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Between the Byzantine and the Islamic worlds? Byzantine Polychrome White Ware

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ABSTRACT

Byzantine Polychrome White Ware (PWW) is special among Byzantine glazed ceramics. It stands out by its sophisticated motifs and its uses, as architectural ceramics and icons, in addition to tableware. This study is based on about 30 sherds of PWW pottery coming from archaeological contexts dated back to the 10th and 11th c., in Greece (Hierissos and other sites in Chalkidiki) and Turkey (Saraçhane in Istanbul). It shows their Constantinopolitan origin, based on kiln material found in the Metro-Marmaray excavations in Istanbul. It also shows how Polychrome White Ware stands out from the traditional Byzantine technological know-how, with the use of lead-alkali glazes, sometimes opacified with tin, and of Co pigments. On the contrary, these features are widespread in Islamic productions of the same period.

1. Introduction

As the most elaborate of Byzantine ceramics, "Polychrome White Ware" (PWW) have attracted the attention of scholars, especially art historians and curators, and also archaeologists and archaeological scientists (Mason and Mundell Mango, 1995; Maguire, 1997; Gerstel and Lauffenburger, 2001; Gerstel, 2010). Some of these ceramics are spectacular by virtue of their motifs and the richness of their decoration, which is sometimes enhanced by gilding. Examples found their way to museum collections such as the Walters Art Gallery, the Louvre, Sèvres, Benaki and Istanbul Archaeological Museums (Durand and Vogt, 1992; Durand, 1997; Papanikola Bakirtzi et al., 1999; Gerstel and Lauffenburger, 2001; François, 2017). PWW exist both as architectural ceramics and as pottery. Previous research focused mostly on the former, which adorned several monuments in the Byzantine capital Istanbul/Constantinople and include remarkable icons, with a comprehensive synthesis proposed in 2001 (Gerstel and Lauffenburger, 2001). PWW pottery is far from being as well known. Yet its study has great potential, especially when it comes from well-defined archaeological contexts, which may give insight into their chronology, uses and social value. Furthermore, the workshop(s) they came from, their area of diffusion and the way in which they were commercialized, the techniques which

were used to manufacture them, are issues which have hardly been addressed.

The last point is of special interest, as PWW presents a remarkable variety of colours unknown in the other Byzantine glazed wares. In addition to stylistic connections, several clues supported by previous archaeometric studies (Henderson and Mundell Mango, 1995; Vogt and Bouquillon, 1996; Vogt et al., 1997; Bouquillon and Durand, 1998; Lauffenburger et al., 2001) such as the turquoise colour implying glazes including alkali fluxes, the dark blue colour provided by cobalt pigments, lead us to consider PWW as a technological link between the Byzantine and Islamic worlds (Waksman, 2021a). This technological connection had remained either undetected (Armstrong et al., 1997), or unnoticed (Vogt and Bouquillon, 1996; Vogt et al., 1997; Lauffenburger et al., 2001), or misunderstood (Armstrong, 2020, with a reply by Freestone, 2021), and we intended to investigate it further.

Another issue which deserved further research was the question of provenance. Although production in Nicomedia (Izmit, Turkey) is supported by texts and finds in that area (Mason and Mundell Mango, 1995; Gerstel, 2010), and workshops of PWW were excavated in Preslav (Bulgaria) (for a synthesis of the Bulgarian evidence: Kostova, 2009; Goryanova and Grozdanova, 2019), the majority of scholars, following Hayes (1992), attribute the main production of PWW to the region of

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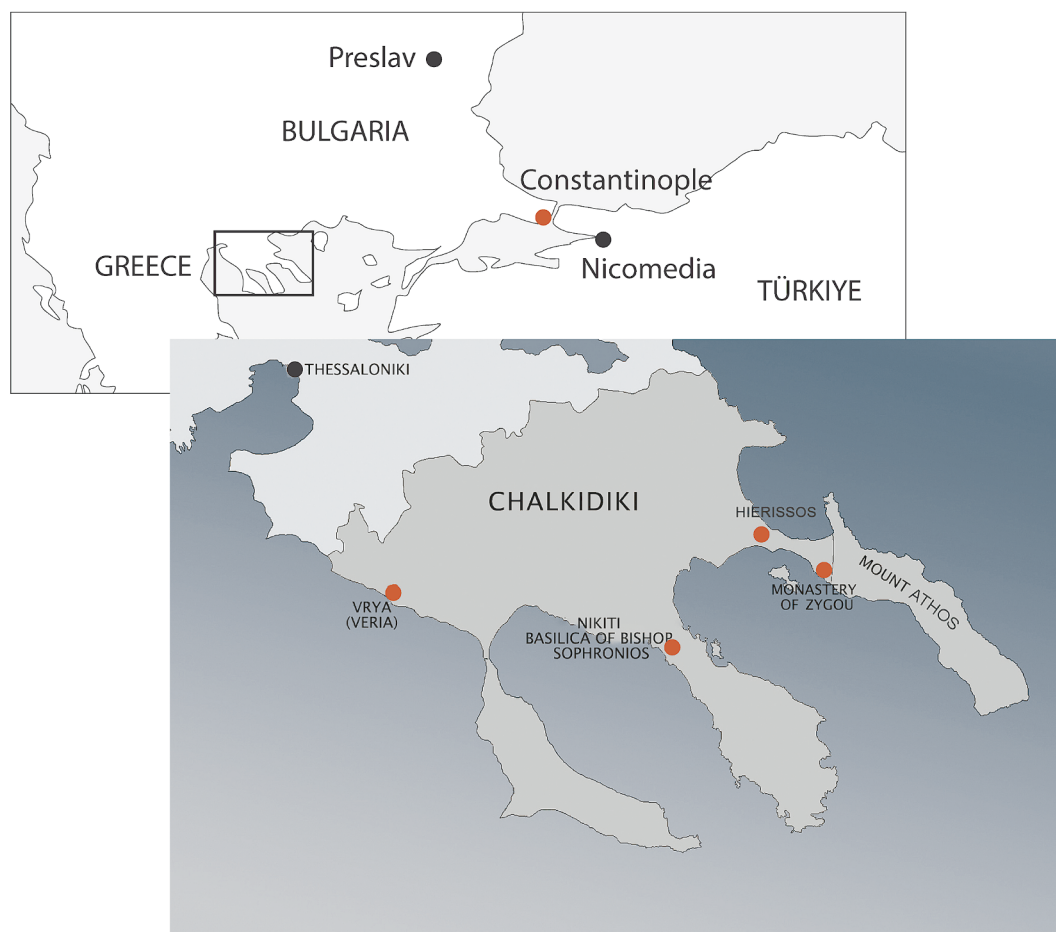


Fig. 1. Location of the sites sampled (in red) or mentioned in the text (D. Giovis, S.Y. Waksman). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Constantinople. Two pottery workshops found in the large-scale Metro-Marmaray excavations in Istanbul recently provided for the first time the opportunity to reconsider pottery production in the Byzantine capital, based on material evidence (Kızıltan, 2007; Waksman and Girgin, 2008; Waksman, 2012, 2021b).

This paper presents the first steps of our investigations, through the archaeometric study of 29 PWW pottery samples found in archaeological excavations in Istanbul (Turkey) and in several sites of Chalkidiki (Greece) (Fig. 1), using WD-XRF (provenance studies) and SEM-EDS (technological studies). It focuses on the main features of their body and glazes, while further research will develop more specific aspects such as the provenance of the pigments.

2. Sites and samples

The site of Saraçhane in Istanbul has been used as a reference for Byzantine pottery studies ever since the publication of its assemblages by J.W. Hayes (1992). We (S.Y. Waksman) had the exceptional privilege to access to a very small part of this material back in the early 2000s. Although only three samples of PWW come from Saraçhane (Table 1, Fig. 2),¹ including one published by Hayes (1992, BP14, plate 8f), they enable us to inscribe our research in the main typo-chronology of Byzantine White Ware in general, and PWW in particular (see also Sanders, 2001), thanks to material from the very site where it was established.

Most of the samples come from excavations conducted by the Ephorate of Antiquities of Chalkidiki and Mount Athos (former 10th Ephorate of Byzantine Antiquities) in different sites of the peninsula of Chalkidiki in Northern Greece – namely the medieval cities of Hierissos and Vrya (modern Veria), the basilica of Bishop Sophronios in Nikiti and the fortified monastery of Zygos (Fig. 1, Table 1). They yielded impressive assemblages of PWW (approximately 87 sherds, an exceptional number outside the capital, to be compared to the 175 sherds found at Saraçhane: Hayes, 1992, p. 35). The majority of the PWW – about three quarters of the material – comes from prosperous dwellings, storage places and workshops of the *extra muros* area and from the port district of the medieval town of Hierissos (Tsanana, 2024, with bibliography). In this site located in the close vicinity of the Mount Athos, PWW were found in well-defined archaeological contexts dating from the second half of the 10th to the end of the 11th century, along with a large quantity of other glazed ceramics and a significant number of coins. It mainly belongs to Hayes' classes I and III (Table 1), the former including examples of human and animal representations (BZN412, BZN413, BZN432) (Fig. 2). A detailed archaeological and stylistic presentation of the PWW from excavations in Chalkidiki may be found elsewhere (Tsanana and Amprazogoula, 2021; see also Poulou, 2021 for other examples found in Greece).

3. Experimental procedures

3.1. WD-XRF

Chemical analyses of the bodies were carried out by Wavelength-

¹ One of these samples was very small and is not illustrated.

Table 1

List of the samples of Polychrome White Ware considered; the site of discovery and the class according to Hayes (1992) are indicated.

Lyon id.	site	Inventory n°	Hayes class
BZN409	Hierissos	AE 13775	III
BZN410	Hierissos	AE 13781	III
BZN411	Hierissos	AE 13785	III
BZN412	Hierissos	AE 13712	I
BZN413	Hierissos	AE 13726	I
BZN414	Hierissos	AE 13734	I
BZN416	Hierissos	AE 13733 + 13735	II
BZN417	Hierissos	AE 13722	III
BZN418	Hierissos	AE 13723	III
BZN419	Hierissos	AE 13768	I
BZN420	Hierissos	AE 13766	III
BZN422	Hierissos	AE 13745	I
BZN424	Hierissos	AE 13754	II
BZN425	Hierissos	AE 13747	III
BZN426	Hierissos	AE 13748	III
BZN427	Hierissos	AE 13744	III
BZN428	Hierissos	AE 13788	I
BZN429	Hierissos	AE 13715	I
BZN430	Hierissos	AE 13740	I
BZN431	Sofroniou basilica	AE 13711	I
BZN432	Sofroniou basilica	AE 6707	I
BZN433	Zygou monastery	Z312	III
BZN434	Veria	AE 13875	III
BZN436	Veria	AE 13793	II
BZN437	Veria	AE 13866	III
BZN438	Hierissos	AE 13778	I
BZY778	Saraçhane, Istanbul		?
BZY779	Saraçhane, Istanbul		I
BZY780	Saraçhane, Istanbul	BP14	I

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, in a way which alters as little as possible the form and the decoration of the sherd. The glazes were 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. Twenty-four major and trace elements were quantified, after calibration of the set-up using 40 geological standards (CRPG, USGS, NIST, British Chemical Standards, ...). The calibration is frequently checked using three in-house pottery standards. Out of the 24 elements determined, seventeen 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.

3.2. SEM-EDS

Glazes analyses were carried out by SEM-EDS at the “Centre Technologique des Microstructures” in Lyon (CTμ, Lyon 1 University), and at the Center for research and restoration of the museums of France (C2RMF) in Paris.

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 μm 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.

At the CTμ, 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 tested by measuring reference glasses and geological standards (Corning Brill B, C and D, DR-N).

At the C2RMF, the chemical characterization was performed using a JEOL 7800F SEM coupled with two SDD Bruker AXS 6|30 Energy-Dispersive X-Ray Spectrometers. The experimental conditions were an acceleration voltage of 15 kV using a 2 nA electron beam current. The software Bruker Esprit allows us to quantify the results using a library of standards and the φ(ρz) method.

The compositions of the glazes are given as an average of three to five measurements on different zones selected within the regions of interest, avoiding the weathered areas and the glaze-body interface. Analysed zones range in size from 500 to 15,000 μm² due to variations in the thickness of the weathered layers. Some inclusions such as cassiterite crystals are included in these zones, while others were investigated separately by spots analysis.

4. Results and discussion

4.1. Chemical analyses of the bodies and provenance study

The PWW bodies have high contents in silicium and aluminium (SiO₂ + Al₂O₃ in the range 87.5–95.5 %), and usually low ones in alkali, alkali-earth and manganese, which indicates a dominant proportion of kaolinitic clays (Table 2). These features are common to all the Byzantine White Wares as defined by Hayes (1992) (Bouquillon and Durand, 1998; Waksman et al., 2007; Waksman and Girgin, 2008; Bouquillon, 2017; Waksman, 2021b). Hierarchical clustering analysis² of the PWW samples from Chalkidiki and Istanbul (Fig. 3) shows one main group, which is not very homogeneous, and samples which are more or less marginal to it. There is no apparent correlation between potential sub-structures and either the typological classes of PWW according to Hayes, or the site the samples come from (Fig. 3, Table 2). Various trends are observed in the marginal samples, including higher contents in Zn and/or Ba, V, Mn, interpreted as pollutions during burial (e.g. Picon, 1991). A sub-group of three samples (BZN410, BZN438, BZN420) has much higher Fe and Mn concentrations, related to large reddish inclusions visible to the naked eye. Nodules of iron oxides of various sizes are frequent in kaolinites, and Fe, Mn and V are quite variable in the main group too, so that these differences may not be significant. The most marginal sample (BZN422) stands out especially with its much higher concentrations in REE and associate element Y.³ But even the latter may be found in kaolinites due to the occasional presence of monazites (e.g. Waksman et al., 2003).

Whether these samples may all have the same origin can better be approached when examining the chemical features of the presumed sources. Unlike previous archaeometric studies of PWW (Mason and Mundell Mango, 1995; Vogt and Bouquillon, 1996; Vogt et al., 1997; Armstrong et al., 1997; Bouquillon and Durand, 1998; Lauffenburger et al., 2001; Bouquillon, 2017), we could rely on the extensive body of comparative data of CERAMO, the Lyon laboratory database of chemical analyses. Out of its 40.000 samples or so, about 4000 correspond to medieval Eastern Mediterranean ceramics, especially Byzantine ceramics including Byzantine White Wares dated from the 7th to the 13th

² Using normalized data, Euclidean distances and average linkage, e.g. Picon, 1984.

³ The concentrations in La and Y, not indicated in Table 2 as several values are close to or below detection limits, are the following for sample BZN422: 64 ppm La, 48 ppm Y.



Fig. 2. Samples of Polychrome White Ware analyzed and associated class according to Hayes (1992). Lyon laboratory ids. are indicated (D. Giovis, S.Y. Waksman).

c. AD. Previous studies showed them to constitute different chemical groups well correlated with Hayes' classification, in particular: Glazed and Unglazed White Ware I, further abbreviated WWI, Glazed White Ware II (GWWII), and late Glazed White Ware (late GWW) which may

include and continue his Glazed White Ware IV (Waksman et al., 2007; Waksman and Girgin, 2008; Waksman, 2019, forthcoming). Our WD-XRF and XRD data also concerned clays collected during surveys, which showed the kaolinitic clays Byzantine White Wares are made of to

Table 2
Chemical composition of the bodies of the PWW samples 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; elements between brackets were not used in the HCA, data with an asterisk were not used in the calculation of m and σ).

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	Ba	V	Ce
BZN429	0.42	1.95	1.067	0.61	72.63	22.43	0.55	0.0184	0.13	0.04	143	33	29	42	76	12	170	200	46
BZN430	0.39	1.98	1.076	0.57	72.37	22.73	0.57	0.0182	0.15	0.04	144	27	28	44	76	14	112	202	39
BYZ780	0.35	1.56	1.114	0.77	71.49	23.62	0.55	0.0172	0.35	0.05	142	32	35	54	47	19	168	200	38
BZN412	0.44	1.67	1.083	0.72	73.34	22.02	0.50	0.0174	0.07	0.04	139	34	35	44	60	16	210	186	47
BZN418	0.47	1.82	1.063	0.95	75.52	19.44	0.50	0.0209	0.05	0.05	136	38	35	41	54	13	212	165	39
BZN434	0.29	2.01	1.087	0.83	75.39	19.62	0.48	0.0137	0.13	0.03	137	40	34	36	59	11	200	206	49
BZN428	0.42	3.90	1.140	0.52	70.17	23.02	0.55	0.0248	0.09	0.06	141	37	32	72	53	17	197	187	43
BZN431	0.42	3.70	1.161	0.63	69.91	23.38	0.56	0.0298	0.06	0.05	150	39	32	80	54	17	174	160	48
BZN419	0.36	2.60	1.142	0.49	71.26	23.35	0.55	0.0265	0.10	0.03	145	31	28	55	71	16	208	179	51
BZN411	0.38	1.83	1.197	0.35	69.58	25.86	0.53	0.0189	0.11	0.04	164	35	21	52	61	21	165	166	62
BZN437	0.42	4.16	1.213	0.51	69.73	23.18	0.53	0.0196	0.05	0.04	162	35	24	57	67	18	154	185	43
BZN417	0.44	2.97	1.208	0.42	69.84	24.11	0.55	0.0162	0.28	0.04	145	38	24	72	45	17	230	157	50
BZN426	0.37	2.90	1.215	0.38	70.05	24.17	0.52	0.0154	0.22	0.05	144	36	21	67	47	16	249	186	45
BZN413	0.54	2.03	1.167	0.46	68.69	26.23	0.59	0.0165	0.14	0.03	148	41	26	59	48	20	263	170	53
BZN425	0.46	2.04	1.141	0.60	69.52	25.31	0.60	0.0206	0.14	0.04	138	36	25	53	46	21	207	168	54
BZN433	0.35	3.06	1.097	0.40	68.97	25.23	0.50	0.0129	0.07	0.19	148	29	20	54	70	19	173	155	37
BYZ779	0.56	1.53	1.106	0.85	69.24	25.50	0.56	0.0161	0.33	0.15	142	40	36	69	59	24	220	219	51
BZN409	0.39	3.73	1.074	0.72	68.12	25.03	0.62	0.0309	0.07	0.05	166	27	31	40	89	16	185	223	46
BYZ778	0.37	1.41	1.056	0.63	64.70	30.66	0.53	0.0135	0.31	0.11	139	30	32	86	40	25	215	162	49
BZN410	0.46	*7.41	1.130	0.65	63.85	25.54	0.62	*0.0396	0.12	0.06	142	36	38	81	64	17	191	210	43
BZN438	0.56	*9.13	1.113	0.67	62.45	25.05	0.63	*0.0505	0.18	0.07	139	37	37	83	56	17	192	206	46
BZN420	0.50	*7.05	1.091	0.66	66.76	23.06	0.57	*0.0424	0.08	0.07	137	37	35	76	59	14	206	192	44
BZN414	0.44	4.70	1.111	0.74	67.47	24.61	0.64	0.0356	0.05	0.08	137	36	35	*167	73	15	186	242	55
BZN416	0.41	1.82	1.048	1.09	75.72	19.22	0.45	0.0210	0.06	0.04	128	45	46	29	55	10	301	160	38
BZN424	0.35	1.96	1.034	1.31	73.71	20.82	0.49	0.0151	0.14	0.05	136	63	53	25	73	9	267	257	35
BZN432	0.78	3.71	1.149	0.78	68.80	23.04	0.61	0.0442	0.47	0.48	137	50	28	83	49	17	291	179	45
BZN436	0.72	2.53	1.137	0.99	70.06	23.47	0.64	0.0316	0.18	0.08	137	80	33	65	57	13	314	201	46
BZN427	0.45	3.80	1.194	1.41	67.60	24.32	0.67	0.0238	0.26	0.06	231	35	70	79	88	48	219	177	80
m	0.45	2.61	1.122	0.70	69.89	23.72	0.56	0.0216	0.16	0.08	146	38	33	59	61	18	210	189	47
σ	0.11	0.97	0.052	0.26	3.26	2.33	0.05	0.0077	0.11	0.09	19	11	10	18	13	7	46	26	9
BZN422	0.31	2.20	1.147	1.87	70.37	22.71	0.82	0.0159	0.32	0.05	248	43	133	41	115	41	395	143	201
Istanbul Sirkeci (Waksman and Girgin, 2008)																			
Glazed White Ware II																			
m	0.79	2.17	1.144	0.75	71.51	22.31	0.50	0.0112	0.10	0.27	140	66	27	64	49	29	210	188	37
σ	0.35	0.65	0.074	0.22	1.94	2.23	0.05	0.0031	0.13	0.28	11	29	6	8	9	5	55	29	8
IST 2	0.25	3.17	1.081	3.01	71.44	19.87	0.84	0.0070	0.11	0.06	266	40	172	27	117	55	440	126	209
IST 3	0.25	3.01	1.072	3.11	71.57	19.88	0.84	0.0090	0.02	0.07	268	40	170	29	117	56	423	128	216

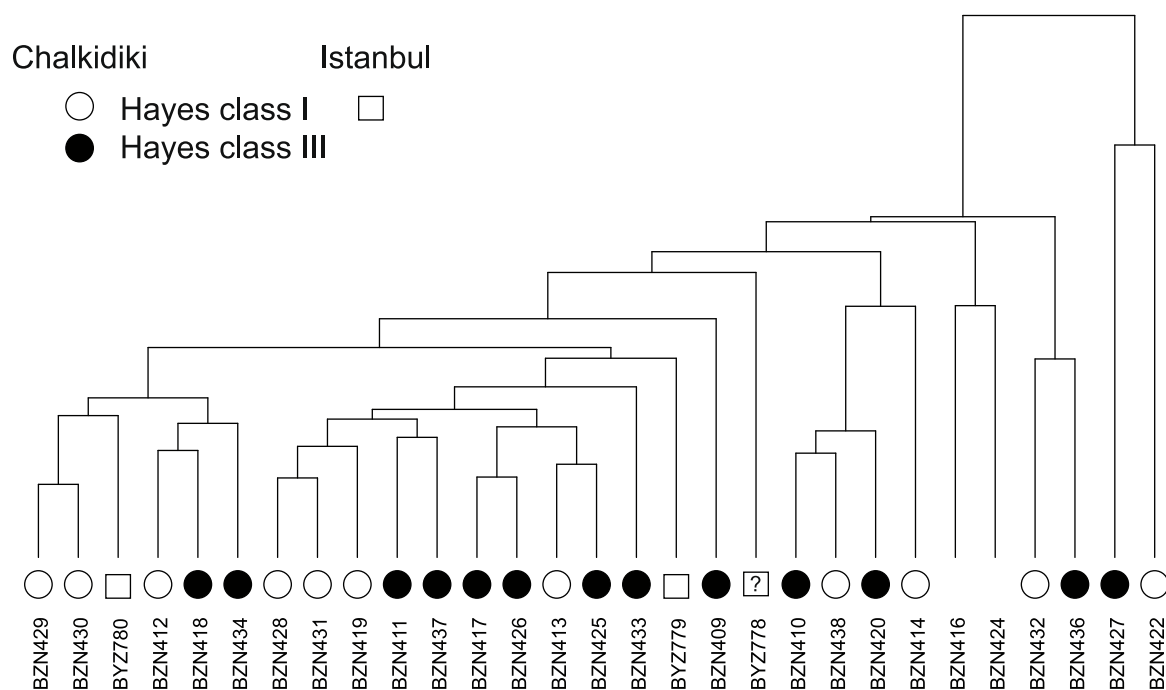


Fig. 3. Hierarchical clustering analysis, based on the concentrations of 17 elements in the bodies of the Polychrome White Ware samples (see text). Symbols refer either to the sites of discovery, or to the main classes according to Hayes (1992) represented in the sampling (S.Y. Waksman).

be abundant in the region between the historical peninsula of Istanbul and the Black Sea (Waksman, 2006, 2019, forthcoming).⁴ These large-scale resources extend over a wide area and have quite variable chemical and mineralogical compositions, which makes it difficult to locate those used in the Byzantine and Ottoman periods precisely. The discovery in the Metro-Marmaray excavations of two pottery workshop contexts enabled us to circumvent this difficulty and provided safe local references for Constantinopolitan productions, including Byzantine White Ware (Waksman and Girgin, 2008; Waksman, 2012, 2021b). GWWII were shown to be local thanks to these references, and the inclusion in the same chemical group of the three PWW from Saraçhane suggested that they were local as well (Waksman, 2021a). The analyses of the Chalkidiki examples now confirm this point (Table 2).

The binary plot aluminium-zirconium (Fig. 4) shows some of the features which differentiate the three main groups of Byzantine White Ware, as well as the close similarity between the group of GWWII and most of the PWW samples (see Table 2 for the complete range of elements). As for the marginal PWW, similar trends may be found in other Constantinopolitan samples (Table 2: high contents in trace elements in BZN422 compare to those in IST 2, a waster, and IST 3: Waksman and Girgin, 2008). Only the highest concentrations in iron (>7% Fe₂O₃) did not find close parallels so far in our corpus of Byzantine White Wares.

The alternative hypotheses of Preslav and Nicomedia as the origin of our PWW samples were still considered on the basis of the few presently available data. Eight tiles, six of which were found among thousands close to Izmit and now in a private collection (Gerstel, 2010), had been analyzed by INAA at the MURR archaeometry laboratory.⁵ The elements determined both by INAA and by WD-XRF show similar concentrations,⁶ somehow casting doubt on the local origin of the “Nicomedia tiles”. As

for Preslav PWW tiles, they were shown to be well differentiated chemically from the ones presumed to be Constantinopolitan (Vogt and Bouquillon, 1996; Bouquillon and Durand, 1998), with indications of chemical features (K₂O close to 3%: Vogt and Bouquillon, 1996, p. 109) which do not support a Bulgarian origin for our PWW samples. Further analyses are planned in order to confirm this point.

To sum up, although the analyzed PWW samples do not form a homogeneous chemical group, their chemical features match those of Constantinopolitan GWWII, with few exceptions. The latter would find parallels in the wide range of chemical concentrations of kaolinitic clayey materials available in the region of Istanbul *lato sensu*, and there is presently no evidence which would support another origin. The heterogeneities in the fabrics and chemical compositions suggest the extraction of clays in different locations, with no obvious correlation so far with stylistic groups which may be interpreted as different Constantinopolitan workshops.

4.2. Glazes analyses and technological issues

Glazes analyses were carried out by SEM-EDS on a sub-sampling of 10 sherds, selected among the main Constantinopolitan group according to the chemical analysis of the bodies. The colour palette of this collection is as follows: white, turquoise blue, dark blue and a range of shades from honey-brown to deep black (Table 3). With few exceptions, the glazes are applied directly on the white body, without a slip layer.⁷ Most of them are heavily weathered, crizzled and even powdered, showing, in cross-section, a typical laminated appearance of the vitreous matrix (Bouquillon, 2022), sometimes to the full thickness (over 300 μm in some cases, see Figs. 8 and 9, left). Particular attention was therefore paid to the location of the sampling, to ensure that the chemical and structural information gathered was as representative as possible.

All the glazed areas studied belong to the lead-alkali glaze family,

⁴ Although not in Arnautköy on the Bosphorus, as has been repeatedly mentioned, quoting the pioneer work of Megaw and Jones (1983).

⁵ Our very warm thanks to M. Glascock (MURR) for giving us the opportunity to examine these data mentioned by J. Lauffenburger in Gerstel (2010).

⁶ The match is not very good for some elements (e.g. Zr), an expectable result for laboratories using different analytical methods and which did not go through an intercalibration procedure.

⁷ A red slip, present in rare cases, will be the subject of further studies. It contrasts with the white (or clear) slip, applied on a red body, typical of most Byzantine glazed ceramics from the 12th c. onwards (see e.g. Papanikola Bakirtzi et al., 1999).

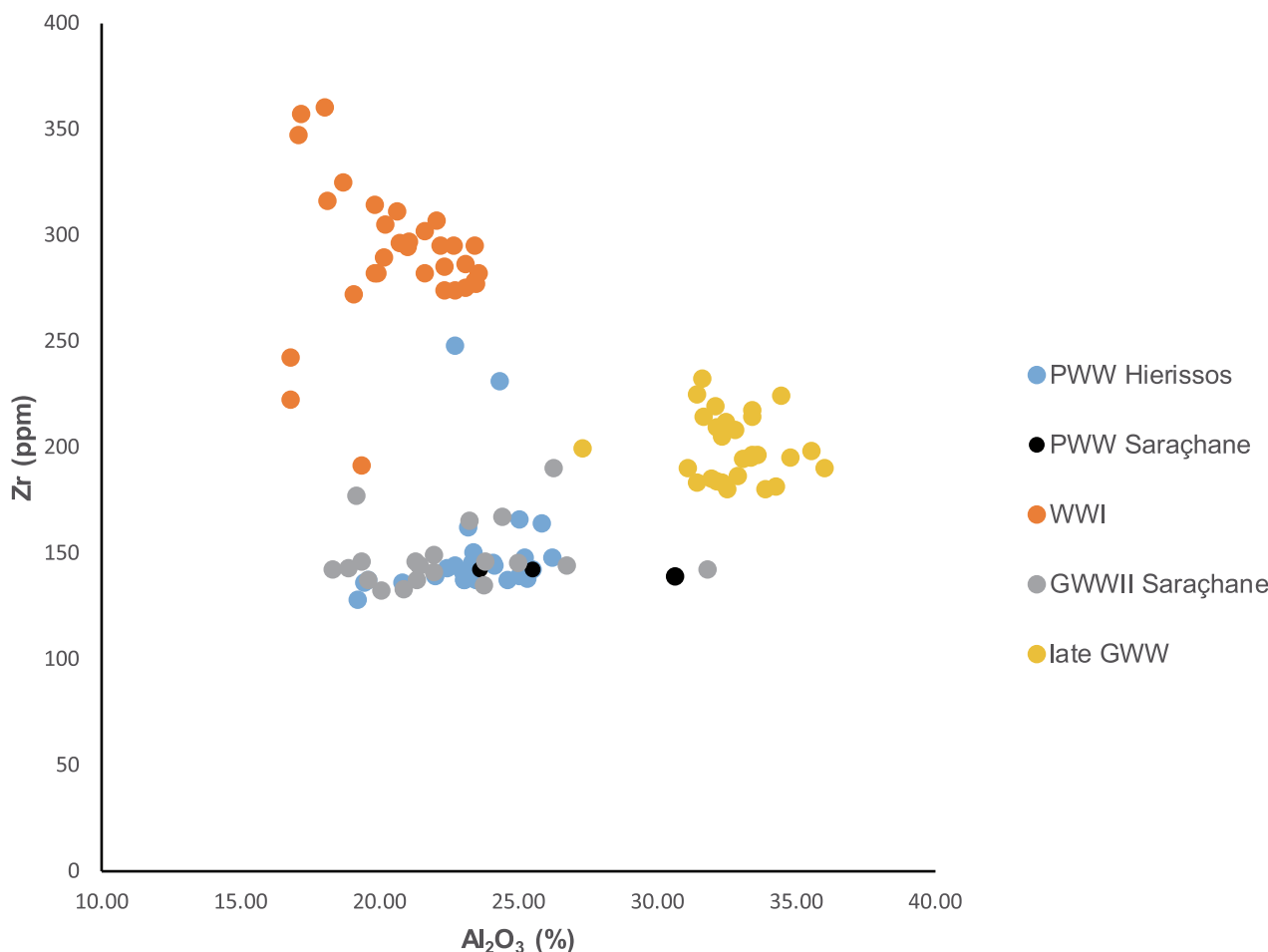


Fig. 4. Binary plot Al_2O_3 -Zr, showing different trends in the bodies of the main categories of Byzantine White Wares as defined by Hayes (1992) and analyzed in Lyon (Waksman, forthcoming). Most of the Polychrome White Wares are included in the group of Glazed White Ware II (for other elements see Table 2) (S. Y. Waksman).

with a noticeable amount of calcium (mostly in the range 3 to 6 % CaO). Whatever the colour, the sodium content varies between 7 and 15 % Na_2O , while K_2O is mostly below 1 %. Lead oxide rarely exceeds 30 % PbO, only a few transparent ochre glazes contain around 40 % PbO (Table 3).

4.2.1. Tin opacified white and turquoise glazes

All the white and turquoise glazes, which correspond to the ceramics of Hayes class III, contain significant levels of tin oxides (over 10 % SnO_2), more than sufficient to obtain a good quality opacification (Tite et al., 2015). The PbO/ SnO_2 ratios, between 1 and 4, seem to suggest the use of a traditional calcine (Matin et al., 2018). The microstructures of these opacifiers are varied, with isolated microcrystals, sometimes grouped in clusters, or larger, well-crystallised grains (Figs. 5, 6).

Turquoise glazes have the same general characteristics, with the exception of the presence of 3 % copper oxides combined with low levels of iron (1 % Fe_2O_3), responsible for the blue-green hue. As for white glazes, the proportions of lead and tin in the vitreous phase vary considerably from one sample to another. At this stage of our research, we do not know yet whether this reflects recipes that were not fully mastered, different workshop practices or varying levels of alteration.

4.2.2. Co-blue glazes

These dark blue glazes, present on both ceramics of Hayes class I and III, are always completely transparent (less than 0.1 % SnO_2) (Fig. 7). They are coloured with cobalt oxide (0.45 to 0.75 % CoO) and are also distinguished from other colours by a clear increase in sodium and

calcium, and to a lesser extent in silica, aluminium and iron (Table 3). Lead contents, on the other hand, are much lower (less than 10 % PbO).

The presence of rare small grains of unfused Co-bearing pigments is noticeable, which may not necessarily reflect the initial raw material⁸ (Fig. 7). All contain zinc, iron and sometimes copper associated to Co, but we noted a great chemical variability from one grain to another in the relative proportions. The amounts of nickel are very low, and traces of chromium were detected in some areas. Further analyses are planned to specify these associations and take advantage of the extensive body of comparative data from provenance studies of Co pigments (Gratuze et al., 2018).

On the sherds of Hayes class I, blue cobalt glazes are associated with transparent glazes, which appear white due to the white background of the kaolinitic bodies. These glazes do not contain tin, and show a significant increase in aluminium (10 % Al_2O_3), titanium and, to a lesser extent, silica, alkalis and iron. Lead contents are lower than in class III glazes. High alumina contents are frequently found in transparent high-lead glazes laid on alumina-rich bodies, due to a diffusion of Al_2O_3 from the paste to the glaze during firing (Walton, 2004; Roisine et al., 2017). In our case, the very high alumina contents, combined with very low thicknesses of the glassy cover (less than 20 μm), suggest that these could be highly altered glassy zones and that the compositions would rather reflect the body/glaze interface.

⁸ We thank N. Schibille (pers. comm.) for attracting our attention to the fact that some elements may preferentially remain concentrated in the inclusions.

Table 3

Chemical composition of the glazes of a sub-sample of PWW determined by SEM-EDS (in oxide weight %; --: under detection limits). The main features and the typological class are indicated.

Lyon id.	glaze colour	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Cl	K ₂ O	CaO	TiO ₂	MnO ₂	Fe ₂ O ₃	CoO	CuO	ZnO	SnO ₂	PbO	main features	Hayes class
BZN409	Opaque white	5.48	0.37	1.06	48.96	0.04	0.21	0.33	3.25	0.07	0.04	0.43	–	–	0.18	10.16	29.40	Sn, white	III
	Turquoise	11.05	0.87	2.03	60.83	0.14	0.57	0.79	6.13	0.08	0.41	1.01	–	2.94	0.51	2.75	9.88	Sn, turquoise	
	Black	6.31	0.22	3.86	38.16	0.10	–	0.99	4.71	0.22	6.54	1.69	0.06	4.37	0.38	0.20	32.18	Mn-black	
BZN411	Opaque white	6.43	0.39	1.80	41.63	0.00	0.34	0.31	2.40	–	–	0.64	–	–	–	14.45	31.62	Sn, white	III
	Turquoise	7.98	0.33	1.44	53.65	0.14	0.28	0.44	3.58	0.06	0.19	0.67	–	2.58	–	9.79	18.88	Sn, turquoise	
	Dark blue	15.83	0.75	2.87	59.82	0.06	0.85	0.71	5.42	0.12	0.20	4.49	0.49	0.95	1.20	–	6.23	Co-blue	
	Black	9.83	0.50	7.74	49.46	0.09	0.23	0.78	3.72	0.28	7.08	0.98	–	4.50	–	0.79	14.02	Mn-black	
BZN413	Honey	6.86	0.67	1.71	32.03	0.07	0.26	0.40	3.13	–	0.26	11.69	–	0.22	–	–	42.71		I
	Black	9.95	0.55	2.97	36.79	0.11	0.44	0.64	2.92	0.11	0.83	22.65	–	2.15	–	–	19.90	Fe-black	
BZN417	Opaque white	7.62	0.33	5.70	47.75	0.01	0.18	0.57	1.63	0.13	0.07	0.94	–	–	0.20	9.52	25.35	Sn, white	III
	Black	10.71	0.08	11.47	55.59	0.20	0.29	1.70	3.27	0.24	3.63	1.80	0.09	2.95	0.40	0.02	7.56	Mn-black	
BZN418	Opaque white	6.17	0.40	1.24	50.30	0.00	0.31	0.50	2.87	–	–	0.56	–	–	–	10.06	27.58	Sn, white	III
	Turquoise	6.42	0.32	2.15	44.51	0.01	0.32	0.37	2.23	–	–	0.76	–	3.03	–	13.96	25.91	Sn, turquoise	
	Black	9.77	0.64	3.14	51.35	0.12	0.32	0.76	4.36	0.21	9.47	1.28	–	3.94	–	3.14	11.50	Mn-black	
BZN425	Opaque white	5.81	3.57	2.31	46.18	0.04	0.10	0.61	2.85	0.09	0.17	1.48	–	–	0.21	16.71	19.87	Sn, white	III
	Dark blue	11.69	2.71	2.41	59.72	0.08	0.70	0.76	5.70	0.11	0.23	3.12	0.45	1.30	1.57	0.10	9.34	Co-blue	
BZN431	Transparent	10.65	0.46	8.55	55.78	0.06	0.36	0.97	3.19	0.27	–	1.17	–	–	–	0.58	17.95		I
	Dark blue	15.37	0.75	3.63	62.45	0.08	0.92	0.84	5.45	0.15	0.09	4.51	0.75	0.19	0.56	–	5.58	Co-blue	
	Honey	7.36	0.51	3.72	34.71	0.10	0.18	0.42	3.49	0.35	–	9.79	–	–	–	–	39.37		
	Black	7.20	0.38	2.29	28.56	0.16	0.27	0.49	2.28	0.11	0.48	45.53	–	0.31	–	–	11.94	Fe-black	
	Black	6.82	0.45	1.91	30.29	0.14	0.32	0.35	3.12	0.09	0.21	23.84	–	–	–	–	32.45	Fe-black	
BZN433	Opaque white	6.46	0.42	1.97	49.45	0.00	0.22	0.42	2.94	0.03	–	0.66	–	–	–	7.98	29.46	Sn, white	III
	Turquoise	13.34	0.62	1.96	65.69	0.03	0.81	0.60	4.45	0.06	0.13	0.99	–	2.89	–	1.78	6.66	(Sn), turquoise	
	Black	11.27	1.36	3.07	54.76	0.11	0.28	1.08	6.13	0.17	5.32	2.07	–	5.40	–	0.53	8.46	Mn-black	
BZN434	Opaque white	5.98	0.47	3.91	46.39	0.11	0.16	0.93	2.13	0.07	0.10	0.75	–	–	0.20	17.61	21.19	Sn, white	III
	Black	10.99	0.11	10.48	56.61	0.13	0.21	1.94	2.79	0.24	4.46	1.25	0.05	1.60	0.43	0.11	8.60	Mn-black	
BZN438	Transparent	9.50	0.61	6.24	61.69	0.13	0.34	0.90	4.06	0.23	0.05	1.57	–	2.33	0.55	0.07	11.74		I
	Dark blue	13.83	0.73	3.03	64.97	0.16	0.94	0.71	6.14	0.13	0.07	4.69	0.63	–	1.06	0.03	2.87	Co-blue	
	Yellow	8.44	0.48	2.77	50.97	0.22	–	0.72	4.70	0.16	0.08	7.69	0.04	2.25	0.48	0.38	20.61		
	Dark brown	6.80	0.48	3.07	34.70	0.26	0.10	0.51	3.28	0.10	0.17	29.55	0.11	–	0.44	0.23	20.21	Fe-dark brown	
	Dark brown	3.39	0.26	2.34	25.55	0.26	0.01	0.46	1.80	0.10	0.12	55.70	0.22	0.89	0.34	0.07	8.51	Fe-dark brown	

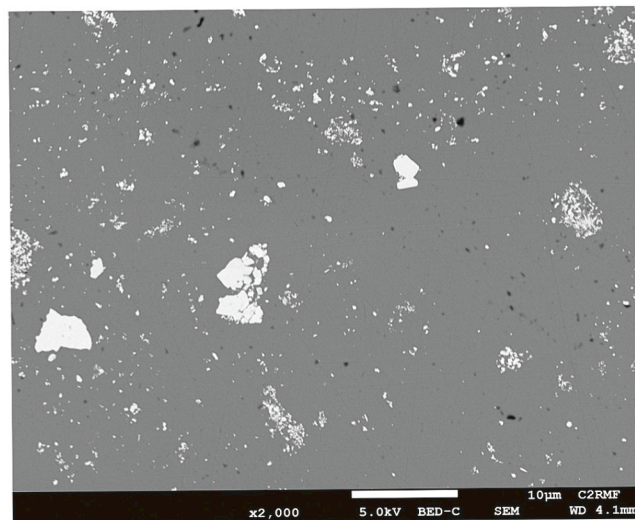
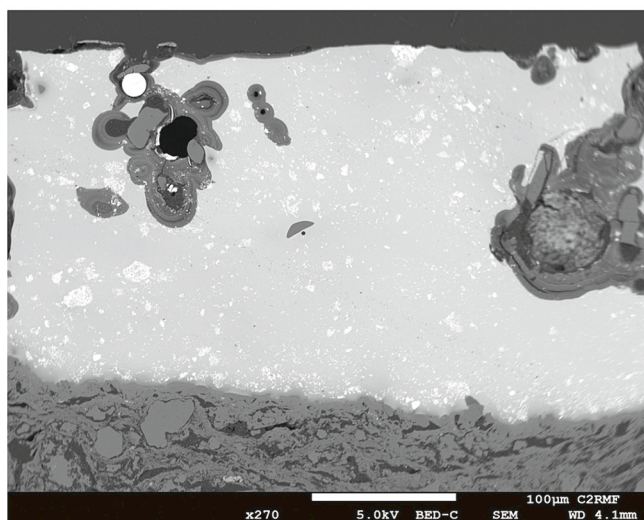


Fig. 5. Tin-opacified white glaze, BSE images, general view (left) and Sn-rich crystals (right) (sample BZN418) (© C2RMF).

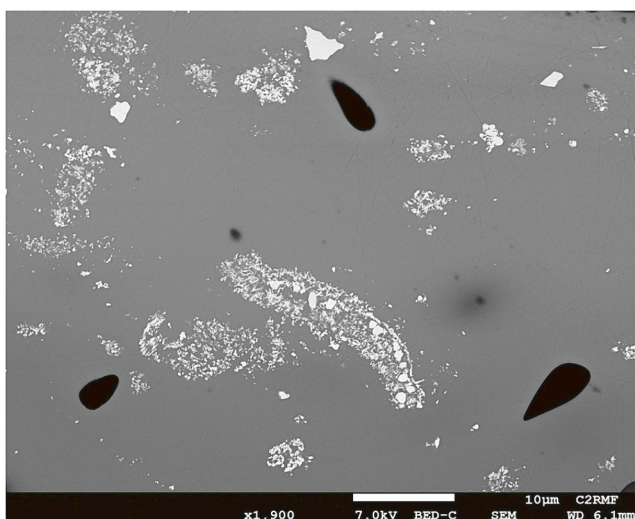
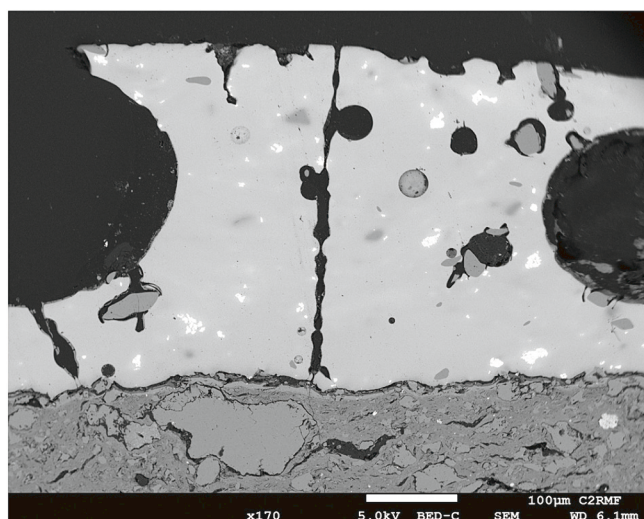


Fig. 6. Tin-opacified turquoise glazes, BSE images, general view (left, sample BZN433) and Sn-rich crystals (right, sample BZN411) (© C2RMF).

4.2.3. Honey glazes

This coloration is obtained by iron oxides, more or less abundant depending on the shade, from yellow to light brown. While iron is dissolved in the transparent brown glazes, where it is exceptional to find small Fe-rich grains, numerous crystals appear both on the surface and in the thickness of a yellow glaze (Fig. 8). These crystals all contain iron systematically combined with copper (between 5 and 10 % CuO, Fig. 8, Table 4).

4.2.4. Dark brown to black glazes

Their thickness is often more important than for the previous coloured areas and their level of alteration is sometimes extreme (Fig. 9, left). All of them present complex microstructures. There are two very different types depending on the dominant colouring oxide: iron, often in concentrations over 25 % Fe₂O₃, or manganese with contents reaching up to 10 % MnO (Table 3).

Manganese-rich black glazes appear very black. Manganese oxides are associated with iron and sometimes copper. In some cases, manganese is completely dissolved in the glaze matrix; in others, highly weathered complex grains with strong reaction halos appear in a totally altered vitreous matrix (Fig. 9). From one grain to another, manganese is associated with other metals (Cu, Fe), the distribution of which varies

greatly.

Iron-rich black glazes are characterized by large grains containing Fe and O which appear in the whole thickness. Some of them are surrounded by a recrystallisation halo suggesting chemical reactions with the lead-alkali glaze matrix during firing (Fig. 10).

Table 3 sums up the most specific features of the glazes, which point out two associations: tin-opacified glazes (turquoise and/or white) and Mn-blacks, which correspond to ceramics of Hayes class III, on the one hand; on the other hand transparent glazes and Fe-blacks, for ceramics of Hayes class I.

The first group follows a technical tradition of glazes which is otherwise unknown in Byzantine pottery, but widespread in the Islamic world. Turquoise glazes are ubiquitous in the latter, following previous Parthian and Sasanian traditions in Mesopotamia (Pace et al., 2008). The introduction of tin-opacified glazes, for instance in Egypt in the 9th c. (Gayraud and Vallauri, 2017), was the subject of several recent studies (e.g. Tite et al., 2015; Matin et al., 2018; Matin, 2019). The use of cassiterite as an opacifier in glazes is considered to be one of the major developments in ceramic art, replacing calcium antimonate, a common opacifier in ancient glazes, especially Mesopotamian and Roman. Tin is introduced in the form of calcine whose PbO/SnO₂ ratios vary depending on chronology and geography; here, PbO/SnO₂ is in the order

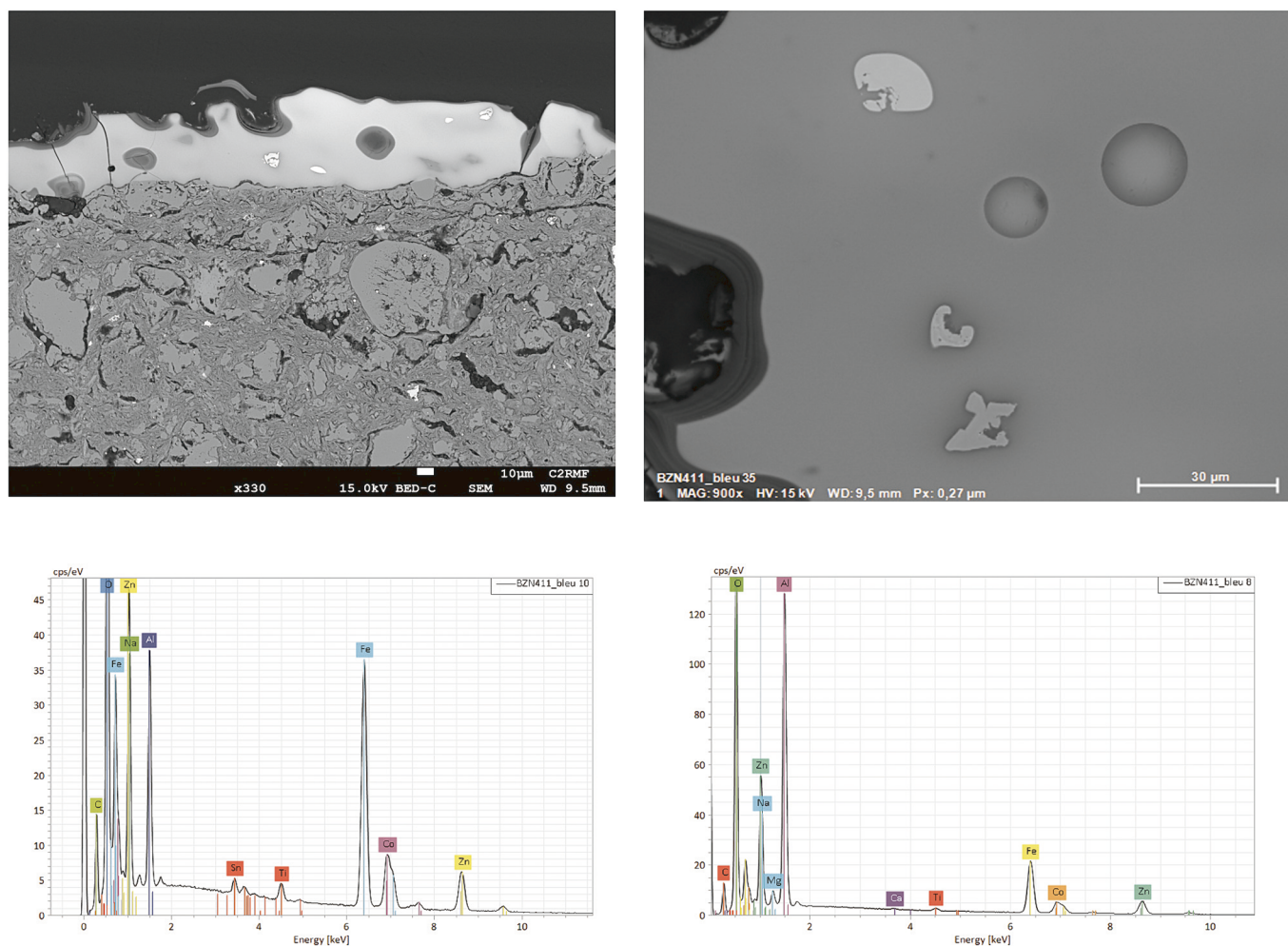


Fig. 7. Cobalt-coloured glazes, BSE images (above), general view (left, sample BZN431), Co-rich grains (right, sample BZN411) and SEM-EDS spectra of two of these grains (below, sample BZN411) (© C2RMF).

of 3, which is within the usual range as defined by [Matin \(2019\)](#).

With its transparent glazes, the second group of Polychrome White Ware may seem closer to other types of Byzantine ceramics. But it has in common with the first group the use of lead-alkali glazes and the occasional one of Co-based pigments. Although archaeometric studies of Byzantine glazes are still scarce, only high-lead glazes were identified so far on Byzantine wares as defined by [Hayes \(1992\)](#), from the first “Byzantine Glazed White Ware I” (7th c. AD) to the late Byzantine productions of Western Anatolia and Constantinople (14th c. AD) ([Armstrong et al., 1997](#); [Waksman et al., 2007](#); [White, 2009](#); [Budak Ünal, 2013](#); [Palamara et al., 2016](#); [Burlot, 2017](#); [Burlot et al., 2020, 2021](#); [Liard et al., 2022](#)). The only exception is Polychrome White Ware, whose glazes belong to a technical tradition alien to Byzantine pottery.

5. Concluding remarks

This paper presents the first results of archaeometric investigations of Polychrome White Ware pottery from archaeological contexts of the 10th–11th c. in Greece (Hierissos and other sites in Chalkidiki) and Turkey (Saraçhane in Istanbul). They point to technical features of the glazes alien to other Byzantine wares but well known from contemporary Islamic ceramics: Co-based pigments, lead-alkali glazes, tin-opacified in some cases. The former were already known from previous studies of architectural Polychrome White Ware ([Vogt and Bouquillon, 1996](#); [Vogt et al., 1997](#); [Lauffenburger et al., 2001](#)), but their significance had escaped notice with few exceptions ([Armstrong, 2020](#)).

Tin-opacified glazes had never been identified in Byzantine pottery before.

The samples examined belong to two technical groups which differ in several respects. The first one is characterized by tin-opacified white and turquoise glazes, and Mn-based blacks. Opaque and transparent glazes may coexist on a same sherd. Stylistically, these ceramics belong to Hayes class III. The ceramics in the second group are part of Hayes class I. Their glazes are not tin-opacified, and the black motifs are due to high concentrations in iron.

Both groups have similar kaolinitic bodies, and do not seem to be correlated with variations in fabric and in chemical composition. They are mostly attributed to a Constantinopolitan chemical reference group, defined after pottery workshop contexts were discovered in the Metro-Marmaray excavations in Istanbul ([Waksman, 2021b](#)). There is however no evidence that these were the workshops of Polychrome White Ware. Their location in Constantinople or its suburbs, the organization of production and its possible connexion to different stylistical groups and glaze technologies, more or less closely related to Islamic ceramics glazes, are still unknown.

The introduction of these technologies in the manufacture of Polychrome White Ware is also a subject for further study and debate. The hypothesis of potters coming to Constantinople from the Islamic world seem to have been favoured so far ([Cutler, 2001](#)). But alternative hypotheses, of techniques transmitted by Byzantine glassmakers or mosaicists, should also be considered ([Biron, 2015](#); [Gómez-Morón et al., 2021](#)). In both cases, why the production of Polychrome White Ware was

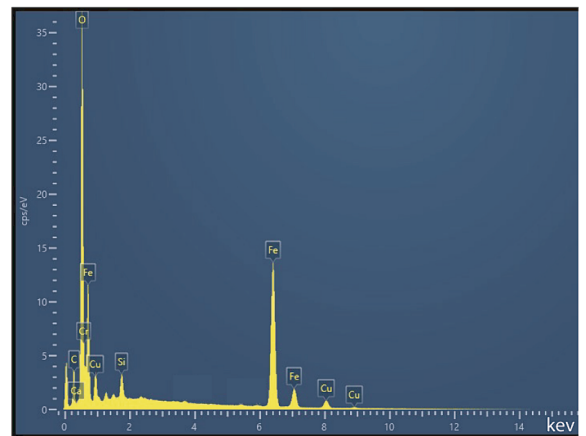
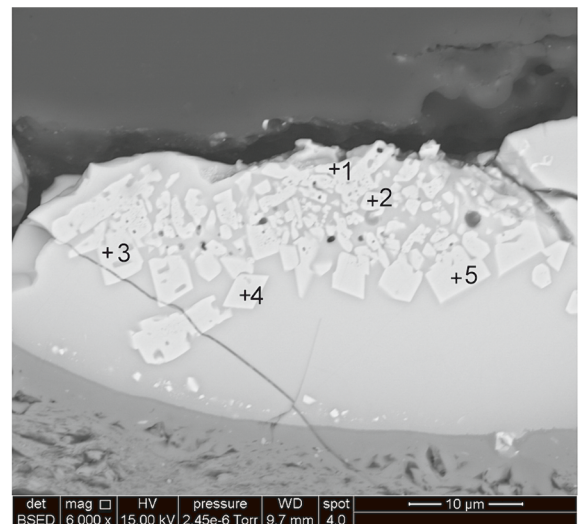
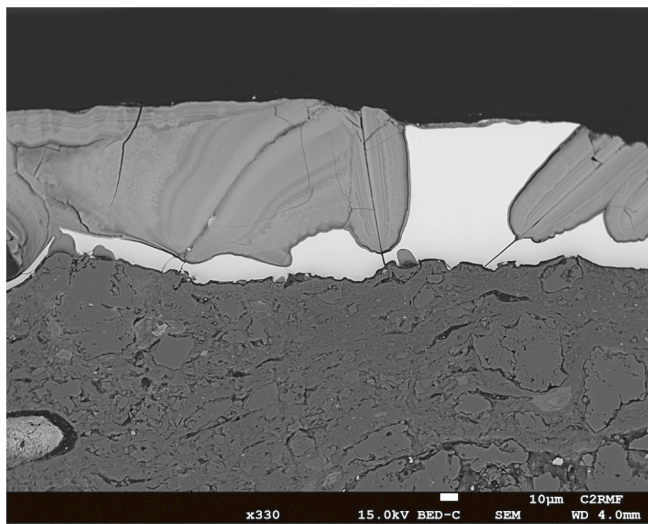


Fig. 8. Honey glazes: BSE images, general view (above left, sample BZN413, © C2RMF), Fe- and Cu-rich crystals and representative SEM-EDS spectrum of their spot analyses (above and below right, sample BZN438, © J. Burlot).

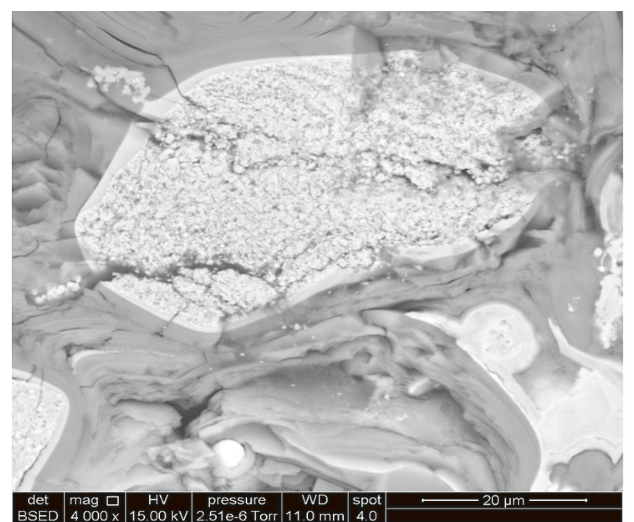
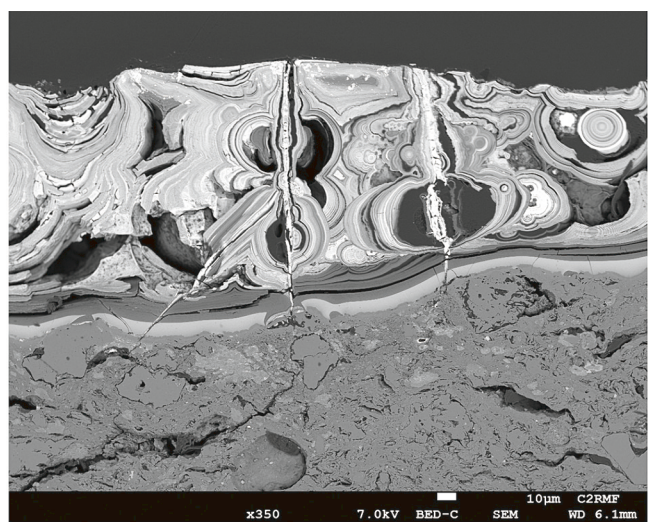


Fig. 9. Mn-rich black glazes, BSE images, general view of a very weathered example (left, sample BZN411, © C2RMF) and Mn- and Al, Cu, Ni, Zn-rich inclusion (right, sample BZN417, © J. Burlot).

Table 4

Chemical composition of inclusions in the brown glaze of sample BZN438 (spot SEM-EDS analyses, cf. Fig. 8).

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	MnO	FeO	CuO	ZnO	PbO
Spectrum 1	–	1.0	0.4	2.5	0.3	0.6	82.4	9.6	1.1	0.6
Spectrum 2	0.2	1.2	0.6	3.3	0.2	0.4	79.8	10.8	1.1	0.5
Spectrum 3	–	1.1	0.4	2.5	0.2	0.5	81.5	10.5	1.0	1.0
Spectrum 4	–	1.2	0.2	0.7	0.1	0.4	84.2	11.3	0.9	0.1
Spectrum 5	–	1.2	0.2	0.4	0.1	0.3	82.6	12.0	1.6	0.1

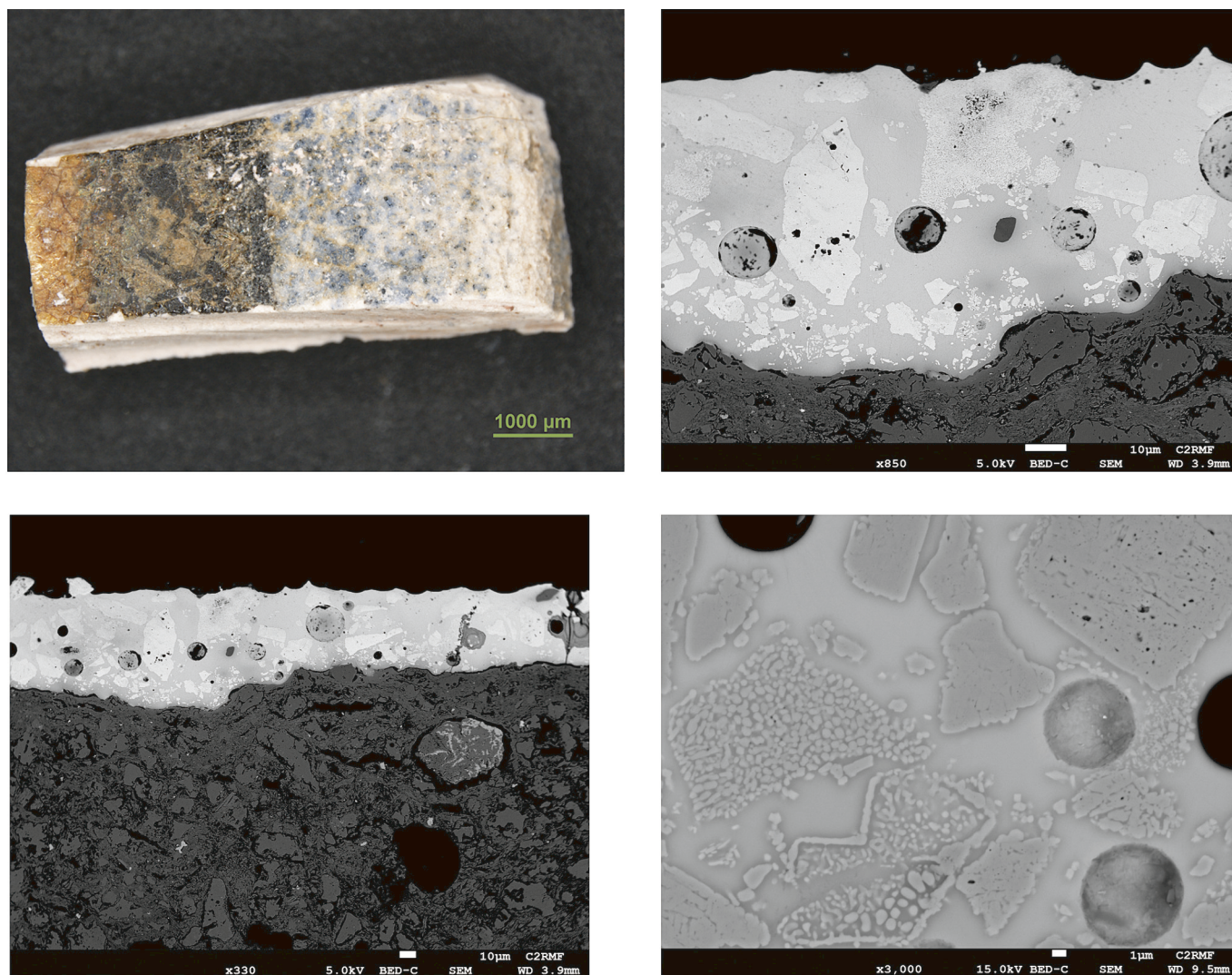


Fig. 10. Fe-rich black glaze (sample BZN431): sample photo from top (above left) and BSE images at various magnifications of the glaze and of Fe-rich inclusions (© C2RMF).

so restricted in time and space, and did not have followers in Byzantine pottery manufacture, are questions which are still open. At any rate, “Byzantine” Polychrome White Ware suggests more complex interactions and exchanges of know-how and craftsmen between the Byzantine and Islamic worlds than was considered before (François, 2017; Waksman, 2021a).

CRediT authorship contribution statement

S.Y. Waksman: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **A. Bouquillon:** Writing – original draft, Methodology, Investigation. **J. Burlot:** Investigation. **C. Doublet:** Investigation.

K. Amprazogoula: Writing – original draft, Investigation. **A. Tsanana:** 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.

Data availability

Data will be made available on request.

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