

Connecting Late Roman and Early Byzantium: Investigating the technological tradition of 6th c. AD glazed wares from Northern Greece and Bulgaria

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Connecting Late Roman and Early Byzantium: Investigating the technological tradition of 6th c. AD glazed wares from Northern Greece and Bulgaria

S.Y. Waksman ^{a,*}, G. Giannaki ^{a,b}, J. Burlot ^a, E. Todorova ^c, M. Daskalov ^c, S. Goryanova ^c, G. Guionova ^d, P. Petridis ^b

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ABSTRACT

Glazed wares found in Thasos (Greece) and in a pottery workshop in Sofia (Bulgaria) in 6th c. AD contexts were investigated using WD-XRF (body analysis) and SEM-EDS (glaze analysis). In both cases, they associate low-calcareous bodies and high-lead glazes, with lead compounds probably applied without the addition of silica before a single firing. This technical tradition is common to the 4th—5th c. Late Roman glazed wares studied so far, from the Balkans to Northern Italy, and to the 7th c. AD "Byzantine Glazed White Ware I". Our corpus may thus be seen as the "missing link" between the Late Roman and the Early Byzantine glazed wares, before glazed tableware meet with a remarkable development later on in Byzantium.

1. Introduction

For many ceramologists, the transition between the Late Antique and the Early Byzantine pottery repertoire was defined by J.W. Hayes, in his study of the pottery excavated at the site of Saraçhane in Istanbul (Hayes, 1968, 1992). This transition in the 7th c. AD initiates the development of Byzantine glazed wares, a phenomenon which will actually not take off before the beginning of the 12th c., as emphasized by Sanders' quantitative data in Corinth (Sanders, 1995, 2003). Glazes were know well before the 7th c. and used in the Roman and Late Roman worlds as well, but a gap seemed to persist between the Late Roman productions of the 4th-beginning of the 5th c., attested by numerous workshops from the Balkans to Northern Italy (Magrini and Sbarra, 2005; Cvjetićanin, 2006; Magrini and Sbarra, 2009, Magrini et al., 2010; Hárshegyi and Ottományi, 2013), and the Early Byzantine glazed wares of the 7th c. present in Sarachane and in the Yassı Ada shipwreck (Hayes, 1968; Bass et al., 1982; Hayes, 1992). Trivyzadaki (Trivyzadaki, 2008, p. 22) and Petridis (Petridis, 2013, p. 187; Petridis, 2015, p. 441-442; Petridis, 2022, p. 333) suggested a clear connection between the glazed pottery discovered in Philippi and Thasos respectively and the

earlier Balkan productions and proved that glazed pottery was well in use already in the 6th c. Indeed, glazed wares excavated in Thasos (Greece) and Sofia (Bulgaria) (Fig. 1) in contexts dated back to the 6th c. may represent the missing link, and are studied by G. Giannaki in the framework of a PhD in archaeology at the universities of Athens (Greece) and Lyon (France).

The present paper investigates the provenance and technology of a sampling of the corpus studied by Giannaki, focusing on the archaeometric characterization of the bodies and glazes and the technical tradition their association may be related to. Both Late Roman and Early Byzantine glazed wares, including the first "Glazed White Ware I" defined by Hayes in Saraçhane (Hayes, 1992), were the subject of previous archaeometric studies which provide a body of comparative data we could build upon (Walton, 2004; Walton and Tite, 2005; Waksman et al., 2007, 2008; Capelli et al., 2009, 2010a, 2010b; Walton and Tite, 2010).

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 $^{^{1}}$ for preliminary results on the Sofia material: Waksman et al., 2024.

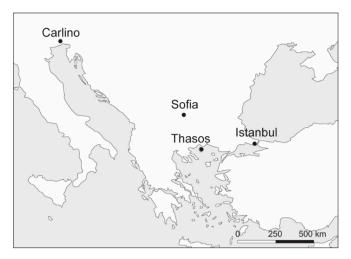


Fig. 1. Map of the main sites mentioned (base MAP O. Barge).

2. Material and methods

2.1. Corpus

The corpus of glazed wares is composed of two batches. The first one comes from a 6th c. pottery workshop excavated in the early 2000s at the site of Lozenets (Sofia, Bulgaria), by a team of the National Archaeological Institute with Museum at the Bulgarian Academy of Sciences directed by M. Daskalov and S. Goryanova (Daskalov and Goryanova, 2009; Daskalov, 2024). The detailed study of the pottery material was carried out in 2022–2023 by E. Todorova, G. Giannaki, S. Goryanova and G. Guionova, in the framework of a French-Bulgarian PHC RILA and of a Bulgarian National Science Fund program (Todorova, 2024). Besides its chronology, the status of the site as workshop was of particular interest. Both glazed and unglazed wares were manufactured there, some in the same forms, and the typological repertoire includes both table and cooking wares. A sampling of 40 sherds well identified typologically, including 23 glazed wares² and 5 wasters, was selected for analysis (Fig. 2).

The second batch came from the excavations carried out in Limenas, Thasos (Greece), by the French School at Athens, the National and Kapodistrian University of Athens, the University of Lille and the Ephorate of Byzantine Antiquities of Kavala. The presence of glazed pottery in 6th c. contexts had already been pointed out by Blondé (Blondé et al., 2003) and Petridis (Petridis, 2013, p. 187; Petridis, 2015, p. 441-442; Petridis, 2022, p. 333) before its study was developed by Giannaki (Giannaki, 2024). No evidence of glazed pottery production was found in Limenas, but the extensive corpus of chemical data on Thasos in Lyon laboratory database was expected to help identifying local wares (Picon and Garlan, 1986; Blondé and Picon, 1999; Blondé, 2007). Within the highly fragmented glazed material of Thasos, 25 sherds among the best preserved typologically were selected for analysis (Fig. 2).

3. Analytical methods

The sherds were first examined under the binocular microscope, to gather basic information on the fabrics, the microstructures and the firing conditions.

They were all sampled for body analysis, carried out by Wavelength-Dispersive X-Ray Fluorescence (WD-XRF) at the ceramology platform of the "Archéologie & Archéométrie" laboratory in Lyon (CNRS UMR 5138, Lyon University), using a Bruker S8 Tiger spectrometer. Samples were cut out with a diamond-coated saw, the glazes were removed and subsampled for further analyses; when absent, an external layer, whose chemical composition is more liable to be altered during burial, was removed. After heating at 950 °C (to eliminate residual water, volatile elements and organics), cooling and grinding, 800 mg of ceramic powder was mixed with 3200 mg of flux (lithium metaborate and tetraborate). The mix was heated to liquid state in a gold and platinum crucible, then cast into a bead. Analyses were carried out on these homogeneous beads, of fixed geometry, which correspond to a mean chemical composition representative of the clayey material of the sherds. Twentyfour major and trace elements are quantified, after calibration of the setup using 40 geological standards (CRPG, USGS, NIST, British Chemical Standards...). The calibration is frequently checked using three in-house pottery standards.³ Out of the 24 elements determined, 17 major (MgO, Al₂O₃, SiO₂, K₂O, CaO, TiO₂, MnO, Fe₂O₃) and trace elements (V, Cr, Ni, Zn, Rb, Sr, Zr, Ba, Ce) are usually taken into account in subsequent multivariate statistical treatments.

A sub-sample of 14 sherds was selected for glaze analysis, based on the results of body analysis. Glaze analysis was carried out by SEM-EDS at the "Centre Technologique des Microstructures" in Lyon (CT μ , Lyon 1 University). Samples were embedded in a polyester resin, cut in a cross section in order to expose all the layers (ceramic body, slip if present, glaze), polished with a 0.25 μ m diamond paste and then coated with a layer of carbon. Prior to coating with carbon, the cross-sections were observed under a binocular microscope with magnifications in the range 10x to 115x. The study of the microstructures was mainly performed using backscattered electron (BSE) images which allow differentiating the various phases according to their atomic number.

Analyses were carried out using a FEI Quanta FEG 250 coupled to an Oxford Instruments Ultim® Max 65 mm² silicon drift detector. All measurements were operated at 15 kV acceleration voltage in 60 s by setting the working distance at about 10 mm. Standardless quantification was performed using a PAP correction method of the intensities. AZtecLive software was used for data acquisition and evaluation, and the reliability of the results was checked by measuring reference glasses and geological standards (Corning Brill B, C and D, DR-N).

4. Results and discussion

4.1. Body analysis and provenance issues

As the Sofia batch is workshop material, the provenance issues concern mostly the Thasos one. In both cases, chemical analysis was intended to identify the category of clay used for these glazed productions. Fig. 3 shows the classification of the whole sampling of glazed wares by hierarchical clustering analysis (HCA), based on the concentrations of 14 major and trace elements, 4 using standardized data, Euclidean distances and the average linkage aggregation criterium (e.g. Picon, 1984). A general feature of all the samples is that they are made of low-calcareous clays. Different chemical groups may be distinguished according especially to the Fe, Ti, K, Mg contents. One sample (TCW 93) stands out by its high contents in Si and Al (SiO $_2+{\rm Al}_2{\rm O}_3>90$ %), Ti and Zr, and low ones in alkali, alkali-earths and Mn, an association typical of kaolinitic clays. We will come back to this specific sample *infra*.

The samples from Sofia workshop form a homogeneous chemical group, with few marginal samples (BZN463, and BZN468 not represented in Fig. 3). A noticeable point is that glazed and unglazed wares have similar compositions (Table 1), indicating the use of the same

² these exclude sherds bearing only drops and drips of glaze, which probably dripped from a glazed ware stacked in the same kiln during firing.

 $^{^{3}}$ for further details on the analytical conditions and performances: Thirion-Merle, 2024.

⁴ In this specific case study, the concentrations in Sr, Ba and Zn were not included in the variables, as several were affected by pollutions during burial (Picon, 1991; Blondé, 2007).



Fig. 2. Representatives examples of the samples analyzed: Sofia workshop (above), Thasos (below), and specific cases (middle left: waster or second choice, Sofia; middle right: "Glazed White Ware I", Thasos) (Lyon lab. ids. are indicated, photos S.Y. Waksman).

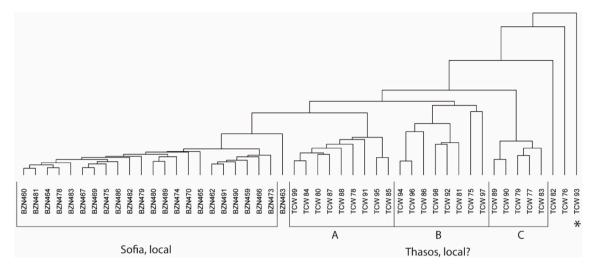


Fig. 3. Hierarchical clustering analysis based on the chemical composition of the bodies, whole sampling of glazed wares. The main chemical groups and sub-groups are underlined. The asterisk marks a sample (TCW 93) distinguished by a kaolinitic body.

clayey material which would have been appropriate for cooking uses too (e.g. Picon, 1995).

Thasos glazed wares are more heterogeneous. Most of them may however be gathered in a large group further sub-divided into 3 subgroups (Fig. 3, Table 1). The most consistent sub-group (C) has higher Fe, Mg, Cr, Ni, V contents than the others, with values remaining in the low ranges. The most distinctive sub-group (A) has low Fe and Ti contents (mean values \sim 5 % Fe₂O₃ and \sim 0.45 % TiO₂), a rather uncommon feature in low-calcareous bodies. The investigations carried out by M. Picon on Thasos clay procurement to manufacture various categories of wares (mostly amphorae, but also black gloss, common and, to a lesser extent, cooking wares), show the chemical variability of the clay materials exploited, which he relates to the restricted availability of the clay resources and their dissemination in small-scale deposits (Picon and Garlan, 1989; Blondé and Picon, 1999). Several workshops are identified on the island, mostly for the production of amphorae. Their chemical features may be differentiated from those of the glazed wares, with the possible exception of Molos workshop, the closest to Limenas (Picon and Garlan 1989, Garlan 2004). A group of amphorae from Thasos, including several collected on the workshop site of Molos, shows some chemical similarities, although not a close match (Table 1). The same may be said of other local references, tripod stilts related to a production of glazed wares of undefined chronology,⁵ and of cooking wares and lamps found in Limenas excavations, roughly dated to the same period as the glazed wares under study (5th-7th c.) (Petridis, 2013; Bia, 2023). Among a sampling of cooking wares and lamps⁶ of the Early Byzantine period studied together with F. Blondé (Waksman and Blondé, 2011), a small number, including a lamp interpreted as an overfired waster, presents fairly close chemical features (Fig. 4). The chemical compositions of most of the glazed wares and of a large part of the cooking wares with a micaceous fabric actually vary in a wide range of composition, which includes Thasian local references (Fig. 4). However, we cannot consider their local status as proven at this stage of research.

Another, kaolinitic, fabric is represented in Thasos by lamps, cooking wares and glazed wares (Petridis, 2013; Bia, 2023). Only one example was part of our corpus (Fig. 2, TCW 93), and a few kaolinitic lamps were analyzed in our previous study with Blondé. These are probably related

to another example bearing traces of glaze, found in Thasos in contexts dated to the end of the 6th – beginning of the 7th c. (Blondé et al., 2011; Petridis, 2013; Giannaki, 2024). The present study shows that sample TCW 93 is related neither to the kaolinitic lamps, nor to the kaolinitic cooking wares previously analyzed (Fig. 4). It is an import, as the histogram of distances with our reference group of glazed and unglazed "White Ware I" shows that it is well integrated into the latter (Fig. 5).

4.2. Glaze analysis and production techniques

A sub-sample of 14 sherds was selected for glaze analysis by SEM-EDS. The Sofia samples selected (BZN467, BZN469, BZN475, BZN478) are representatives of the most common glazed forms (jugs, mortars, Fig. 2) and of the main chemical group. In addition, 2 samples were expected to bring further information on the manufacturing techniques: BZN473 considered either a waster or a second choice due to many blisters on the surface of the glaze (Fig. 2), and BZN487, where the glaze is present only as drops with a central pinhole. 9

Thasos selection (TCW 75, TCW 80, TCW 84, TCW 88 to TCW 90) was taken among samples of the three chemical sub-groups (A, B, C, Figs. 3 and 4), and also included TCW 93, identified as an import of "Glazed White Ware I".

Observation of cross-sections of the sherds under a binocular microscope already brings a range of information. In all cases, the glaze is applied directly on the body, without an intermediate slip. The bodies of most of the Sofia samples are only partly reoxidized, a few remaining completely reduced (Fig. 6). In the former case (Fig. 6, left), the reduced part of the sherd always corresponds to the glazed side, which supports a single firing process, where reoxidation during cooling could only occur through the unglazed side. The blisters, occasional on many sherds and particularly abundant at the surface of sample BZN473, appear to be bubbles trapped at the surface (Fig. 6, right). The pinholes (Fig. 2) would be another aspect of the same phenomenon, due to

⁵ for a sub-contemporary production including glazed wares at Molos: Papadopoulos, 1995.

 $^{^6\,}$ The corpus of lamps is studied by P. Petridis and will be published as part of the final reports of the Thanar excavations in Thasos.

⁷ Although not a reference group *stricto sensu* as its Constantinopolitan origin has not been proven so far, it includes the very samples from Saraçhane used by Hayes to define this ware (Hayes, 1992; Waksman, 2017, 2019).

 $^{^{\}rm 8}$ The chronology of this glazed sample in Thasos contexts will be discussed by Giannaki in her PhD.

⁹ for more details on this sample, especially the high content of bismuth in inclusions present in its glaze as clue for the provenance of the lead compounds: Waksman et al., 2024.

¹⁰ for the firing cycle and the reducing or oxydizing atmosphere in the kiln during this cycle, e.g. Picon, 2002.

Table 1
Chemical composition of the bodies determined by WD-XRF, ranked as in Fig. 3, and comparative data (major and minor elements in oxide weight %, trace elements in ppm; m: mean, σ: standard deviation, n: number of samples; elements between brackets were not used in the HCA).

TCW 98 0.93 4.25 0.438 3.16 67.77 20.49 1.05 0.0211 1.55 0.14 158 113 139 78 38 13 57 675 53 TCW 92 1.44 4.33 0.453 3.07 68.44 19.26 0.95 0.0338 1.42 0.35 158 106 122 69 42 19 49 762 60 TCW 81 0.99 4.54 0.520 3.32 68.67 18.73 1.13 0.0246 1.62 0.21 178 109 130 74 48 16 56 724 59	Lyon id.	CaO	Fe_2O_3	TiO_2	K_2O	SiO_2	Al_2O_3	MgO	MnO	(Na_2O)	(P_2O_5)	Zr	(Sr)	Rb	(Zn)	Cr	Ni	La	(Ba)	V	C
BZN461 1.48	Sofia, Lozenets workshop																				
BZNA76 1.4 0.54 0.58 0.75 0.59 0.24 0.58 0.045 0.58 0.045 0.58 0.045 0.10 1.00 1.00 1.00 1.00 1.05 0.16 0.15 0.16 0.10 1.0	BZN460	1.46	5.45	0.671	2.70	65.95	20.27	1.55	0.0463	1.65	0.06	164	198	142	85	74	25	35	571	115	7
BZM478 1.44 5.31 0.681 2.64 6.29 20.22 1.54 0.0400 1.67 0.10 170 100 104 85 81 24 35 551 16 BZM460 1.45 5.45 0.690 2.09 6.59 19.05 1.46 0.0458 1.59 1.10 11 77 18 18 148 84 73 22 42 555 123 BZM460 1.47 5.50 0.680 2.59 6.51 19.05 1.46 0.052 1.51 1.10 1.10 10 18 18 148 84 73 22 42 555 123 BZM460 1.40 5.50 0.652 1.51 0.000 1.51 0.000 1.51 0.000 1.51 170 11 170 19 143 84 73 22 42 555 123 BZM460 1.40 5.50 0.652 1.50 0.000 1.51 0.00	BZN481	1.48	5.42	0.670	2.68	66.20	20.17	1.50	0.0427	1.56	0.11	163	187	144	87	74	24	29	556	111	7
BZX4467 1.45 5.56 0.679 2.06 0.554 1.98 1.49 0.018 1.59 0.11 1.70 1.89 1.41 8.6 7.4 2.5 4.1 5.56 1.25 1.50 1.25	BZN464	1.49	5.44	0.680	2.71	65.98	20.25	1.56	0.0450	1.58	0.09	166	192	148	85	76	25	39	544	117	8
BZNA96	BZN478	1.44	5.31	0.681	2.64	66.29	20.22	1.54	0.0460	1.57	0.10	170	190	145	85	81	24	35	551	116	8
BEZM469 1.49 5.70 0.680 2.65 6.11 2.000 1.51 0.0725 1.53 0.11 170 199 143 84 74 23 29 539 120	BZN483	1.45	5.45	0.679	2.60	66.54	19.89	1.49	0.0458	1.59	0.11	177	189	143	86	74	23	41	572	116	8
BZX446 1.4 5.56 0.672 2.63 06.21 1.987 1.47 0.0264 1.53 0.028 1.53 0.028 1.53 0.028 1.53 0.028 1.53 0.028 1.53 0.028 1.03 1.038 1.03	BZN467	1.42	5.56	0.680	2.59	66.59	19.95	1.46	0.0502	1.41	0.12	166	181	143	84	73	22	42	565	123	7
B224466 1.41 5.56 6.852 2.60 6.508 2.040 1.53 0.0434 1.54 0.08 174 184 141 88 74 24 34 569 115 0.08 174 184 141 88 74 24 34 569 115 0.08 174 184 141 88 74 24 34 569 115 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 88 74 24 34 569 116 0.08 174 184 141 141 141 141 141 141 141 141 14	BZN469	1.49	5.70	0.680	2.65	66.11	20.00	1.51	0.0522	1.53	0.11	170	199	143	84	74	23	29	593	120	7
BEZNHS6 1.41 5.56 0.682 2.00 6.598 2.0.40 1.53 0.045 1.55 0.085 17.7 148 141 88 7.4 2.4 3.4 5.60 115 12NHS2 1.75 5.70 0.045 2.01 6.05 19.86 1.41 0.045 1.53 0.041 1.05 0.08 17.3 178 150 83 7.4 2.4 3.4 5.60 115 12NHS2 1.55 1.05 1.05 1.05 1.05 0.05 1.05 1	BZN475	1.65	5.55	0.672	2.63	66.21	19.87	1.47	0.0526	1.53	0.20	173	209	138	83	74	24	39	652	111	7
BZY482 1.37 5.70 0.646 2.99 66.55 19.86 1.41 0.049 1.50 0.08 173 178 150 83 74 23 31 532 106 122 124 124 144 5.49 0.66 124 145 5.57 0.647 0.25 1.25 1.25 0.0431 1.50 0.047 1.53 0.14 196 191 143 83 72 24 32 5.62 12 12 12 12 12 12 12 12 12 12 12 12 12																74				115	7
BZM499 1.48																74					7
BZN489 1.43 5.67 6.67 6.67 6.02 2.71 6.602 2.013 1.50 0.0499 1.58 0.07 163 187 151 87 77 2.5 30 5.58 112 BZN489 1.45 5.57 6.062 2.04 6.574 20.25 1.55 0.0476 1.50 0.10 169 186 147 89 77 24 39 5.50 115 BZN470 1.51 5.45 6.66 6.069 2.02 1.56 0.0476 1.59 0.12 192 190 149 89 77 24 39 5.56 115 BZN476 1.54 5.65 6.069 3.12 6.009 2.007 1.68 0.046 1.75 0.15 188 186 143 89 80 25 35 567 115 BZN465 1.48 5.36 0.630 2.46 6.03 1.969 1.44 0.0452 1.59 0.08 153 187 140 82 71 24 37 543 126 BZN490 1.41 5.78 0.774 2.54 6.516 2.133 1.64 0.0454 1.39 0.08 153 187 140 82 77 2.5 33 557 104 BZN490 1.41 5.96 0.748 2.44 64.51 2.150 1.71 0.0438 1.40 0.08 173 181 141 93 84 27 31 542 129 BZN490 1.41 5.79 0.774 2.55 6.522 2.094 1.60 0.0478 1.38 0.14 170 184 143 89 78 2.5 35 556 127 BZN473 1.97 5.64 0.066 2.52 6.507 2.024 1.55 0.0533 1.71 0.17 178 2.13 153 83 74 24 36 578 278 BZN463 2.00 5.38 0.638 3.51 6.567 19.15 1.55 0.0533 1.71 0.17 178 2.13 153 83 74 24 36 578 278 BZN463 2.00 5.38 0.638 3.51 6.567 19.15 1.55 0.0533 1.71 0.17 178 2.13 153 83 74 24 36 578 794 122 BZN463 2.00 5.38 0.638 3.51 6.567 19.15 1.55 0.0533 1.71 0.17 178 2.13 153 83 74 24 36 578 794 122 BZN463 1.00																					7
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BZNA74 1.51 5.45 5.069 2.64 66.95 20.27 1.56 0.0476 1.59 0.12 190 149 89 77 23 30 5.76 115 158 186 143 89 25 23 55 567 115 158 186 186 143 89 25 23 55 567 115 158 186 186 143 89 25 25 567 115 187 186 143 89 25 25 25 25 201 2																					8
BENAYO 1.54 5.66 0.669 3.12 6.509 20.07 1.68 0.0446 1.75 0.15 1.88 186 143 89 80 25 25 35 567 115 16 BENAYOS 1.48 5.36 0.630 2.64 6.91 1.969 1.44 0.046 1.75 0.15 1.89 1.80 1.33 187 140 82 71 25 33 557 104 182 182 182 182 182 182 182 182 182 182																					8'
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TCW 98 0.93 4.25 0.438 3.16 67.77 20.49 1.05 0.0211 1.55 0.14 158 113 139 78 38 13 57 675 53 TCW 92 1.44 4.33 0.453 3.07 68.44 19.26 0.95 0.0338 1.42 0.35 158 106 122 69 42 19 49 762 60 TCW 81 0.99 4.54 0.520 3.32 68.67 18.73 1.13 0.0246 1.62 0.21 178 109 130 74 48 16 56 724 59 TCW 75 1.06 4.22 0.485 3.51 69.79 17.80 0.87 0.0563 1.55 0.28 186 126 149 83 50 23 56 1019 64	TCW 96	1.18	5.26	0.614	2.73	66.43	20.63	1.22	0.0228	1.47	0.21	171	89	119	71	54	17	42	498	86	9
TCW 98 0.93 4.25 0.438 3.16 67.77 20.49 1.05 0.0211 1.55 0.14 158 113 139 78 38 13 57 675 53 TCW 92 1.44 4.33 0.453 3.07 68.44 19.26 0.95 0.0338 1.42 0.35 158 106 122 69 42 19 49 762 60 TCW 81 0.99 4.54 0.520 3.32 68.67 18.73 1.13 0.0246 1.62 0.21 178 109 130 74 48 16 56 724 59 TCW 75 1.06 4.22 0.485 3.51 69.79 17.80 0.87 0.0563 1.55 0.28 186 126 149 83 50 23 56 1019 64	TCW 86	1.10	4.76	0.694	2.83	67.01	19.71	1.40	0.0317	1.82	0.23	194	114	106	66	88	32	56	647	82	11
TCW 92 1.44 4.33 0.453 3.07 68.44 19.26 0.95 0.0338 1.42 0.35 158 106 122 69 42 19 49 762 60 TCW 81 0.99 4.54 0.520 3.32 68.67 18.73 1.13 0.0246 1.62 0.21 178 109 130 74 48 16 56 724 59 TCW 75 1.06 4.22 0.485 3.51 69.79 17.80 0.87 0.0563 1.55 0.28 186 126 149 83 50 23 56 1019 64																					ç
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(continued on next p	1GW /3	1.00	7.22	0.403	5.51	07.79	17.00	0.07	0.0303	1.55	0.20	100	120	17)	0.5	50	23				
																			(continue	ı on nex	t pag

Lyon id.	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	SiO ₂	Al ₂ O ₃	MgO	MnO	(Na ₂ O)	(P ₂ O ₅)	Zr	(Sr)	Rb	(Zn)	Cr	Ni	La	(Ba)	V	Ce
TCW 97	1.10	4.97	0.662	3.62	67.58	19.05	1.07	0.0258	1.53	0.21	230	129	170	92	70	20	52	678	77	101
sub-group C																				
TCW 89	1.62	6.39	0.657	3.40	64.60	18.70	2.28	0.0805	1.77	0.19	189	229	159	145	120	76	48	663	133	89
TCW 90	1.45	6.00	0.664	3.43	65.10	18.86	2.20	0.0748	1.81	0.18	188	232	165	144	118	72	47	675	133	89
TCW 79	1.93	5.92	0.667	3.38	64.26	18.96	2.36	0.0568	1.75	0.45	185	234	151	136	125	72	40	644	118	92
TCW 77	2.20	5.88	0.614	3.43	64.59	18.71	2.13	0.0563	1.77	0.37	177	256	160	143	114	66	42	731	121	88
TCW 83	2.66	5.76	0.656	3.49	63.84	18.62	2.31	0.0678	1.93	0.40	184	267	159	135	116	65	45	718	107	100
TCW 82	5.21	6.00	0.576	3.29	64.47	16.58	2.27	0.0581	1.20	0.14	123	226	154	82	103	71	29	584	101	73
TCW 76	3.12	6.45	1.013	4.27	56.98	23.31	2.18	0.0678	0.51	1.28	226	82	149	149	170	85	33	953	128	96
Thasos, Glazed White Ware I																				
TCW 93	0.27	3.68	1.251	1.69	71.94	20.37	0.51	0.0168	0.03	0.06	316	26	82	36	89	28	52	371	92	112
Comparative data																				
Sofia, Lozenets workshop, glazed and unglazed wares (n =																				
38, (Waksman et al., 2024)																				
m	1.55	5.58	0.681	2.65	65.86	20.25	1.52	0.0461	1.53	0.15	170	201	142	87	76	25	35	610	117	77
σ	0.23	0.16	0.027	0.13	0.62	0.47	0.09	0.0034	0.08	0.13	10	31	4	3	3	1	4	112	7	6
Thasos, Molos workshop, amphorae ($n = 27$)																				
m	2.15	4.75	0.614	3.37	64.41	21.86	1.83	0.0877	0.14	0.61	208	69	101	95	64	45	61	652	67	99
σ	1.44	0.53	0.073	0.30	1.17	1.20	0.40	0.0191	0.19	0.68	16	19	17	12	14	7	27	137	13	6
Takenhal County Class I White Wass I (c. 16 Walsons																				
Istanbul, Saraçhane, Glazed White Ware I (n = 16, Waksman et al. 2007)																				
m	0.78	5.71	1.104	1.44	69.22	20.37	0.61	0.0229	0.45	0.12	285	41	71	45	86	32	45	330	112	91
σ	0.78	0.77	0.114	0.26	2.44	20.37	0.01	0.0229	0.43	0.12	36	10	15	43 5	12	6	8	78	21	17
	0.00	0.77	0.211	0.20		_,11	0.10	0.0007	3.50	3.07	30	10	10		12	-	-	, 0	21	

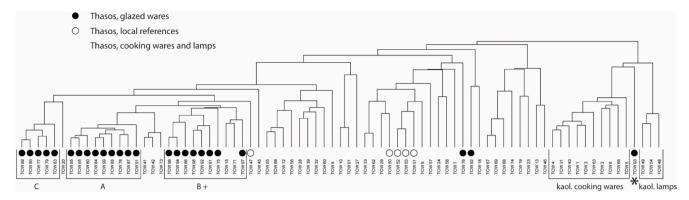


Fig. 4. Hierarchical clustering analysis based on the chemical composition of the bodies, Thasos glazed wares together with Thasos cooking wares and lamps found in Late Roman contexts, micaceous and kaolinitic fabrics (after Waksman and Blondé, 2011). The asterisk marks a glazed sample (TCW 93) distinguished by a kaolinitic body.

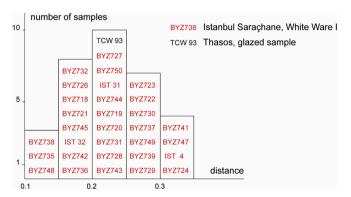


Fig. 5. Histogram of Euclidean distances between the reference group of "Byzantine White Ware I" and Thasos sample TCW 93.

bubbles of gases either trapped in the glaze (blisters) or which exploded leaving a cavity (pinholes). Both would be favoured by a single firing, as a first, biscuit firing prior to glazing and second firing would have liberated gases due e.g. to organic material contained in the clayey body, and thus avoid such glazing defects.

The firing conditions of Thasos samples are less consistent and display various aspects (bodies completely reduced, or completely reoxydized even with both surfaces glazed, and several intermediate cases) which do not provide such a clear picture.

SEM-EDS analyses of the glazes indicate that they are high-lead ones, with Na₂O + K₂O contents usually below 1 % (Table 2). The iron concentrations between 1.5 and 3 % FeO may account for the greenish to brown colour of the glazes, when applied on a reduced or oxidised body surface, respectively. The glaze compositions are not very homogeneous, but may be seen as variants of a similar "recipe", with no clear pattern related either to the site (Sofia or Thasos) or to the chemical subgroup of the bodies. One sample stands out, though, the import of "Glazed White Ware I" (TCW 93), with lower lead, higher alumina and much higher silica concentrations (more than 30 % SiO2, versus an average of c. 20 % for the other samples, Table 2). These features are in good agreement with previous data on "Glazed White Ware I" (Waksman et al., 2007). Fairly developed interfaces between the body and glaze (Fig. 7) tend to support the hypothesis of a single firing, although several other parameters should theoretically be taken into account (Molera et al., 2001; Cormier and Godet, 2022 with further literature). Most of the inclusions present at the interfaces are rich in Pb, Si, and to a lesser extent Al and K, which suggest that they may be lead felspars, which may develop at the interface between high-lead and lowcalcareous bodies (Molera et al., 2001, Cormier and Godet, 2022 with further literature).

The technical tradition our samples belong to may be better understood when compared with other Roman, Late Roman and Early Byzantine glazed wares, as seen on the binary plots presented Fig. 8.¹ The CaO/SiO₂ + Al₂O₃ plot (left) differentiates samples having low- and high-calcareous bodies. On the right hand side of the figure, the SiO₂ content of the body is plotted against the SiO2 content of the glaze, recalculated without the contribution of PbO. This diagram may been used to evaluate if a glazing mix containing an addition of silica was used (SiO2 glaze recalculated > SiO2 body), or if the lead compounds (usually sulfides or oxides) combined with the silicon of the body to form the glaze during firing (dots around the first bisector) (Hurst and Freestone, 1996; Walton, 2004; Waksman et al., 2008; Walton and Tite, 2010; see also Cormier and Godet, 2022 for details and requests for caution in the use of such diagrams). Fig. 8 (left and right) illustrates two technical traditions: on the one hand the association of calcareous bodies with a (possibly pre-fritted) glazing mix containing an addition of silica, on the other hand non-calcareous bodies on which lead compounds were applied as such (or mixed with the same clay). The Late Roman batches examined, including Sofia's and Thasos', belong to the second tradition, as well as the Early Byzantine "Glazed White Ware I" (Waksman et al., 2007, 2008). These results are in good agreement with previous studies by Capelli et al. on Late Roman glazed wares found in Northern Italy, Hungary, and Bulgaria, and on the 5th c. production site of Carlino (Walton and Tite, 2005; Capelli et al., 2009, 2010a, 2010b).

5. Concluding remarks

The archaeometric study of ceramics from Bulgaria and Northern Greece provided the opportunity to investigate little known 6th c. AD glazed wares, at the transition between the Late Antique and the Early Byzantine periods. In Sofia (Bulgaria), they came from a workshop context, and are shown to be made of the same clayey material as unglazed common and cooking wares fired in the same kilns. The analyses suggest that their high-lead glazes were manufactured with lead compounds which combined with the silica of the body to form the glaze during a single firing. In Thasos, the same technical features are observed, with an association of high lead-glazes applied on low-calcareous bodies. For the majority of the glazed samples of Thasos, a local origin is possible but not demonstrated. On the other hand, the analyses clearly show the presence of an example of Byzantine "Glazed White Ware I", which is actually the only import of this ware confirmed

¹¹ adapted from Waksman et al., 2008, where the description of the comparative material considered may be found.

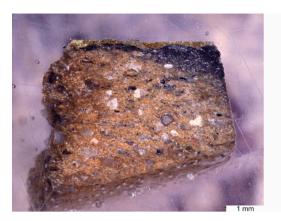




Fig. 6. Polished cross-sections under the binocular microscope, showing total reduction (right, BZN473) or partial reduction (left, BZN469) of the clayey body on the glazed side. A large bubble at the surface of the glaze covered by crusting is also visible (right). Sofia workshop samples (photos J. Burlot).

Table 2Chemical composition of the glazes determined by SEM-EDS (in oxide weight %).

Lyon id.	Na ₂ O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	PbO
Sofia, Lozenets workshop									
BZN466	0.3	0.6	7.1	20.9	0.4	0.8	0.3	2.4	67.1
BZN467	0.4	0.5	5.9	18.2	0.6	0.7	0.2	1.8	71.7
BZN469	0.2	0.5	5.8	16.3	0.4	0.9	0.2	1.8	73.9
BZN473	0.3	0.4	5.2	15.7	0.3	1.3	0.2	1.7	74.9
BZN475	0.2	0.5	5.3	17.9	0.6	0.7	0.2	2.8	71.8
BZN478	0.3	0.5	6.0	19.8	0.5	0.5	0.2	1.8	70.3
BZN487	0.6	0.7	7.5	22.4	0.7	0.9	0.3	2.4	64.6
Thasos, local?									
TCW75	0.3	0.5	6.4	20.4	0.6	0.7	0.3	2.1	68.7
TCW80	0.6	0.9	6.6	25.7	0.9	2.0	0.2	2.2	60.8
TCW84	0.2	0.7	5.7	19.8	0.6	1.2	0.2	2.3	69.3
TCW88	0.4	0.5	5.2	17.7	0.4	0.6	0.1	1.7	73.2
TCW89	0.4	0.9	6.2	22.5	0.7	1.0	0.3	2.0	66.0
TCW90	0.4	1.0	6.8	22.1	0.6	1.5	0.3	2.4	65.0
Thasos, Glazed White Ware I									
TCW93	0.2	0.2	8.6	30.8	1.0	0.5	0.6	1.6	56.5

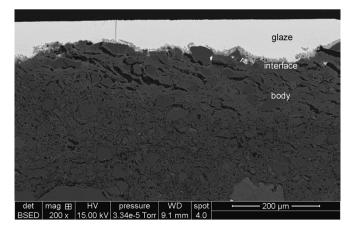


Fig. 7. Representative example of a glazed ware as seem under the SEM, BSE mode: the high-lead glaze is applied directly on the low-calcareous body, without intermediate slip; inclusions are visible at the interface between the body and the glaze (sample BZN466, Sofia) (photo L. Geay, $CT\mu$).

by chemical analyses so far.¹² Also noticeable in Thasos is the presence in the same contexts of other wares having a kaolinitic body, possibly including glazed lamps, which are distinct from the series of "Byzantine Glazed White Ware" attributed to Constantinople (Waksman, 2019).

Our data seem to fill what was previously seen as a gap between the 4th — early 5th c. Late Roman glazed productions, well identified archaeologically from the Balkans to Northern Italy, and the 7th c. Byzantine "Glazed White Ware I" defined in Constantinople/Istanbul and confirm Trivyzadaki's and Petridis' earlier suggestions. They suggest the continuity of a technical tradition which may last in the Byzantine mainlands until the short-lived emergence in the 10th c. of glazing techniques coming from the Islamic world, with the "Polychrome White Ware" (Waksman et al., 2024), and fade away at the beginning of the 12th c., with the spectacular development of glazed wares productions (Sanders, 1995, 2003) using a wide variety of clay

The results of the state of the

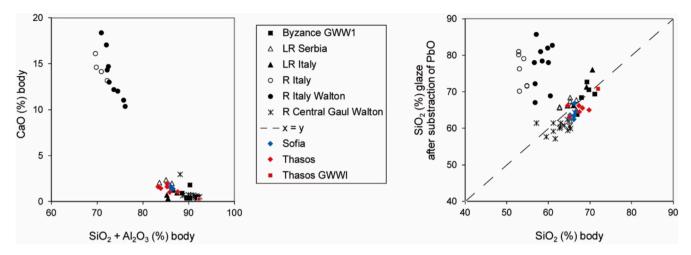


Fig. 8. Binary plots showing selected chemical features of the bodies and glazes of the samples, together with data from the literature; two different technical traditions are illustrated: a glazing mix mainly involving Pb and Si compounds applied on calcareous bodies, as opposed to low-calcareous bodies on which Pb compounds were applied directly or mixed with the same clay (R: Roman, LR: Late Roman, GWWI: "Glazed White Ware I"; adapted from Waksman et al., 2008).

bodies and decoration techniques enabled by the introduction of underglaze slips.

CRediT authorship contribution statement

S.Y. Waksman: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft. G. Giannaki: Funding acquisition, Investigation. J. Burlot: Investigation, Methodology. E. Todorova: Conceptualization, Funding acquisition, Investigation, Methodology, Writing – review & editing, Project administration. M. Daskalov: Investigation, Project administration. G. Guionova: Investigation. P. Petridis: Conceptualization, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data are contained in the manuscript

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