2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October19-21, 2022

Archaeometry of Basilicata Graffita ware: provenance and technology

Ester Maria Annunziata[1], Grazia Lubraco[1], Barbara Bravo[2], Luca Medici[3]

[1]*School of Specialization in Archaeological Heritage, SSBA DiCEM – Department of European and Mediterranean Cultures, University of Basilicata, Matera, Italy, grazialubraco@gmail.com, esterinaannunziata@gmail.com*
[2]*Thermo Fisher Scientific S.p.A., Rodano (MI), Italy,*
[3]*I.M.A.A. – C.N.R., Tito Scalo (PZ), 85050, Italy,*

***Abstract* – The Graffita ware from the Moliterno Castle showed compositional peculiarities (relative to both ceramic body and glaze-decoration) that give indications on the technologies used for the itsproduction in Basilicata and on the circulation of raw materials. Different technologies seem to have been adopted for the production ofGraffita ware in the diyacrony. There is a Graffita ware characterized by a lead coating with traces of tin, containing abundant quartz and cristobalite, implying firing at high temperatures. The bright green decoration consists of a copper-based pigment with aggregates of cassiterite. The olive-green decoration consists of bivalent and trivalent iron. On the other hand, a Graffita ware with arsenic in the glaze and in the blue pigment has also been identified. The presence of arsenic suggests dating them to early 16th century. Besides, there are evidence that bone dust was intentionally used to make the engobe. A possible non-local provenance can be hypothesized for a fragment of Graffita ware from Moliterno Castel.**

I. INTRODUCTION

The technique of graffito ware has a remote eastern origin; transmitted from China to Persia in the 9th-10th centuries, it then moved from there to the Mesopotamian and Syrian areas, and finally to the Byzantine empire (Annunziata 2020). Glazed Graffita ware are generally characterized by a production process consisting of distinct stages: engobing, scratching, first firing, coloring, glazing, and second firing. The engobe is generally made of a thin layer of kaolinitic clay and has the purpose of masking the color of the original ceramic body. Scratching is practiced using a pointed or stick tool, which highlighting the contrast between the darker color of the ceramic body and the whitish engobebrings out the "graffito" decoration. Finally, the ware is decorated mainly usinginorganic based pigments (e.g. iron-brown and copper-green) and eventually subjected to a second firing after being coated with lead glaze that makes the object waterproofed (Patitucci 2002). Seldom, the scratching is performed directly on the wet ceramic bodyso that the incisions, which characterize the decoration, appear less deep and sharp, as the color of the ceramic body is not highlighted (Annunziata, 2020 and references therein).

The present study is addressed to the archaeometric characterization of ceramic bodies and of glaze and decoration of the Graffitaware from Moliterno Castle (Basilicata region, southern Italy)attested at the 14th and 15th centuries. This is achieved through the acquisition of elemental distribution maps bymicroX-Ray fluorescence (μ-XRF) using Bruker's M4 Tornado apparatus. Besides, the possible presence of organic based pigments as well as of mineralogical phases bearing metals in glaze and decorations is underlined by microX-Ray Diffraction (μ-XRD) and micro Raman spectroscopy, using respectively DMAX Rapid from Rigaku and the DXR3 for ThermoFisher Scientific.

II. THE GRAFFITA WARE AT MOLITERNO CASTLE

The Graffita ware from Moliterno Castle, despite the finely crafted and variety of decorations - referable to both open and closed forms (Annunziata, Gargiulo 2019) - is represented by a small number of sherds (6%) and only 4 individuals (3 dishes and a jug from US 2014) have been partial reconstructed. The decorations, refer mainly to variegated plant motifs exhibiting almost yellow, green and blue colors (the decorations follow both the graffito and trace bands independent of it). The brims of the reconstructed dishes are often ornamented with a decorative motif consisting of concentric circumferences, delimiting a space occupied by a continuous field of semi-circles making an embricked pattern. Such artifacts find comparison with fragments of polychrome Graffita ware at Torre di Mare (Metaponto, MT; Bertelli, Roubis 2002), Grottaglie (De Vincentis, 2006) and Senise (PZ) (Marino, 2016) where production scraps and semi-finished products are also attested (Annunziata, Gargiulo 2019). Other fragments of Graffitaware pertaining to both open and closed forms

present brim decorations depicting plant motifs, similar to those present on the polychrome Graffito ware "Castrignano type" from the excavations of Mesagne and dated to the 16th century, as well as to those of materials from the excavation of the castle of Salerno (Patitucci Uggeri 1977; De Crescenzo 1990) and finally to those found in Bovino (FG), defined as "Torre Alemanna" type (Dell'Aquila 2016). The latter are characterized by grooves that appear sharp and less deepas they are probably produced with a different technique in which the scratching phase is performed directly on the wet ceramic body, before engobing (Dell'Aquila 2016).

III. *ARCHAEOMETRY OF GRAFFITA WARE FROM MOLITERNO CASTLE*

Five samples (CM 44, 48, 49 and 51) of Graffita ware from Moliterno Castle were analyzed. The ceramic bodies ofCM44, CM 48 and CM49 have compositional characteristics compatible with *Argillesubappennine* outcropping in Basilicata region (Tursi, MT) and seem to have been fired at temperature higher than 900C° whereas sample CM51 has not (Annunziata 2022). The compositional analysis of the glaze from Graffita ware from Moliterno Castell revealed the existence of a lead-type glaze. Tin was not found in the glaze in detectable amount in sample CM44but was significantly present in the form of cassiterite, the mineralogical phase bearing Sn (SnO_2), in samples CM49.

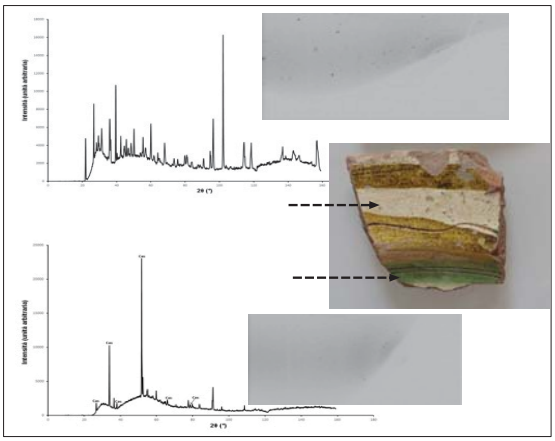

Fig.1. μX-ray diffraction patterns form CM49 sample. Two-dimensional spectra and diffraction figures for white coating and green decoration.

Specifically, μ-XRD revealed the presence of well-crystallized cassiterite (SnO_2) - as the most abundant phase together with traces of Cu compounds (likely oxides) in the green decoration from CM49. Only traces of this mineralogical phase have been detected in the remaining portion of the fragment glaze. Quartz and cristobalite were also abundant in the glaze of this fragment.If the cristobalite found in the white coating is from thermaltransformation of quartz, then the temperature of the second firing of the artifact-after it was coated with lead glaze to make the object impermeable-must have reachednecessarily temperatures higher than 900 °C (Patitucci 2002).Micro-XRF mapping confirmed the presence of a lead-glaze with a significant amount of tin (SnO_2) in the CM49 coating (Fig. 2). Tin, as also suggested by XRD, seems to have been better preserved under the decoration, as it was mostly concentrated in the fragment portion exhibiting the bright green decoration. Copper is the chromophore responsible for the bright green decoration (compare Fig.1 and Fig. 2). On the other hand, the chromophore Fe is responsible for the color of the olive-green decoration in fragment CM49 (Fig. 2). It is well known that for Graffita ware, olive-green (yellowish-green) decoration is widely used but the pigment responsible for such color is based on cobalt antimonates (Sb, Co) (Carratoni, 2002). In the Graffita ware from Moliterno Castlethe olive-green decoration - which appears not to be too opaque - the presence of antimony or cobalt (Sb or Co) is ruled out,and Fe is present in large quantities. It is likely that a natural pigment consisting of "clay" containing goethite, alpha-FeO(OH)as well as silica-aluminates with hydrated Fe oxides (limonite-type) has been used for such decorations. Besides, a pigment obtained by grinding the minerals glauconite (hydrated silicate of iron and potassium) and celadonite could have also been used to obtain this color. The interactions between the chromophore Fe(II), with its blue coloration, and Fe(III), with its yellow coloration, are responsible for the olive-green (yellowish-green). The color can vary from dull green to yellowish green depending on the origin and content of oxides and hydroxides. A pigment with these characteristics, and with such a color, was already known to the Greeks and Romans and was used in all painting techniques during the Middle Ages, the Renaissance until the 19th century. In Apulia, in the province of Lecce, quarries of a variety of *Pietraleccese* are indeedknown to have a greenish coloration due to the presence of glauconite (Laviano 2006).

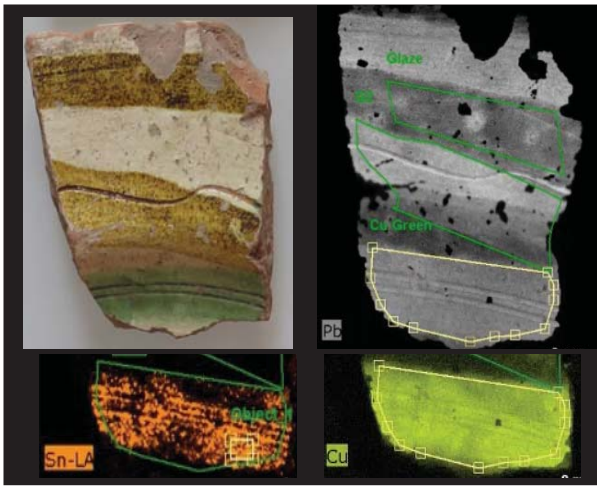

Fig. 2. Elemental distribution maps of the CM 49 graffito fragment acquired in micro XRF with Bruker's M4 Tornado

The lead-glaze from Graffita ware CM44 does not contain any tin. However, μ-XRF mapping revealed the presence of large amount of phosphor in the coating. Apossible deliberate addition of phosphates (mainly inorganic apatite)during the lead-type preparation of the glaze can be hypothesized due to the presence of large amount of P in the glaze (Fig. 3). The use of this technology, with the function of a flux (an agent to lower the melting temperature of the glass), is indeed a common practice (De Crescenzo, 2002 and references therein), although this function is already largely explicated by the high percentages of PbO (which acts as both a lattice-former and a flux). However, the ratio between calcium and phosphorus (<1), allowed to establish the organic nature of the apatite (the mineralogical phase bearing P) and to hypothesize the use (intentional or accidental) of bone dust (the main constituent of bone is calcium phosphate, i.e., hydroxyapatite) in the analyzed Graffito warefragments. The most probable hypothesis, given the relative distribution of P and Ca, is that bone dust (which has also the function of whitening the ceramic body) was intentionally used to make the engobe, normally made using kaolin, given the difficulty in recovering the latterin the Lucanian geographical area (Annunziata 2022).From the engobe, the Ca and P elements present in the crystal lattice of this mineral - due to chemical diffusion during firing - may have thus migrated to the glaze.

The presence of arsenic in the glaze of the Graffitaware fragment CM44 (Fig.3) - as well its high concentration in the blue pigment used for the graffito, is a rather peculiar finding.In the blue pigment, elements such as Bi and Ni(not shown) were also found in addition to the main chromophore Co. Arsenic is thought to be an element that can provide information about the period of production of majolica.This element begins to appear in the blue pigment from around 1520s and its presence could be related to different treatment of cobalt ores from this time(Zucchiatti et alii, 2006). Before 1520, cobalt sourced from Erzgebirge in Germany was a by-product of silver smelting: arsenic, which also accompanies cobalt in the raw material in the form of arsenates, was thus dispersed during this process asextremely volatile. Starting from 1520s, however, genuine sapphire manufacture was established in Schneeberg and the use of the reverberatory furnace was introduced, which made it possible to recover some of the arsenic as it cooledresulting in enrichment of this element in the blue pigment. The presence of arsenic thus testifies a change in the preparation of the pigment in the early 1500s.The presence of nickel is closely related to that of cobalt, being this element substituent of Co (probably as an impurity), and it is also an important indicator of raw material origin and technology. Cobalt often results in association with nickel, copper, arsenic, manganese and zinc in pigments.

The close correlation between cobalt and nickel observed in the CM44 sample could therefore suggest an origin of raw material used to obtain the pigment from the central Europe. The bright green decoration of the fragment CM44, similarly to what observed for the CM49 fragment,also contains the chromophore Cu (see Fig. 3).

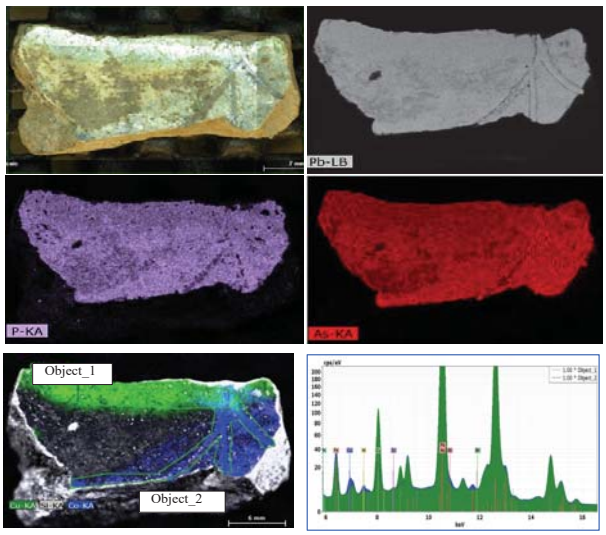

Fig. 3. Elemental distribution maps of the CM 44 graffito fragment acquired in micro XRF with Bruker's M4 Tornado

Micro-Raman spectroscopy allowed also to identifynewly formed mineral phases in the olive-green decoration from fragment CM51. They consist of silicates such as lovozerite - $Na_2Ca(Zr, Ti)(Si_6O_{12})[(OH)_4O_2]*H_2O$ - and of the zeolite amicite $K_2Na_2Al_4Si_4O_{16}$ - $5H_2O$ (Fig. 4).

I. CONCLUTIONS

The Graffita ware from the MoliternoCastle showed compositional peculiarities (relative to both ceramic body and glaze-decoration) that give indications on the technologies used for the itsproduction in Basilicata and on the circulation of raw materials.Specifically, CM49 and CM44 present compositional characteristics compatible with a local production (Annunziata 2022). This hypothesis is supported by the evidence of kiln scraps and semi-finished products found in the surrounding area of Senise. From a stylistic point of view, in fact, the Graffita wares from MoliternoCastle show similarities with those attested in Torre di Mare (De Crescenzo 2002) and Senise (Marino 2016), where semi-finished artifacts were also found.
Sample CM 49 is characterized by a lead coating with traces of tin, containing abundant quartz and cristobalite, thus implying firing at high temperatures. The bright green decoration consists of a copper-based pigment with aggregates of recrystallized cassiterite. The olive-green decoration consists of a mixture of bivalent and trivalent iron.

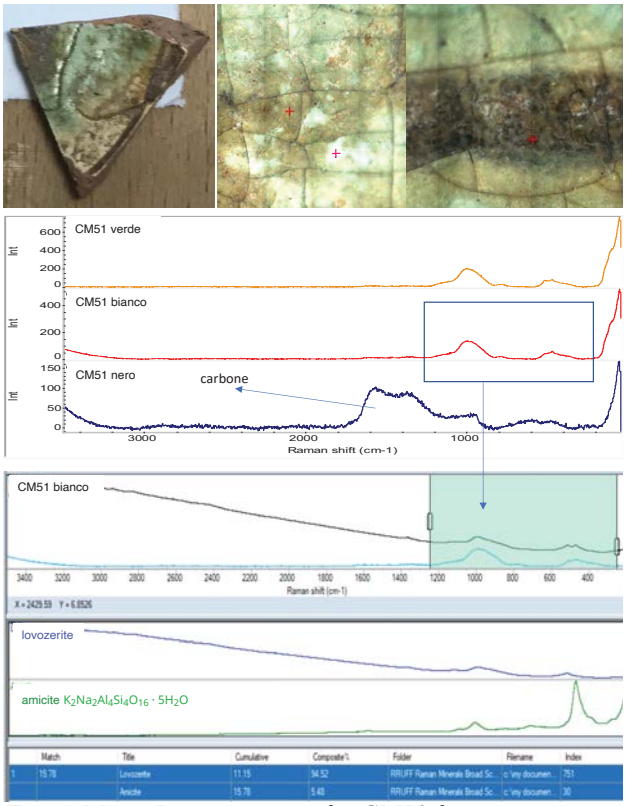

Fig. 4. Micro-Raman spectra for CM51 fragment

Sample CM 44 differs from CM49 for the presence of arsenic in the glaze and in the pigment of the blue decoration, for which cobalt and nickel arsenates were used. The presence of arsenic suggests dating them to early 16th century.Besides, there areevidencethat bone dust (which has the function of whitening the ceramic body) was intentionally used to make the engobe, normally made using kaolin, given the difficulty in recovering the latter in the Lucanian geographical area.This lead to hypothesize that different technologies were adopted for the production ofGraffita ware in Basilicata in the diachrony.
A possible non-local provenance can be hypothesized for the fragment CM51. The presence of newly formed mineral phases in the olive-green decoration from fragment CM51, coupled with considerations about the body characteristic of thisfragment whose composition differs from those of other Graffito ware from Moliterno Castel, confirms this hypothesis.

REFERENCES

[1]ANNUNZIATA E.M (2022) - Archeologia e Archeometria della ceramica medievale: un approccio multidisciplinare per ladiagnostica dei manufatti ceramici della Basilicata", Tesi di Dottorato di Ricerca, Università degli studi della Basilicata, 2022.
[2]ANNUNZIATA E.M. (2020) - La circolazione della maiolica arcaica e della graffita nelle Marche centro-meridionali, MOSCATELLI U. (a cura di), Marca Marche, rivista di storia regionale, pp. 119-137.
[3]ANNUNZIATA E. M., GARGIULO B. (2019)- Economia e società dal Castello di Moliterno: analisi del contesto attraverso i dati materiali, in atti del convegno Storie di Ceramiche (Pisa)
[4]ARTHUR P. (2007)- Byzantine and Turkish glazed ceramics in southern Apulia, Italy, in Böhlendorf-Arslan, B., Osman Uysal, A., Witte-Orr, J. (a cura di), Canak. Late Antique and Medieval Pottery and Tiles in Mediterranean Archaeological Contexts, ≪Byzas≫ 7, 239-254.
[5]BERTI G., GELICHI S., MANNONI T. (1995) - Trasformazioni tecnologiche nelle prime produzioni italiane con rivestimenti vetrificati (secc. XII-XIII), in VIe Congrès International sur la Céramique Médiéval en Méditerranée, Aix-en-Provence, pp. 383-403.
[6]BRIANO A. (2017)- indagini archeometriche preliminari sulle invetriate in monocottura dal castello di
[7]DONORATLCO, in M. Giorgio (a cura di), Storie di ceramiche4. Ceramica e archeometria, pp. 29-36.
[8]DELL'AQUILA C. (2016)- La ceramica graffita policroma tipo di Torre Alemanna, in Dell'aquila C. (a cura di), Le ceramiche di Torre Alemanna: la graffita policroma e le altre tipologie: dai cavalieri teutonici agli abati commendatari, pp. 49-108.
[9]DE CRESCENZO A. (1990) - La ceramica graffita del Castello di Salerno, Napoli.
[10]DE CRESCENZO A. (2002) – I Manufatti ceramici, IN Torre di Mare I, Ricerche archeologiche nell'insediamento medievale di Metaponto (1995-

1999), Adda Editore, Bari, 2002.
[11]MARINO G. (2016), La ceramica medievale e postmedievale del convento di San Francesco d'Assisi a Senise (PZ), tesi di specializzazione, Scuola di Specializzazione in Beni Archeologici di Matera.
[12]PATITUCCI UGGERI S. (2002) - Le prime ceramiche ingubbiate in Italia. Savona e Venezia, in E. Deminicis, A. M. Giuntella, a cura di, Le ceramiche di Roma e del Lazio in età medievale e moderna, V, Ed. Kappa, Roma 2002, pp. 9-39.
[13]SAJAI N., ET-TABIROU M., CHAHINE A. (2016) - Structure, thermal behavior, and chemical durability of lead–calcium–phosphate glasses, A Multinational Journal, Volume 89, 2016.