

Matera “foggials” (Southern Apennines): Multi-analytical characterization of the natural coatings of local grain storage structures

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Article

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ABSTRACT

This paper focuses on a multi-analytical characterization of Matera (Basilicata region, southern Italy) foggials used to collect and store grain commodities to define their uses and the mineralogical, petrographic and geochemical features. The old district of Matera (Sassi) was recognized as a UNESCO heritage site since 1993. Fifteen samples of rock fragments (generally limestone or calcarenites) and coatings were collected from 4 different sites in the centre of Matera. Petrographic observation with optical microscope and mineralogical analysis showed that the mineralogical assemblage mainly consists of calcite and quartz and subordinately, Fe-hydroxides. The most abundant major oxides are CaO, Al₂O₃ and SiO₂ while among the trace elements, the most enriched are Pb, Sr, Cr, Ba and V. The REEs pattern shows a general flat distribution with no enrichment or depletion of LREEs and HREEs. A negative correlation between CaO and Σ REEs content suggests that REEs has no affinity for carbonate phases. The multi analytical characterization let us to hypothesize that Apulia region, in particular the Apulian “red earth” from Murge area, could be among the areas of origin of the materials used to produce the Matera foggials coatings.

KEYWORDS: Matera foggials; multi-analytical characterization; petrography, geochemistry, archaeometry.

INTRODUCTION

In the old district of Matera (Sassi), which are a rupestrian settlement excavated and built in the Pleistocene Gravina Calcarenite, recognized as a UNESCO heritage site since 1993,

the presence of the “foggials” have been recognized (Bonomo et al., 2019, 2020). The so called “foggials” are deep pits, excavated in predominantly carbonate rocks (Fig. 1), used to collect and store grain commodities which storage was ensured by using a Fe-rich local clay (Sogliani & Marchetta, 2010). The technique of covering the surfaces of Matera’s foggials ensured perfect preservation of the foodstuffs, which, managed to be preserved for several years (even a decade) while the replacement of the straw coating had to take place frequently (De Troia, 1992; Bernacchia, 2006). This technique of conditioning pits has been observed in Capitanata where some rather large silos were lined with bricks and then plastered (De Troia, 1992). Another type of covering with straw or mats is documented in Mandolfo and more generally in the contexts of the Marche and Sicily (Bernacchia, 2006; Bresc, 1979). In Matera, this technique has been widespread since the late Byzantine and early Norman period. The technique of storing grain inside airtight pits, called “silos” or “silo” in technical parlance, appears to be one of the most widespread. Silos, which appear as early as Neolithic times and have been until modern times (17th-19th centuries) among the main systems of long-term grain storage, are in fact known over such a vast area that it seems easier to identify areas where no traces of them are preserved than to list all those in which their presence is known with certainty. These underground city granaries represented areas of great economic interest in the 12th-15th centuries, since they were not isolated silos associated with individual dwellings,



Fig. 1 - Granary related to the San Falcione complex

but a large number of units concentrated in real storage areas of the city. The important socio-economic role played by the possession of these pits is also underscored by the abundant written documentation regarding the transfer of ownership, sale, and dowry of these underground structures. In the complex of the rupestrian church of San Falcione (Murgia Timone), a granary was studied that originally must have been about 2.00 meters deep. The underground rooms, in fact, after the earliest use as granary pits or cisterns documented in the sources, were used as cellars and dwellings with substantial transformations of the original layout (Sogliani & Marchetta, 2010). Some excavation data in San Giovanni Square made it possible to determine the chronology of a core of thirteen contiguous granary pits, belonging to the medieval period, that occupied the space below the excavation area. In fact, the calcarenite quarry planned for the construction of the church of Santa Maria la Nova considered the location of the underground rooms. This is evidence that the pits predated the quarry and consequently the church. (Sogliani & Marchetta, 2010). The granary pits, observed in this work, all show a covering consisting mostly of fragments showing a colour ranging from red to brown. The aim of this work was the multi-analytical characterization of the material used for the realization of Matera foggials to obtain insight about the minero-chemical, petrographic features and origin of the raw materials used to make the coatings under study.

GEOLOGICAL FRAMEWORK

The Matera area is characterized by a rocky structural high (Murge di Matera or Matera Horst), standing out from surrounding upper Pliocene–lower Pleistocene clays (Channel et al., 1979; Ciaranfi et al., 1979, 1988; Pieri, 1980; Iannone & Pieri, 1982) (Fig. 2a). The Matera Horst is located between the Murge area, in the Apulia region (part of the southern Apennines foreland), and the Bradano River Trough (the south-Apennines foreland basin) (Ciaranfi et al., 1983; Doglioni, 1993; Doglioni et al., 1994). The Murge area is characterized by some NW–SE trending karstic plateaux whose elevation decreases toward northeast from about

600 m above sea level (Murge Alte Plateaux) down to the Adriatic Sea (Murge Basse Plateaux and Apulian Adriatic shelf) (Tropeano et al., 2002). The Murge Plateaux are flanked by smaller and narrower displaced blocks that variably dip SW, NW, and SE (Pieri, 1980; Ricchetti, 1975). This simple structure is cut by NW–SE trending narrow grabens (Iannone & Pieri, 1982). The westward displaced blocks represent the south-Apennines foreland ramp (the Bradano Trough) and are covered by Pliocene–Pleistocene foredeep deposits. The foreland ramp is characterized by a horst and graben system (Tropeano et al., 1994). The Matera Horst is one of the most elevated and well-exposed up-thrown blocks of the system (Tropeano, 1992; Pieri et al., 1997). The Murge area, the Matera Horst and the foreland ramp are made of Mesozoic limestone belonging to the Apulian Platform, a relic of the African passive margin (Channel et al., 1979), emerged at the end of the Cretaceous (Ricchetti et al., 1988). During the Neogene, the Apulian platform became part of the foreland of the south-Apennines chain (Pescatore et al., 1999) and was divided into three structural domains (Gargano, Murge and Salento structural highs). From the middle Pliocene the Apulian foreland underwent a relatively rapid increase in regional subsidence because of the progressive eastward migration of the south-Apennines orogenic system (Iannone & Pieri, 1982). It was in response to this subsidence that regional transgression resulted in the progressive drowning of the Murge structural high which became a large island archipelago composed exclusively of Cretaceous limestone. Transgression led to the deposition of a thin (no more than few tens' metres thick) upper Pliocene–lower Pleistocene mantle of bioclastic and/or lithoclastic carbonates (Calcarenite di Gravina Fm) on the faulted Cretaceous succession of the Murge high (Tropeano & Sabato, 2000). During the Pleistocene, this carbonate-dominated system was drowned by clays of the Argille sub-apennine Fm, supplied by erosion of the Apennines thrust belt (Pieri et al., 1996). Since the middle Pleistocene the Murge region and the Bradano Trough experienced regional uplift (Doglioni et al., 1994). After the Quaternary uplift and subsequent erosion, the Matera Horst is at present partially exposed and deep canyons (the so-called *Gravine*) formed in the Cretaceous bedrock (Altamura Limestone Fm).

SAMPLING AND ANALYTICAL TECHNIQUES

A total of 15 samples were collected from 4 different sites (Fig. 2b) in the centre of Matera. The samples (Fig. 3), consisting of both rock samples, generally limestone/calcarenitic aggregates and foggials lining, were taken at the San Falcione Complex; the hypogea of Piazza San Giovanni; the Church of San Francesco (Bank of Italy); and the hypogea of Piazza San Francesco (Tab. 1). The samples belonging to the F1-San Falcione group show a matrix in which various fragments of *cocciopesto*, iron hydroxides, quartz and benthic foraminifera are immersed. Group F2-San Giovanni shows a carbonate matrix in which various fragments of *cocciopesto* are immersed. The F3-Banca d'Italia group consists of two coverings, one in the middle and in contact with calcarenite, showing fragments of earthenware rich in inclusions

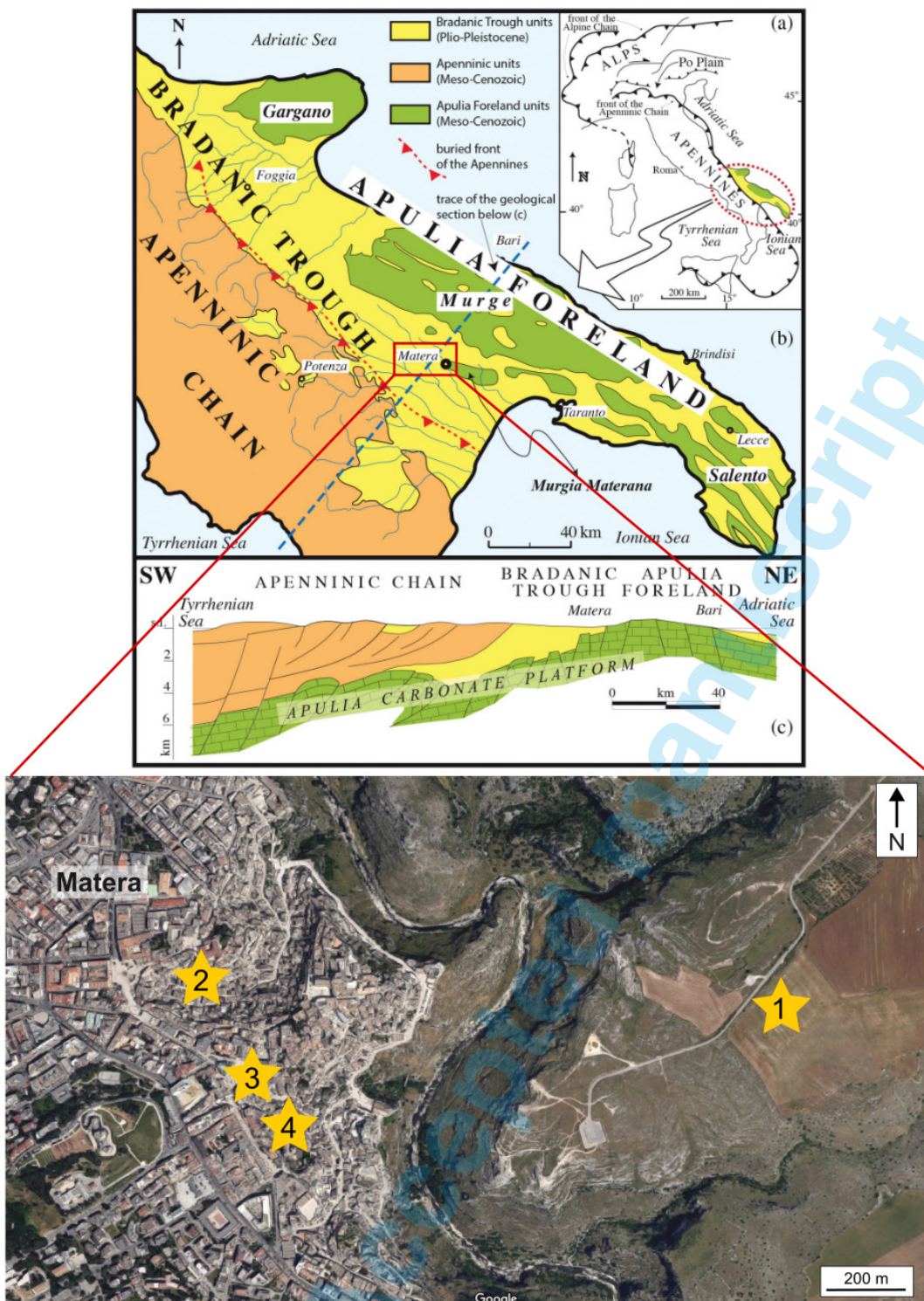


Fig. 2 - a) Geological sketch map of the studied area (modified after Tropeano et al., 2018); b) sampling locality; Point 1 is San Falcione, Point 2 is San Francesco, Point 3 is Banca d'Italia, Point 4 is Piazza San Francesco.

the other, more external, is characterised by smaller fragments with fewer inclusions. The F4-Piazza San Francesco group consists of a matrix composed mainly of microcrystalline calcite in which quartz crystals, calcite in the form of rounded granules and fragments of *cocciopesto* are immersed. The latter have a squat shape and angular edges. Group F5-San Giovanni presents different characteristics to the groups observed with a matrix with a phyllosilicate composition in which crystals are chaotically dispersed. The latter show homogeneous sizes, except for rare clinopyroxene crystals.

Petrographic and microstructural observations were performed by using a Nikon Alphaphot-2 YS2 optical microscope at the Department of Science, University of Basilicata, Potenza. Microchemical and micromorphological analysis was made with scanning electron microscopy (ESEM) and an XL30 Philips LaB6 ESEM instrument equipped with an energy dispersive X-ray spectrometer (SEM-EDS) at the SEM laboratory of the Department of Science, University of Basilicata, Potenza. This instrument employs a Schottky based gun design using a point-source cathode of tungsten with a resolution of 2 nm @ 30 kV and

Table 1 - Collected samples with code name, locality, and sample group.

Sampling site	Samples group	Sample name
San Falcione	F1	UF 1A
		UF 1B
		UF 1C
San Giovanni	F2	UF 2B
		UF 2C
Banca d'Italia	F3	UF 3A
		UF 3B
		UF 3C
		UF 3D
		UF 3E
		UF 3F
Piazzazza San Francesco	F4	UF 4A
		UF 4B
		UF 4C
San Giovanni	F5	UF 2A

2 nm @ 30 kV. EDS delivers high quality data, with a max energy resolution of 121 eV for Mn K α , providing high-resolution analysis. XRPD analyses were performed on bulk samples, at the XRPD laboratory of the Department of Science, University of Basilicata, on powdered rock and *cocciopesto* samples by using a Siemens D5000 equipment with CuK α radiation, 40 kV and 32 mA. Data were collected between 0° and 70° 2 θ for all samples, with step size of 0.02° and scan speed of 2 seconds. Major and trace elements concentrations were determined on one representative pulverised sample for each sample group, by ICP and ICP-MS

analysis at Activation Laboratories (Ancaster, Canada). The used analysis package was the 4Litho - Lithium Metaborate/Tetraborate Fusion - ICP and ICP-MS.

RESULTS

Petrography

Petrographic analyses revealed five types of samples: F1-San Falcione, F2-San Giovanni, F3-Banca d'Italia, F4-Piazza San Francesco and F5-San Giovanni. The samples belonging to the F1-San Falcione group are characterized by two clearly visible layers: one consisting of the calcarenitic layer, belonging to the rock in place (Gravina calcarenite), excavated for the construction of the foggials; the other, reddish in colour, concerns the coating of these works, which was important for ensuring proper preservation of cereal commodities (Tropeano, 1994; Tropeano & Sabato, 2000; Pomar & Tropeano, 2001) (Fig. 4a). In the F1-San Falcione samples the presence of ooids, showing a typical sub-circular structure dispersed in a fine matrix and characterised by alternating mineralogical compositions (Mongelli et al., 2015), was detected (Fig. 4b). The calcarenitic layer shows a clastic structure, characterized by fragments of sedimentary rocks, crystals, and microfossils. Calcite is found both in anhedral crystalline aggregates of minute size (5-10 μ m) and in crystals with rhombohedral habit of medium size. Quartz is subordinately present in single crystals or in small aggregates (5-10 μ m) associated with calcite. At parallel Nicols it appears transparent and clear, showing no evidence of flaking, sometimes fractured. The reddish layer consists of a red matrix paste, due to the abundant presence of iron oxides showing a microcrystalline structure, most likely consisting of clay-based minerals. Within it is a poorly graded aggregate (100-150 μ m),

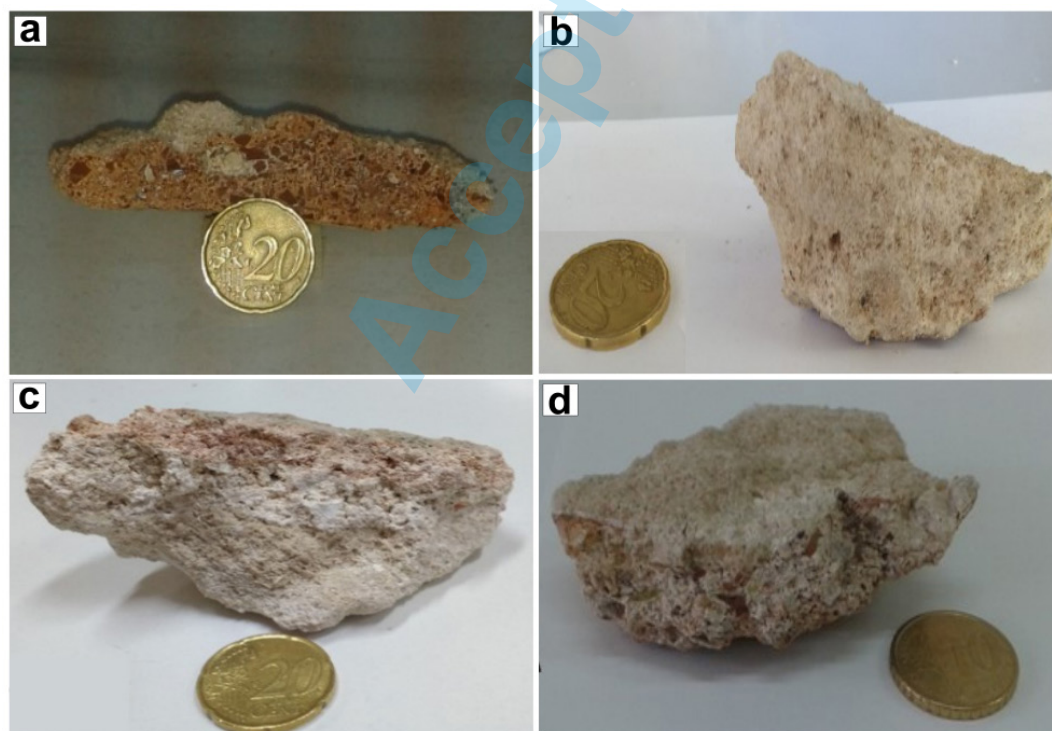


Fig. 3 - Macroscopic features of selected collected samples. a) sample from F1-San Falcione group; b) sample from F2-San Giovanni group; c) sample from F3-Banca d'Italia group; d) sample from F4-Piazza San Francesco group.

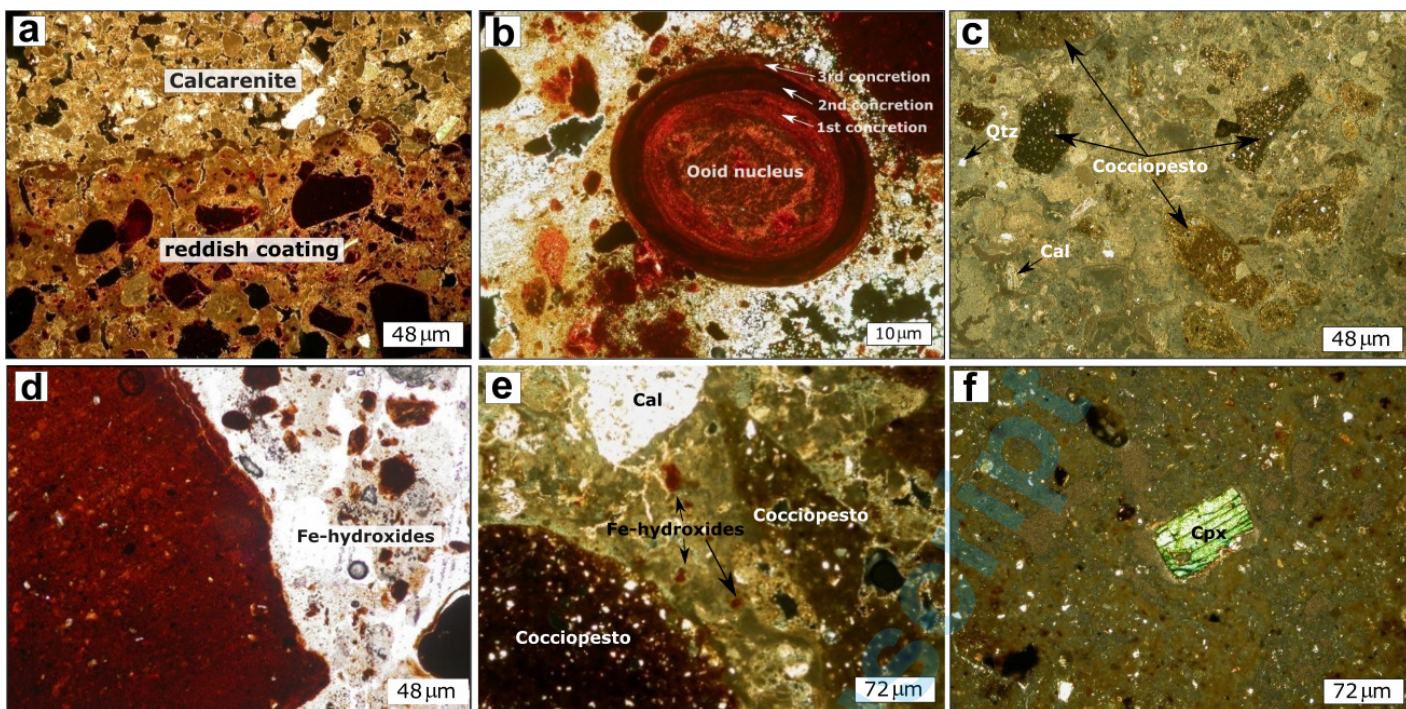


Fig. 4 - Microphotograph of selected sample using optical microscope. a) contact between calcarenite and reddish coating layers (sample from F1-San Giovanni group); b) Ooid structure of a sample from F1-San Giovanni group; c) *cocciopesto* with calcite and quartz crystals (sample from F2-San Giovanni group); d) *cocciopesto* and Fe-hydroxides in the external coating (sample from F3- Banca d'Italia group); e) *cocciopesto* with calcite and Fe-hydroxides (sample from F4-Piazza San Francesco group); f) clinopyroxene crystal (sample from F5-San Giovanni group).

containing mainly earthenware, minerals of various kinds and microfossils or fragments of them. The *cocciopesto* appears red and/or brown in colour, with sub-rounded to strongly angular contours. Group F2-San Giovanni is characterized by samples showing two distinct layers: one related to the calcarenitic fraction, the other to the coating. The latter shows a greyish matrix paste most likely consisting of micritic calcite, in which are immersed brick fragments of various sizes, calcite aggregates (50-100 μm), and rare quartz crystals and opaque minerals (Fig. 4c). The earthenware fragments vary in shape from angular to rounded and are rich in inclusions (quartz, mica, biotite, and iron oxides). Samples belonging to the F3-Banca d'Italia group show a lower abundance of iron oxides. It is also possible to observe the presence of three layers, one characterized by a calcarenitic composition, an intermediate layer in which brick fragments rich in inclusions are observed, up to 5 mm in size and brown in colour, an outer layer characterized by *cocciopesto* fragments of small size (up to 1.5 mm) with a bright red colour (Fig. 4d). Group F4-Piazza San Francesco includes samples in which the contact between the calcarenite fraction and the coating can be observed. They show a greyish matrix paste consisting of micritic calcite and clay-based minerals. Scattered in it are fragments and/or aggregates of calcite and fragments of *cocciopesto* of varying nature and size (up to 6 mm). The latter show a colour ranging from light brown to brown with sometimes angular, sometimes rounded edges. They are characterized by a great quantity and variety of inclusions (Fig. 4e). The mineralogical association that distinguishes this group consists of muscovite, biotite, quartz, plagioclase, calcite, k-feldspar, and iron oxides. Group F5-San Giovanni is characterized by a massive structure

and, unlike the previous groups studied, is devoid of *cocciopesto* fragments. It consists of a very fine-grained, greenish brown matrix paste in which rare clinopyroxene crystals are included (Fig. 4f).

Micromorphological and microchemical analysis (sem-eds)

F1-San Falcione samples show a matrix in which various fragments of *cocciopesto*, iron hydroxides and quartz. Calcite can be observed both in microcrystalline form and in larger crystals (Fig. 5a). Group F2-San Giovanni shows a carbonate matrix in which various fragments of *cocciopesto* are immersed with several inclusions and reach a size of about 1.5 mm (Fig. 5b). Group F3-Banca d'Italia consists of two coverings, one intermediate and in contact with calcarenite, showing fragments of earthenware rich in inclusions; the other, characterized by smaller fragments with fewer inclusions essentially given by white mica (muscovite), quartz, k-feldspar, calcite, iron hydroxides, ilmenite, and titanium oxides. The middle layer consists of a carbonate matrix in which rare quartz crystals, phyllosilicates, and sodium plagioclase (albite) are dispersed in addition to lateritic. Among the inclusions, quartz, iron hydroxides, titanium oxides, zircon, and ilmenite were detected (Fig. 5c). The F4-Piazza San Francesco group consists of a matrix consisting mainly of lime-based minerals in which quartz crystals, calcite in the form of rounded granules and fragments of *cocciopesto* are immersed (Fig. 5d). Group F5-San Giovanni shows different characteristics than the groups observed so far. A matrix with phyllosilicate composition is present in which minerals such as quartz, biotite, mica, apatite and Fe-hydroxides are chaotically dispersed. The rare clinopyroxene crystals are characterized by larger size and stubby prismatic habit (Fig. 5e). In particular, the

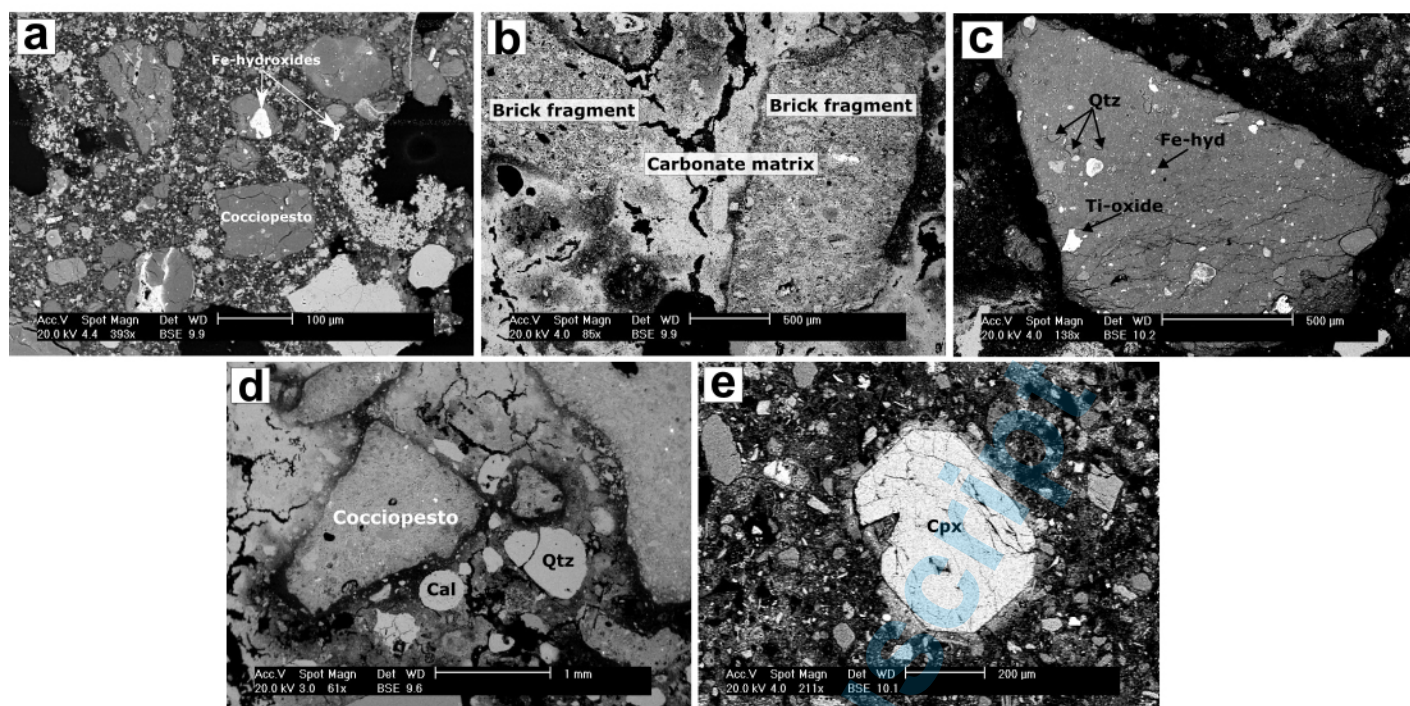


Fig. 5 - Microphotograph of selected samples by using Scanning Electron Microscope. a) fragments of *cocciopesto* and Fe-hydroxides; b) bricks fragments in carbonate matrix; c) *cocciopesto* with several mineral inclusions; d) fragments of *cocciopesto*, calcite and quartz; e) clinopyroxene crystal.

chemical composition made on the detected pyroxene revealed the typical composition of a diopside crystal ($\text{CaMgSi}_2\text{O}_6$).

Mineralogy

X-ray powder diffraction analyses were performed on five samples representative of each analysed group using the X'Pert HighScore software. All the samples examined mainly consist of calcite and quartz (Tab. 2; Fig. 6). The presence of hematite was observed in each of them, except for group F5-San Giovanni. Maghemite and ilmenite are also present in the F1-San Falcione group. In all samples, except for group F1-San Falcione, k-feldspar and plagioclase are present; the latter is also absent in group F5-

San Giovanni. Kaolinite is found only in the first group and F3-Banca d'Italia, while muscovite in groups F2-San Giovanni, F3-Banca d'Italia, F4-Piazza San Francesco and F5-San Giovanni. The only group in which dolomite has been observed is F3- Banca d'Italia, while clinopyroxene is characteristic of group F5-San Giovanni.

Geochemistry

Geochemical analyses were performed on one selected representative sample from each group of studied samples (Tab. 3). Concentrations are similar for all samples except for group F5-San Giovanni, which shows different values regarding major and trace elements values. The most abundant major oxides are SiO_2

Table 2 - Mineralogical composition of the studied foggials samples.

Samples	UF 1A	UF 2B	UF 3A	UF 4B	UF 2A
Sample site	F1-San Falcione	F2-San Giovanni square	F3-Bank of Italy	SF4-San Francesco square	F5-San Giovanni square
Calcite	>50%	>50%	>50%	>50%	>50%
Dolomite	n.d.	n.d.	n.d.	n.d.	n.d.
Quartz	25-50%	25-50%	25-50%	25-50%	25-50%
Hematite	0-10%	0-10%	0-10%	0-10%	n.d.
Kaolinite	0-10%	n.d.	n.d.	n.d.	n.d.
Muscovite	n.d.	0-10%	0-10%	0-10%	0-10%
K-Feldspar	n.d.	0-10%	0-10%	0-10%	0-10%
Plagioclase	n.d.	0-10%	0-10%	0-10%	n.d.
Clinopyroxene	n.d.	n.d.	n.d.	n.d.	0-10%
Maghemite	0-10%	n.d.	n.d.	n.d.	n.d.
Ilmenite	0-10%	n.d.	n.d.	n.d.	n.d.

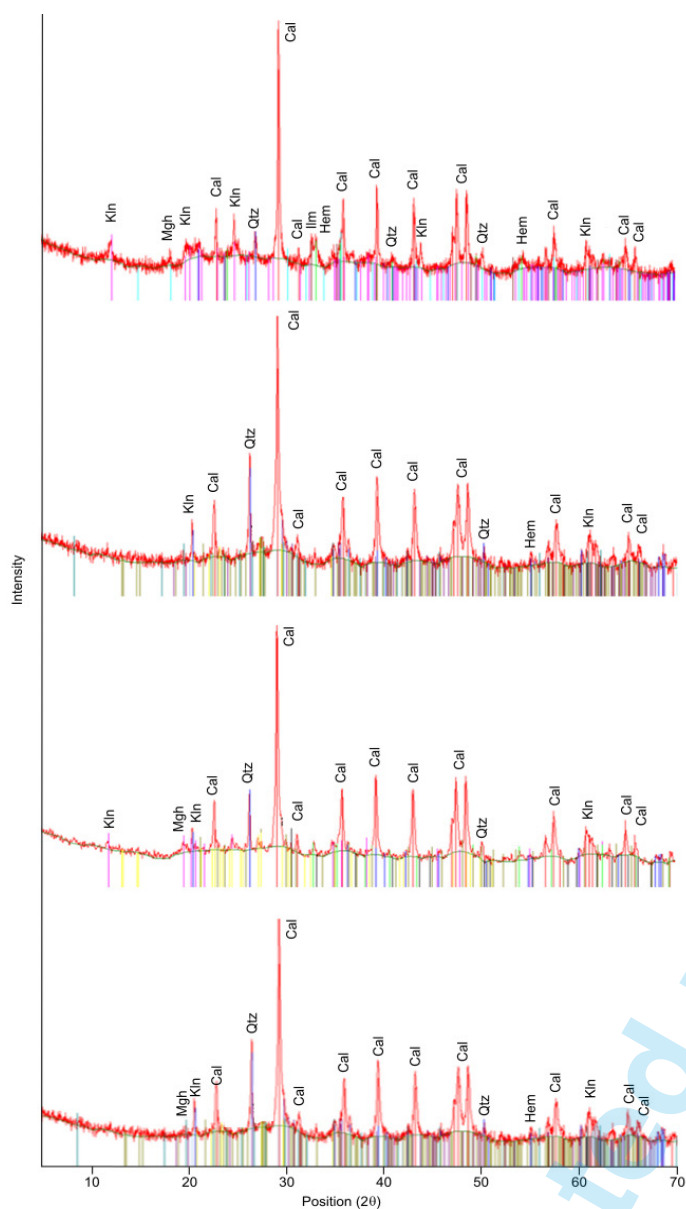


Fig. 6 - X-Ray Powder diffraction patterns, with related sample name, of four selected samples.

(median = 18,44 wt.%), Al_2O_3 (median = 6,52 wt.%), Fe_2O_3 (median = 3,11 wt.%) and CaO (median = 35,78 wt.%) which exhibits higher values. CaO enrichment appears evident for each group, especially for F5-San Giovanni showing a value of 50,73 wt.% while the F1-San Falcione group shows lower abundances of CaO (25,89 wt.%), but in turn shows higher concentrations, of Al_2O_3 (13,08 wt.%) and Fe_2O_3 (6,83 wt.%), respect the other groups. The most abundant trace elements are V (median = 42,01 ppm), Cr (median = 55,02 ppm), Sr (median = 205 ppm), Ba (median = 104 ppm) and Pb (median = 149 ppm). Pb shows very high values in F2-San Giovanni and F4-PIAZZA San Francesco samples reaching a maximum value of 1435 ppm and 1434 ppm respectively as also highlighted by the presence of PbO phases by SEM-EDS analysis, while in the rest of samples F1-San Falcione, F3- Banca d'Italia and F5-San Giovanni the content of Pb is 31,49 ppm, 149 ppm and 133 ppm, respectively. Considering the total REEs amount, the F1-San Falcione samples

Table 3 - Major oxides (wt.%) and trace elements (ppm) composition of the analysed samples. n.d. (not detected).

Sample	UF 1A	UF 2B	UF 3A	UF 4B	UF 2A
%					
SiO ₂	18.44	19.99	16.32	20.86	3.71
TiO ₂	0.85	0.3	0.52	0.35	0.05
Al ₂ O ₃	13.08	6.49	7.82	6.52	1.06
Fe ₂ O ₃	6.83	3.09	3.83	3.11	0.43
MnO	0.04	0.03	0.03	0.05	0.01
MgO	0.95	2.04	2.35	2.07	0.58
CaO	25.89	35.72	36.12	35.78	50.73
Na ₂ O	0.07	0.39	0.12	0.41	0.1
K ₂ O	1.47	1.49	0.8	1.51	0.2
P ₂ O ₅	0.14	0.11	0.07	0.13	0.26
LOI	32.24	29.19	32.01	29.21	42.88
Total	100	98.84	99.99	100	100
ppm					
V	126.89	42.01	68.6	41.96	19.76
Cr	164.46	55.02	70.74	54.91	30.72
Co	14.5	6.44	6.21	6.4	3.6
Ni	60.11	38.91	40.35	36.89	26.12
Cu	26.5	33.7	16.88	33.67	9.03
Zn	73.55	56.72	70.48	56.7	29.73
Sr	107	245	170	242	205
Rb	28.35	37.04	27.68	37.01	19.02
Ba	94.22	116	104	112	69.34
Pb	31.49	1435	149	1434	133
La	49.76	16	25.27	15.98	8.19
Ce	133.51	31.07	53.58	31.55	1.91
Pr	11.59	3.82	5.93	3.8	1.95
Nd	37.44	11.55	18.14	11.53	5.81
Sm	6.91	2.36	3.49	2.34	1.18
Eu	1.5	0.55	0.76	0.53	0.27
Gd	7.36	2.53	3.69	2.51	1.29
Tb	0.89	0.36	0.48	0.34	0.18
Dy	4.51	1.86	2.63	1.84	0.95
Ho	0.84	0.43	0.51	0.4	0.19
Er	2.44	1.08	1.51	1.06	0.55
Tm	0.35	0.16	0.22	0.15	0.08
Yb	2.35	0.98	1.4	0.96	0.49
Lu	0.37	0.16	0.22	0.15	0.08
ΣREEs	259.82	72.91	117.83	73.14	23.12
(La/Yb) _{PAA}	1.56	1.21	1.33	1.22	1.23
Ce/Ce*	1.28	0.92	1.01	0.93	0.86

is the most enriched with a value of 259,82 ppm while the less enriched sample is F5-San Giovanni with a total REEs of 23,12 ppm. Geochemical results were normalized using the PAAS (Post-Archean Australian Shale) (Taylor & Mc Lennan, 1985) to identify any enrichment or depletion relative to the upper continental crust standard. The major (Fig. 7a) and trace elements (Fig. 7b) diagram shows that all groups of samples analysed follow the same pattern, except for group F5-San Giovanni, which is comparable with the other groups only for CaO and P₂O₅ content. The group less enriched in Pb is F1-San Falcione, which shows a slight enrichment in Cr, probably due to the greater presence of clay minerals. The REEs pattern (Fig. 7c) shows a general flat distribution with no evident enrichment or depletion of LREEs and HREEs. The F1-San Falcione group is slightly enriched in LREEs compared to PAAS, unlike all

other groups that show depletion, respect to PAAS, and a positive anomaly of Ce. This could be explained by the fact that in this group, as evidenced by mineralogical and petrographic analyses, both the matrix and the *cocciopesto* fragments are composed of phyllosilicates and Fe oxides, according to Poli et al. (1977) regarding the affinity of these mineralogical phases with REEs. To account for the Ce and Gd anomalies, their concentrations were compared with Fe₂O₃ content showing a strongly positive correlation (Fig. 7 d,e), suggesting a particular affinity of Ce and Gd with Fe phases. The other groups, on the other hand, being characterized by a carbonate matrix, are depleted in REEs compared to PAAS, due to the dilution effect. Furthermore, it was observed that a factor regulating this behaviour is given by the lower or higher content in *cocciopesto*, in fact the F5-San Giovanni group appears

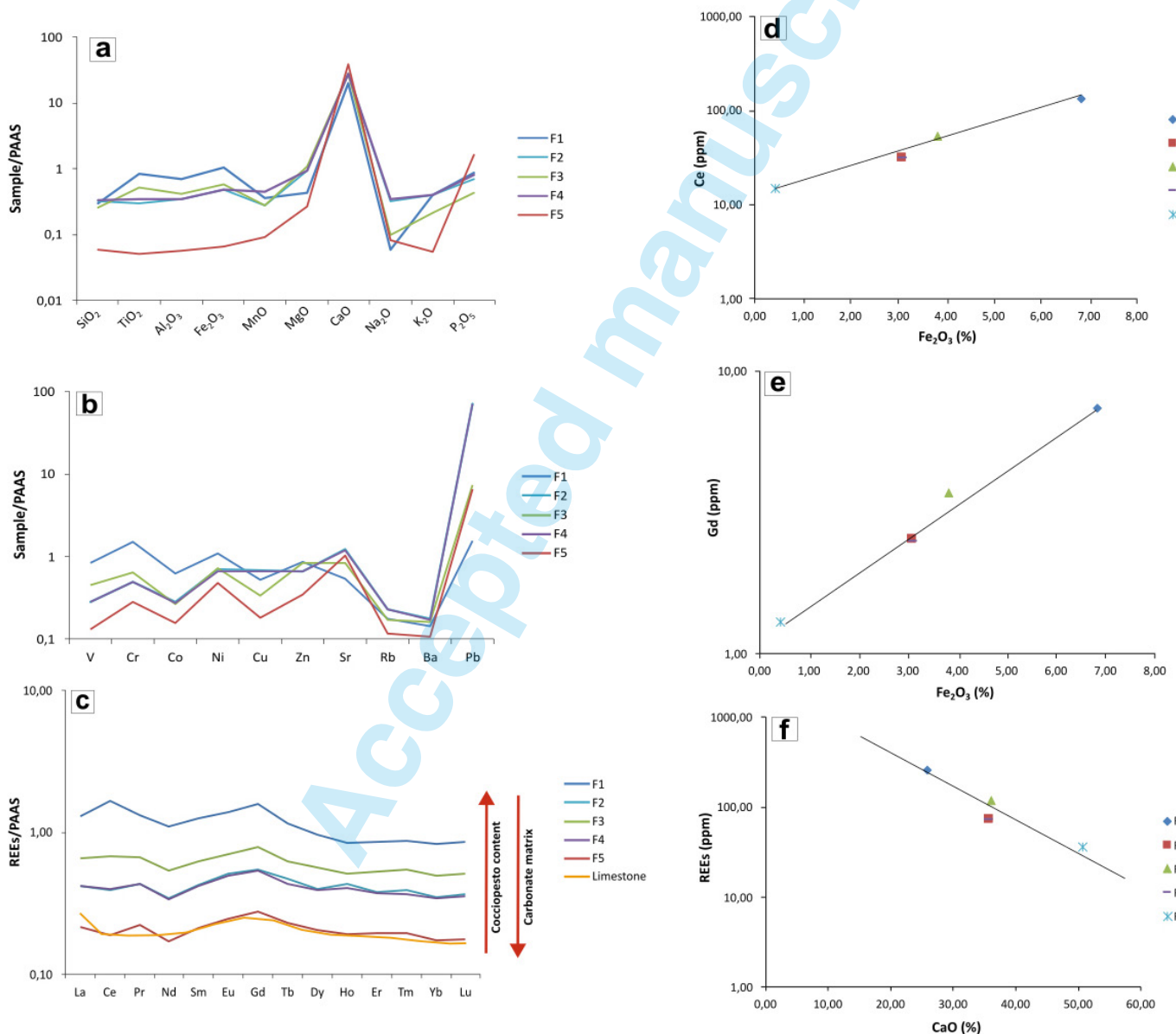


Fig. 7 - a) PAAS normalized major oxides spider diagram of the studied samples. CaO is the most abundant oxide in the studied samples; b) PAAS normalized trace elements spider diagram of the studied samples. Cr, Ni, Sr and in particular Pb are the most enriched trace elements in the analyzed samples; c) REEs pattern distribution of the studied samples. The content of REEs is correlated with the amount of *cocciopesto* in the samples; d) positive correlation between Ce and Fe₂O₃; e) positive correlation between Gd and Fe₂O₃; f) negative correlation between Σ REEs and CaO. Limestone values are from Bellanca et al., 1997.

as the most depleted. Since the samples studied contain high CaO contents, these were compared with some northern Italy (Veneto region) limestone samples studied by [Bellanca et al. \(1997\)](#). All the samples under examination approximately follow the limestone trend, in particular the F5-San Giovanni group sample (UF 2A) which is made up of sample with higher concentrations of CaO. The group that deviates most from this trend is F1-San Falcione, which is made up of the highest concentrations of SiO_2 and Al_2O_3 . The F2-San Giovanni, F4-Piazza San Francesco and F5-San Giovanni groups present anomaly values comparable with those of the carbonate rock, while the others differ, mainly the F1-San Falcione group, showing a positive Ce anomaly. The $(\text{La}/\text{Yb})_{\text{PAAS}}$ ratio values confirmed that the fractionation of the REEs in the studied samples is different compared to that of the limestone. Finally, it is possible to observe a negative correlation between the amount of CaO and ΣREEs content (Fig. 7f), suggesting that REEs has no affinity for carbonate phases.

DISCUSSION

The composition of the samples studied defines parameters that provide insight into the nature and origin of the raw materials used to make the coatings under study. All the coatings analysed consisted of a fine-grained matrix and *cocciopesto* fragments, except for group F5-San Giovanni. This mixture was to ensure good oxygenation and waterproofing of the pits, protected from moisture and weathering. The matrix, which had to act as a binder and be easily workable to adhere to the walls of the foggials, does not have a homogeneous composition in all the samples analysed. Some differences are noticeable especially according to the sites to which the samples belong. The San Falcione complex samples, located near Murgia Timone (group F1-San Falcione), differ from the others in the presence of a reddish-coloured matrix, consisting mainly of clay minerals and iron oxides that were observed in the different analyses that were carried out on the samples. Therefore, for the hypothesis of the origin of these coatings, it has been proposed that so-called “red earths,” taken from nearby Apulia and mixed with terracotta, were used in their making. Red earth was observed in the karst landscape of the Murge area and are related to the multiple exposure phases of the Apulia Carbonate Platform reaching thickness from some centimetres to several meters ([Ciaranfi et al., 1988](#); [Spalluto et al., 2005](#); [Mongelli et al., 2014](#); [Micheletti et al., 2023](#)). It is interesting to note that in the same area where the red soils were found, there are also rocks of a calcarenitic which is the same calcarenite lithology outcropping in Matera area (Gravina calcarenite). Red earth can be considered as a polygenetic relict soil formed during the Tertiary and/or hot and humid Quaternary periods ([Durn et al., 2003](#); [Muhs et al., 2010](#)). In some cases, the genesis of red earth can be linked to a variety of parent materials including aeolian dust, volcanic material and/or terrigenous clastic inputs ([Durn et al., 2003](#); [Singer, 2007](#); [Muhs et al., 2010](#)). The mineralogical composition of Apulian red earth mainly consists of iron and aluminium oxides and hydroxides along with discrete amounts of clay minerals. The composition of Apulian red earth is composed of large SiO_2 , Al_2O_3 , Fe_2O_3 and CaO amounts

occurring as a reddish clayey to silty-clay material, which covers karstified limestones ([Moresi & Mongelli, 1988](#); [Morelli et al., 2000](#); [Micheletti et al., 2023](#)). There are similar mineralogical and geochemical features composition were observed between Apulian red earth and the studied samples supporting the hypothesis that, the material used in the Matera foggials may likely derive from these residual deposits. Furthermore, in the samples of the F1-San Falcione group, we detected the presence of so-called ooids, typical sub-circular structures characterised by alternating mineralogical compositions mainly composed of Al and Fe oxides and hydroxides, dispersed in a clay matrix ([Mongelli et al., 2015](#)). These structures have been widely reported in the Apulian residual deposits reflecting different climate periods ([Mongelli et al., 2014, 2016](#); [Buccione et al., 2016](#)). Recent work has made it possible to obtain information on the provenance of raw materials of archaeological interest through a multi analytical approach ([Rizzo et al., 2023](#)). A final consideration concerns the presence of variable and sometimes abundant Pb contents, which suggests that Pb oxide was probably used in the manufacture of pottery, which was then destined to be crushed to obtain the earthenware used. It is known that varying amounts of PbO were added to clays for their low-melting properties, which served to lower the firing temperature of artifacts. The maximum temperature that could be reached in a wood-fired kiln rarely exceeded 950 °C, so the composition of the clay was modified to ensure satisfactory firing of its artifacts; in fact, lead oxide (PbO) has a melting temperature of 890 °C and dioxide (PbO_2) melts at 290 °C decomposing. The variability in concentration found in the finds can be justified not only by the manufacturer’s arbitrary additions, but also by the fact that, during the production cycle, significant amounts of lead accumulated in the kiln firing chamber, where glazes containing Pb had been fired several times, creating an “internal environment” that progressively allowed the diffusion of this element during the firing of subsequent ceramics ([Mantovani, 2012](#)).

CONCLUSIONS

A multi-analytical approach has allowed us to distinguish the Matera foggials coatings into two main types which are the covering related to the granaries of San Falcione is composed of a mixture of “red earths” and “*cocciopesto*” and the coating of the foggials found in the hypogea of Piazza San Giovanni, Piazza San Francesco and near the Bank of Italy, show a composition given by lime and *cocciopesto* fragments. The petrographic and mineralogical study defined five cladding groups, differentiated based on the presence or absence of earthenware, its colour and size. The distinction was also made in relation to the abundance of inclusions in the brick fragments. Basically, the samples belonging to group F1-San Falcione, differ from the others, by the presence of a reddish matrix and relatively small and poorly inclusions *cocciopesto* fragments. The other groups (F2-San Giovanni, F3-Banca d’Italia, F4-Piazza San Francesco), on the other hand, show a lighter matrix and larger and variable-sized fragments rich in inclusions. Group F5-San Giovanni, on the other hand, appears to be devoid of *cocciopesto*. The geochemistry showed that all samples are enriched in Pb,

especially those belonging to the F4-Piazza San Francesco and F2-San Giovanni groups; this can be correlated with the presence of Pb oxide phases, observed by scanning electron microscopy. Based on these considerations and on the fact that the amount of Pb is highly variable in the analysed samples, it can be assumed that the Matera foggials fragments come from different areas of ceramic production and are probably distinguished by different ages, as they have compositional characteristics that sometimes differ from each other. Furthermore, a relevant CaO content for all groups of samples was observed, especially for F5-San Giovanni. As the CaO content increases, the REEs content decreases, from which it can be inferred that they lack affinity for carbonate phases. In fact, all groups are depleted in REEs except F1-San Falcione, which has a predominantly siliciclastic composition and, therefore, enrichment in light REEs. It also has a positive anomaly of Ce and Gd, showing an affinity for Fe phases. This work, which was based on a multi-analytical characterization of Matera's foggials, evidenced their compositional and petrographic features and brought to light some considerations on the origin of the natural materials used. The similarity between compositional and petrographic data between studied samples with Apulian red earth, and the presence in this area of the same calcarenitic lithologies, can suggest that these residual deposits may have been used in foggiali linings, particularly because of their clay characteristics. This information would suggest that nearby Apulia, and particularly Murge area, could be among the areas of origin of the materials used to produce the Matera foggials coatings. Of course, given the lack of specific data on the origin and the provenance of these materials, this hypothesis deserves to be validated and confirmed through further studies.

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