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The Medieval lead-glazed pottery from Nogara (north-east Italy): a multi-methodological study

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ABSTRACT

The present work focuses on the archaeometric characterisation of 10th–11th-century lead-glazed pottery from Nogara (Verona, north-east Italy), with the main aim of defining the production technology of both glaze and clay body, through a multi-methodological approach.

All the glazes, transparent and yellow to green in colour, are $20-100 \ \mu m$ thick, texturally homogeneous and variable in composition, with high lead content (PbO: 53-76 wt%), variable silicon (SiO₂: 17–31 wt%), low aluminium (Al₂O₃: 4–7 wt%) and alkalis (Na₂O + K₂O: 0.6–1.7 wt%) and iron, acting as colourant (FeO about 2 wt%). The ceramic bodies are illitic non-calcareous clay-based, the textural features of which indicate neither depuration nor tempering, and firing temperatures generally under 850 °C. Microstructural, chemical and mineralogical evidence suggests that the Nogara glazes were produced by applying to the unfired ceramic body a lead compound flux, which caused partial melting and chemical diffusion phenomena in and outside the ceramic body. Small (<5 µm) newlyformed K-Pb feldspar crystallites, with euhedral morphologies, were also identified at the body-glaze interface of all samples, suggesting uniform firing techniques. The glaze colour, related to chromophorous FeO, must be considered as unintentional. Comparisons between Nogara samples with the same type of ceramics from various sites of the Mediterranean area and European countries, covering a wide time-span (Roman times to Modern age) show general chemical uniformity of the lead coating composition over the centuries, from whichever archaeological site the samples come. In addition, the results reported here further support the hypothesis that, in Italy, the tradition of using non-calcareous clay in combination with lead compound by itself, appeared in late antiquity, continued until mid-Medieval times.

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1. Introduction

The custom of coating pottery with one or more layers of different materials with respect to the composition of the ceramic body is attested since prehistory and developed for practical and aesthetic needs, especially to make the ceramic body easily washable and waterproof and to modify its appearance in colour or brightness. From the fourth millennium BC onwards, glazes, intended as transparent glassy coatings, were used in the Near East and Egypt, first on steatite and faiance and then, from the 16th century BC, on clay bodies. The first use of glazes in Italy, and in particular in the northern part of the country, is attested in the Roman period (1st century BC). This practice continued here without interruption until the late-Roman period (5th–6th

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centuries AD). During the early Middle Ages (7th–10th centuries AD) production of these artefacts moved from northern to southern Italy (Sannazzaro, 1994), as also documented by the few findings of these materials in the north of the country, and mainly in the Emilia and Veneto regions, before the 12th century AD (Fig. 1). Also in the Venetian hinterland, few attestations of glaze pottery are documented, examples being the two glazed spindle-whorls found in Verona (Fig. 1, site 37), one base sherd of a jug found in Gazzo Veronese (Fig. 1, site 20) and some spindle-whorls found in Conselve (Fig. 1, site 38), until the discovery of more than a hundred glazed potsherds at Nogara, a site 35 km south of Verona, near the river Tartaro, and not far from the rivers Adige and Po (Fig. 1).

Extensive excavations by the University of Padova (2003–2007) in this site has brought to light wooden structures (quays and harbour structures, houses) and many types of artefacts (pottery, glass, metals, wooden spoons, *pietra ollare*, etc.), among which are the most numerous assemblage of Medieval glazed pottery in





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Fig. 1. Geographic locations of sites in northern Italy, in which mid-Medieval glazed wares (1–25) and 6th–11th century glazed pottery spindle-whorls (sites 26–39) have been found (from Buzzo, 2007, modified). Sites: 1. Torino; 2. Alba; 3. S. Michele di Trino; 4. Brescia; 5. S. Stefano di Poviglio; 6. S. Agata Bolognese; 7. Bologna; 8. Casalecchio di Reno; 9. Budrio-Bagnarola; 10. Medicina; 11. Medicina-Triforce; 12. Sellustra; 13. Imola; 14. Forlì; 15. Ravenna; 16. Ferrara; 17. Argenta; 18. Comacchio; 19. Codigoro-Pomposa; 20. Gazzo Veronese; 21. Venezia; 22. Venezia-Murano; 23. Venezia-Mazzorbo; 24. Venezia-Torcello; 25. Concordia; 26. Aosta; 27. Frugarolo; 28. Castel S. Pietro; 29. Pellio Intelvi; 30. Monte Barro; 31. Milano; 32. Pavia; 33. Cerete; 34. Desenzano; 35. Piadena; 36. Ledro; 37. Verona; 38. Conselve; 39. Verzegnis.

northern Italy. The site may be viewed as a flourishing crafts and trade centre in Medieval times, as supported by other archaeological evidence, such as the finding of harbour structures near the ancient bank of the river Tartaro (Saggioro et al., 2001). Notwithstanding the trade feature of Nogara, the glazed sherds come mainly from the residential buildings of the site. In the absence of any evidence of trading nor storing of glazed pottery, we presume that these objects were only used in domestic settings (Saggioro, 2011).

Although the area was frequented for a longer period, from the 9th to the 16th centuries, its date ranges mainly between the first half of the 9th century to the end of the 11th century. For all these reasons, Nogara represents the perfect context for a detailed study of glaze production technology in northern Italy in mid-Medieval times, a chronological period poorly documented in the literature of this area.

Macroscopic and archaeological characterisation of the glazed pottery from Nogara describes it as transparent high lead-glazed, single-fired ceramic, produced from a calcareous, iron-rich baseclay tempered with grog (Buzzo, 2011a,b) and depurated (understood as the result of a series of preparatory techniques for removal of coarse inclusions, by hand, decanting and levigation). These archaeological hypotheses were verified by a multi-analytical approach, based on a combination of microscopic, mineralogical, microchemical and textural analyses on both glaze and ceramic body.

The main aims of this paper are therefore to define production technology in terms of preparation, application and firing, as well as the nature of the raw materials used to produce both ceramic body and glaze. All this information will contribute to extending knowledge on 10th–11th-century glazed pottery in Italy, poorly studied until now.

2. Materials and methods

The glazed pottery from Nogara is in different colours and was archaeologically defined, according to Buzzo's classification (Buzzo, 2011a), as glaze type A and type B when green to brown or red coloured, respectively, the former representing about 98% of the findings and the latter only 2%. Archaeometric analyses were carried out on 10 fragments of glaze pottery type A, due to the scarcity of those of type B. In particular, nine fragments of tableware wall sherds, glazed only on the external side and referable to jug shapes, and one fragment of a pottery spindle-whorl, glazed on both sides, were selected (Table 1). They were mainly from the 10th–11th centuries AD in age, according to the dating of many residential buildings in Nogara from which the fragments come.

All the samples were microscopically analysed under both transmitted polarised light microscope on thin sections, following the procedure and terminology proposed by Whitbread (1986, 1989, 1995) and reflected light microscope on polished sections, in order to characterise the ceramic body and the glaze, respectively. Microstructural and microchemical analysis was carried out on the scanning electron microscope (SEM) coupled with an EDS spectrometer with a CamScan MX 2500 microscope, equipped with a LaB₆ cathode, and operating at 20 kV and 160 nA, and with a working distance (WD) of about 22 mm. Microchemical

Table 1	
ist of samples analysed, with indicative dates and type of potsherd.	

Sample	Date (cent. AD)	Potsherd type
NGI 2045/1	10th-11th	Jug with spout
NGI 2045/2	10th-11th	Jug
NGI 3031/K	10th-11th	Spindle-whorl
NGI 3006	10th-11th	Small jar
NGI 3045	10th-11th	Jug
NGI 2051	11th-12th	Jug
NGI 3025/C	10th-11th	Jug
NGI 3028	10th-11th	Jug
NGI 3044/A	10th-11th	Jug
NGI 3047/B	10th-11th	Jug

characterisation of the glaze and compositional profiles from the glaze in the ceramic body were performed on a CAMECA-SX50 electron microprobe (EMPA), equipped with four wavelengthdispersive spectrometers, operating according to the analytical conditions listed in Table S1 (Appendix. Supplementary data). In more detail, glaze bulk compositions were obtained by random point microanalyses, generally based on the average of 15 points per sample, avoiding the most unhomogeneous areas of glaze (i.e., surface and ceramic body–glaze interface). Chemical profiles were carried out along a line crossing the whole thickness of glaze from surface to ceramic body.

The ceramic body was mechanically separated from the glaze and the surface layers were removed with a micro-drill, to avoid possible contamination, ground and analysed by X-ray powder diffraction (XRPD) on a PANalytical X'Pert PRO diffractometer in Bragg–Brentano geometry, equipped with a Cu X-ray tube (40 kV and 30 mA, Cu–Ka radiation) and X'Celerator detector in the $3^{\circ}-70^{\circ}$ 2θ range, 0.02° step size and 1 s count per step. In addition, quantitative chemical analyses of major, minor (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅) and trace elements (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd, Pb, Th and U) were carried out on the ceramic bodies by X-ray fluorescence (XRF) on a WDS Philips PW2400 spectrometer, equipped with a Rh tube and operating at 3 kW as maximum power. Samples were prepared as beads by mixing calcined powder and Li₂B₄O₇ in a dilution ratio of 1:10. A set of geological standards, analytically tested by the international scientific community (Govindaraju, 1994), was used for calibration. Detection limits for major and minor elements correspond to 0.01 wt% for Al₂O₃, MgO and Na₂O, 0.02 wt% for SiO₂, 0.005% for TiO₂, Fe₂O₃, MnO, CaO, K₂O and P₂O₅, and to following ppm for the trace elements: Sc = 2, V = 5, Cr = 6, Co = 2, Ni = 3, Cu = 2, Zn = 2, Ga = 5, Rb = 2, Sr = 2, Y = 2, Zr = 2, Nb = 2, Ba = 3, La = 10, Ce = 10, Nd = 10, Pb = 3, Th = 3, U = 3. FeO content was determined by titration with potassium permanganate. Fe₂O₃ was obtained by the difference from Fe₂O_{3tot} determined by XRF, according to the formula $Fe_2O_3 = (Fe_2O_3)_{tot} - 1.111^*FeO_2O_3$

3. Results and discussion

3.1. Ceramic body

The ceramic body of all Nogara samples macroscopically shows wheel-throwing traces and various paste colours, varying from red to grey, in some cases also in the same potsherd.

Microscopic analysis indicated that the potsherds were homogeneous from a petrographic viewpoint. They are all characterised by homogeneous and poorly optically active groundmass, with a speckled birefrangent fabric, due to the presence of mica-like minerals, and not a carbonatic groundmass as presumed by Buzzo (Buzzo, 2011a). Pores are scarce (3-5%) and mainly represented by tens to some hundred micron-sized vughs, intended as relatively large, irregular voids (Kemp, 1985). Only the pottery spindle-whorl fragment (NGI 3031/K) is more porous (5-10%), containing abundant vesicles and channels. All the samples contain only argillaceous inclusions as clay pellets and not grog, as hypothesised by Buzzo (2011a,b). Inclusions are always very abundant, having a coarse:fine ratio between 50:50 and 60:40, close-spaced related distribution with grains having points of contact, angular and sub-angular shape, and silty and sandy grain size. They are composed of predominant crystals of quartz, associated with abundant mica flakes, scarce opaque minerals, and rare, sporadic fragments of metamorphic rocks (micaceous levels of schist-like rocks), rhyolite groundmass, chert, limestone, crystals of microcline, plagioclase, green amphibole, garnet, epidote and pyroxene. The minero-petrographic composition of inclusions in the ceramic bodies is consistent with the geology of the Adige alluvial deposits, on which the archaeological site of Nogara lies. In more detail, fragments of metamorphic rocks and garnet and rhyolite groundmass are related to the Alpine basement and the Early Permian Atesine Porphyric Platform, respectively.

Samples were divided into two petrographic groups on the basis of the inclusion grain-size distribution, one (samples: NGI 2045/1, NGI 2045/2, NGI 3031/K, NGI 3006, NGI 3045) being characterised by grains mainly around 250 μ m in size, and the other (samples: NGI 2051, NGI 3025/C, NGI 3028, NGI 3044/A, NGI 3047/B) with smaller inclusions, mostly around 150 μ m. Differences in terms of relative abundance of lithic and mineral fragments, as well as grain-size distribution among the studied potsherds reflect the textural heterogeneity in the alluvial deposits of the Adige.

Microscopic analysis also showed that the groundmass immediately under the glaze, at the glaze-ceramic body interface, is less porous and darker in colour when observed in parallel polar. In the scanning electron microscope back-scattered (SEM-BSE) images, this portion of the potsherds appears lighter in colour, having a higher medium atomic number than the ceramic body (Fig. 2a).

The chemical composition of major and minor elements in the ceramic body is substantially homogeneous, as indicated by the scarce variance, expressed by the low standard deviation values, whereas trace elements have higher variability (Table 2). This composition matches ranges of non-calcareous, low-alumina clay, normally used in Italy for lead-glazed pottery production of late Roman and early Medieval age (Paroli et al., 2003; Walton and Tite, 2010). As regards the firing technology, although the iron content is very similar in all samples, the division between Fe²⁺ and Fe³⁺, and therefore the reduction index (RI), expressed by the FeO/FeO_{tot} ratio (Maggetti and Galetti, 1981), is very variable (Table 2). Only samples NGI 2045/1 and NGI 2045/2, having RI values lower than 0.2, are referable to oxidising firing conditions, whereas all the others, with RI over 0.2, are consistent with reduction firing conditions. From a mineralogical viewpoint, on the basis of XRPD data, all the samples contain quartz, K-feldspar, plagioclase, illite and, in some cases (samples NGI 2045/1, NGI 2045/2, NGI 3006), also haematite. This mineralogical association, and in particular the lack of chlorite and the presence of illite peaks, indicates that this pottery was fired in the 750-850 °C temperature interval. Only the pottery spindlewhorl (sample NGI 3031/K) exceeded 900 °C, as testified by the lack of illite and the presence of hercynite. These indications are also supported by the microstructure of the ceramic body, as observed in the SEM-BSE images, in which the groundmass of some samples (NGI 2045/2, NGI 3006, NGI 3044/A) appears only partially vitrified, with a network of glass embedding still crystallized mica flakes. In most cases (NGI 2045/1, NGI 3045, NGI 2051, NGI 3025/C, NGI 3028, NGI 3047/B) vitrification is more extensive, showing a more pervasive network of glass and fewer pores, and only the spindlewhorl (NGI 3031/K) has an extensively and highly vitrified groundmass.

3.2. Glaze

Preliminary optical examination reveals that all the glazes from Nogara are transparent and amber-yellow to olive-green in colour, ranging from a few tens to one hundred μm in thickness and showing small gaps, crackles, bubbles and fractures, variable in size and number.

From the textural and compositional viewpoints, all the glazes have a homogeneous texture (Fig. 2) and chemical composition very high in lead (PbO = $65 \pm 7 \text{ wt\%}$), high in silicon (SiO₂ = $23 \pm 5 \text{ wt\%}$) and low in aluminium (Al₂O₃ = $5 \pm 1 \text{ wt\%}$), calcium (CaO = $1.01 \pm 0.6 \text{ wt\%}$), iron (FeO = $2 \pm 0.4 \text{ wt\%}$) and alkalis (Na₂O = 0.40 ± 0.1 and K₂O = $0.98 \pm 0.13 \text{ wt\%}$) (Table 3). In more



Fig. 2. SEM-BSE images of Nogara glaze. Note that, due to great difference in mean atomic number between ceramic body and glaze, BSE images were obtained with suitable brightness and contrast settings, in order to highlight compositional differences in glaze. Thus, ceramic body appears black and glaze as light grey layer. Note also inter-diffusion zone between glaze and ceramic body. a: Homogeneous texture of glaze and diffusion of lead into ceramic body, marked by arrows. b: Newly-formed crystals at body–glass interface (probable Pb, K-feldspar, SEM–EDS data). c: Detail of a relict crystal of K-feldspar showing corona-like structure of Pb, K-feldspar (grey); d: Metallic lead inclusions at body–glaze interface.

detail, lead content is variable among the samples, ranging between 53 and 75 wt%. The other chemical elements show lower variability with respect to PbO (Table 3). In addition, PbO and SiO₂ have a negative correlation ($R^2 = 0.95$), whereas both SiO₂ and Al₂O₃, and Na₂O and K₂O show positive correlations ($R^2 = 0.90$ and 0.84, respectively), with the exception of sample NGI 3031/K, which has a Na₂O content lower than all the other samples (Fig. 3).

Glazes of samples from Nogara are also characterised by the presence of air bubbles, the number of which is quite variable and is related to the different viscosity of the glaze. Samples with few bubbles (NGI 3025/C, NGI 3028, NGI 3044/A, NGI 3047/B, NGI 2051), having a glaze sufficiently fluid to allow the gas bubbles to escape during firing, are characterised by high PbO (>65 wt%), whereas those with many bubbles (NGI 2045/1, NGI 2045/2, NGI 3031/K, NGI 3006, NGI 3045), having a more viscous glaze which trapped gas bubbles, contain lower PbO (<65 wt%). The difference in viscosity and consequently in bubble contents, is therefore due to the different content of PbO, which acted as flux.

In addition, all samples with high PbO content (NGI 2051, NGI 3025/C, NGI 3028, NGI 3044/A, NGI 3047/B), also contain inclusions of metallic lead at the body–glaze interface (Fig. 2d). According to Comodi et al. (2004), when firing is carried out in reducing conditions, as deduced for most of the studied samples, the higher the lead content, the greater the probability of reduction of lead oxide to metallic lead. It is very interesting to note that the chemical composition of samples, which have PbO content lower than 65 wt % and do not contain drops of metallic lead, is close to that of the

eutectic in the PbO–SiO₂–Al₂O₃ system (31.7% SiO₂, 61.2% PbO, 7.1% Al₂O₃, as reported in Bansal and Doremus, 1986). The cooling of such a melt, eutectic in composition, limited the formation of crystalline phases and thus maintained high glaze transparency and brightness. On the contrary, glazes with high PbO content, have a composition differing from that of the eutectic, the cooling of which, in reducing conditions, caused the separation of metallic lead drops.

In attempting to establish the production technology of lead glazes, interactions between the glaze mixture and the clay body should be considered (Tite et al., 1998; Walton and Tite, 2010). As discussed by Hurst and Freestone (1996), when a lead compound (oxide, sulphide or carbonate) is used by itself, the lead diffuses into the body during firing, reacting with it to form a glaze. Therefore, subtracting the lead oxide content from the glaze composition and recasting the obtained data to 100%, the resulting composition should be close to that of the ceramic body. In addition, contents of other elements of glaze should remain constant throughout its thickness (De Benedetto et al., 2004) for firing time of at least one hour (Walton and Tite, 2010). In contrast, when a lead-silica mixture is used, the lead and silica react during firing to form the glaze, into which there will be some subsequent diffusion of body components (e.g., aluminium, calcium, iron, alkalis). In this case, the glaze composition, after subtraction of the lead oxide content and recasting to 100%, will depend on the relative diffusion rates of the different body components. Therefore, it will not normally match that of the ceramic body (Tite et al., 1998).

Table 2

Chemical composition of major, minor (expressed as oxide wt%), and trace elements (expressed as ppm) of Nogara potsherds, except for sample NGI 3031/K (XRF data); average (A), standard deviation (SD), FeO, obtained by titration, Fe₂O₃ values, calculated for difference from Fe₂O₃tot, reduction index (RI) and L.O.I. (loss on ignition) also reported.

wt%	NGI 2045/1	NGI 2045/2	NGI 3006	NGI 3045	NGI 2051	NGI 3025/C	NGI 3028	NGI 3044/A	NGI 3047/B	А	SD
SiO ₂	68.90	68.53	69.09	67.57	70.52	70.00	68.12	68.64	69.41	68.97	0.91
TiO ₂	0.82	0.82	0.81	0.82	0.82	0.84	0.81	0.84	0.86	0.84	0.02
Al_2O_3	16.14	16.08	16.60	17.28	15.83	15.40	16.86	16.31	15.61	16.23	0.60
Fe ₂ O _{3tot}	5.90	5.83	5.87	5.83	5.11	5.18	5.60	5.69	5.61	5.62	0.29
MnO	0.13	0.12	0.11	0.11	0.10	0.11	0.11	0.11	0.12	0.11	0.01
MgO	2.00	2.01	1.98	2.10	1.81	1.88	2.20	2.06	1.95	2.00	0.12
CaO	1.47	1.67	1.40	1.48	1.49	1.59	1.55	1.64	1.66	1.55	0.10
Na ₂ O	1.73	1.76	1.66	1.70	1.97	1.74	1.75	1.63	1.55	1.72	0.12
K ₂ O	2.98	2.95	2.90	3.20	2.69	2.75	3.19	3.10	2.95	2.97	0.18
P_2O_5	0.12	0.18	0.10	0.11	0.17	0.19	0.19	0.19	0.19	0.16	0.04
L.O.I.	1.16	1.33	1.32	1.35	1.23	1.03	1.57	1.09	1.28	1.26	0.04
FeO	0.69	0.64	1.23	2.18	3.71	3.18	1.31	2.49	2.28	1.97	1.16
Fe ₂ O ₃	5.13	5.12	4.50	3.41	0.99	1.65	4.14	2.92	3.08	3.44	1.44
RI	0.13	0.12	0.23	0.42	0.81	0.68	0.26	0.49	0.45		
ppm											
Sc	26	16	22	24	19	23	22	17	20	21	3
V	108	106	116	112	95	108	119	114	114	110	7
Cr	125	124	126	130	120	131	183	140	158	137	20
Со	18	16	20	17	15	15	18	16	16	16	1
Ni	71	69	69	74	80	61	86	71	85	74	8
Cu	27	30	28	23	25	22	28	23	20	25	3
Zn	88	100	99	103	80	85	104	97	98	94	8
Ga	11	8	<5	<5	<5	6	<5	11	<5		
Rb	139	137	134	145	122	125	148	134	127	134	9
Sr	130	132	128	130	132	128	132	125	119	128	4
Y	40	39	37	35	35	40	37	39	41	38	2
Zr	257	254	254	224	292	298	245	259	295	264	25
Nb	15	17	16	16	21	24	17	15	19	17	3
Ba	455	469	489	557	550	490	527	539	514	510	36
La	38	34	37	50	50	42	37	47	45	42	6
Ce	87	80	86	89	98	83	82	79	87	85	5.7
Nd	27	27	31	12	20	29	29	20	24	24	6
Pb	93	318	251	122	729	1056	342	136	525	397	321
Th	<3	<3	<3	<3	<3	<3	<3	<3	<3		
U	<3	3	<3	<3	<3	<3	<3	4	<3		

The comparison between the chemical compositions of Nogara glazes, recast to 100% without the lead contribution, and those of ceramic body shows substantial chemical similarity (Table 4). This match supports the hypothesis that glaze was produced by applying only a lead compound to the ceramic body. In the case of application of a lead-silica mixture, the SiO_2 content would be higher in the recast glaze and the alumina and other oxide contents lower, when compared with that of the ceramic body (De Benedetto et al., 2004). In addition, the EMPA chemical profiles of the glaze, through the glaze-ceramic interface to the outermost part of the ceramic body (Fig. 4) show substantial uniformity of concentrations of lead, aluminium and silicon within the glaze itself, except for the sudden variation of these elements at the glaze-ceramic body interface. This chemical evidence, together

with the good negative correlation between PbO and SiO_2 (Fig. 3a), further supports the hypothesis of use of only a lead compound for glaze production.

It should be stressed here that the use of body clay, itself mixed with the lead compound to produce the glaze suspension, could result in a match between the body composition and the recast glaze composition (Tite et al., 1998). In the case of the Nogara samples, this hypothesis is not reliable, because the body clay is poorly depurated and rich in aplastic fragments and heavy minerals, which would worsen the quality of glaze suspension, making the production process less efficient. All other elements found in the glaze (silicon, aluminium, sodium, potassium, iron, magnesium, manganese, titanium, calcium) come from the ceramic body itself and are related to diffusion processes, induced by the

Table 3	
Chemical composition of Nogara glazes (EMPA data) Average standard deviation	and number of analytical points (A P) reported

Sample	A.P.	SiO ₂	SD	PbO (wt%)	SD	FeO (wt%)	SD	Al_2O_3	SD	MgO (wt%)	SD	Na ₂ O	SD	K ₂ O (wt%)	SD	CaO (wt%)	SD	TiO ₂ (wt%)	SD	MnO (wt%)	SD
		(1110)		(1100)		(1100)		(1100)		(110,0)	_		_	(1100)		(110,0)		(1100)		(1100)	_
NGI 2045/1	20	30.31	0.83	53.52	1.57	2.75	0.28	7.47	0.35	1.06	0.10	0.59	0.10	1.19	0.13	1.07	0.09	0.40	0.05	0.05	0.04
NGI 2045/2	10	24.99	0.50	61.32	1.01	2.08	0.17	5.83	0.20	0.92	0.06	0.53	0.06	0.93	0.08	1.86	0.49	0.27	0.06	0.11	0.08
NGI 3031/K	12	31.07	1.14	57.12	1.66	2.29	0.24	6.64	0.40	0.49	0.06	0.10	0.06	0.59	0.06	0.35	0.04	0.38	0.06	0.05	0.05
NGI 3006	11	24.06	1.26	63.90	1.31	1.95	0.23	5.59	0.42	0.78	0.10	0.50	0.17	0.83	0.16	1.05	0.24	0.30	0.07	0.04	0.06
NGI 3045	20	22.67	0.65	65.63	0.89	2.06	0.18	5.62	0.31	0.81	0.07	0.42	0.10	0.76	0.08	0.59	0.09	0.31	0.10	0.07	0.06
NGI 2051	20	20.71	1.33	69.98	1.84	1.54	0.17	4.58	0.22	0.66	0.08	0.38	0.13	0.66	0.12	0.90	0.24	0.22	0.05	0.06	0.04
NGI 3025/C	11	16.75	8.33	75.89	3.66	1.24	0.17	3.61	6.75	0.49	1.61	0.34	0.12	0.51	0.07	0.47	0.14	0.22	0.10	0.04	0.03
NGI 3028	9	18.06	0.80	72.71	1.08	1.82	0.12	4.42	0.31	0.64	0.05	0.28	0.07	0.50	0.06	0.54	0.02	0.24	0.04	0.04	0.06
NGI 3044/A	18	20.02	0.82	70.60	1.18	1.42	0.12	4.08	0.19	0.62	0.09	0.43	0.10	0.78	0.08	0.88	0.26	0.25	0.06	0.04	0.04
NGI 3047/B	10	21.53	1.33	66.24	1.68	1.78	0.16	4.56	0.43	0.79	0.06	0.44	0.10	0.98	0.13	2.38	0.40	0.26	0.05	0.07	0.04



Fig. 3. Diagrams of mean values of EMPA data, with relative standard deviation, for: a) SiO₂ vs PbO, b) SiO₂ vs Al₂O₃, and c) Na₂O vs K₂O contents of glazes from Nogara. Note negative correlation between PbO and SiO₂ ($R^2 = 0.95$) and positive correlation between SiO₂ and Al₂O₃ ($R^2 = 0.90$) and Na₂O vs K₂O ($R^2 = 0.84$).

application of a lead compound, which acted as flux. The SEM-BSE images indicate an intermediate layer between ceramic body and glaze, with a thickness of several tens of micrometres and a higher average atomic number than the ceramic body, but lower than that of the glaze, which represents the diffusion zone of lead into the ceramic body (Fig. 2a). The EMPA chemical profiles clearly indicate diffusion processes between body and glaze (Fig. 4). The lead content, constant in the glaze, shows a sharp decrease at the body-glaze interface and a subsequent gradual decrease within the ceramic body, indicating that it diffused for some tens micrometres into that body (Figs. 2a and 4). A different trend can be observed for silica and alumina, which diffused from ceramic body into glaze. The good positive correlations found between SiO₂ and Al₂O₃ and between Na₂O and K₂O (Fig. 3) further support the chemical diffusion of these elements from ceramic body to glaze, due to melting of the feldspathic and illitic phases of the body. According to this model, iron, the only chromophorous element identified in the glazes, was not intentionally added, as often reported in the literature (Cuomo di Caprio, 2007) but derived from the ceramic body.

Many newly-formed crystals, generally less than 5 μ m in size and prismatic or acicular in habit, were observed at the glazeceramic body interface (Fig. 2b). They have composition $(SEM-EDS data: SiO_2 = 45.7 wt\%, Al_2O_3 = 14,5 wt\%, K_2O = 8.1 wt\%,$ PbO = 30.1 wt%, FeO = 1.6 wt%) consistent with lead-potassium feldspars. The same types of crystals were also identified around some K-feldspar relicts in the glaze, forming a corona-like structure (Fig. 2c). The formation of Pb-K feldspar crystallites and their extent depends on factors such as the type of clay used, firing and cooling times, firing temperatures reached. In particular, the type of clay used is an important parameter which influenced the formation of Pb-K feldspar crystallites and their extent: the use of noncalcareous illitic clays at the same firing temperature and glaze application method, determines the development of the most extended interface and the crystallisation of numerous Pb-K feldspars, related to the breakdown of illite, which make many K⁺ ions available for the nucleation and growth of Pb–K feldspar (Molera et al., 2001). This is also verified in the case of the Nogara pottery, which was produced with an illitic non-calcareous clay. The euhedral habitus of the crystals and their small size ($<5 \mu m$) in all the Nogara samples suggest comparable firing conditions, probably between 750 °C and 850 °C (Molera et al., 2001; Walton and Tite, 2010) with short heating time. The relatively low temperature of firing was still sufficient to allow the growth of a great number of crystallites; however, firing time and temperatures were too low to allow the crystallites to exceed the size of

Table 4

Chemical composition of ceramic body "b" (XRF data) and that of glaze "g" (EMPA data, recalculated to 100 without lead content). Note: sample NGI 3031/K not included, due to lack of XRF data.

Samples	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)
NGI 2045/1 b	68.90	0.82	16.14	5.90	0.13	2.00	1.47	1.73	2.98
NGI 2045/1 g	66.43	0.87	16.38	6.04	0.12	2.33	2.34	1.29	2.61
NGI 2045/2 b	68.53	0.82	16.08	5.83	0.12	2.01	1.67	1.76	2.95
NGI 2045/2 g	65.83	0.70	15.36	5.49	0.29	2.42	4.90	1.41	2.44
NGI 3006 b	69.09	0.81	16.60	5.87	0.11	1.98	1.40	1.66	2.90
NGI 3006 g	67.88	0.85	15.77	5.49	0.11	2.20	2.95	1.40	2.34
NGI 3045 b	67.57	0.82	17.28	5.83	0.11	2.10	1.48	1.70	3.20
NGI 3045 g	67.32	0.92	16.70	6.13	0.20	2.40	1.76	1.26	2.27
NGI 2051 b	70.52	0.82	15.83	5.11	0.10	1.81	1.49	1.97	2.69
NGI 2051 g	69.48	0.74	15.36	5.18	0.21	2.23	3.04	1.26	2.21
NGI 3025/C b	70.00	0.84	15.40	5.18	0.11	1.88	1.59	1.74	2.75
NGI 3025/C g	70.46	0.92	15.19	5.22	0.15	2.05	1.99	1.43	2.14
NGI 3028 b	68.12	0.81	16.86	5.60	0.11	2.20	1.55	1.75	3.19
NGI 3028 g	67.52	0.90	16.51	6.81	0.16	2.39	2.01	1.06	1.89
NGI 3044/A b	68.64	0.84	16.31	5.69	0.11	2.06	1.64	1.63	3.10
NGI 3044/A g	69.56	0.88	14.16	4.95	0.13	2.17	3.07	1.51	2.72
NGI 3047/B b	69.41	0.86	15.61	5.61	0.12	1.95	1.66	1.55	2.95
NGI 3047/B g	65.05	0.77	13.76	5.38	0.20	2.38	7.18	1.34	2.96



Fig. 4. Concentration profiles for SiO₂, PbO, and Al₂O₃, obtained by EMPA analyses on sample NGI 2051 from external surface of glaze into ceramic body. Same trends shown by all other samples.

 $5 \mu m$ (Molera et al., 2001). According to these considerations, the lead content of the Nogara glazes, although varying from one sample to another, is due to the maximum temperature reached during firing and the cooling rates: the growth of newly-formed K–Pb feldspars and the body–glaze interface cause progressive decrease of the lead, potassium and aluminium contents of the glaze.

Textural and compositional differences do not allow us to distinguish whether the lead compound was applied on unfired or biscuit objects. However, some data suggest that the glazes from Nogara were produced by applying a lead compound on an unfired body. The presence of a blackened zone in the Nogara ceramic body immediately below the glaze, identified by both macroscopic and microscopic observations, may support the hypothesis of a lead compound applied to an unfired body. This blackened zone may be due to incomplete oxidation of the ceramic body immediately under the glaze, which protected the clay from oxygen during firing (Tite et al., 1998). A uniform ceramic body, or at least without any blackened zone under the coating, would have been expected if the body had been fired before it was glazed. Further support to the above method of glaze application comes from the finding of metallic lead inclusions at the glaze-body interface in some samples (Fig. 2d), the precipitation of which, in addition to the high lead content of the glaze, was probably also "stimulated" by the "local" reducing conditions, due to the application of a lead compound on the unfired body.

It should be stressed that chemical and minero-petrographic data on Medieval lead-glazed pottery from Italy are scarce, particularly those of mid-Medieval age like the Nogara assemblage, and when these data are available, they only focus on characterisation of the ceramic body (e.g., Bonifay, 1986; Paroli et al., 2003). The results obtained in the present study cannot at the moment be compared with others on samples similar in date and geographical area of provenance. Comparisons between Nogara glazes and lead glazes already archaeometrically studied, dated from Roman times to the Modern period in various sites in the European and Mediterranean area, show general chemical uniformity of the composition of the lead coating over the centuries, from whichever archaeological site the samples come (Fig. 5). Nevertheless, the recent work of Walton and Tite (2010) revealed some general trends, useful in tracing the history of technological transfer in the



Fig. 5. Ternary diagram of SiO_2 -PbO-(Na₂O + MgO + Al₂O₃ + K₂O + CaO + FeO) for glazes from Nogara (open triangles) and other 1st–18th century sites (full dots: data from Tite et al., 1998, modified; dotted area: data from Walton and Tite, 2010).

production of lead-glazed pottery over the studied period of approximately 800 years. The two glazing techniques seem to have been used in eastern Anatolia since the 2nd century BC and then introduced in Italy during the Augustan age. Between the 1st and 4th centuries, only a lead-silica mix seems to have been employed in Italy. The use of lead oxide by itself appears in Italy during the 4th–5th centuries AD, as the exclusive glazing technique on illitic, low-calcareous clay bodies; from that period onwards, silica-lead mixtures appear to have been used only on calcareous ceramic bodies. According to these results, we assume that, around the 4th-5th centuries, a technological change in glazing methods occurred in Italy. Although Italian glazed sherds are poorly documented for Early and mid-Medieval centuries, the few findings analysed, reported in Walton and Tite (2010), seem to follow the same trend, with a lead compound applied to non-calcareous clay. The results obtained on the Nogara samples further support the hypothesis that in Italy the tradition of using non-calcareous clay in combination with lead compound by itself continued until mid-Medieval times.

4. Conclusions

The present multi-methodological study, carried out on glazed pottery from Nogara (north-east Italy), allowed us to define the production technologies used in mid-Medieval times in northern Italy, and to answer questions still open after archaeological characterisation. The glazed pottery from Nogara can be defined as high lead-glazed pottery, due to its content (up to 75 wt% in PbO), the variability of which is related to firing time and temperature. The body–glaze interface, characterised by many micron-sized ($<5 \mu m$) newly-formed Pb-K feldspars, shows diffusion of lead from the glaze into the ceramic body and a blackened zone in the ceramic body immediately below the glaze. This microstructural, chemical and mineralogical evidence, together with the chemical similarity between glaze, without lead contribution, and ceramic body, suggests that the Nogara glaze was produced by the application of a lead compound which acted as a flux, on an unfired object and in similar firing conditions. This lead compound causes partial melting of the clay body and chemical diffusion phenomena, as testified by the occurrence of silicon, aluminium, sodium, potassium, iron, magnesium, manganese, titanium, and calcium in the glaze, and by good positive correlations between SiO_2 and Al_2O_3 and Na_2O and K_2O .

The Nogara glazed pottery was produced with an illitic noncalcareous clay, neither depurated nor tempered, and without the addition of grog. The petrographic nature of the inclusions indicates that the pottery was locally produced and, on the basis of the mineralogical associations, fired at temperatures between 750 °C and 850 °C, except for sample NGI 3031/K, which exceeded 900 °C. These data match the firing temperature defined for other leadglazed pottery, and are sufficiently high to allow the coating to vitrify. The RI index also suggests that the samples were fired in a non-uniform atmosphere, indicating poor control of firing conditions, responsible for the various colours of the ceramic body.

The colours of the glaze, variable both among samples and within the same sherd, must be considered unintentional because of the iron content, which derived from the clay body, due to chemical diffusion phenomena.

The absence of any kind of decoration or intentional colouring or decolouring elements, as well as poor control of firing conditions suggest little interest in the aesthetic aspects of these artefacts, in accordance with their functional use. The use of illitic non-calcareous clays may have been intentional, since these materials have an expansion coefficient very similar to that of lead glazes.

The variable lead contents of the Nogara glazes match data for lead-glazed pottery reported in the literature until now, and is due to variable firing conditions. Although the lead-glazed pottery from various European and Mediterranean sites, dated from Roman times to the Modern Age, show general compositional analogies, the Nogara pottery is perfectly inserted in the Italian Late Antique tradition of the use of non-calcareous clay in combination with lead compound by itself. In addition, the present study testifies that the above tradition continued in Italy until mid-Medieval times.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jas.2012.03.016.

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