ArcheoSciences

Revue d'archéométrie

34 | 2010

Varia

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Electronic version

URL: <https://journals.openedition.org/archeosciences/2618>

DOI: 10.4000/archeosciences.2618

ISSN: 2104-3728

Publisher

Presses universitaires de Rennes

Printed version

Date of publication: 10 April 2010

Number of pages: 45-57

ISBN: 978-2-7535-1407-2

ISSN: 1960-1360

Electronic reference

Claudio Capelli and Roberto Cabella, "Archaeometric analyses of Mediterranean glazed cooking wares.", *ArcheoSciences* [Online], 34 | 2010, Online since 10 April 2013, connection on 28 January 2022.
URL: <http://journals.openedition.org/archeosciences/2618> ; DOI: <https://doi.org/10.4000/archeosciences.2618>

This text was automatically generated on 28 January 2022.

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Archaeometric analyses of Mediterranean glazed cooking wares.

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*Analyses archéométriques de céramiques culinaires glaçurées méditerranéennes
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Claudio Capelli and Roberto Cabella

- 1 The medieval (*ante* 14th c.) stratigraphic layers of the excavations carried out in the '80s at the Palazzo Ducale of Genoa (Liguria, NW Italy) are rich in ceramic wares coming from a large part of the Mediterranean (Cabona *et al.*, 1986; Rabino, 2006-2007). However, the high degree of fragmentation of the pottery is an obstacle to a classification only based on typological characteristics, in particular as for the coarse and the glazed monochrome wares, which are very poor in discriminant features. On the other hand, little is known about production centres and diffusion of these classes also at a Mediterranean scale, and few archaeological/typological published data are available for comparative studies (for instance: Grassi, 1999; Waksman, 2002).
- 2 Previous investigations on some medieval glazed monochrome types found in Ligurian and Provençal contexts (Capelli *et al.*, 2002; Capelli *et al.*, 2006) demonstrated the utility of thin section analyses in order to identify different productions and to localise the areas of provenance. On these bases, a interdisciplinary study was carried out on 12th-13th c. glazed cooking wares found at Palazzo Ducale (Capelli *et al.*, 2007a). The integrated petrographic and archaeological study allowed the identification of seven groups (1-7), three of which (1, 4, 5) dominate. Moreover, provenance information was obtained by the comparative study of geological data and the thin section database of Mediterranean ceramics available at the DipTeRis of Genoa. Finally, diffusion data were also attained for a few groups by integrated archaeometric and archaeological analyses of other north Tyrrhenian coeval contexts.

- 3 In this paper we will present the results of the thin section study, as well as those of new XRPD and SEM-EDS analyses on selected samples, mainly aimed at better characterising the seven different productions from a technical point of view, finding out further distinctive elements and evaluating preliminarily if more accurate analytical methods (such as XRF applied on bodies and microprobe, laser ablation, PIXE on glazes) could significantly improve the results.
- 4 In Table 1 are listed the analysed samples of Palazzo Ducale, with a few archaeological data. In addition, a reference sample (7530, Group 7*) from the production of Uzège, southern France (Leenhardt, 1995) was analysed for comparison with the Group 7 sample. In Figure 1 are shown some diagnostic sherds representative of the groups identified by the analyses.

Figure 1: Diagnostic sherds representative of the groups identified by the analyses.
 Figure 1: Quelques tessons représentatifs des groupes identifiés par les analyses.

1.

1. Analytical methods

- 5 After the observation of all the recovered sherds (more than 650) of that class by a 10x-magnifying lens, 29 representative samples (all the typologically diagnostic sherds, chosen in collaboration with the archaeologists) were submitted for thin section analysis.
- 6 Among them, 16 samples were selected for SEM-EDS analysis. All samples showing strong evidence of weathering, affecting body and/or glaze, have not been taken into consideration.

Finally, seven representative samples were also analysed by XRD (Tab. 1).

- 7 XRD analyses were carried out using a Philips PW3710 diffractometer. Powdered samples were run between 2.5° and 70°2 θ ^[9], with a generator potential of 30 kV, a generator current of 22 mA (using a CuK α ^[9] radiation), a Ni filter, and a scan speed of 1°/min. The software used for XRD data reduction was Philips PC-APD Diffraction Software and MacDiff 3.0.6c.

Table 1: List of the samples analysed by optical microscopy (OM), XRD, SEM-EDS with a few archaeological data.

Tableau 1: Liste des échantillons analysés par microscopie optique (OM), XRD, SEM-EDS avec quelques données archéologiques.

GR	SAMPLE	STR. LAYER	CHRONOLOGY	OM	XRD	SEM-EDS
1	6892	92	1st half 12th c.	X		X
	6901	88	12th c.	X		X
	6902	87	end 12th c.	X		
	6889	83	end 12th c.-beginning 13th c.	X		
	6884	84	beginning 13th c.	X	X	X
2	6890	71	1st half 13th c.	X	X	X
3	6891	78	end 12th c.-beginning 13th c.	X	X	X
	6888	79	end 12th c.-beginning 13th c.	X		X
4	2414	92	1st half 12th c.	X		
	6898	92	1st half 12th c.	X	X	
	6886	91	half 12th c.	X		X
	6896	91	half 12th c.	X		
	6899	83	end 12th c.-beginning 13th c.	X		X
	6885	85	beginning 13th c.	X		
	6900	84	beginning 13th c.	X		X
5	2415	93	1st half 12th c.	X		
	6905	92	1st half 12th c.	X		
	6894	91	half 12th c.	X		
	6903	91	half 12th c.	X		
	6906	85	beginning 13th c.	X		X
	6908	84	beginning 13th c.	X		
	6909	84	beginning 13th c.	X		
	6907	76	beginning 13th c.	X		X
	6904	76	beginning 13th c.	X		
	6895	72	beginning 13th c.	X	X	X
	6897	64	beginning 14th c.	X		X
6	6893	90	2nd half 12th c.	X		X
	6887	87	end 12th c.	X	X	X
7	6883	83	between 12th c. and 13th c.	X	X	X

- 8 SEM-EDS images and analyses were carried out on polished thin sections with a Philips SEM 515 equipped with an energy-dispersive spectrometer (EDAX PV9100). Quantitative analysis calibration was accomplished with synthetic (glass) and natural standards. The results of SEM-EDS analysis of glazes and pastes (major and a few minor elements) have been normalised to 100wt%. Microanalyses of glazes were carried out on selected points (spot mode) avoiding alterations, reaction zones and mineral inclusions; the reported values are the mean of at least three analyses. For paste analysis, the window mode (150x corresponding to 0.5 mm²) was used, avoiding the outer parts of the body, which are influenced by the glaze, and the coarsest inclusions; the reported values are the mean of two or more analyses. SEM-EDS analyses of pastes (bearing in mind the limits due to the small number of samples – in particular as for some groups consisting of one or very few available samples – and the low accuracy of that method, especially for heterogeneous materials) were carried out in order to obtain preliminary data about the chemical composition of the seven groups and to search for possible relationships with petrographic features.

1.

2. The seven groups. Mineralogical, petrographic and textural analyses of pastes and glazes

- 9 The main features of the different groups resulting from optical and electron microscopy are described below and summarised in Table 2 (pastes) and Table 3 (glazes). Table 2 also shows the mineral phases identified by XRD.

Table 2: Main petrographic features of the ceramic bodies of the groups discussed in the text.
Tableau 2 : Caractéristiques pétrographiques principales des pâtes des groupes décrits dans le texte.

group	clay matrix	oxidation degree	texture	qtz	Kf	mica	am	ep	granitoid rocks	ophiolitic rocks	acid metam.	others	accessory minerals	XRD
1	Fe-rich	xxx	c	xxx	xxx	x			xxx		x	Fe-nod	tm, rt, ilm, am	qtz, ab, hm
2	Fe-rich	xxx	c	xxx	xxx	x			xxx		x (vol?)		tm, rt, ilm, am	qtz, ab, Kf
3	Fe-rich	xxx	m	xxx	xxx	xxx			x		x (vol?)		am, ep, rt, tm	qtz, ab, hm
4	Fe-rich	x-xxx	m	xxx		x					xxx			qtz, cc
5	Fe-rich	xx-xxx	m-c	xxx	xx	xxx	xx	xx		xx	xxx		op, tt, rt, grt, cpx	qtz, ab, mu/ill, tre, hm
6	Fe-Ca-rich	xx-xxx	f-m	xxx	xxx	xxx	xx				xxx	Si-mf	ep, tt, tm, grt	qtz, ab, mu/ill, hm
7	Al-rich	xx	m	xxx								Fe-nod ARF	rt, tt, zir	qtz

Abbreviations: ab: albite; acid metam.: acid metamorphic rocks; am: amphibole; ARF: argillaceous rock fragments; c: coarse; cc: calcite; cpx: clinopyroxene; ep: epidote; f: fine; Fe-nod: Fe-nodule; grt: garnet; hm: hematite; Kf: K-feldspar; ilm: ilmenite; m: medium; mu/ill: muscovite/illite; op: opaque minerals; qtz: quartz; rt: rutile; Si-mf: microfossils; tm: tourmaline; tre: tremolite; tt: titanite; vol: acid volcanicite; zir: zircon.

Abréviations : ab : albite ; acid metam. : roches métamorphiques acides ; am : amphibole ; ARF : fragments d'argilites ; c : grossière ; cc : calcite ; cpx : clinopyroxène ; ep : epidote ; f : fine ; Fe-nod : nodule ferrique ; grt : grenat ; hm : hématite ; Kf : K-feldspath ; ilm : ilménite ; m : moyenne ; mu/ill : muscovite/illite ; op : minéraux opaques ; qtz : quartz ; rt : rutile ; Si-mf : microfossiles siliceux ; tm : tourmaline ; tre : trémolite ; tt : titanite ; vol : roche volcanique acide ; zir : zircon.

1. 1.

Group 1

- 10 **Body.** Paste inclusions are angular, abundant, medium-sorted and often coarse-grained (Figs. 2-3, n. 1). Most of them are composed of weakly metamorphic quartz+feldspar (granitoid?) rock fragments (up to 1-2 mm in size) and derived minerals (<0.3-0.5 mm): feldspars, sometimes rich in Fe-oxide micro-inclusions (Fig. 4, n. 1), quartz, and rare micas. Fine-grained quartz-micaschist fragments are also present in minor amounts. The clay matrix is generally oxidised and partially vitrified. The macroscopical colour of the body is generally red-orange and homogeneous in the cross section.

Figure 2: Thin section microphotographs (crossed polars, actual dimensions: 1.3 x 1 mm) of the ceramic body of representative samples.

Figure 2 : Microphotographies en lame mince des pâtes d'échantillons représentatifs.

1) 6901, Group 1; 2) 6891, Group 3; 3) 2414, Group 4; 4) 6904, Group 5; 5) 6893, Group 6; 6) 6883, Group 7. mgr: metagranitoid; gns: gneiss; qrt: quartzite; qrts: quartzshist; qtz: quartz; serp: serpentinite.
1) 6901, Groupe 1 ; 2) 6891, Groupe 3 ; 3) 2414, Groupe 4 ; 4) 6904, Groupe 5 ; 5) 6893, Groupe 6 ; 6) 6883, Groupe 7. mgr : metagranitoïde ; gns : gneiss ; qrt : quartzite ; qrts : quartzshiste ; qtz : quartz ; serp : serpentinite.

- 11 **Glaze.** Macroscopically, glazes are bright orange in colour. In thin section they are not coloured or, rarely, light yellow. Their thickness is low (<0.10-0.15 mm) but homogeneous (Fig. 3, n. 1). Relic quartz inclusions are rarely observed. In sample 6901, one cluster of cassiterite micrograins was found out in the glaze (Fig. 4, n. 2). The glaze-body interface, with neoformed K-Al-Pb silicates (K-Pb feldspars; Molera *et al.*, 2001) is rather thin (Fig. 4, nos. 1, 2).

Group 2

- 12 It consists of few samples (only one analysed here) slightly different from Group 1 in typological features, fabric texture and composition. It could possibly be considered a sub-group of the former.
- 13 **Body.** In the coarse fraction (up to 2 mm in size) there are several clasts of fine- or medium-grained quartz +/- feldspar metamorphic rocks, rarely showing possible relic volcanic textures, associated to granitoid (?) rock fragments very similar to those characteristic of Group 1.

Glaze. In thin section, the glaze is light yellow in colour, very thin (ca. 0.06 mm) and regular.

Table 3: Main petrographic features of the glazes of the groups identified by optical microscopy.
Tableau 3 : Caractéristiques pétrographiques principales des glaçures des groupes identifiés par la microscopie optique.

group	macrosc. colour	colour in thin section	thickness (mm)	glaze-body interface	neoformed phases	bubbles	homogeneity
1	bright orange	colourless-light yellow	<0.10-0.15	thin	K-Pb-f (IF)		xxx
2	bright orange	light yellow	<0.07	thin	K-Pb-f (IF)		xxx
3	bright orange	light yellow	<0.1	thin	K-Pb-f (IF)		xxx
4	green-yellow	green-yellow	0.1-0.4	thick	K-Pb-f (IF)	xxx	x
5	brown	yellow	<0.10-0.2	thick	K-Pb-f (IF), Fe-rich + Mg-rich phases (GL)	xx	xx
6	brown-green brown	yellow	0.1-0.2	thick	K-Pb-f (IF), di, wo (IF, GL)		xx
7	greyish	colourless	<0.05	thick	Pb-f (IF)		x

Abbreviations: di: diopside; f: feldspar; wo: wollastonite; GL: in the glaze; IF: at the glaze-body interface.

Abréviations : di : diopside ; f : feldspath ; wo : wollastonite ; GL : dans la glaçure ; IF : à l'interface glaçure-pâte.

Group 3

- 14 **Body.** Aplastic inclusions are abundant, poorly sorted and mostly composed of generally fine-grained (<0.3 mm) quartz, feldspar and mica individuals (Figs. 2-3, n. 2). Some coarser fragments (up to 1 mm in size) of quartz-feldspar rocks (meta-granitoids?), as well as fine-grained quartzites and possible acid meta-volcanites, are also present.
- 15 **Glaze.** The glaze, light yellow in colour under the microscope, is thin (<0.1 mm) but homogeneous (Fig. 3, n. 2). The reactions at the glaze/body interface are little developed (Fig. 4, n. 3).

Figure 3: Thin section microphotographs (plain polarised light, actual dimensions: 1.3 x 1 mm) of the ceramic body and glaze of representative samples.

Figure 3: Microphotographies en lame mince (nicols parallèles, dimensions réelles: 1.3 x 1 mm) des pâtes et des glaçures d'échantillons représentatifs.

1) 6901, Group 1; 2) 6888, Group 3; 3) 2414, Group 4; 4) 6906, Group 5; 5) 6893, Group 6; 6) 6883, Group 7.

1) 6901, Groupe 1 ; 2) 6888, Groupe 3 ; 3) 2414, Groupe 4 ; 4) 6906, Groupe 5 ; 5) 6893, Groupe 6 ; 6) 6883, Groupe 7.

Group 4

- 16 **Body.** Paste inclusions are subangular, abundant and medium-sorted. They are mainly composed of fine-grained acid metamorphic rock fragments (quartzite, quartz-schist, mica-schist, and phyllite, up to more than 1 mm in size) and of smaller quartz grains (Figs. 2-3, n. 3; Fig. 4, n. 4). The clay matrix is variably (from poorly- to well-) oxidised, even in a same sherd; the macroscopical colour of the body varies from grey or brownish to red.

The minor presence of calcite, identified by XRD analysis, could be considered of secondary origin.

- 17 **Glaze.** Glazes are bubble-rich and inhomogeneous in thickness, even if generally thin (<0.1 mm) (Fig. 3, n. 3). Their colour varies from yellow to green depending on the redox conditions. The glaze-body interface is thick and rich in neoformed K-Pb feldspars (Fig. 4, n. 4).

Figure 4: SEM images showing glaze-body interactions.

Figure 4 : Images au SEM montrant les réactions pâte-glaçure.

1) 6901, Group 1; 2) 6901, Group 1; 3) 6891, Group 3; 4) 6886, Group 4. Feox: Fe-oxides; Kf: K-feldspar; KPf: K-Pb-feldspar; px: pyroxene; qtz: quartz; Sn: cassiterite.

1) 6901, Groupe 1 ; 2) 6901, Groupe 1 ; 3) 6891, Groupe 3 ; 4) 6886, Groupe 4. Feox : oxydes de fer ; Kf : feldspath potassique ; KPf: K-Pb-feldspath ; px : pyroxène ; qtz : quartz ; Sn: cassiterite.

Group 5

- 18 **Body.** Paste inclusions are abundant, subangular and medium-sorted (Figs. 2-3, n. 4). They are composed of elements derived from both acid metamorphites and ophiolites: quartzite, quartz-micaschist, micaschist, paragneiss fragments prevailing on serpentinite (generally transformed into Mg-rich olivine during firing) and quartz+albite+epidote metabasite clasts (sometimes >1 mm in size); single mineral grains (<0.3 mm) of quartz, mica (abundant), feldspar, amphibole, epidote and several accessory minerals. The clay matrix is in general partially or totally oxidised and vitrified.

Figure 5: SEM images showing glaze-body interactions.
 Figure 5 : Images au SEM montrant les réactions pâte-glaçure.

1) 6897, Group 5; 2) 6906, Group 5; 3) 6893, Group 6; 4) 7530, Group 7*. Ab: albite; F: undetermined Fe-rich lamellar phase; Feox: Fe-oxide; Kf: K-feldspar; Kpf: K-Pb-feldspar; mi: mica; Ol: Mg-olivine; qtz: quartz; Pf?: Pb-feldspar?; Sn: cassiterite.

1) 6897, Groupe 5 ; 2) 6906, Groupe 5 ; 3) 6893, Groupe 6 ; 4) 7530, Groupe 7*. Ab: albite ; F : phase lamellaire indéterminée riche en fer ; Feox: oxide de fer ; Kf : feldspath potassique ; Kpf: K-Pb-feldspath ; mi : mica ; Ol : Mg-olivine ; qtz: quartz ; Pf ? : Pb-feldspath ? ; Sn : cassiterite.

- 19 **Glaze.** The glaze colour is typically brown macroscopically and yellow in thin section. The glaze thickness is variable (<0.1-0.2 mm) (Fig. 3, n. 4). The glaze-body contact is irregular and the interface, rich in neoformed K-Pb feldspars growing on mica and feldspar grains of temper, is rather thick (Fig. 5, nos. 1-2).
- 20 Many micro-crystals of an undetermined Fe-rich neoformed lamellar phase are often included in the glaze (Fig. 5, n. 1), enhancing its brown-red macroscopical colour. Several bubbles are also present and, only in 6897, a few cassiterite clusters are scattered in the glaze (Fig. 5, n. 1). Occasionally, serpentinite fragments (transformed into Mg-rich olivine by firing) from the outer part of the body are embedded by the glaze. In that case, these fragments develop thick reaction rims, which are characterised by a spongy glassy texture including scattered Mg-rich phases indeterminable by SEM-EDS (Fig. 5, n. 2).

Group 6

- 21 **Body.** Paste inclusions are abundant (Figs. 2-3, n. 5). They are composed of fine-grained quartz, mica, feldspar, amphibole and several heavy mineral individuals (<0.2 mm), rare larger gneiss fragments (up to 0.8 mm in size) and siliceous microfossils. In the oxidised

clay matrix, micro grains of carbonates are associated with dominant Fe-oxides. Macroscopically, the body is rather homogeneously red-orange in colour.

- 22 *Glaze.* The glaze colour is generally brown, rarely green-brown macroscopically, and yellow in thin section. Its thickness is about 0.1 mm in one sample and 0.2 mm in the other sample (Fig. 3, n. 5). The glaze-body contact is irregular and the interface is evidenced by the growth of abundant K-Pb feldspars, while many micro-crystals of Ca-rich neoformed phases (diopside and rarer wollastonite) are scattered in the glaze (Fig. 5, n. 3).

Group 7

- 23 This group consists of very rare sherds, only one of which showing discriminant typological features. The reference sample 7530 (Group 7*) from Uzège is very similar to Group 7 in both fabric and glaze features.
- 24 *Body.* Paste inclusions are almost exclusively composed of quartz grains. The largest ones (up to 1 mm in size) are rounded in shape and relatively scarce, while in the groundmass (<0.1 mm) they are subrounded and more abundant (Figs. 2-3, n. 6). The clay matrix is kaolinite-rich, as suggested by the peculiar brown-grey colour and the Al-rich composition obtained by SEM-EDS analysis.

Figure 6: Body chemical compositions of representative samples of the groups identified by optical microscopy in the CaO+MgO-SiO₂-Al₂O₃ (above) and CaO+MgO-Fe₂O₃-Al₂O₃ (below) ternary diagrams.

Figure 6 : Compositions chimiques de la pâte d'échantillons représentatifs des groupes décrits dans le texte dans les diagrammes ternaires CaO+MgO-SiO₂-Al₂O₃ (en haut) et CaO+MgO-Fe₂O₃-Al₂O₃ (en bas).

- 25 *Glaze.* The glaze is very thin (<0.05 mm) and irregular (Fig. 3, n. 6). The glaze-body interface is well developed. Differently from the other groups, Al-rich silicates (possibly Pb-feldspars) grew instead of K-Pb feldspars at the glaze-body interface (Fig. 5, n. 4) because of the K-poor (kaolinite-rich) body composition.

1. 1.

Summary of the discriminant features

- 26 In conclusion, simple macroscopical and microscopical features allow the distinction of the seven groups. The main of them are listed below.
- 27 *Group 1 to 3:* bright orange (light yellow in thin section) glaze, body with granitoid inclusions (accessory volcanites in Group 2 and 3; finer grain size in Group 3; thin glaze in Group 2). *Group 4:* low-quality green to yellow glaze (bubble-rich, irregular thickness), body with fine-grained acid metamorphic rock inclusions. *Group 5:* brown (light yellow in thin section) glaze with abundant Fe-rich neoformed microinclusions, body with acid metamorphic and ophiolitic inclusions. *Group 6:* brown (yellow in thin section) glaze, body with acid metamorphic inclusions and siliceous microfossils. *Group 7:* very thin and irregular greyish (colourless in thin section) glaze, body with kaolinitic clay matrix and rounded quartz grains.

3. Chemical composition of ceramic bodies

- 28 SEM-EDS chemical analyses show that the pastes of all groups are Si, Al-rich and Ca-poor (CaO<2.1 wt%; Table 4). Such compositions reflect the use of Fe-rich alluvial (Groups 1-6) or kaolinitic clays (Group 7/7*) and silicate-rich temper, confirming the thin section observation. In the ternary diagram CaO+MgO-SiO₂-Al₂O₃ (Fig. 6 above), the compositions fall in a relatively restricted field of the *Ca-poor clays*. In the ternary diagram CaO+MgO-Fe₂O₃-Al₂O₃ (Fig. 6 below), the higher Al₂O₃ / Fe₂O₃ ratios discriminate Group 7/7* from the other Groups.
- 29 The Groups identified by optical microscopy show minor chemical peculiarities (Table 4) related to their mineralogical and petrographic features. While Al, Ti-rich and Fe, alkali-poor compositions clearly discriminate Group 7/7*, the other Groups show only moderate differences in alkali contents: K values are higher in Groups 4, 5, and 6; Na values are lower in Group 4 and higher in Group 1.

Table 4: Bulk chemical compositions (by SEM-EDS, normalised to 100wt%) of the ceramic body of representative samples of the groups identified by optical microscopy.

Tableau 4 : Compositions chimiques (par SEM-EDS, normalisés à 100 wt %) des pâtes d'échantillons représentatifs des groupes identifiés par la microscopie optique.

group	1			2	3		4			5				6		7	7*
sample	6884	6892	6901	6890	6888	6891	6886	6899	6900	6895	6897	6906	6907	6887	6893	6883	7530
Na ₂ O	2.43	3.88	4.13	1.73	1.44	2.12	<0.5	0.52	0.61	1.84	2.21	1.32	1.74	1.63	1.49	<0.5	<0.5
MgO	1.14	0.99	0.88	0.97	1.37	1.24	1.75	1.43	1.55	2.93	1.78	2.63	2.41	2.53	2.71	0.23	0.47
Al ₂ O ₃	24.45	22.43	19.74	21.68	23.21	20.10	23.55	18.96	20.61	24.11	18.39	21.29	23.45	18.87	20.77	28.83	34.74
SiO ₂	58.26	59.44	63.65	63.12	60.57	60.31	60.85	69.11	65.43	55.36	65.54	57.36	53.50	64.89	59.91	66.48	59.45
K ₂ O	1.42	0.72	0.77	1.66	1.81	1.64	3.18	2.46	2.56	2.83	2.88	3.47	2.95	2.66	3.21	0.33	0.28
CaO	1.05	1.01	1.26	0.91	1.28	1.16	1.31	0.67	0.98	1.55	0.97	1.11	1.29	0.84	2.10	0.78	1.25
TiO ₂	1.07	0.62	0.97	0.57	0.86	1.01	0.91	0.73	0.81	0.99	1.09	1.08	0.94	0.93	0.74	1.35	1.67
Fe ₂ O ₃	10.18	10.91	8.60	9.36	9.46	12.42	8.45	6.12	7.45	10.39	7.14	11.74	13.72	7.65	9.07	2.00	2.14

- 30 At present, no statistical treatment is possible because of the limited number of analysed samples. However, the important dispersion of the chemical results obtained

by SEM-EDS even inside of most of the Groups suggests that a precise distinction of groups and origins would be difficult even improving the number of samples.

- 31 The use of advanced chemical methods that analyse trace elements as well, such as XRF, could improve the distinction between the productions. Concerning provenance, however, little results could be obtained in this case by chemical analysis compared to optical microscopy: archaeological hypotheses about the origin are scarce and few reference materials of known production centres are available.

4. Chemical composition of glazes

- 32 Representative glaze samples were investigated by SEM-EDS in order to both improve the technical characterisation of the artefacts and search for variations in chemical composition of glazes to be related to the typological/petrographic groups.
- 33 All glazes show Si, Pb-rich, Ca, alkali-poor composition (Table 5) and fall in the field of the *high lead glazes* (Fig. 7; Tite *et al.*, 1998). Fe, which is the only colouring agent (the greenish or yellow colours depending on reducing or oxidising conditions), shows variable contents. Both intentional opacifiers and relic components of the glaze mixture are generally absent.

Figure 7: Glaze chemical compositions (mean values) of representative samples of the groups identified by optical microscopy in the ternary diagram PbO-SiO₂-NAKCFM (from Tite *et al.*, 1998). NAKCFM=Na₂O+Al₂O₃+K₂O+CaO+FeO+MgO.

Figure 7 : Compositions chimiques moyennes des glaçures d'échantillons représentatifs des groupes identifiés par la microscopie optique dans le diagramme ternaire PbO-SiO₂-NAKCFM (d'après Tite *et al.*, 1998) ; NAKCFM=Na₂O+Al₂O₃+K₂O+CaO+FeO+MgO.

- 34 A moderate chemical zoning was generally observed, which is related to glaze-body interactions (Molera *et al.*, 2001): in particular, Si, Al, and, in most cases, K contents

increase from the surface to the base of the glaze, while Pb decreases and diffuses into the outer parts of the body enhancing the vitrification of the clay matrix.

- 35 No clear chemical clusters are generally recognisable in the analysed glazes, even if, taking into account the typological-petrographic groups, some differences could be observed (Tab. 5, Fig. 7): in particular, with some exceptions, Groups 1, 2, 3 show higher Si contents, in Groups 5 and 6 Mg contents are higher, while Group 7-7* is characterised by higher contents of Al and lower contents of Fe.

Table 5: Mean chemical compositions (by SEM-EDS, normalised to 100wt%) of the glazes of representative samples of the groups identified by optical microscopy.

Tableau 5 : Compositions chimiques moyennes (par SEM-EDS, normalisés à 100 wt%) des glaçures d'échantillons représentatifs des groupes identifiés par la microscopie optique.

group	1			2		3		4		5				6		7	7*
sample	6884	6901	6892	6890	6891	6888	6886	6899	6900	6895	6897	6906	6907	6887	6893	6883	7530
Na ₂ O	<0.5	1.53	<0.5	<0.5	0.50	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.18	<0.5	1.26	1.09	<0.5	<0.5
MgO	0.21	0.30	0.30	0.36	0.21	0.48	0.46	0.49	0.55	0.88	0.47	0.95	0.65	0.48	1.01	0.22	0.14
Al ₂ O ₃	2.37	5.19	3.83	3.75	4.35	3.92	6.03	4.50	5.18	5.49	3.53	6.47	4.53	3.27	6.22	7.90	7.06
SiO ₂	32.85	34.58	27.92	28.98	32.52	31.32	26.09	23.25	27.93	23.41	17.56	26.59	25.47	24.65	27.16	31.72	25.38
PbO	61.73	53.48	64.24	63.31	58.46	60.13	63.37	67.59	62.45	65.84	75.48	59.25	65.24	66.78	58.75	56.15	64.98
K ₂ O	0.21	0.55	0.21	0.38	0.55	0.30	0.44	0.24	0.55	0.38	0.18	0.49	0.34	0.24	0.69	0.26	0.12
CaO	0.53	0.69	0.80	0.38	0.81	0.77	0.29	0.22	0.51	0.57	0.27	0.32	0.29	0.26	1.61	1.52	0.76
TiO ₂	0.36	0.59	0.38	0.25	0.34	0.57	0.44	0.33	0.42	0.39	0.22	0.51	0.50	0.29	0.44	0.74	0.51
FeO	1.74	3.09	2.32	2.59	2.26	2.51	2.88	3.38	2.41	3.04	2.28	4.24	2.98	2.77	3.03	1.49	1.05

- 36 In conclusion, SEM-EDS analysis of glazes does not seem to be a powerful tool in order to precisely discriminate the various productions identified, even improving the number of samples. The use of more accurate and sensitive microanalytical techniques taking into account also trace elements could provide further markers in some cases, but the fairly homogeneous recipes may reduce the possibility of a clear distinction between all these groups.

5. Discussion

Provenance and diffusion

- 37 *Group 1.* It can be referred to the so-called “Pseudo-ligure” type, which is diffused in a large part of the Mediterranean: from Spain to Israel, including Provence, Liguria and Tuscany (Capelli *et al.*, 2006; Baldassarri *et al.*, 2007). The former archaeological hypothesis of a Ligurian (Savona) origin is not supported by the analytical results. In fact, inclusions (weakly metamorphic granitoids, without Alpine metamorphic overprint) are not consistent with Savona and regional rocks (Vanossi, 1991; Giammarino *et al.*, 2002). Moreover, fabrics are quite different from the numerous reference samples of the local ceramic production (Capelli & Cabella, 2005; Capelli *et al.*, 2007b), represented by Group 6. Then, the atelier of Group 1 must be located in other Mediterranean productive areas (such as Spain, Provence, Tuscany and the Aegean-Anatolian sector) where acid metamorphic rocks outcrop.
- 38 A similar hypothesis could be made for *Group 2* and *Group 3*, which are partially comparable with Group 1. Therefore, the possibility of three different centres/workshops located in the same geological/technological area cannot be excluded.
- 39 *Group 4.* Ceramics attributable to Group 4 were found at Hyères, Provence and Andora, Liguria (Capelli *et al.*, 2006; 2007c). A Ligurian production is possible, because the metamorphic inclusions are consistent with some rock formations (Palaeozoic meta-sediments and meta-volcanites of the Briançonnais Domain) outcropping in the Finale-

Noli area, western Liguria (Vanossi, 1991; Giammarino *et al.*, 2002). Provence, Tuscany and the Aegean-Anatolian sector are among the alternative provenance areas.

- 40 *Group 5.* The peculiar association of acid metamorphic and ophiolitic fragments in the ceramic paste limits the provenance investigation to few geological sectors. The integration with archaeological data points to a probable origin of the Group 5 production from the Aegean-Anatolian area. Even if also in western-central Liguria (as well as in Corse and Tuscany) both rock types outcrop, a regional origin could be excluded on chronological bases. In fact, most of the sherds of Group 5 were found in stratigraphic layers dated to the first half of the 12th c., while Savona production is thought to start in the second half of the 12th c. (Cabona *et al.*, 1986).
- 41 *Group 6.* The origin from Savona (western Liguria) workshops is established by the close relationships between the fabrics of Group 6 samples and kiln wasters of other ceramic classes produced in Savona (Capelli & Mannoni, 2001; Capelli *et al.*, 2007a).
- 42 *Group 7.* The typological and petrographic features of Group 7 exactly match those of the production of Uzège, Languedoc (Leenhardt, 1995), a reference sample of which (Group 7*) was analysed for comparison. The compositional features of pastes are consistent with a provenance from south-eastern France, where kaolinitic raw materials are diffused and commonly used.

Technical features

- 43 Thin section, SEM-EDS, and XRD analyses show that all samples form a group relatively homogeneous in mineralogical and chemical composition, due to the general use of Ca-poor (Fe-rich or kaolinitic) clays with dominant silicate (quartz) inclusions (temper), which give the cooking wares a good resistance to thermal shocks (Picon & Olcese, 1994; Tite *et al.*, 2001).
- 44 A precise evaluation of firing temperature by XRD is difficult due to the lack of Ca-rich phases (Table 2). In most samples, however, the absence of phyllosilicate peaks and the partial or total vitrification of the clay matrix, observed by microscopy, suggest fairly high firing temperature (>900°C; Maniatis & Tite, 1981; Cultrone *et al.*, 2001). One exception is sample 6895 of Group 5, where peaks of white mica are still present (as well as those of tremolitic amphibole, from the ophiolitic temper; however, the coarse grain of inclusions could be responsible for the preservation of mineralogical relics at temperatures above their thermal stability field). The weak hematite peaks observed in Groups 1, 5, 6 samples are related to the transformation under oxidising conditions of Fe-oxides/hydroxides scattered in the clay matrix.
- 45 All the glazes are Pb, Si-rich and Ca, alkali-poor. Similar recipes were used for the various productions. In all cases, the clear divergence between the paste and glaze composition after subtraction of the PbO content and recasting to 100% points to the addition of Si-rich raw materials to Pb compounds (Tite *et al.*, 1998), which are the only or main fluxing agents.
- 46 No intentional opacifier was used. The occasional presence of cassiterite in only two samples might be explained by casual contamination of the glaze mixture.
- 47 The slight variations in some elements showed by the glazes of a few groups could depend either on slightly different recipes for the glaze mixture or contamination processes by different ceramic bodies (Tite *et al.*, 1998). For example, the partial

assimilation of ophiolitic inclusions and kaolinitic matrix could be responsible for the higher Mg and Al contents in glazes of Group 5 and 7-7*, respectively.

- 48 The relatively important presence of Fe (FeOwt% always >1) might be due either to impure silica sources or, less probably, to mobilisation processes from the clay body (Fe contents do not increase from the glaze rim to the glaze-body interface). The hypothesis of an intentional use of Fe as colouring agent can be excluded, as the main function of glaze in that rough cooking pottery is to impermeabilize the vessel, while appearance is less important.
- 49 A greater degree of variability must be supposed for the atmosphere of kilns and the number of firings. The analyses of the macroscopical features (homogeneity, colour, oxidation) of glaze and body and the small-scale glaze-body interactions (extent of mobilisation of chemical elements and growth of neoformed phases) point to a single firing for Group 4 and, possibly, 7-7*, and to a double firing for Groups 1-3 (Tite *et al.*, 1998). More doubts exist as regards Groups 5 and 6, characterised by a thick glaze-body interface, which is generally referred to single-firing processes (Molera *et al.*, 2001). However, in this case the homogeneous oxidation of both body and glaze may suggest double firing and the presence of abundant reaction phases might be explained by slow cooling rates at high temperatures (Parmelee, 1948; Tite *et al.*, 1998).

Conclusions

- 50 The archaeometric study of the 12th-13th c. pottery assemblage of Palazzo Ducale allowed a precise typological classification, never attained before, and provided new data about provenance, diffusion and technique of Mediterranean glazed cooking wares, contributing to improved knowledge of the routes of trade and technology in a critical period of the Middle Ages.
- 51 Because of the technical and compositional homogeneity as well as the scarceness of reference materials, XRD, SEM-EDS and other chemical analyses demonstrated in this case to be less useful than optical microscopy for the distinction of the different productions of glazed cooking wares as well as for provenance and diffusion studies.
- 52 Fabric analyses led to the distinction of seven groups (1-7), which are different from each other in compositional, technical and typological characteristics. They can be referred to at least five workshops or production centres, three of which (Groups 1-3, 4, and 5) are the most represented in terms of sherds abundance.
- 53 The comparative study of fabrics with both geological data and our pottery thin section database points to the import to Genoa, during the 12th-13th c., of cooking wares produced in the northern Mediterranean area included between Provence and the Aegean-Anatolian sector. In contrast with former archaeological hypotheses, only a minor amount of regional products was found. On the other hand, an early Savona production of glazed cooking ware (Group 6) was recognised. It came before the “Graffita arcaica tirrenica”, which started in the late 12th c. (Varaldo, 1997). Moreover, the analyses do not exclude the possibility of another regional production (from western Liguria), started at the beginning of the 12th c. (Group 4).
- 54 It is noteworthy that no imports were found at Palazzo Ducale of glazed cooking wares coming from other important production areas, such as North Africa, western Sicily

and southern Spain, even if numerous glazed tablewares came to Genoa from these regions in the same time span (Cabona *et al.*, 1986).

- 55 The results of this study may point to the existence, in most cases, of specialised productions of glazed cooking ware, also located in different workshops or production centres from those of tablewares (because of the necessity of peculiar raw materials?). In spite of the plurality of workshops, a fairly homogeneous technical knowledge in the production of glazed cooking wares was diffused in the Mediterranean during the 12th-13th centuries AD. Similar quartz-rich, Ca-poor raw materials were generally chosen for ceramic bodies and similar recipes (impure quartz-rich sands mixed with Pb compounds as fluxes) were used for the glazes.

This work is dedicated to Tiziano Mannoni, deceased on october 2010. He also contributed to our research with useful discussions about typological and archaeological problems. We are grateful to: A. Rabino for the help in the choice of the samples; L. Vallauri, who helped us to identify the origin of Group 7 and provided the reference sample; A. Cucchiara and L. Negretti, who performed XRD and SEM-EDS analyses; two anonymous referees for their helpful suggestions and criticism. This work has been carried out in the framework of the Research Cooperation Program for archaeometric analyses between DipTeRis and Soprintendenza per i Beni Archeologici della Liguria.

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ABSTRACTS

Thin section, XRPD, and SEM-EDS analyses were carried out on pastes and glazes of 12th-13th c. glazed cooking wares found out at Palazzo Ducale of Genoa (Liguria, NW Italy). Seven productions different in compositional, technical and typological characteristics were recognised. Imports from centres located in the northern Mediterranean sector included between Spain and the Aegean-Anatolian area, as well as an early local production (from Savona workshops), were identified. The comparison between all these specialised productions shows a fairly homogenous technical knowledge. Ca-poor (Fe-rich alluvial or kaolinitic) clays with quartz-rich temper were generally used for the body, which give the cooking wares a good resistance to thermal shocks. Firing temperatures were relatively high, while both single- and double-fired productions have been identified. All glazes are non-opacified and show Si, Pb-rich, low-alkali, low-Ca composition; no clear chemical clusters are generally recognisable. Fe is the only colouring agent of the glazes, but its presence could be unintentional in most cases.

Les pâtes et les glaçures de céramiques culinaires (XII^e-XIII^e siècles) retrouvées au Palazzo Ducale de Gênes (Ligurie, Italie du Nord-ouest) ont été étudiées en lame mince au microscope polarisant, au microscope électronique (SEM-EDS) et par diffraction des rayons X (XRD). On a reconnu sept productions différentes par leurs composition, technique et typologie. À côté de plusieurs importations, dont les centres d'origine sont localisables dans la Méditerranée du Nord (entre l'Espagne et la région égéenne-anatolienne), on a découvert aussi une production locale (des ateliers de Savone) précoce. La comparaison entre les différentes productions montre un niveau technique relativement homogène. Généralement, les pâtes sont constituées d'argiles pauvres en calcium (alluviales, riches en fer, ou kaolinitiques) et de dégraissants riches en quartz, qui donnent une bonne résistance aux chocs thermiques. Les températures de cuisson sont relativement hautes, tandis que mono- et double cuissons sont évidentes. Toutes les glaçures sont transparentes, riches en Si et Pb et pauvres en Na, K, et Ca; aucun groupement compositionnel n'est bien visible. Le fer représente l'unique colorant, mais, dans la plupart des cas, sa présence n'est probablement pas intentionnelle.

INDEX

Mots-clés: analyse minéralogique, analyse pétrographique, céramique glaçurée

Geographical index: Italie, Italie du Nord

Keywords: glazed ceramic, petrographic analysis, mediterranean trade, mineral analysis

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