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Chemical characterization of ancient potteries from Himera and Pestavecchia necropolis (Sicily, Italy) by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES)

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ABSTRACT

Thirty-eight samples of pottery were analyzed for determining chemical composition in order to establish their provenance. The potteries tested in the present research come from Himera and Pestavecchia archaeological sites. After digestion in microwave oven, the samples have been analyzed for fourteen minor elements (Ba, Cd, Co, Cr, Cu, Ga, Li, Mn, Ni, Pb, Sr, Ti, Tl, and Zn) and six major elements (Al, Ca, Fe, K, Mg, and Na). Chemical analysis was carried out by Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES). The most abundant minor elements are Cr, Ba and Ni. Cr concentration ranged from 66 to 3635 mg kg^{-1}, Ba concentration ranged from 388 to 2677 mg kg^{-1} and Ni concentration ranged from 35 to 1758 mg kg^{-1}. The relative standard deviation (RSD) of the replicates on the concentrations of analyzed metals ranged from 0.07% to 14%.

The aim of this study is to assign the local or non-local provenance of the examined potteries, in particular validating and clarifying archaeological hypothesis based on the simple visual examination and stylistic characterization of ceramic objects. Principal component analysis performed on the dataset, together with the application of cluster technique and non statistical analysis, allowed the identification of three main groups of samples and a lonely one (R 97). In particular, sample R 97 shows high Cr concentration (3635 mg kg^{-1}) and high Ni concentration (1758 mg kg^{-1}), typical of Corinthian pottery. The results of chemical analysis show that the stylistic features are not always sufficient to correctly identify the origin of a ceramic object.

1. Introduction

Southern Italy and Sicily have been important cultural and economical areas of the central-western Mediterranean, especially in Archaic age (600–475 B.C.) and Classical period (475–323 B.C.). The complex history of Sicily has seen a succession of different cultures and civilizations. The Greeks, in particular, have built important monumental works such as temples [1] and theaters, many of them being still well preserved. Pottery was one of the main materials used to construct common objects, *amphorae* and vases, principally. Ceramic objects were obtained by firing clay and were used for many purposes: food containers, cooking pots, dishes, and pots funeral. This paper presents the chemical characterization of thirty-eight samples of pottery recovered during an archaeological excavation at Pestavecchia and Himera necropolis, in the archaeological site of Himera. Himera was situated along the northern coast of Sicily and Greeks have founded the colony in 648 B.C. The analyzed objects represent *tiles* having local provenance according to archaeologists, *pithoi*, usually employed for burying the dead bodies of children, *olla* and *scannas*, containers used in cooking, and various types of *amphorae*. The *amphorae* were used primarily as food containers, especially during shipping from one city to another. The large number of *amphorae* found in archaeological excavations testifies the intense commercial viability of Himera. All *amphorae* are dated in the Archaic period and have Etruscan, Punic, and Greek (in particular Corinthian) style.

Provenance studies of ceramic materials are widely performed by determining the chemical composition of shreds excavated on an archaeological site; this allows discrimination of locally produced objects from imported wares and getting information on trade routes and relations concerning the excavation site. Thanks to the determination of chemical composition of ceramic ware it is possible to explore its origin.

The aim of this study is to assign the local or non-local provenance of the examined potteries, in particular validating and clarifying archaeological hypothesis based on the simple visual examination of ceramic objects.

The samples have been analyzed for fourteen minor elements (Ba, Cd, Co, Cr, Cu, Ga, Li, Mn, Ni, Pb, Sr, Ti, Tl and Zn) and six major elements (Al, Ca, Fe, K, Mg and Na); chemical analysis was carried out by Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES).

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Some of the most exploited techniques in the study and characterization of ancient ceramics are Atomic Absorption Spectroscopy (AAS) [2], total reflection X-ray fluorescence spectrometry (TXRF) [3], neutron activation analysis (NAA) [4,5], Raman [6–8], IR [9–11], and ICP–OES [12,13].

ICP–OES is one of the most important multi-elemental analytical techniques for the characterization of samples in materials science. This technique has excellent analytical characteristics such as high precision, selectivity, as well as low detection limits. The sample preparation is the most crucial stage in multi-element analysis of silicate matrices, like ancient pottery using ICP–OES. Until recently, decomposition of such materials has been carried out almost exclusively by wet acid decomposition in open vessels [14] or by alkaline fusion [15–17]. In this study microwave-assisted wet decomposition in closed-pressurized vessels was used, because it allows to reduce the extraction time [18], as demonstrated also for other matrices [19].

In order to identify groups of potteries that can be clustered on the basis of their provenance and chemical composition, in this research, PCA and cluster analysis have been carried out. Many examples of applications of principal component analysis [20–22] and cluster analysis [14] for classification purposes and provenance studies in literature are present.

2. Experimental

2.1. Samples

Thirty-eight samples of pottery were analyzed for determining chemical composition in order to establish their provenance. The potteries tested in the present research come from two archaeological sites:

- Fifteen ceramic samples were recovered during an archaeological excavation at the necropolis of Himera, a Greek colony founded in 648 B.C., located near Himera river mouth, along the northern coast of Sicily, at east of Palermo (Fig. 1). The samples of this excavation are labelled as “T”.
- Twenty-three samples come from Pestavecchia necropolis, another necropolis of Himera city, located at east of Himera river mouth. The samples of this excavation are labelled as “R”.

The samples represent *tiles*, *pithoi*, *olla* and *scannas* containers used in cooking, and various types of transport *amphorae* of Etruscan, Punic, and Greek (in particular Corinthian) style.

Table 1
Description of the pottery samples.

Sample	Type[a]	Characteristics	Provenience
T 67	P	Red-orange	Himera necropolis
T 70	E A	Beige-dark	
T 71	C A	Pink-beige	
T 80	Tl	Red-orange	
T 97	Tl	Red-orange	
T 109	E A	Beige-pink dark	
T 154	Tl	Red-orange	
T 164	P	Red-orange	
T 223	Tl	Red-orange	
T 293	P	Red-orange	
T 307	C A	Beige	
T 321	E A	Beige-dark	
T 326	C A	Grey-brown	
T 328	C A	Beige	
T 329	E A	Reddish-brown	
R 2	C A	Pink-beige	Pestavecchia necropolis
R 3	C A	Pink-beige	
R 15	K A	Reddish	
R 21	L A	Grey-beige	
R 24	E A	Reddish	
R 27	E A	Reddish	
R 43	P	Reddish	
R 47 *int*	P	Grey-beige	
R 47 *ext*	P	Reddish	
R 67	S	Reddish	
R 88	O	Reddish-brown	
R 91	E A	Pink-beige	
R 93	P A	Pink-grey	
R 97	N.I.	Beige	
R 99	E A	Reddish	
R 110	O	Reddish	
R 115	O	Grey-dark	
R 130	A A	Reddish	
R 131 *ext*	P A	Grey-dark	
R 131 *int*	P A	Reddish	
R 136	Tl	Pink-beige	
R 142	C A	Reddish	
R 152	P A	Reddish	

[a] P = Pithos; Tl = Tile; E A = Etruscan type amphora; C A = Corinthian type amphora; K A = Kiota type amphora; L A = Laconic type amphora; A A = Attic type amphora; P A = Punic type amphora; O = *olla*; S = *scannas*; N.I. = not identified by archaeologists.

Fig. 1. Location of archaelogical site.