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Thermal and mineralogical investigations of historical ceramic

A case study

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Cultural Heritage Special Chapter

Abstract The selected sample for this study represents a piece of pavement ceramics from a private collection. The ceramic (approximately XVIIIth century) comes from Campania region, Naples province. A chemical, mineralogical and morphological characterization of a Campagna ceramic piece received from a particular collection has been performed. Inductively coupled plasma-atomic emission spectroscopy—(ICP-AES) was used for the determination of Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, and TiO_2 as major constituents and Cu, Cr, Ni, Pb, and Zn as minor and trace selected elements. There is a very important characterization method used for the control of the reaction process and of the properties of the materials obtained. Physical and mineralogical analyses were made by using the thermal behavior (thermogravimetric analysis (TG) and differential thermal analysis (DTG)) and X-ray diffraction spectrometry for the mineralogical composition. The results of these analyses allow the establishment of conclusions about several aspects of their manufacture, the origin of the raw materials and their provenance (local or imported). They provide information supporting certain archeological hypothesis. The performed analysis revealed some very interesting characteristics: lower amount of silica and increased concentration of alumina, the presence of calcium in relatively low concentration (Ca-poor ceramic) and a mineralogical composition.

Keywords Archaeometry · Ceramics · Analytical techniques · Ceramic · Campania region

Introduction

The history of ceramics practically overlaps the history of mankind. Since ancient times, people have produced, through various methods, vases, ornaments, and many other items of ceramics. The oldest ceramic artifact discovered was dated back to the period 29000–25000 B.C. [1].

The chemical analysis, used in provenance, technological, and usage studies, must be defined between chemists and archeologists in order to provide as much information as possible with enough analytical accuracy of the results. Several analytical methods are currently applied, especially due to the development of the instrumental analytical techniques in the last decades. Traditional methods with a largely archeological and typological basis did not enable us to obtain enough information about several aspects regarding the nature and origin of ancient ceramic materials. This is the reason why a large number of articles have recently emerged devoted to study these materials using physical and chemical analyses. Among these studies, geological and ceramic reference materials have been used in order to establish decomposition procedures and analysis schemes using different techniques, such as ICP-AES and XRF [2, 3]. In these sense, tile fragments [4], amphorae shreds and fine ware [5], ancient bricks [6], figure vases [7], etc., were analyzed by different techniques in order to

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classify ceramic pieces into compositional groups, where the obtained results often supported archeological hypothesis previously established. Thermal analytical methods are often used to characterize archeological materials, such as waterlogged archeological woods [8], black crusts on buildings [9], parchments [10], or ancient concrete [11].

In this article, some important points in the analytical methodology development for ceramic analysis are presented, supported in some case studies. Campania volcanic arc zone (situated in Campania region, Naples province) consists of a number of active volcanoes. The most active volcano is Mount Vesuvius, which since antiquity has produced major damage. It has erupted many times. The famous eruption of 79 A.D., when the cities of Pompeii and Herculaneum were fully covered with lava, has been repeated almost every 100 years, some very strong eruptions darkening the sky over Europe to Constantinople (in 1631).

The use of some analytical techniques for the study of various artifacts (including historical paper or metal artifacts) was previously reported by the group [12, 13].

The composition of ceramic artifacts is extremely important; from these data, one could extract both information about the commercial activities of ancient peoples, as well as preliminary information toward the identification of possible counterfeits.

The purpose of this article was to study some ceramic pieces found during the archeological excavation in the area of Campania region, Naples province, and to establish if they apart to the local settlement workshop or maybe they were imported from others counties through Roman Legion.

The analytical chemistry is an essential and indispensable discipline to tackle these studies. Therefore, a chemical, mineralogical, and physical characterization of ceramic (approximately XVIIIth century) from Campania region (Naples province) was made to carry out this investigation. The archeometric study offers indicators for the typology of Campania's ceramic production and provides chemical, mineralogic and petrographical references which allow the pottery to be recognized outside of its area of production. This study aims to determine the chemical and mineralogical characteristics of a ceramic piece in order to distinguish the technological character of artifacts.

Materials and methods

Description of the samples

Samples were obtained by taking a minimum part of the archeological object, with the aid of a scalpel with diamond tip, to minimize any damage and contamination. These samples were ground in an agate mortar and pestle before analyses, in order to reduce the particle size and to secure homogeneity.

Fig. 1 The analyzed sample

The examined specimen is a part of a private collection. Ceramic sample analyzed dates at least to the eighteenth century (during which the piece entered the collection by purchase from the region of Campania, Naples Province), if not earlier. The sample is hexagonal in shape, with sides about 2 cm (Fig. 1). The piece is supposed to be a part of pavement from the area of ancient city of Pompeii.

Physicochemical analyses

Sample preparation and analytical techniques

Chemical analysis of pottery samples involved the application of different analytical techniques. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to determine major element and Ba, Sr, V, Y, and Zr contents and Ag, Bi, Cd, Cu, Ni, Pb, and Zn contents. Above all, the mineralogical investigation has demonstrated that SiO_2 and CaO are the most representative in the sample. The sample dissolution was carried out in the following way: a minimum amount of sample was treated with hydrofluoric acid in an open vessel and heated on a hot plate. It was followed by addition of aqua regia, heating again until dryness. The residue was dissolved with 1 mL of concentrated hydrochloric acid and diluted with water to the mark in Teflon volumetric flasks. Care was taken to keep the contamination to a minimum. Ultrapure water was used throughout and all reagents used were of analytical grade. In all flame and emission spectroscopy determinations, blanks of reactive were analyzed giving signals under the detection limits.

Apparatus

A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. Multielement, matrix matched standards were used for the quantitative determinations. Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control. In particular, 0.1 g of each sample was placed in the Teflon PFA digestion vessels and a mixture of fluorhydric acid (40%) and azotic acid (69.5%) was added. This technic was employed for determining several major and minor elements, including Al, Ca, Cu, Cr, Fe, Mg, Mn, Ni, Pb, Ti, and Zn. K and Na were measured using the same instrument in flame emission mode.

X-ray fluorescence analysis was performed with an energy dispersive X-ray fluorescence spectrometer, ED-XRF PW4025, Minipal 2-PAnalytical, with a Si(PIN)-detector, having a resolution of 150 eV at 5.89 keV (Mn-Kα-line).

The thermal analyses were performed on a TGA/SDTA 851 Mettler Toledo equipment, in a temperature range 35–1200 °C (10 °C min^{-1}) in an air stream with a heating rate of 5 °C min^{-1}, using alumina crucible.

The XRD patterns were recorded on a DRON UM1 diffractometer using an iron filter for the CoK_{α} radiation (1.79021 Å).

Fourier transform IR spectroscopy FT–IR standard spectra were collected by using a Perkin Elmer Spectrum GX spectrometer, equipped with a diffuse reflectance unit. It was possible to use the drift accesory with the powdered pure substance, thereby allowing for a better and easier analysis. The resolution was 4 cm^{-1} and 64 scans were obtained and averaged. The background spectrum was obtained against an aluminum plate. Transmittance percentage (%) was collected in the range of 4000–400 cm^{-1}.

Results and discussion

The archeological area

The integration of historical archeological data with archaeometric data revealed that the coarse wares found at the archeological site of Naple can be ascribed to the local production to a wider territory corresponding to the whole regional extension of Campania region.

Pompeii was a provincial sea-port town, with about 30.000 inhabitants coming form a hybrid population. The artifact is the subject to four behavioral practices: manufacture, use, maintenance, and discard. Manufacture consists in making the object from materials obtained from nature (clay, sand), use is the utilization of the artifact for the purpose or the purposes it was manufactured [14].

The manufacturing process for a mostly pottery involves most of the times this six stages: raw materials procurement, the preparation of the paste, forming, drying, firing, sometimes it was needed two times, post firing handling, and storage in a constant atmosphere. The process difficult to control involves the drying and firing. If a vessel was dried too fast it might developed weak spots that could become cracks threw out the firing process. If the vessels were not enough dried could cracked or exploded threw the firing stage. The artifacts exploded too much to the firing gases inside the kiln or exposed to an oxygen-rich, or an oxygen-poor atmosphere can lose their colors. Also the vessels that were put in a cold atmosphere after the firing process could crack, and lose their attachments, such as handles, very easily.

Chemical and mineralogical analysis

Major constituents, such as Si, Al, Ca, Fe, K, Mg, Mn, Na, and Ti, were determined in the samples and the results calculated as percentage of their respective oxides (SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, and TiO_2). The content of some minor elements (Cu, Cr, Ni, Pb, and Zn) were also detected by ICP-AES and EDXRF.

The EDXRF results obtained in the analyzed sample are presented in Fig. 2 and Table 1, and from those results, the sample could be categorized as a Ca-poor ceramic. The quantitative determination was performed trough ICP-AES (Table 1), while the quantitative mineralogical composition was determined trough XRD (Fig. 3).

The variables were grouped in three different studies: (i) 14 corresponding to chemical data (SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, TiO_2, Cu, Cr, Ni, Pb, and Zn), (ii) nine variables corresponding to data of total mineralogical composition (calcite, quartz, dolomite, gehlenite, anorthite, feldspars, phyllosilicates, piroxenem, and wollastonite), and (iii) those 12 for heavy mineralogical fraction (tourmaline, zircon, rutile, garnet, andalusite, distene, epidote, diopside, apatite, hornblende, sillimanite, and staurolite).

CaO contents are modest, the matrices are ferric, and mineral assemblages comprise mostly quartz, anorthoclas, hornblende, and muscovite. Except for quartz, the mineral association in this sample is similar to that in trachytes from Etna consisting of "plagioclase (An40), augitic clinopyroxene, FeTi oxides, some olivine and kaersutite set in a groundmass containing alkali-feldspar (anorthoclas), clinopyroxene, Ti-magnetite, biotite and sporadic sodalite, and nepheline" [15]. The composition of glass within the ceramic bodies may be compared to that of lava in numerous other areas [16, 17]. Lastly, note that the olivine in rocks from Etna is mainly forsteritic [18], whereas that in the studied ceramic specimens is Feric. Gravimetrically determined concentration of silicon dioxide (the total SiO_2) is 60.2%. Chemical analysis results are confirmed by

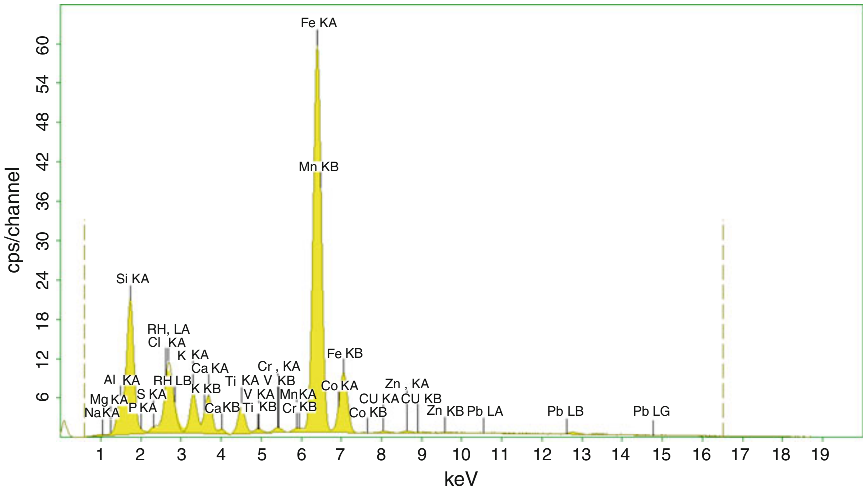

Fig. 2 EDXRF spectrum of the analyzed sample

Table 1 Chemical composition of the sample (EDXRF and ICP-AES) compared with other studied ceramic [19]

Compound	Concentration through EDXRF/ %	Element	Concentration through ICP-AES/ %	Element	Concentration in other ceramics/% [19]
Al_2O_3	21.3	Al	8.67	Si*	23.9
Fe_2O_3	6.86	Na	4.15	Ca	8.31
K_2O	2.33	Fe	3.07	Ti	3.52
MgO	2	K	2.94	Al	1.69
CaO	1.75	Ba	1.38	Fe	1.06
TiO_2	0.93	Ca	1.23	Na	1.06
Cr_2O_3	0.09	Mg	0.74	K	0.36
MnO	0.06	Ti	0.45	Pb	0.18
ZnO	0.02	Cr	0.048	Mg	0.13
CuO	0.02	Mn	0.034	Ba	0.09
		Zn	0.019	Mn	0.03
		Cu	0.0075	Zr	0.007
				Zn	0.002
				Cr	0.0017

* In the studied sample, the SiO_2 was present in a concentration of 60.2%, gravimetrically determined

EDXRF analysis. The concentrations of muscovite, hematite and anorthoclas were determined by correlation of the mineralogical analysis with the chemical analysis. Quartz concentration was determined from the diffraction data, compared with a standard quartz sample. The concentration of the amorphous $Al(OH)_3$ was determined by correlation of the thermogravimetric analysis with chemical analysis: loss on ignition of 3.1% between 80 and 760 °C corresponds exactly to concentration of aluminum unbound in the form of muscovite and anorthoclas. 1% loss in the range 760–1200 °C corresponds to the concentration of water resulting from the decomposition of muscovite (Fig. 4 and Table 2). The mineralogical results show a relatively low amount of silica and an increased concentration of alumina, by comparison with other analyzed samples [19].

Thermal analysis

The thermal effect observed in the temperature range from 25 °C to 1000 °C was comparable to those previously obtained in similar Roman materials [20]. A more detailed study showed two variations in the ranges of 550–650 °C and 750–900 °C. The expansive effect of about 600 °C can be attributed to the quartz transformation (α–β transformation). The material contracts slightly until a temperature of 750 °C is reached, in this moment the synterization step starts. The presence of calcium carbonate causes a second expansive effect about 700 °C due to the formation of CO_2. In the same way, the thermal effect observed around 800 °C is probably due to the transformation of calcite in gehlenite. In these materials with high contents of calcium carbonate, up to 15%, an additional expansible effect is

Fig. 3 The XRD pattern of ceramic sample—*m* muscovite, *a* anorthoclas, *h* hematite, *q* quartz

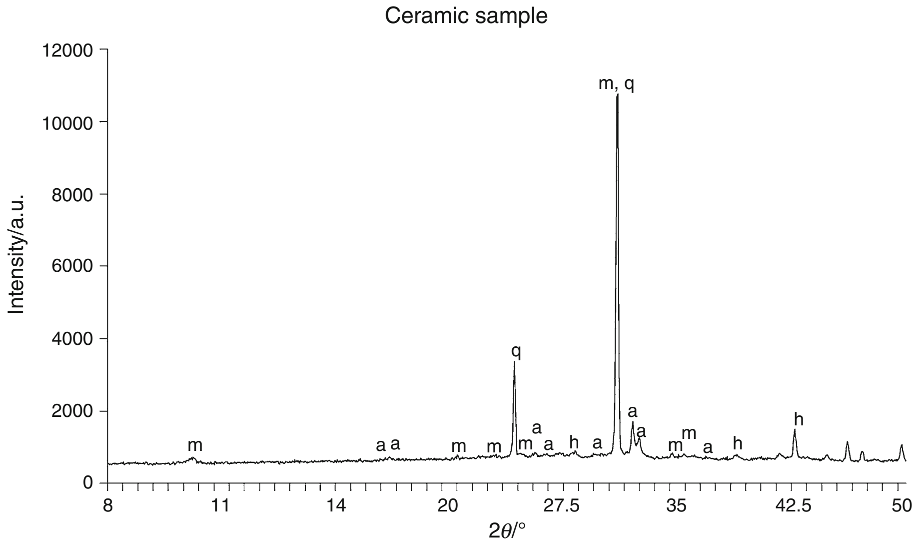

Fig. 4 TGA results for the analyzed sample

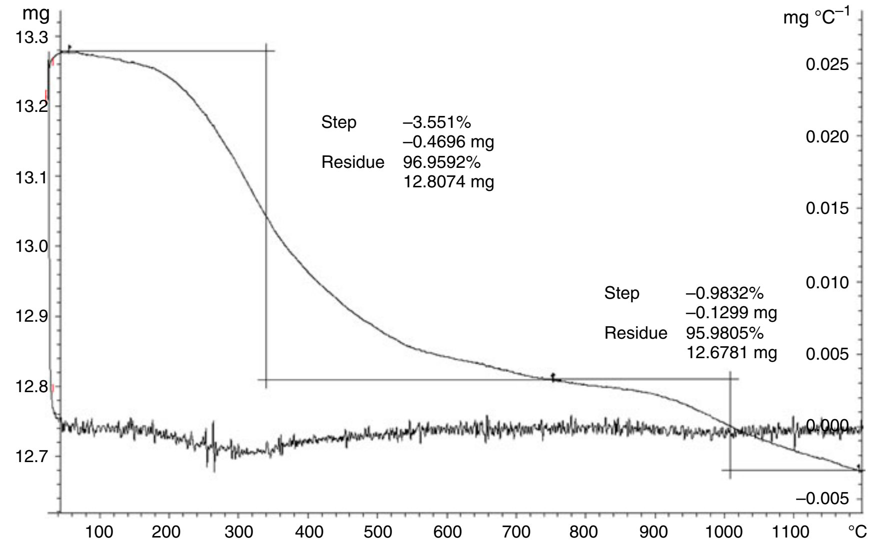

Table 2 Mineralogical composition of the analyzed sample

Minerals	Concentration/%	ASTM
Quartz [α SiO_2]	36.4	33–1161
Muscovite [$KAl_2Si_3AlO_{10}(OH)_2$]	20.0	7–25
Anorthoclas [$Na_xK_{1-x}AlSi_3O_8$]	25.1	10–361
Hematite [α Fe_2O_3]	4.4	13–534
Amorphous $Al(OH)_3$	9.0	
Unidentified compounds	5.1 (by difference)	

observed, at around 900 °C, attributed to the formation of crystalline calcium silicate (wollastonite type) from breakdown of the previous amorphous materials. At temperatures greater than 1050 °C, at which the fusion begins, a new contraction appears, probably due to the transformation of gehlenite in mullite [21].

In the kaolinitic clays with calcium carbonate, the formation of gehlenite at 850 °C from the lime has been recognised by Maniatis et al. [22], who also reference the carbonate destruction between 850 °C and 1050 °C [23] with the incorporation of calcium causing a vitrification process. A quick diffusion of calcium ions toward quartz grains, feldspar, and clay minerals was observed and melilite type, gehlenite, and iron-gehlenite had to be formed from CaO around 850 °C. According to Schüller [24], the growth is controlled by the interface, and the range of diffusion is higher when the concentration of silica and alumina is not similar than calcium concentration.

Thermal analysis is often a very useful tool to discern among different ceramic pastes since their thermal behavior depends on the raw materials employed. But in this particular case, the thermal study carried out does not allow us to distinguish samples according to their origin.

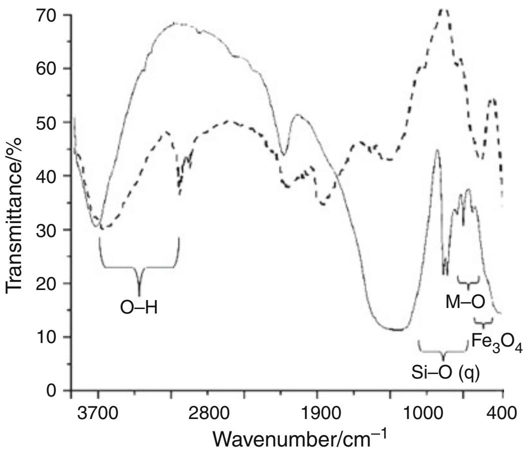

Fig. 5 FTIR spectra for magnetite (*dotted lines*) and Campania ceramic with magnetite (*continues line*)

From the morphological and mineralogical studies, the authors could conclude that the presence of large quantities of SiO_2 indicates that the reached temperature was not high enough for silicates formations. These effects were a consequence of a short and heterogeneous heating process that provides decarbonatation processes followed by the elimination of CO_2, as well as the cracking of the ceramic material caused by the quick transformation of calcite in CaO [22]. The presence of mineral geothermometers [14] in the Italian ones, such as gehlenite ($SiO_2{\cdot}Al_2O_3{\cdot}2CaO$), a compound formed at the same time as $CaCO_3$ decomposition (about 800 °C), and wollastonite ($SiO_2{\cdot}CaO$), a compound formed after gehlenite at higher temperature, is a consequence of a treatment at temperatures close to 900 °C or higher.

Fourier-transform IR technique (FTIR) spectroscopy is a good analytical tool to determine the changes of chemical components in ceramic caused by different treatments [25]. The ceramic is not transparent for light, so the DRIFT (diffuse reflectance infrared Fourier-transform) technique can be applied.

Figure 5 shows IR spectrum for the ceramics from Campania. The similar bands assigned to typical O–H (3700–3000 cm^{-1}; 1635 cm^{-1}), Si–O in quartz (1160, 1082, 797, 778, 695, 512 cm^{-1}) and M–O (725, 645, 585 cm^{-1}) vibrations are very well resolved in the IR spectrum of ceramic sample. A specific band from 575 cm^{-1} could be assigned to magnetite, in good correlation with composition of Campania volcanic arc zone (situated in Campania region, Naples province) magnetite being one of the components of active volcanoes lava [26].

Conclusions

A suitable combination of the physicochemical analytical techniques used for studying ceramic provided useful information about chemical and mineralogical composition. It helps to shed more light on the nature of the raw materials used in the manufacture of the pieces, possible origin, production, and firing technology, providing arguments to predict and to confirm archeological hypothesis.

The test results show that the material under study is different from regular ceramics (presented in another paper by the group [19]), both in terms of chemical composition and in terms of mineralogical composition, however, in good agreement with literature data concerning the ceramic artifacts from Naples [27].

This is a proof of the possibility of creating maps of origin for the ceramics, which could provide information on the origin and authenticity of the pieces studied.

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