

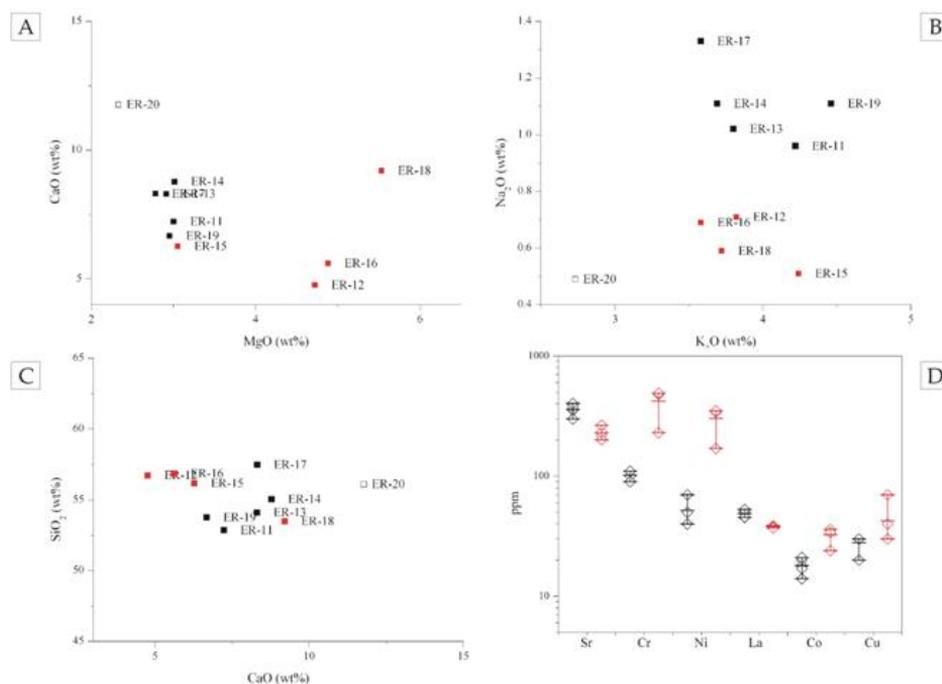


Fig. 5. (A, B, C) Binary diagrams of some major oxide elements for black-glazed Attic ceramic; (D) Box plots showing compositional ranges of trace elements: 'first subgroup' (in black), second 'subgroup' (in red).

Discussion

The Archaic ceramic with painted geometric decoration (but also engraved or embossed) is a typological class that has been attested in numerous sites of central and western Sicily. In the last decade it has been subjected to several archaeometric studies aimed to its compositional characterization and to the identification of the manufacturing centers [8-15]. The chemical analyzes after [11], carried out by NAA (Neutron Activation Analysis) on 62 ceramic artefacts (representative of the local archaic engraved/impressed/painted ceramics) from various sites of western Sicily, allowed the same authors to hypothesize at least five different production centers in the territory. However, despite this encouraging incipit, up to date only one dedicated production center has been definitely attested. It is located at Entella in the heart of the Sicanian Mountains. Specifically, it was possible to define for the first time a 'reference compositional group', carrying out, in addition to the conventional mineralogical-petrographic and chemical analyzes of significant ceramic finds, also the analyzes of overfired production wastes and local clayey raw materials after experimental firing tests [15]. It should also be noted that one of the aforementioned archaeometric studies suggests the Monte Polizzo site among the production centers of this class of ceramic artifacts, although no kiln has yet been brought to light [14]. Finally, studies still being soon published would confirm the same hypothesis for the important settlements of Iato and Segesta.

The data acquired on the studied sample set allow stating that all analyzed findings possess consistent compositional and textural characteristics up to the point to consider more

than likely their assignment to a single ‘paste group’. Specifically, it was put in evidence the use of a clay material particularly rich in calcareous bioclasts among the aplastic inclusions and relatively poor in quartz and mica between the detritic components.

The use of archaeometric analyses, in addition to the simple characterization of the ceramic pastes, would also investigate the place of production of the corresponding artefacts (local/imports). Clearly a research with these purposes should provide an increase of the studied individual ceramic samples (also entering into the details of forms and functionality) and, at the same time, give the analysis of the clays available in the surroundings of the site. Nevertheless, thanks to the data available in the literature, some preliminary considerations can be made being based on the results here presented. In particular, in figure 6A the CaO/SiO₂ concentration ratios of the analysed matt painted ceramic samples were plotted with those that correspond to the attested coeval production of Entella. These latter productions are represented by a satisfactorily coherent group (with a slight ‘physiological’ dispersion of the CaO/SiO₂ ratio), which, moreover, is very different with respect to the Erice’s set of samples. In fact, the content of CaO of the Entella’s manufactories is clearly lower. Regarding the fitting with the data concerning the ceramic raw materials of western Sicily, it seems clear the excellent compositional convergence between the manufactures of Entella and the clays of the Terravecchia Formation, while, at the same time, the other clay formations which are distinctly more calcareous seem to better overlap the ceramic samples from Erice. Two considerations can be drawn from this comparison: i) the archaic matt painted ceramic found at Erice was not produced in Entella, which is the only Elimian site where, up to date, a dedicated kiln for the production of this ceramic class has been attested and where only the clays of the Terravecchia Formation were exploited for this purpose; ii) the matt painted ceramic found at Erice may have been produced on site, or elsewhere, however, in any case, through the use of other clays than those of the Terravecchia Formation (also used at Monte Polizzo). In this paper it will not be possible to give a final answer, although it is already interesting to have excluded an import from Entella, and to have at least a scientific base different from the only stylistic-formal comparisons in support of the local production hypothesis. In fact, the most widespread clay deposits on the southern and western slopes of Monte San Giuliano (at the top of which stands the settlement of Erice) are those belonging to the Marne di San Cipirello Formation, known for their abundant fossil microfauna with calcareous composition [7].

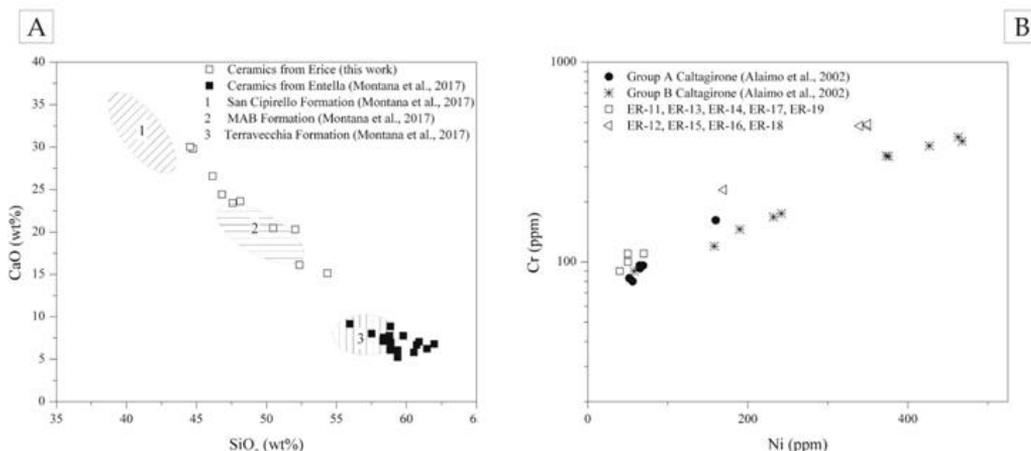


Fig. 6. (A) Compositional comparison (CaO/SiO₂) between Archaic ceramics from Erice (this work), from Entella (after [15]) and compositional field pertaining to clayey raw materials outcropping in the neighbourhood of Entella; (B) Binary diagram Cr-Ni concerning black glazed pottery (this work) compared with similar findings recovered from other Sicilian sites.

As regards the set of samples representative of the black-glazed cup/skyphoi, the evidence derived from mineralogical-petrographic observations and chemical analyzes allowed to countersign their importation from extra insular production centers, with the single exception of the sample E20. As known, the well-known 'black-figure pottery' was born in Corinth in the seventh century BC and developed in Athens and Attica, reaching its apogee in the 5th century BC. It represents the archaeological ceramic material studied for a long time and from numerous points of view (the first essays date back to the second half of the 18th century). However, to date, the vast majority of archaeometric studies have been focused on the manufacture technique of the black-glaze, while, on the contrary, little attention has been paid to the mineralogical-petrographic and chemical characterization of the ceramic body, and even less on the location of the different production centers and the supply points of clayey raw materials. It would seem, in fact, that the clays locally used (even starting from the Mycenaean Age) came from different points of Attica, i.e. Athens and surroundings (alluvial deposits of the Ilissos River), areas surrounding the Mt. Hymettus, Mt. Parnes, the territory of Mesogea and also the well-known mining district of the ancient Laurium (modern Lavrion) about forty kilometers from Athens [16, 17 and references therein]. The mining district of Lavrion, known since the early Bronze Age, was intensively exploited by the Athenians from the end of the 6th century BC, above all for the extraction of lead and more precious silver. A recent experimental archaeometric study recognized the use of the local CaO-poor and metal-rich (specially Zn) illitic clays derived from the hydrothermal alteration of polymetallic sulphides as the raw material specifically used for the preparation of the black glaze [17]. The thesis that the clay used for the black-glaze decoration was not the same used for the manufacture of the ceramic body has been standing for about 25 years [18], supported by the hypothesis that any decanting treatment, necessary to obtain the enrichment of the colloidal particles, could not have completely removed the CaCO₃ which, on the contrary, is present (even if in poor amounts) in the clay material that constitutes the ceramic body, testified by CaO concentrations ranging from about 3% to about 7% by weight [18, 19]. The Lavrion area is part of a complex polymetamorphic belt, comprising Attica and Cyclades, formed in the Alpine Orogenes of the Ellenids. The geological structure of the Attica region, therefore, consists of alternating rocks, dating from pre-Carboniferous to Cretaceous, such as marble, gneiss, schist, volcanic tuff, limestone, sandstone and, in some points, ophiolitic successions. Specifically, the placing of a granitic pluton in the middle-upper Miocene caused the formation of marbles by contact metamorphism and the setting up of large deposits of polymetallic sulfides by hydrothermal fluids (T = 125- 280°C). This could explain the anomalous values of Zn (and to a lesser extent of other base metals) present in the black glaze of the Attic vases produced from local clays. Athens is located in a large topographic basin surrounded by Mt. Aigaleos to the west by the M. Hymettos and Penteli to the north-east and by Mt. Parnes to the north. The basin was formed by the accumulation of sediments mainly eroded by the so-called 'Athens Schists' (medium grade metamorphites with chlorite and sericite alternated with shales, lenses of sandstones, crystalline limestones and calcirudites) and, to a lesser extent, from the above pelagic limestones of the Upper Cretaceous 'Tourkovounia Formation' (which constitute the Acropolis and the other hill reliefs included in the area [20]). During the Quaternary period, layers of alluvial deposits up to 20 meters thick covered most of the central and western basin sector, consisting of breccias and weakly coherent conglomerates, gravels, sands, silts and clays [21]. Many outcrops of clay deposits have been exploited in the past for the production of ceramics and some continue to be exploited today.

This geological premise offers an interpretative key to the data derived from the petrographic and chemical analyzes of the studied ceramic samples. The petrographic analysis by the observation of thin sections in transmitted polarized light showed a clear difference between the samples ER-11, ER-13, ER-14, ER-17, ER-19 (first paste subgroup) and the samples ER-12, ER-15, ER-16, ER-18 (second paste subgroup). Both the subgroups are

characterized by poor aplastic inclusions (packing generally less than 5% area) even small sized (mostly between 0.04-0.2mm). They are also characterized by the presence of tiny flakes of white mica in the groundmass (characteristically abundant in the samples of the first paste subgroup) and, among the larger inclusions, sporadic fragments of metamorphic rocks of low-medium grade (shales and micaceous schists) in addition to quartz and feldspars. It is important to emphasize that ceramic pastes with these microfabrics have already been recognized for Attic black-glazed vases found in other Sicilian sites. In particular, the petrographic analyzes of 5th century BC ceramics from Caltagirone have highlighted the presence of numerous samples (in total 20 among craters with black figures, craters with red figures, kotyliskos, pelike and lekytos,) well distributed in the two microscopic fabrics above described [22]. Similarly, a large number of ceramic finds classified as black-figure Attic pottery found in the area of Messina showed a microfabric analogous to the one of the second paste subgroup described in this paper [23]. It is equally important to underline that the mineralogical and textural recurrences above described are in both cases perfectly agree to the chemical data, although the same analytical methods have not been used. In fact, the anomalous values of concentration in Cr and Ni have been attested to be recurrent in all the ceramic bodies with paste corresponding to our second paste subgroup. The paste with abundant mica in the groundmass (our first paste subgroup), even if not showing correspondingly anomalous values, presents an enrichment in the concentration of trace elements (above all base metals, arsenic and lead) with respect to what is known for the Sicilian clays and of the Appennine ones from the Magno-Greek area [24]. In figure 6B a Ni-Cr binary diagram shows the good compositional correspondence between the Attic black-glazed samples analyzed in this paper and the materials from other Sicilian sites taken from the cited previous studies.

In conclusion, the compositional characteristics of the black-glazed ceramics from Erice leave no doubts about their origin from production centers located in the Attica region. Abnormally high concentrations of some major elements (MgO, Fe₂O₃ and K₂O on all) and a large number of trace elements (Cr, Ni, Co, As, Pb, Zn, Cu, Sc, Be, V, Ga, Ge, Sn and Tl) are in agreement with the geological features of the area, characterized in particular by metamorphic rocks of medium-low grade and metabasites (metamorphosed basic volcanic rocks). The clays with high values of chromium and nickel could, in fact, derive from the serpentinization of the femic minerals of the basic volcanic products typical of ophiolitic sequences, while all the other trace elements (in particular As, Pb, Cu and Zn) can be correlated with hydrothermal mineralization, spread in the same area and subject to specific mining activities for thousands of years.

Conclusion

This contribution, although representing a preliminary study, offers interesting insights for the future development of archaeological research on the Elymian settlement of Erice.

Particularly interesting is to have pointed out that Erice, with good probability, might have been a center of production of painted tableware with geometric decoration. This result enriches the panorama of the production centers already attested in western Sicily. Moreover, given that the excavations carried out until now have not allowed the discovery of production facilities, the number of samples belonging to this class to be subjected to archaeometric analysis will be increased and the analytical characterization of locally available clayey raw materials will be carried out.

The results for the black-glazed Attic pottery class are equally stimulating. The data obtained from the analyses only focused on ceramic body, in fact, allow us to confirm the presence of at least two distinct production centers active in the same period in the region. This theme will also be examined in parallel in the course of a specific project that includes sampling, experimental firing and analysis of clayey raw materials.

Acknowledgments

Fritz Thyssen Stiftung, Freie Universität Berlin and Excellence Cluster TOPOI. THE FORMATION AND TRANSFORMATION OF SPACE AND KNOWLEDGE IN ANCIENT CIVILIZATIONS.

References

- [1] S. De Vincenzo, *Modelli mediterranei ed elaborazioni locali. Le mura di Erice nel quadro delle fortificazioni del Mediterraneo occidentale alla luce delle indagini stratigrafiche*, **Analysis Archaeologica. An International Journal of Western Mediterranean Archaeology**, Monograph Series N° 2 (Rome), 2016.
- [2] C. Blasetti Fantauzzi, *Tra Elimi e Greci. La ceramica di età arcaica dai contesti di fondazione della cinta muraria di Erice*, **Analysis Archaeologica. An International Journal of Western Mediterranean Archaeology**. Monograph Series N° 3 (Rome), 2018.
- [3] D. Gulli, G. Montana, A.M. Polito, C. Trombi, *Nuovi dati archeologici e archeometrici sulla produzione di ceramica indigena della Sicilia occidentale*, **La Sicilia in età arcaica: dalle apoikiai al 480 a.C.**, Caltanissetta-Roma: Salvatore Sciascia Editore s.a.s., ISBN: 978-88-8241-408-5, 2012, pp.589-599,
- [4] A.J. Matthew, *Spots before the eyes: new comparison charts for visual percentage estimation in archaeological material*, In: A. Middleton, I. Freestone (Eds) **Recent Developments in Ceramic Petrology**, British Museum Occasional Paper, 81, 1991, pp. 399–409.
- [5] Y. Maniatis, M.S. Tite, *Technological Examination of Neolithic-Bronze Age Pottery from Central and Southeast Europe and from the Near East*, **Journal of Archaeological Science**, 8(1), 1981, pp. 59-76.
- [6] M.A. Cau Ontiveros, P.M. Day, G. Montana, *Secondary calcite in archaeological ceramics: evaluation of alteration and contamination processes by thin section study*, In: V. Keklikoglou, A. Hein, Y. Maniatis (Eds.), **Proceedings of the 5th European Meeting on Ancient Ceramics** (Athens, 18-20 October 1999), Modern Trends In Scientific Studies on Ancient Ceramics. British Archaeological Reports (BAR), International Series 1011 Archaeopress Oxford, UK, 2002, pp. 9–18.
- [7] G. Montana, M.A. Cau Ontiveros, A.M. Polito, E. Azzaro, *Characterisation of clayey raw materials for ceramic manufacture in ancient Sicily*, **Applied Clay Science** 53(3), 2011, pp. 476–488.
- [8] G. Montana, A. Corretti, A.M. Polito, F. Spatafora, *Ceramic production in the indigenous settlement of Entella (western Sicily) during archaic age*, In: Memmi Turbanti I (ed) **Proceedings of the 37th International Symposium on Archaeometry**, 13th-16th May 2008, Siena, Italy, Springer-Verlag (Berlin, Heidelberg), Vol 1, 2011b, pp. 113–118.
- [9] I. Sandu, V. Cotiuga, A.V. Sandu, A.C. Ciocan, G.I. Olteanu, V. Vasilache, *New Archaeometric Characteristics for Ancient Pottery Identification*, **International Journal of Conservation Science**, 1(2), 2010, p. 75-82.
- [10] I. Sandu, V. Cotiuga, A. V. Sandu, A.C. Ciocan, M. Praisler, *The determination of some archaeometric characteristics of ancient ceramics*, **International Symposium on Applied Physics: Materials Science, Environment and Health ISAP 1**, Ed. University Press GUP (ISSN 1843-5807), Galați, 2009, pp. 421-425.

- [11] M.J. Kolb, R.J. Speakman, *Elymian regional interaction in Iron Age western Sicily: a preliminary neutron activation study of incised/impressed tablewares*, **Journal of Archaeological Science**, **32**, 2005, pp. 795-804.
- [12] G. Montana, A.M. Polito, A.T. Lavore, A. Caruso, C. Trombi, *Indagini archeometriche funzionali all'individuazione dei centri di produzione ceramica attivi in età arcaica nella Sicilia centro-occidentale: Monte Adranone (Sambuca di Sicilia, Agrigento)*, In: C. D'Amico (Ed.), **Atti del IV Congresso Nazionale di Archeometria**, Pisa 1-3 Febbraio 2006, Pàtron Editore, Bologna, 2007, pp. 447-457.
- [13] G. Montana, I. Iliopoulos, V. Tardo, C. Greco, *Petrographic and Geochemical Characterization of Archaic-Hellenistic Tableware Production at Solunto, Sicily*, **Geoarchaeology**, **24**(1), 2009, pp. 86-110.
- [14] G. Montana, C.E. Heinzl, A.M. Polito, L. Randazzo, *Archaeometric evidence attesting production of indigenous archaic pottery at Monte Polizzo (Western Sicily)*, **Periodico di Mineralogia** **81**(1), 2012, pp. 107-130.
- [15] G. Montana, A.M. Polito, A. Corretti, A. Serra, *Compositional reference for the documented Archaic production of indigenous matt-painted pottery at Entella (Western Sicily)*, **Archaeological and Anthropological Sciences**, **9**, 2017, pp. 693-708.
- [16] H. Mommsen, *Attic pottery production, imports, and exports during the Mycenaean period by Neutron Activation Analysis*, **Mediterranean Archaeology and Archaeometry**, **Vol. 3**(1), 2003, pp. 13-30.
- [17] A. Chaviara, E. Aloupi-Siotis, *The story of a soil that became a glaze: Chemical and microscopic fingerprints on the Attic vases*, **Journal of Archaeological Science Reports** **7**, 2016, pp. 510-518.
- [18] Y. Maniatis, E. Aloupi, A.D. Stalios, *New evidence for the nature of Attic black gloss*, **Archaeometry**, **35**(1), 1993, pp. 23-34.
- [19] M.S. Tite, M. Bimson, I.C. Freestone, *An examination of the high gloss surface finishes on Greek Attic and Roman Samian wares*, **Archaeometry**, **24**(2), 1982, pp. 117-126.
- [20] P. Gaitanakis, *Geological Map of Greece 1:50.000. Athinaï-Pireus sheet*, **Institute of Geology and Mineral Exploration**, Greece, 1982.
- [21] M. Regueiro, M. Stamatakis, K. Laskaridis, *The geology of the Acropolis (Athens, Greece)*, **European Geologist**, **38**, 2014, pp. 45-52.
- [22] R. Alaimo, R. Giarrusso, I. Iliopoulos, G. Montana, *Archaic and classical ceramic artefacts from Caltagirone (Sicily): a first attempt for distinguishing imports and local imitations through petrography and chemistry*, **Periodico di Mineralogia**, Special Issue: Archaeometry and Cultural Heritage, **71**, 2002, pp. 17-31.
- [23] G. Barone, S. Ioppolo, D. Majolino, C. Branca, L. Sannino, G. Spagnolo, G. Tigano, *Archaeometric analyses on pottery from archaeological excavations in Messina (Sicily, Italy) from the Greek archaic to the Medieval age*, **Periodico di Mineralogia**, **74**(1), 2005, pp. 11-41.
- [24] P. Mirti, A. Casoli, *Analysis and classification of ceramic material excavated on a South Italian archaeological site*, **Annali di Chimica**, **85**(9-10), 1995, pp. 519-530.

Received: May 08, 2019

Accepted: November 16, 2019