2020 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Trento, Italy, October 22-24, 2020

Characterization of Etruscan non-vascular ceramic fragments

Margherita Cantelli [1], Alberta Facchi[2], Francesca C. Izzo[1], Elisabetta Zendri[1]

[1] *Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Via Torino 155 eta, 30170, Mestre, Venice, Italy.*
854492@stud.unive.it, fra.izzo@unive.it, elizen@unive.it
[2] *National archaeological Museum of Adria, Ministry of Cultural Heritage and Activities, alberta.facchi@beniculturali.it*

***Abstract* – This work focuses on the importance of Archaeometry aiming at defining some archaeological uncertainties concerning the use of distinctive materials. More precisely, the goal of this study is the interpretation of spectroscopic and thermogravimetric data, as well as water absorption measurements, for the characterization of non-vascular ceramic fragments found in two different Etruscan settlements dated back to 6th-4th century BC and situated in the Po Delta region (San Basilio di Ariano nel Polesine and Adria – Rovigo, Italy). A multi-analytical approach was applied in order to clarify the role of these ceramic findings, which were supposed to be building materials used to cover house walls, as internal or external plasters.**

I. INTRODUCTION

The current study deals with the materials found in two different archaeological sites identified as settlements of clear Etruscan cultural field in the Po Delta region, Italy. Etruscans were a civilization of ancient Italy that covered a wide period, from the 9th to the 1st century BC, establishing mainly in the area corresponding to Tuscany, Umbria, Lazio, Emilia-Romagna and some areas of Campania, but it was not until the 6th century BC that the Po Valley was colonized by them. The settlements taken into consideration were situated in the village of San Basilio di Ariano nel Polesine (Rovigo) and in the small town of Adria (Rovigo) [1, 2]. They both were commercial ports also connected with the harbour of Spina (Ferrara, Italy), becoming important multi-cultural centres, where Etruscans, ancient Veneti and Greek merchants and sailors met for trading.

The samples analysed in this study are: 1) non-vascular ceramic fragments (called *concotto* by the archaeologists) different in size and shape with heterogeneous surfaces presenting a particular groove, 2) several fragments of *incannucciato* showing circular longitudinal impressions on some sides.

Similar materials were found also during the excavation in the shore of Spina. The literature associated with these findings suggests the use of *concotto* as plaster in the bottom part of the wall being more water-resistant, and *incannucciato* as daub fragments to cover the upper part of the wattle structure, even if excavation reports do not clarify the doubts concerning the use of these materials [3, 4].

Considering the uniqueness of the findings, how can Archaeometry help to clarify their role? A multi-analytical approach was carried out by means of spectroscopic measurements, such as Fourier-transform infrared (FTIR) and FTIR in attenuated Total Reflection (ATR) mode spectroscopies, and thermogravimetric analysis coupled with a differential scanning calorimetry (TG-DSC). Moreover, based on the results obtained by spectroscopic techniques water absorption analysis was considered to investigate the total open porosity of the findings.

II. MATERIALS AND METHODS

A. Materials description

The fragments, stored in the depository of the Museo Archeologico Nazionale di Adria (Rovigo), are different in size and shape, with a surface of approximately 10 cm^2 to 110 cm^2 and a non-uniform thickness around 1.5 cm. They generally show two different sides: one smoothed, while the other rough and irregular. A substantial portion of fragments has, on one side, a repetitive groove which differs between the sites; 70 pieces from San Basilio show a deep and tight sign, whereas, 109 findings from Adria feature a large, flat and shallow groove (Fig. 1).

According to this preliminary observation, the fragments were subdivided into groups depending on chromatic features [5], that could indicate differentiations in firing temperature and/or in mineral composition. Most of the pieces colouration goes from light red (2.5YR 6/6) to light brown (7.5YR 6/4), but some of them are rather heterogeneous presenting a violet coloration and efflorescences.

To facilitate comparisons with materials whose ancient purpose is known, some of the 210 fragments of *incannucciato* from San Basilio were also considered.

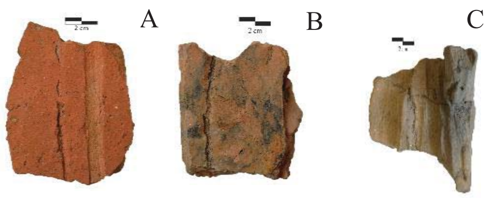

Figure 1. Samples: San Basilio (A), Adria (B) and incannucciato (C) samples.

These pieces, showing clear evidence of wattle impressions suggesting a wattle and daub construction process, present a granular composition, since they are prone to powdering to the touch (Fig 1).

Table 1. Groups sub-division of San Basilio and Adria concotto samples

Site	Groups	Pieces	Munsell colour indication
SB83	A	14	-
SB83	C1	18	2.5YR 6/6
SB83	C2	31	7.5YR 6/4
AER16	1	16	2.5YR 6/6, 5YR 6/6
AER16	2	14	2.5YR 6/4, 2.5Y 8/2
AER16	3	20	7.5YR 7/4, 10YR 7/3
AER16	4	19	10YR 6/2, 2.5Y 7/1
AER16	5	22	2.5YR 5/6, 2.5YR 6/4
AER16	6	12	-

B. Analytical methods

Considering the high number of samples stored in the depository of the museum, a micro-destructive in-situ investigation approach was primarily chosen in order to select the most representative fragments.

All the fragments were firstly analysed with a portable Bruker ALPHA spectrometer equipped with ATR modulus based on a single-bounce diamond ATR crystal. Sample were placed on the crystal head and were directly examined without any preparation. Spectra were recorded in the range 4000–400 cm^{-1}, 32 single-beam scans at 4 cm^{-1} resolution. To detect more punctual information about surfaces and bulk composition infrared spectra on selected samples were obtained by FT-IR Nicolet Nexus 670/870 spectrometer in transmission configuration using KBr pellets (1:100-wt.% sample/KBr). Spectra were recorded in the range 4000–400 cm^{-1} as a ratio of 32 single-beam scans at 4 cm^{-1} resolution.

Based on the spectroscopic results, water absorption by total immersion was performed on selected fragments to investigate the porosity, measuring the amount of absorbed water by the material submerged into water at room temperature and pressure, as well absorption rates and drying values.

Thermogravimetry couple with Differential Scanning Calorimetry (TG-DSC) were performed providing information about mineral phase transitions. TG and DSC analyses were carried out simultaneously with a Netzsch 409/C instrument. About 10 mg of finely powdered samples were heated in an open corundum (Al_2O_3) crucible from 25°C to 1000°C at a heating rate of 10°C min^{-1} with flow rate of 80 ml min^{-1} of N_2.

III. RESULTS AND DISCUSSION

Figure 2 shows the FTIR-ATR spectrum of sample 303Y (side A, group 5), chosen as the representative for the majority of the ceramic artefacts analysed. Table 2 lists the IR frequencies of selected samples with the corresponding vibrational assignments. The interpretation of these data allowed to identify the compounds present in the samples, revealing as main component as silicate, like quartz [6], [7] and feldspars (orthoclase [8] and albite [9]), iron oxides (hematite and magnetite [7], [10]) and clay minerals (kaolinite [11] and montmorillonite [7]).

In addition, some samples (Figure 3) present iron-rich clay minerals signals [6], and diopside [12] in the surface, but not in the bulk. Moreover, some spectra display distinctive peak of gypsum on the surface that can be related to the efflorescence observed by naked eye.

Table 2. FTIR-ATR results of sample 303Y and 41W (surface) and corresponding vibrational assignments.

Sample	IR frequency (cm^{-1})	Vibrational assignment	
303Y_5	3378	H-O-H str.	Montmor.
	1636	OH deformation	Water
	1164	Si-O str. (asymmetric)	Quartz
	986	Si-O str. (asymmetric)	Quartz
	796	Si-O str. (symmetric)	Quartz
	778	Si-O str. (symmetric)	Quartz
	721	Al-O-Si bend.	Albite
	698	Si-O bend. (symmetric)	Quartz
	643	Al-O coord.	Orthoclase
	556	Fe-O	Magnetite
	448	Si-O def.	Quartz
41W_A	973	Si-O str. (asymmetric)	Quartz
	918	Al-Al-OH bend.	Illite/Kaolinite
	872	Fe(AlOH)	Iron-rich clay minerals
	796	Si-O str. (symmetric)	Quartz
	776	Si-O str. (symmetric)	Quartz
	696	Si-O bend. (symmetric)	Quartz
	637	Al-O coord.	Orthoclase
	504		Diopside
	452	Si-O def.	Quartz

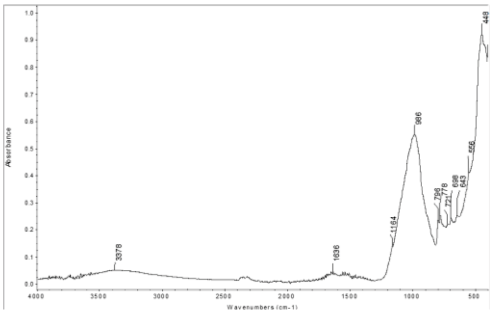

Figure 2. FTIR-ATR spectrum of 303Y_5 sample

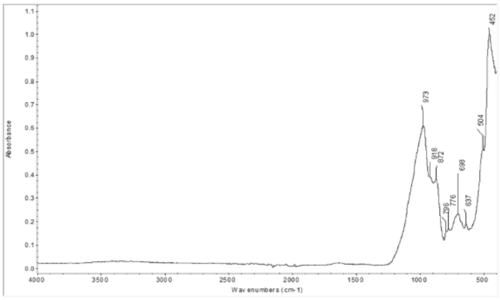

Figure 3. FTIR-ATR spectrum of 41W_A sample

Additional FTIR analysis on bulk were performed in transmittance mode in order to understand the nature and the distribution of the efflorescence and the presence of diopside. The latter is a mineral that can be naturally present in the ceramic body, but it can also form at high temperature (>800°C) [7], so it can be a good indicator of the firing temperature. However, the spectrum of the bulk did not show the peak of diopside, suggesting that only the superficial part of the samples underwent to high temperature. No clear evidences of gypsum were found in the bulk, suggesting its presence as contribution from the soil. Moreover, the *incannucciato* sample displays the frequency characteristic of silicates, clay minerals, iron oxides and calcite [7].

Based on the spectroscopic results it was decided to evaluate total open porosity by water absorption (WA); two representative samples for each group were considered. According to the NORMAL 7/81 [13] samples should have the same shape and width, to directly correlate obtained values with the volume, and should be dried in an oven at 60°C before being weighed. For this study a different approach has been chosen, considering that a non-destructive strategy was recommended.

Samples were firstly weight to register the initial value, and subsequently submerged in water and weight after some specific periods of times in order to estimate the quantity of WA. Sample 1_INC was the faster to reach saturation (30 minutes), while the majority of samples (12) required 120 minutes, 5 fragments needed 150 minutes, only one piece required 240 minutes and two samples even took 420 minutes.

The obtained values range from 14.53% to 21.96%;

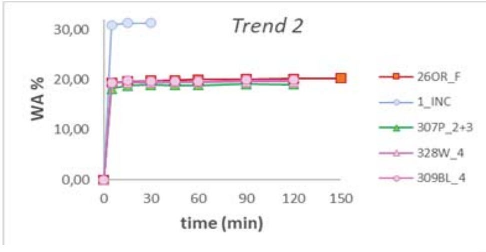

Figure 4. Absorption curve, Trend 2

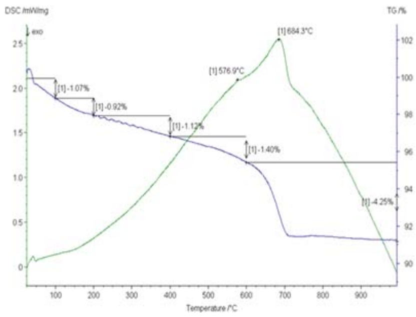

Figure 5. TG-DSC thermogram of sample 1_INC_bulk

since WA increases according to open porosity [14], and high WA values are due to coarse particles [10], it can be deduced that samples with the lowest WA value suggest a low porosity and a composition of fine particles. An *incannucciato* sample (1_INC) was also analysed showing the highest value of WA (31.28%) suggesting higher open porosity and the presence of coarse particles.

Absorption curves were also considered, dividing them into three main classes depending on the absorption trends. Since the dimension of pores can be supposed according the absorption rate [15], it can be suggested that the samples following Trend 2 shown in Figure 4 (high absorption rate) are supposed to have small pores, while samples following Trend 1 should have bigger pores [15].

Few selected samples were chosen in the interest of correlating the firing temperatures with specific groups. TGA–DSC curves were examined considering both the heat flow of samples and the mass loss expressed as percentage, both as function of temperature. The thermograms of all the samples analysed, except for incannucciato, are characterised by a broad endothermic peak around 550÷650°C that indicates the loss of hydroxyl water by clay minerals [16], even if it is difficult to attribute the dehydroxylation phase to one precise clay mineral. This indicates that the firing temperatures of ceramic fragments should have been lower than 500°C, despite the preliminarily subdivision in groups.

Thermogram of incannucciato (Figure 5) displays a DSC peak at 576.9°C referring to the polymorph transformation of α- to β-quartz [17], while the peak at 684.3°C could be ascribable to the decomposition of reformed calcite [18], accompanied by a weight loss of 4.25%. Since the transformation of α- to β-quartz is reversible, the peak at 576.9°C cannot be a significant indication of firing temperature. Usually, the presence of calcite is a good indication to define the firing temperature, but not in the case of reformed calcite [19]. TGA results are expressed in Table 3 as percentages of mass loss considering different temperature ranges and as total weight loss. The most noteworthy feature has been detected in Sample 367BL_6, having the highest value of weight loss (22.26%). This indicates a clear difference in composition attributable to the presence of gypsum related to the mass loss of 12.59% in the 100-200°C temperature range.

Table 3. Percentage of mass losses per T range

	367 BL_6	328 BL_6	2 P_C1	309 P_1	41 W_A	1_INC
<100°C	-2.37%	- 1.11%	- 1.14%	- 1.09%	- 0.17%	- 1.07%
100-200°C	- 12.59%	- 0.69%	- 1.74%	- 0.07%	- 0.62%	- 0.92%
200-400°C	-1.81%	- 0.57%	- 1.70%	- 0.47%	- 0.69%	- 1.12%
400-600°C	-1.00%	- 0.49%	- 0.68%	- 0.67%	- 0.35%	- 1.40%
>600°C	-4.49%	- 0.62%	- 1.55%	- 0.42%	- 0.78%	- 4.25%
Tot weight loss	22.26%	3.48%	6.81%	2.72%	2.61%	8.74%

IV. CONCLUSIONS

Aim of the study was the characterisation of non-vascular ceramic materials found in two distinct Etruscan settlements. A multi-analytical approach was carried out using specific investigation methods such as FTIR and ATR mode spectroscopies, TGA-DSC and evaluation of the open porosity. This approach allowed to collect useful information about the composition of ceramic mixtures, as well as the methodology of firing, suggesting interesting hypothesis about the role of these materials within the construction process: since low water absorption values imply good resistance to the natural environment and a good permeability [20], this study can confirm the interpretation [3, 4] of the use of these ceramics as building materials with specific waterproof properties.

REFERENCES

[1] S. Bonomi and G. Gambacurta, "Adria: l'abitato etrusco," in *Spina - Neue Perspektiven der archäologischen Erforschung*, Zurigo, 2017.

[2] S. Bononi, M. C. Vallicelli and C. Balista, *The etruscan settlement of Adria (Italy - Rovigo): New data from the excavations in Via Ex Riformati (years 2015-2016),* in press.

[3] L. Zamboni, Spina città liquida : gli scavi 1977-1981 nell'abitato e i materiali tardo-arcaici e classici, Rahden: VML Verlag Marie Leidorf, 2016.

[4] L. Cappuccini and M. Mohr, "Strutture a Spina nel IV sec. a.C.," in *Spina - Neue Perspektiven der archäologischen Erforschung*, Zurigo, 2012.

[5] Munsell, Munsell soil color charts (Year 2000 Revised Washable Edition), New Windsor (NY): Munsell Color Company, 2000.

[6] C. M. Müller, B. Pejcic, L. Esteban, C. Delle Piane, M. Raven and B. Mizaikoff, "Infrared Attenuated Total Reflectance Spectroscopy: An Innovative Strategy for Analyzing Mineral Components in Energy Relevant Systems," *Scientific Reports,* pp. 1-11, 2014.

[7] R. Ravisankar, S. Kiruba, P. Eswaran, G. Senthilkumar and A. Chandrasekaran, "Mineralogical Characterization Studies of Ancient Potteries of Tamilnadu, India by FT-IR Spectroscopic Technique," *E-Journal of Chemistry,* vol. 7, no. S1, pp. S185-S190, 2010.

[8] V. Ramasamy and G. Suresh, "Mineral Characterization and Crystalline Nature of Quartz," *American-Eurasian Journal of Scientific Research,* vol. 4, no. 2, pp. 103-107, 2009.

[9] R. G. Annamalai, R. Ravisankar, A. Naseerutheen, A. Chandrasekaran and K. Rajan, "Application of various spectroscopic techniques to characterize thearchaeological pottery excavated from Manaveli, Puducherry, India.," *Optik,* no. 125, pp. 6375-6378, 2014.

[10] G. Velraj, K. Janaki, A. Mohamed Musthafa and R. Palanivel, "Estimation of firing temperature of some archaeological pottery shreds excavated recently in Tamilnadu, India," *Spectrochimica Acta Part A,* vol. 72, pp. 730-733, 2009.

[11] P. Djomgoue and D. Njopwouo, "FT-IR Spectroscopy Applied for Surface Clays Characterization," *Journal of Surface Engineered Materials and Advanced Technology,* vol. 3, pp. 275-282, 2013.

[12] G. De Benedetto, R. Laviano, L. Sabbatini and P. Zambonin, "Infrared spectroscopy in the mineralogical characterization," *Journal of Cultural Heritage,* vol. 3, pp. 177-186, 2002.

[13] N. 7/81, Assorbimento d'acqua per immersione totale e capacita di imbibizione, Roma: CNR - ICR..

[14] T. Kato, K. Ohashi, M. Fuji and M. Takahashi, "Water absorption and retention of porous ceramics

fabricated by waste resources," *Journal of the Ceramic Society of Japan,* vol. 2, no. 116, pp. 212-215, 2008.

[15] P. A. Gane, C. J. Ridgway and J. Schoelkopf, "Absorption Rate and Volume Dependency on the Complexity of Porous Network Structures," *Transport in Porous Media,* vol. 54, pp. 79-106, 2004.

[16] F. Leach, J. Davidson, G. Claridge, G. Ward and J. Craib, "The Physical and Mineralogical Characteristics of Pottery from Mochong, Rota, Mariana Islands," in *Islands of Inquiry: Colonisation, seafaring and the archaeology of maritime landscapes*, Camberra, ANU Press, 2008, pp. 435-452.

[17] C. G. Mothé and M. C. R. Ambrosio, "Process occurring during the sintering of porous ceramic materials by TG/DSC," *Journal of Therman Analysis and Calorimetry,* vol. 87, no. 3, pp. 819-822, 2007.

[18] A. Bakolas, G. Biscontin, A. Moropoulou and E. Zendri, "Physico-chemical characteristics of traditional mortars in Venice," in *Proceedings Structural studies of historical buildings IV*, Southampton, Computational Mechanics Pubblications, 1995, pp. 187-194.

[19] B. Fabbri, S. Gualtieri and S. Shoval, "The presence of calcite in archaeological ceramics," *Journal of the European Ceramic Society,* vol. 34, pp. 1899-1911, 2014.

[20] L. Aouba, C. Bories, M. Coutand, B. Perrin and H. Lemercier, "Properties of fired clay bricks with incorporated biomasses: Cases of Olive Stone Flour and Wheat Straw residues," *Construction and Building Materials,* vol. 102, pp. 7-13, 2016.