

CHEMICAL CLASSIFICATION OF THE SLIP LAYERS IN ITALIAN CERAMICS OF THE 15TH-17TH CENTURY

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Abstract: This work deals with the study of 15th -17th century slipped/glazed and sgraffito ceramics produced by important manufactures of central and northern Italy. Representative samples have been analyzed for the purpose of characterizing and classifying their slip layers. Observations by optical microscopy (OM) on thin section have been carried out in order to determine the structure and the average thickness of the slips. Scanning electron microscopy combined with energy dispersion spectroscopy (SEM-EDS) has been used to individuate the chemical composition, which has been useful for classifying the slips and defining their provenance area.

Keywords: slip, sgraffito ceramics, Italy, archaeometry, SEM-EDS

INTRODUCTION

Slipped and glazed ceramics produced all around Italy from the 15th to the 18th century are characterised by a slip well recognizable for its whitish colour and fine grained texture. Generally, it is an argillaceous coating, made essentially of special clay, applied on the clay body in form of aqueous suspension. It is often associated with red paste, functioning as a cover of the coloured ceramic body. Being it permeable, a transparent glaze is always present on it (Cuomo Di Caprio 2007).

Differently from the contemporary majolica, slipped and glazed ceramics were produced in several sites, capillary spread throughout the territory. Despite some peculiarities, usually in the choice of the decorative subjects, the different productions are not easily distinguishable, all being characterised by quite standardized decorations, painted or engraved.

Aim of this work was to find a further criterion to discriminate the provenance of the archaeological finds of slipped and glazed wares.

Archaeometric analyses have so far been carried out extensively only on pastes and glazes, while our focus is the characterization of the slip layers, hoping that it

can be proposed as specific element of classification of this type of ceramic artefacts.

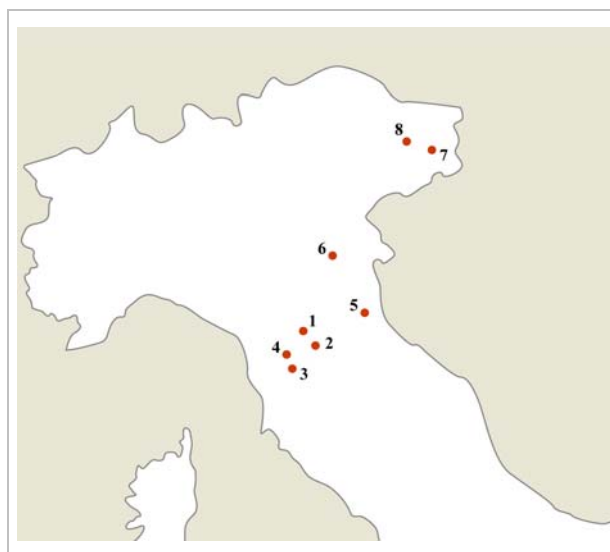


Fig. 1 Map of Central and Northern Italy, showing the eight hypothesised provenances of the studied samples:

1. Cafaggiolo, 2. Borgo San Lorenzo, 3. Castel-fiorentino, 4. Empoli, 5. Faenza, 6. Ferrara, 7. Castelnovo del Friuli and 8. Udine

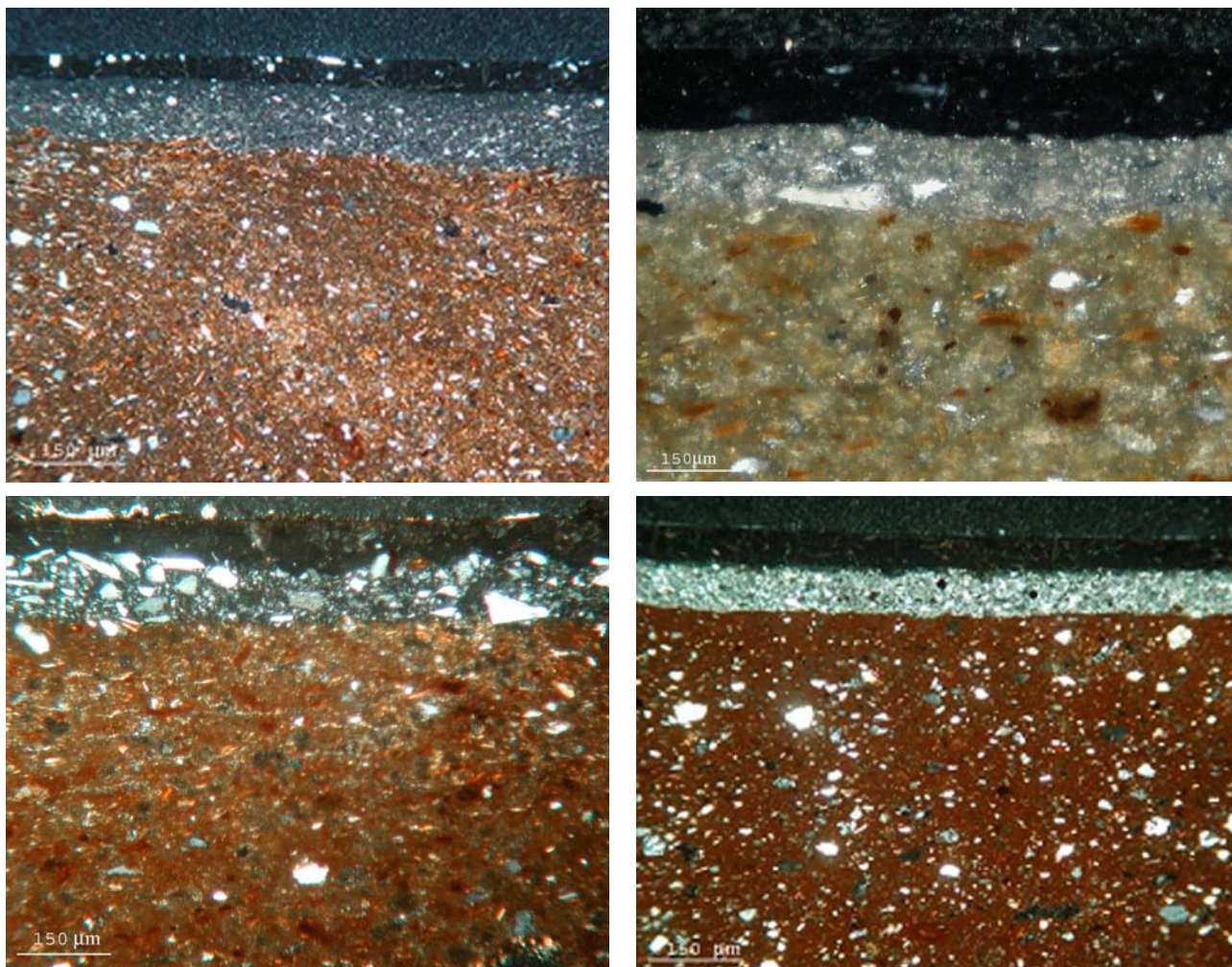


Fig. 2 Micrographs of thin sections of the different type of slips: a. very fine microstructure with few small grains of quartz and feldspar; b. scarce aplastic grains in an amorphous matrix; c. angular quartz grains in a scarce clay matrix; d. microstructure with abundant aplastic fine grains.

EXPERIMENTAL

Some fifty artefacts attributed to eight ceramic manufactures in central and northern Italy have been analysed (**Fig. 1**). They come from:

A) Tuscany: Cafaggiolo 6, Borgo San Lorenzo 9, Castelfiorentino 6 and Empoli 3;

B) Emilia-Romagna: Faenza 3 and Ferrara 4;

C) Friuli Venezia Giulia: Castelnovo del Friuli 9 and Udine 11.

A short description of the samples has been provided in **Table 1**. They are mostly part of open shapes (plates and bowls), with painted or engraved decorations, incised by means of a tip to make lines or using a cutter to obtain

areas with “champlevé” effect, sometimes enriched with coloured brush touches (*Baragatti et al. 2003, Capucci 2007, Casadio et al. 2000, Degasperi & Vannini 2001, Guarnieri 2006, Moore Valeri 2004, Vitri & Casadio 2001*).

Most of these materials have been previously investigated, at least for their ceramic paste (*Amato et al. 2004 and 2006, Fabbri et al. 2000 and 2006*).

In order to prepare the samples for the analyses, a small portion of each finds has been removed. After being wrapped into a resin block, a slice of the fragment has been cut and polished to make a 30 µm thin section, perpendicular to the surface, thin enough to allow the light of an optical microscope to pass easily through. All the samples have been investigated in order to observe the microstructure of the slip layers, to measure their average thickness and to provide information on the applying technique.

Table 1 Short description of the samples selected for the analyses

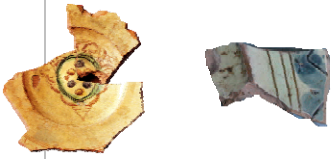







TUSCANY	CAFAGGIOLO (6 samples analysed)	
		Fragments of open shapes, slipped and glazed on the main surface, while only glazed on the other, decorated with incised patterns. Some finds present the Medici coat of arms.
	BORGO SAN LORENZO (9 samples analysed)	
		Part of both open and close shapes, presenting painted or engraved decorations (incised by means of a tip to make lines or using a cutter to obtain areas with “champlevé” effect). Open shapes are slipped and glazed only on recto size.
	CASTELFIORENTINO (6 samples analysed)	
		Portions of plates and bowls, coated only on recto and decorated with scratched monochrome motives, often including coats of arms. One fragment presents the date 1614.
EMILIA-ROMAGNA	EMPOLI (3 samples analysed)	
		Fragments of open shapes of little dimension are slipped and engraved on recto, while the bigger ones are coated and decorated on both size.
	FAENZA (3 samples analysed)	
		Mostly fragments of plates, characterised by whitish pastes and painted decorations imitating the majolica motives.
EMILIA-ROMAGNA	FERRARA (4 samples analysed)	
		Very similar to the Faenza ones, these fragments represent a late production of slipped and glazed ceramics that imitate colours and decorations of the contemporary majolica.
FRIULI VENEZIA GIULIA	UDINE (11 samples analysed)	
		There are two groups of samples: one is constituted by vessels characterised by coloured engraved decorations only on the main surfaces. The other consists on a non-common production of slipped and glazed tiles decorated with a huge repertoire of subjects.
	CASTELNOVO DEL FRIULI (9 samples analysed)	
	Finds of a typical renaissance production of slipped and glazed ceramics: usually coated only on recto surface, engraved with a tip and enriched with green, yellow and brown brush touches.	

Table 2 Normalised chemical composition of the slips (% by weight)

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
CAFAGGIOLO								
CF1g	56.03	23.14	1.24	1.37	8.01	1.38	1.04	7.79
CF3g	55.71	23.46	1.30	1.37	6.33	3.92	1.38	6.54
CF7g	57.02	24.03	0.60	0.88	6.44	2.05	1.06	7.92
CF9g	60.50	18.62	0.86	0.74	8.30	1.20	0.74	8.89
CF10g	57.59	20.75	0.86	1.00	8.49	1.95	0.81	8.55
BORGO SAN LORENZO								
BSL1g	57.20	22.36	1.05	1.41	7.00	2.30	0.91	7.76
BSL2g	55.89	20.46	0.87	1.11	8.30	5.44	0.93	7.00
BSL4g	56.15	24.27	0.84	0.58	8.94	1.70	1.06	6.46
BSL5g	60.36	17.64	0.77	0.80	10.40	1.30	1.41	7.32
BSL6g	65.43	17.91	0.25	0.28	2.45	0.69	0.80	12.18
BSL7g	55.84	22.58	0.55	0.66	7.48	1.67	3.08	8.13
BSL8g	58.44	17.39	1.04	1.16	10.81	2.32	1.79	7.05
BSL9g	62.13	18.88	0.76	1.07	7.03	3.21	1.16	5.75
BSL10g	62.48	17.98	0.47	0.67	6.90	0.96	1.04	9.49
CASTELFIORENTINO								
BE117a	61.80	26.00	0.90	1.04	3.62	0.66	0.83	5.14
CM165	55.34	29.53	0.75	0.68	5.63	0.54	1.31	6.22
CP141	62.53	19.90	0.93	0.81	7.64	1.61	0.88	5.69
PC182	58.25	20.06	0.84	1.26	9.05	1.57	1.15	7.82
SM371a	54.29	28.04	1.11	0.53	5.53	2.33	0.90	7.26
VM275	58.04	24.37	1.01	1.49	4.40	3.76	1.35	5.57
EMPOLI								
EM1	54.55	25.56	0.84	0.86	7.44	2.56	1.23	6.96
EM4	55.38	22.58	1.15	0.71	8.07	2.84	1.59	7.68
EM573	50.85	24.16	0.63	1.26	6.03	6.65	3.00	7.42
FAENZA								
CM1i	55.63	17.14	0.71	1.25	6.22	10.60	2.11	6.34
CM2i	52.18	17.03	0.72	1.04	5.36	15.81	1.09	6.78
CM3i	57.56	15.53	0.72	1.40	5.61	10.85	2.81	5.52
FERRARA								
FE2	80.40	9.33	0.37	1.05	0.72	1.20	0.46	6.47
FE7	82.80	8.93	0.00	0.69	0.50	1.23	1.80	4.05
FE9	77.69	11.41	0.00	1.87	0.64	4.71	0.33	3.35
FE14	60.52	22.06	0.25	1.51	2.06	6.96	0.36	6.28
CASTELNOVO DEL FRIULI								
CNF4	64.57	23.54	0.30	2.51	1.82	1.35	0.48	5.35
CNF6	57.84	28.95	0.30	1.99	1.74	1.51	0.40	7.25
CNF10	63.68	24.67	0.24	2.46	1.37	2.38	0.28	4.86
CNF11	67.09	21.31	0.30	2.25	1.52	2.78	0.39	4.26
CNF12	64.47	21.17	0.37	3.93	2.02	3.13	0.53	4.30
CNF13	67.02	20.28	0.32	2.37	1.64	2.86	0.49	4.93
CNF14	69.23	22.50	0.27	1.24	1.03	1.42	0.11	4.13
CNF19	66.76	24.72	0.32	2.04	1.06	0.87	0.17	3.94
CNF20	62.99	22.64	0.40	3.30	2.06	2.35	0.48	5.65
UDINE								
PA5	68.00	20.23	0.76	1.84	1.44	2.51	0.55	4.67
PA6a	68.85	20.67	0.48	1.33	1.49	2.47	0.45	4.26
PF3	70.42	17.63	0.84	1.87	1.93	2.71	0.47	4.14
PF4	58.45	28.22	0.30	1.36	1.83	2.38	0.39	7.07
PF6	59.21	28.39	0.39	0.94	1.40	2.94	0.20	6.52
PO3	58.60	29.41	0.46	1.70	1.88	1.84	0.37	5.73
PO5	58.62	27.57	0.26	2.15	2.52	2.75	0.66	5.47
PO7	56.89	28.78	0.49	1.73	2.22	2.73	0.72	6.45
PO14	55.74	28.94	0.16	1.94	3.11	3.77	0.39	5.95
PO17	58.67	27.20	0.32	1.28	4.13	2.59	0.63	5.17
PO19	60.10	26.81	0.38	1.84	2.29	2.11	0.66	5.80

Another slice of the fragment has been polished and coated with a graphite film to make it electrically conductive and analysable by means of a scanning electron microscope combined with an energy dispersion spectroscope (SEM-EDS). This analysis has permitted the observation of the texture of the coating with high magnifications and the determination of the chemical composition of the slip layer.

To this purpose, 5 to 10 measurements on different areas of each sample were performed; the average was calculated after eliminating eventual anomalous results.

RESULTS AND DISCUSSION

Observations on thin sections

Observations on thin sections have evidenced some differences among the studied slip layers, that are attributable both to their thickness and microstructure.

All the samples attributed to Tuscan manufactures present homogeneous characteristics. The slips are characterised by a very fine microcrystalline structure in which few and small grains of quartz and feldspar (20 μm in size) are recognisable in a clay matrix more or less anisotropic (**Fig. 2a**). The thickness of the slip layers is around 150 μm on average.

The ceramics from Faenza and Ferrara (Emilia Romagna region) are very different. The slips layers of Faenza, 120 μm thick, show an amorphous clay matrix in which non-plastic silicate grains (20-30 μm in size) are packed into a compact texture (**Fig. 2b**). The slips of Ferrara, on the contrary, belong to the clay-poor and grains-rich type, where angular quartz grains (60-100 μm in size) are supported by a scarce clay matrix (**Fig. 2c**). The average thickness of this layer is 80 μm .

The microstructure of the slips coming from Udine and Castelnovo del Friuli are very similar, being of the clay-rich type like those from Tuscany, but characterised by a more abundant amount of very fine crystal grains (**Fig. 2d**). The thickness of the slip layer is around 120 μm in the pottery, and from 100 up to 250 μm in the tiles.

Comparing these results it is possible to summarize that a raw material with argillaceous components has been used to prepare the slip. This clay, light in colour after firing, seems to be the only raw material for the artefacts from Tuscany, Faenza and Friuli. On the contrary, a ground quartz rich raw material was mixed with a relatively small quantity of clay, for obtaining the slips of the Ferrara samples.

According to the slip classification proposed by *Capelli & Cabella (2007)*, the here studied slips belong to the clay-rich type with coarse grains, with the exception of the slips from Ferrara that are clay-poor with prevalent quartz inclusions.

Chemical analyses

From the results of the chemical investigations presented in **Table 2**, it is possible to point out that samples of the same provenance are very similar to each other, with a very small variability range.

The slips from Tuscan manufactures show Al-values comprised between 20 and 24% Al_2O_3 and K_2O around 7%, but their characteristic feature is the high content of magnesium oxide, from 6% to 8% MgO . This composition is not compatible with the known clayey raw materials outcropping in the area. Therefore, two hypotheses can be done: a) the slips were obtained introducing magnesium-rich material into a clay, light in colour after firing, according to *Casellato et al. 2008*) they were produced using a clay raw material, that is today unknown or exhausted. The presence in the area of alteration products from Mg-rich ultramafic rocks gives value to the first hypothesis (*Pistone 1974*).

The chemical compositions of the slips from Faenza and Ferrara are very different; the formers are characterised by high values of calcium oxides (12% CaO approximately) and around 6% of MgO , while the second ones have very high contents of silica (more than 75% SiO_2). Quartz-rich slips are typical of Middle Eastern ceramic production (*Henshaw 2007*), where they are realised by mixing very fine-ground quartz and clayey material (light in colour after firing).

All the slips from the Friuli region, on the contrary, are characterised by low calcium and magnesium oxide. But they can be divided into two subgroups depending on the Al_2O_3 content. The slips of the vessels from Castelnovo (except CNF6) and three vessels from Udine excavations (PA5, PA6a and PF3) have relatively low concentrations (about 23% Al_2O_3), while the other samples from Udine (and CNF6) show alumina contents of about 28% Al_2O_3 .

These results point out that the analysed ceramics are characterised by four different types of slips, in terms of microstructure and chemical composition:

Magnesium-rich slips (probably with tale), with texture poor of aplastic grains;

Calcium-rich slips (probably with calcite), with amorphous clay matrix;

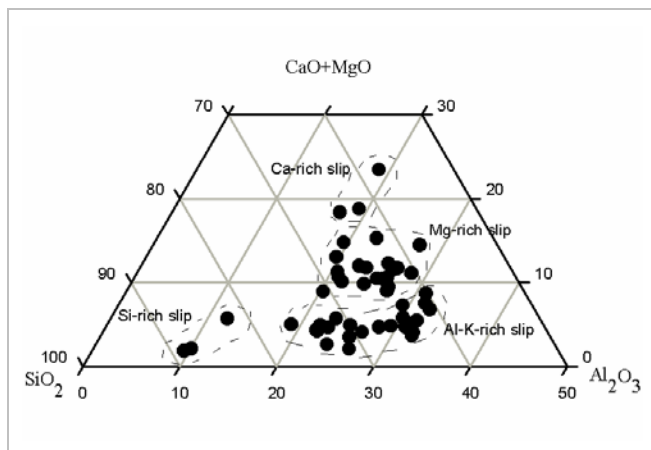


Fig. 3 Ternary diagram of the slips chemical compositions (SiO_2 - $\text{CaO}+\text{MgO}$ - Al_2O_3), in which the four chemical groups are well evidenced

Silicate-rich slips (with abundant quartz), made of quartz grains;

Slips with low concentrations of calcium and magnesium oxides, and relatively high values of aluminium and potassium oxides (probably very rich in Al-K silicates). In this case two subgroups can be evidenced depending on the level of aluminium oxide. The optical structure is relatively rich of aplastic grains.

This situation is well represented in the ternary diagram (SiO_2 - $\text{CaO}+\text{MgO}$ - Al_2O_3) reported in **Fig. 3**, in which the four groups and the two subgroups are easily distinguishable.

As a conclusion, considering the provenance of the slips included in the four groups, a quite clear geographic subdivision of the slips and the corresponding raw materials can be done. All the Mg-rich slips are coincident with the ceramics from Tuscany, all the samples from Faenza fall into the Ca-rich group, while three of the four samples from Ferrara are in the Si-rich group. The ceramic slips from Friuli belong to the Al-K group.

CONCLUSIONS

The results of the archaeometric investigations permit to conclude that there are different types of slips, in terms of raw materials used to obtain a product that turns white during firing. In any case they have the same ornamental and functional role, that is to hide the red colour of the ceramic paste and to offer a white base for the decorations.

A correspondence between chemical and microstructural characteristics of the slip layers and geographical provenance of the ceramics has been pointed out. This is in contrast with the common idea of a unique source from the Vicenza area, in Northern Italy. This provenance can be hypothesised only for the samples from Friuli, where the composition is characterised by high amounts of alumina and potassium oxides, so recalling the chemistry of the so-called “Tretto kaolin”, which is an illite-rich clay with quartz and kaolinite as minor components. On the other hand, the slip of Tuscan production, rich in Mg, is completely different and hardly known up till now. Never identified so far in local clay deposit, its supply source and its preparation procedure have to be investigated. Concerning the slips from Ferrara, they are characterised by a peculiar structure and a chemical composition that is reminiscent of a Middle East practice of making ceramics. As regards the slips from Faenza, the scarce number of samples analysed does not permit conclusive and precise remarks.

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