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COMPOSITION AND TEXTURE OF A SET OF MARVERED GLASS VESSELS FROM 12th CENTURY AD BRANIČEVO, SERBIA

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Abstract – Strongly coloured glass vessels decorated with marvered threads of white glass are a wide-spread and popular, but rarely studied group of high-quality glassware of medieval Islamic origin. Relatively little is known about the composition and production places of these vessels, and their chronological range is not very well defined, as many of the published finds lack contextual evidence. Here, we present detailed chemical and microstructural data on a set of well-dated purple glass vessels decorated with white threads, excavated at the Mali Grad site in Braničevo, Serbia, in an archaeological context dated to the middle/second half of the 12th century AD. The set comprises at least sixteen different vessels, manufactured from two different batches of probably Levantine plant-ash glass coloured by manganese oxide. Significantly, the results demonstrate that these batches are correlated to particular vessel shapes. The base glass of the white threads is comparable to that of the purple vessel glass, but instead of being coloured by added manganese oxide, it contains considerable amounts of tin and lead oxides which provide the effect of opacity and white colour. No difference in composition can be seen between the white glass threads used to decorate the vessels from the two different manganese-coloured batches, thus indicating a likely common production origin of the whole set.

Key words – Islamic glass, Marvering, Braničevo, Serbia, 12th century, LA-ICPMS analysis, SEM imaging, pXRF.

INTRODUCTION

Islamic glass vessels of the High Middle Ages are renowned for their artistic and aesthetic quality. Among the easily recognisable decorated glass objects are vessels consisting of an intensely coloured body trailed with threads of opaque glass, most often of white colour, typically dragged in a festooned fashion (i.e. the so-called combed decoration) when the glass was still soft and often marvered flat into the surface of the vessel walls¹. The first comprehensive survey of these marvered Islamic glasses was published by James

Allan², who surveyed and summarised the earlier literature on the subject as well as detailing his own considerable knowledge of the material based mostly on the Ashmolean Collection, followed by Stefano Carboni's review of the material in the al-Sabah Collection³. Since then, further studies reported more finds, for instance

¹ Pinder-Wilson 1999, 129–130.

² Allan 1995.

³ Carboni 2001, 291–321.

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Fig. 1. Examples of the analysed purple glass vessels with marvered decoration from Braničevo (Cat. Nos 1, 2, 6 from Spasić-Đurić, Jovanović in this volume; photo: Institute of Archaeology, Belgrade)

Сл. 1. Примерци анализираног пурпурног стакла из Браничева украшени апликацијом нишима (Cat. Nos 1, 2, 6 из Spasić-Đurić, Jovanović у овом броју Старицара; фото: Археолошки институт, Београд)

from Bet Shean in Israel⁴, the Wadi al-Tūr in Sinai⁵, and Jerusalem⁶. Beyond this, numerous articles and catalogue entries also depict fragments of such vessels from various sites or museum collections, attesting the wide popularity of this group. Despite this popularity, however, few papers discuss the chemical composition of these vessels, the main one being Julian Henderson's companion piece to the survey by James Allan⁷.

Recent excavations at House No 4 from Braničevo in eastern Serbia have yielded a highly remarkable assemblage of glass vessel fragments (Fig. 1). They were found in a closed context formed with the destruction of the building and dated, on the basis of the numismatic evidence, to the middle/second half of the 12th c. AD⁸. The main finds form a set of at least 16 individual vessels, including bowls, bottles and flasks made from translucent purple glass with opaque white festooned decoration. They have few published parallels from the Balkans⁹, and form the topic of this chemical study. A full presentation of the vessel set, its

context and archaeological interpretation is provided in the preceding paper by Dragana Spasić-Đurić and Sonja Jovanović¹⁰. Here, we report the results of compositional and microstructural analyses done on this assemblage.

MATERIALS AND METHODS

The fragments were recovered during regular excavations in 2011 and visually sorted and assigned to at least 16 different vessels, tentatively identified as six

⁴ Hadad 2002.

⁵ Shindo 1993.

⁶ Brosh 2014; Brosh 2017, 300–301, 303–304.

⁷ Henderson 1995.

⁸ Spasić-Đurić 2016, 113–114, Fig. 56b; Spasić-Đurić, Jovanović in this volume.

⁹ E.g. vessels from Kotor, Montenegro in Križanac 2001, and from Corinth, Greece in Davidson 1952, 115–116, Nos 755–758.

¹⁰ Spasić-Đurić, Jovanović in this volume.

small and two large bowls, two flasks, and three large bottles; other fragments indicate the presence of a further three unidentified, highly fragmented vessels, potentially also flasks. From the much larger total number of sherds excavated, 15 fragments representing at least nine of the different vessels were analysed by Bernard Gratuze¹¹ using Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). On each fragment three spots in the purple glass base and, where possible, a further three spots in the white glass were analysed using well-published conditions and protocols¹². The Appendix reports the average values of the three measurements per sample, separate for the purple and the white glass, together with the results for the reference glass Corning A, whose composition is assumed known¹³ and which was analysed as part of the same analytical sequence as the compositionally unknown glass fragments¹⁴. From the analysis by LA-ICPMS we identified the presence of two different chemical compositions among the purple glasses (see below); this separation was further supported by portable X-Ray Fluorescence (pXRF) analyses done at the National Museum in Požarevac using a hand-held Olympus Delta InnovX instrument with modified calibrations based on the instrument's Soil and Mining Plus modes (see below).

To better understand the manufacturing technology of the opaque white decoration, and to explore the reason for the observed internal heterogeneity of the triplicate LA-ICPMS analyses (see below), six of the 15 fragments analysed by LA-ICPMS were selected for further study by optical and scanning electron microscopy. In preparation for this, the samples were embedded in cold-setting transparent resin in such a way that the cross section of the glass would be exposed after grinding and polishing the flat surface of the resin disc, revealing both the purple glass matrix and the white decoration. They were then investigated using a Leica DM2700 Optical Microscope (OM) and a JEOL Scanning Electron Microscope with Energy-Dispersive Spectrometer (SEM-EDS) at the Archaeological Materials Science Laboratories of UCL Qatar.

RESULTS

There are two main characteristics to report regarding the results of the scientific analysis of these glass fragments. Firstly, there is the chemical composition of the glass, separately for the purple bodies and the white threads, as determined by LA-ICPMS. Secondly, there are the textures of the two glass parts on a microscopic

level, as visualised and determined by SEM Back-Scatter Electron (BSE) images and EDS analyses for six fragments¹⁵ out of the 15 analysed by LA-ICPMS. Knowing the composition enables us to discuss the production technology and the likely origin of this glass, and whether the different vessels were made all at the same workshop during the same production event, or whether they are from different sources. The texture, in addition, provides us some information regarding the working and colouring processes used to make and decorate the glass vessels.

Composition

The purple glass fragments are a typical soda-lime-silica glass, with around 67 wt% silica, 12 to 13 wt% soda, and c 9 wt% lime (Table 1). The presence of 2.5 to 3 wt% magnesia and 1.9 to 2.3 wt% potash indicates the use of plant ash as the flux. The purple colour is due to a manganese oxide content of, on average, 2 to 2.2 wt%, clearly added as a deliberate ingredient of the colouring recipe. Around 2 wt% alumina and around 1 wt% iron oxide are the only other compounds present at the percentage level. This composition matches typical Islamic plant-ash glass compositions known from extensive literature, and is in accordance with the stylistic affiliation of the vessel types and decoration to an Islamic origin.

Within this compositional range we identify two subgroups. Purple 1, with eight analysed samples, has slightly higher concentrations of potash, magnesia (Fig. 2), and lime, while Purple 2, with seven analysed samples, has slightly higher concentrations of iron and

¹¹ At the laboratory of the Institut de Recherche sur les Archéomatériaux (IRAMAT) – Centre Ernest Babelon, UMR 5060 CNRS/Université d'Orléans, France.

¹² Cf. Gratuze 2016. Three separate spots were placed in the cross sections of the fragments, analysing a volume of glass c 0.06 mm wide and c 0.2 mm deep. An exception is sample BRN 1-09 on which, due to the strong glass heterogeneity of the decoration, nine individual spots were measured, spread over three different areas, and then averaged as three separate results; see Fig. 6a, b and the Appendix – samples BRN 1-09.w(i), BRN 1-09.w(ii), and BRN 1-09.w(iii).

¹³ Brill 1972; Adlington 2017.

¹⁴ The comparison of the measured oxide concentration to values published by Brill (1972), Vicenzi et al. (2002), Wagner et al. (2012), and Adlington (2017, Table 3) shows an overall good consistency; the main discrepancy was seen in the determined lime concentration, which was analysed c 13% higher than in the published values.

¹⁵ Fragments BRN 1-04, 1-05, 1-07, 1-09, 1-13 and 1-14b.

wt%	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	P ₂ O ₅	Cl	TiO ₂	Fe ₂ O ₃	
Purple 1	67.4	1.75	12.2	2.25	9.1	2.87	0.30	0.71	0.09	0.73	
Purple 2	66.7	1.90	12.9	1.91	8.7	2.60	0.26	0.77	0.10	1.06	
White (all)	57.8	1.08	9.0	1.81	6.9	2.35	0.24	0.66	0.06	0.44	
ppm	Li ₂ O	B ₂ O ₃	Rb ₂ O	SrO	BaO	V ₂ O ₅	Cr ₂ O ₃	ZrO ₂			
Purple 1	20	315	16	682	1473	27	21	59			
Purple 2	25	414	14	677	1547	31	23	67			
White (all)	4	225	11	456	195	18	11	39			
	MnO	CoO	NiO	CuO	ZnO	As ₂ O ₃	Ag	SnO ₂	Sb ₂ O ₃	PbO	Bi
	wt%	ppm	ppm	ppm	ppm	ppm	ppm	wt%	ppm	wt%	ppm
Purple 1	2.02	7	17	518	67	19	3	0.04	74	0.13	2
Purple 2	2.21	13	17	478	86	24	2	0.10	292	0.33	5
White (all)	0.60	8	33	352	39	44	25	6.6	21	12.3	288
Base glass	SiO ₂ *	Al ₂ O ₃ *	Na ₂ O*	K ₂ O*	CaO*	MgO*	P ₂ O ₅ *	Cl*	TiO ₂ *	Fe ₂ O ₃ *	MnO*
White (all)											
(wt%)	71.4	1.33	11.1	2.24	8.5	2.91	0.30	0.81	0.07	0.54	0.74

Table 1. Average values for the main oxides and selected trace compounds of the compositional glass groups Purple 1, Purple 2 and White from Braničevo, as determined by LA-ICPMS. The lower section reports the base glass composition of the white glass as recalculated after removing the added oxides (SnO₂ and PbO), and recalculating the listed eleven compounds (marked with an asterisk) to 100%, see footnote 32. Full data is in the Appendix

Табела 1. Просечне вредности главних оксида и издвојених једињења у пробама који улазе у састав стакла Пурпур 1, Пурпур 2 и белој стакла из Браничева, утврђених методом LA-ICPMS. При дну табеле приказан је основни састав белој стакла добијен након искључивања доданих оксида (SnO₂ и PbO) и поновно прерачунавања вредности за преосталих једанаест једињења (означених звездицом) до 100%, види нап. 32. Комплетни подаци дају су у прилогу

manganese oxide (Fig. 3), and higher levels of some trace elements such as lead, tin, antimony, boron and lithium (Fig. 4).

The differences in trace element levels between the two subgroups, identified by the LA-ICPMS analyses, were sufficiently clear to be recognised even in the much less accurate and precise pXRF analyses, particularly for antimony, but also tin, lead, and even manganese at the level of major oxide. This enabled us to assign, within the space of a few minutes, specific fragments to either of the two subgroups, as a fast in-situ method without the need for full analysis in a specialist laboratory¹⁶. In order to confirm the feasibility of such an approach, a few fragments already analysed by LA-ICPMS were measured by pXRF, providing an idea of the extent of credibility of the data¹⁷. Screening an additional set of c 30 fragments from the assemblage in this manner indicated that all were compatible with either of the two purple glass subgroups, within the

limitations of the method (Fig. 5a, b)¹⁸. This not only confirmed the consistency of the overall assemblage but also helped in assigning some individual fragments to specific vessels.

The opaque white glass has a similar base composition as the purple glass, in that it is also a plant-ash based soda-lime-silica glass. The main difference is that the white glass contains an additional c 5 to 9 wt% tin

¹⁶ The full pXRF data is on file at the National Museum in Požarevac; the details of this work will be published elsewhere in a more technical paper.

¹⁷ The purple areas of fragments BRN 1-03, 1-05 (Purple 1) and BRN 1-04, 1-10 (Purple 2) were re-analysed using pXRF (see Fig. 5). Based on this internal comparison, we considered the numerical values reported by the pXRF instrument as indicative (labelled as wt% ind. and ppm ind. in the graph) rather than fully quantitative.

¹⁸ For methodology and limitations of the pXRF technique in glass analyses see Adlington, Freestone 2017.

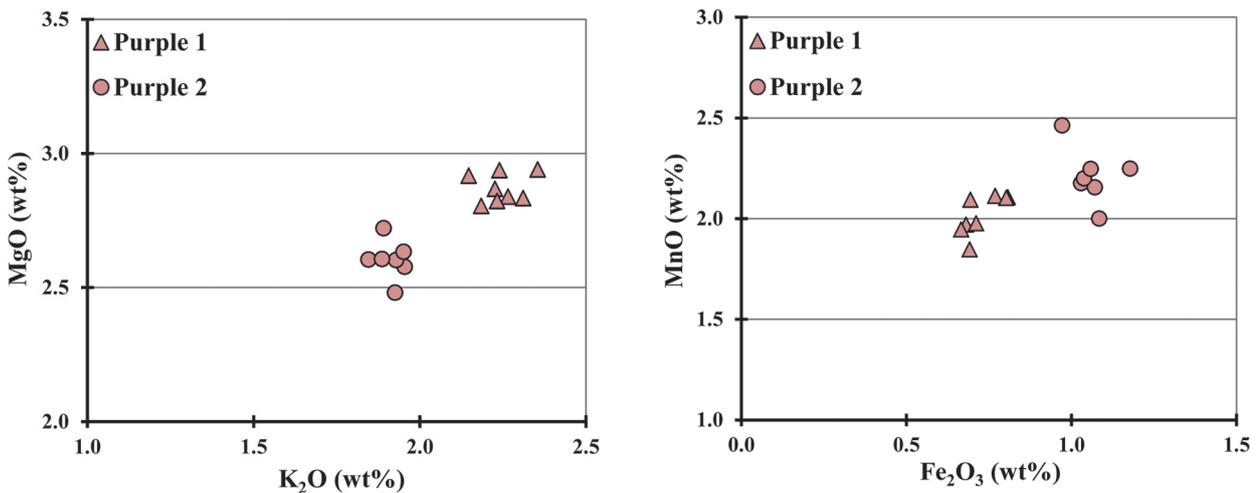


Fig. 2. The magnesia (MgO) and potash (K₂O) contents of Purple 1 and Purple 2 both fall in the range associated with plant ash glass, and differ from each other to show that they form two separate compositional subgroups.

LA-ICPMS data from B. Gratuze, IRAMAT

Fig. 3. The manganese oxide (MnO) and iron oxide (Fe₂O₃) contents of Purple 1 and Purple 2 differ from each other, confirming that they form two separate compositional subgroups. LA-ICPMS data from B. Gratuze, IRAMAT

Сл. 2. Вредности оксида магнезијума (MgO) и оксида калијума (K₂O) у обе подгрупе стакла, извојене као Пурпур 1 и Пурпур 2, улазе у опсег који се везује за стакло на бази биљног пепела, док разлике између ових вредности указују на постојање две подгрупе са различитим саставом.

LA-ICPMS подаци добијени од Б. Грајуза, IRAMAT

Сл. 3. Вредности манган-оксида (MnO) и оксида гвожђа (Fe₂O₃) у стаклу извојеном као Пурпур 1 и Пурпур 2 се разликују, што потврђује две подгрупе стакла различитог састава.

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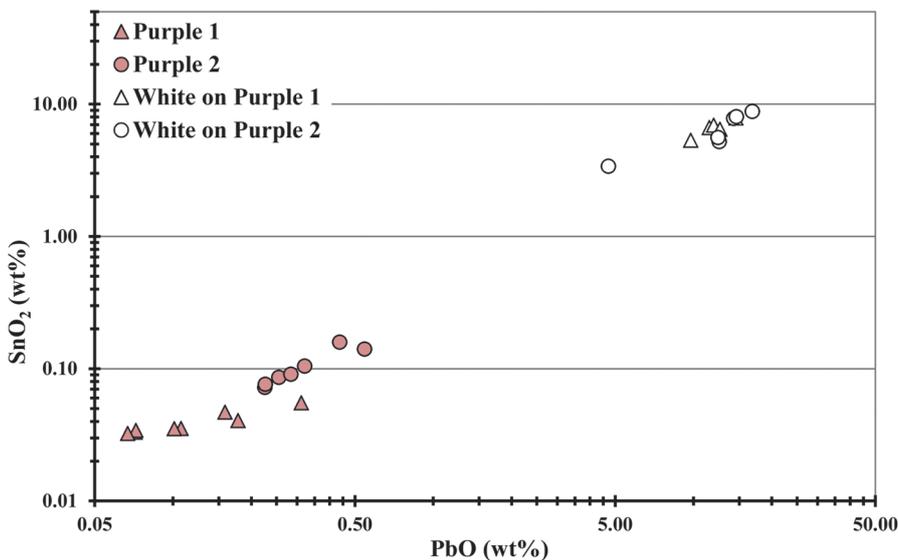


Fig. 4. The tin oxide (SnO₂) and lead oxide (PbO) contents of Purple 1 and Purple 2 fall on the same correlation line as in the white trails, but at different concentrations. Note the logarithmic scale of the two axes.

LA-ICPMS data from B. Gratuze, IRAMAT

Сл. 4. Вредности оксида калаја (SnO₂) и олова (PbO) у стаклу извојеном као Пурпур 1 и Пурпур 2 праће исту линију корелације као код белој стакла, али са другачијом концентрацијом. Види логаритамску скалу две осе.

LA-ICPMS подаци добијени од Б. Грајуза, IRAMAT

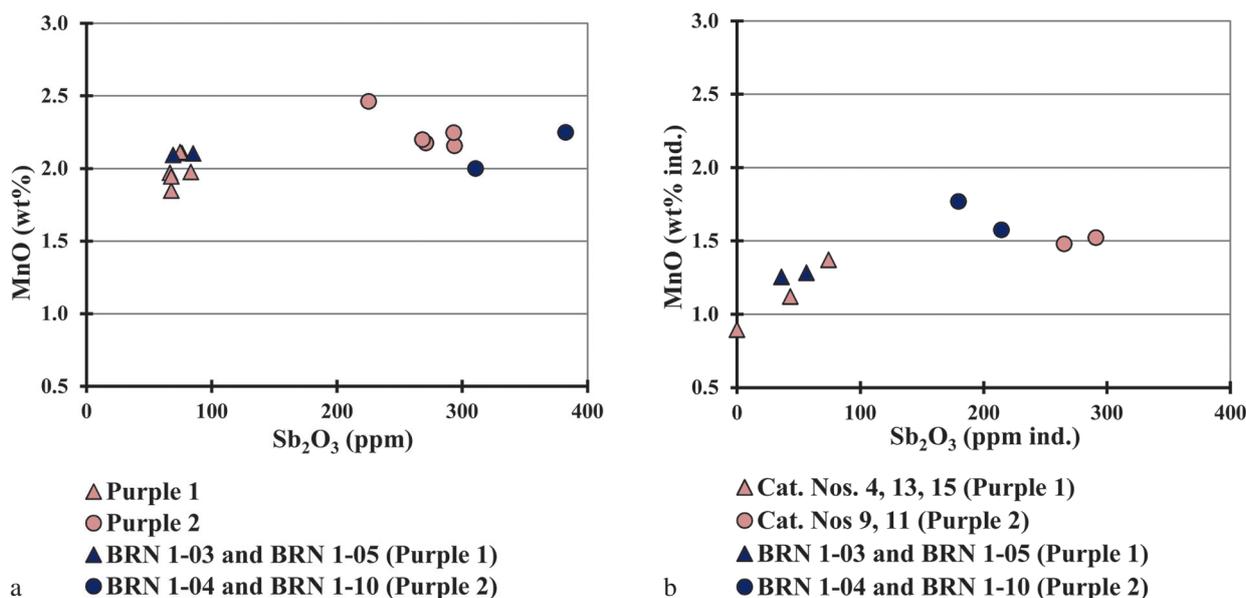


Fig. 5. Purple 1 and Purple 2 can be clearly distinguished by their manganese oxide (MnO) and antimony oxide (Sb₂O₃) contents in the LA-ICPMS data (a). These oxides can successfully separate the two compositional subgroups even in the less accurate and precise pXRF data (b; numerical values on the axes only indicative; uncorrected Soil mode measurements). The pXRF data allow recognition of bottle Cat. No 11 as Purple 2 and three more vessels as Purple 1 – bowl Cat. No 4, flasks Cat. Nos 13, 15 (see Spasić-Đurić, Jovanović in this volume). A loose handle fragment of bottle Cat. No 9, not analysed by LA-ICPMS, is confirmed to belong to Purple 2. LA-ICPMS data from B. Gratuze, IRAMAT

Сл. 5. Пурпур 1 и Пурпур 2 јасно се разликују по вредностима манган-оксида (MnO) и оксида антимона (Sb₂O₃) према LA-ICPMS подацима (a). Ови оксиди могу јасно да раздвоје две хемијски различите подгрупе стакла, што се чак може добити и у мање прецизним мерењима pXRF-ом (b; нумеричке вредности на осам су само индикативне; некорисана „Soil mode” мерења). Подаци добијени методом pXRF опредељују боцу Cat. No 11 као Пурпур 2 и три друге посуде као Пурпур 1 – здела Cat. No 4, мале боце („flasks”) Cat. Nos 13, 15 (види: Спацић-Ђурић, Јовановић у овом броју Старицара). Фрагмент гршке боце Cat. No 9 који није анализиран методом LA-ICPMS, потврђено је да припада подгрупи Пурпур 2. LA-ICPMS подаци добијени од Б. Грајуза, IRAMAT

oxide and around 10 to 17 wt% lead oxide; accordingly, the other components of the initial glass melt are reduced by about 18 to 22 % of their original concentration due to the dilution from the added metal oxides. An exception is sample BRN 1-13.w which has significantly lower levels of tin and lead oxides (adding up to only c 8 wt%) compared to the rest of the opaque white glasses. This compositional peculiarity is possibly a result of insufficient homogenization of the glass melt during the introduction of the tin- and lead-rich additive, when this particular portion of the batch absorbed lower amounts of opacifying substance¹⁹.

When considering the compositional results of the white glass samples, one has to bear in mind that these

are data from LA-ICPMS, which means that they represent only a microscopically small volume of material²⁰. Since the white glass is compositionally heterogeneous (see below), this can result in highly variable measured concentrations, especially of lead and tin oxides, depending on which parts of the heterogeneous glass was ablated by the laser. This is particularly evident in the white decoration of fragment BRN 1-09 analysed in three separate areas (cf. Fig. 6).

¹⁹ Cf. Fig. 8a, b.

²⁰ See footnote 12.

Remarkably, the levels of antimony and copper are significantly lower in the white glass than in the purple glass (Fig. 7); the same is true for other trace elements such as lithium, boron, zinc, strontium and barium. In

contrast, some elements, such as arsenic, silver and bismuth, commonly associated in terms of their geological occurrence with lead, are significantly increased in the white glass.

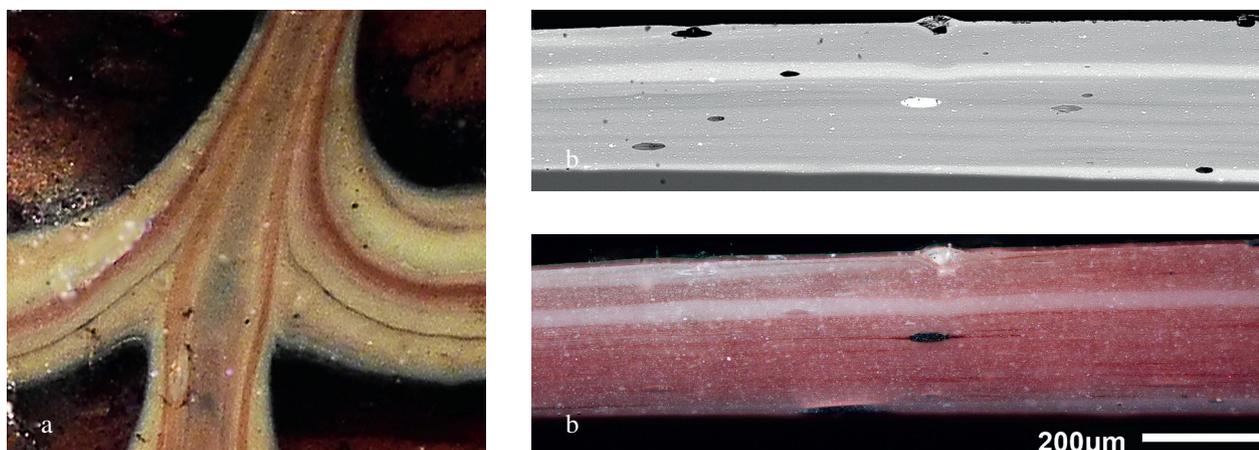


Fig. 6. Close-up photograph of the decorative trails on a fragment of bottle Cat. No 10 showing streaks of purple glass in the white thread (a; width of image c 1.7 mm). Mixing of white and purple glass in the cross section of sample BRN 1-09 (sampled from the same vessel) as seen in the SEM-BSE image as different grey shades and in the OM micrograph in colour (b; scale bar is 0.2 mm). The mixing is potentially due to contamination of the tool during the dragging of the trails, and also explains the differences between the three analyses of the white glass in this sample (BRN 1-09.w(i), (ii), (iii))

Сл. 6. Детаљ декорације на фрагменту боце Cat. No 10 приказује шпратове пурпурног стакла прожеће кроз беле нише (а; ширина слике с. 1,7 мм). Мешање белој и пурпурној стакла у пресеку узорка BRN 1-09 (узорак исте посуде), што се на SEM-BSE слици препознаје у виду различитих сивих сенки, а на OM микрографију у боји (b; размера је 0,2 мм). Мешање је можда резултат контаминације изазване алатком којом су се наносиле стаклене нише, што такође објашњава и разлике у шири мерења белој стакла у овом узорку (BRN 1-09.w(i), (ii), (iii))

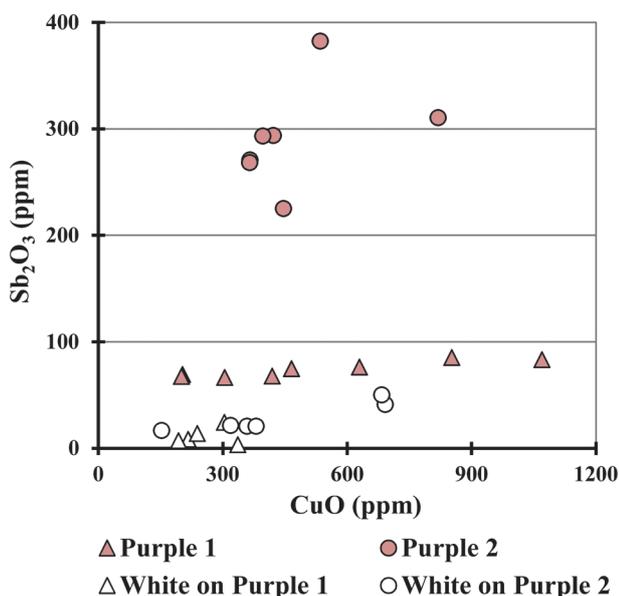


Fig. 7. The antimony oxide (Sb_2O_3) content in the purple glasses is significantly higher than in the white glass, particularly in Purple 2, while copper oxide (CuO) is only elevated in some of the analysed samples compared to the white glass. LA-ICPMS data from B. Gratuze, IRAMAT

Сл. 7. Садржај оксида антимона (Sb_2O_3) у пурпурном стаклу је у значајној мери виши него у белом стаклу, нарочито код узорка подгрупе Пурпур 2, док је бакар-оксид (CuO), у поређењу с белим стаклом, повишен само у неким испитаним узорцима. LA-ICPMS подаци добијени од Б. Грагуза, IRAMAT

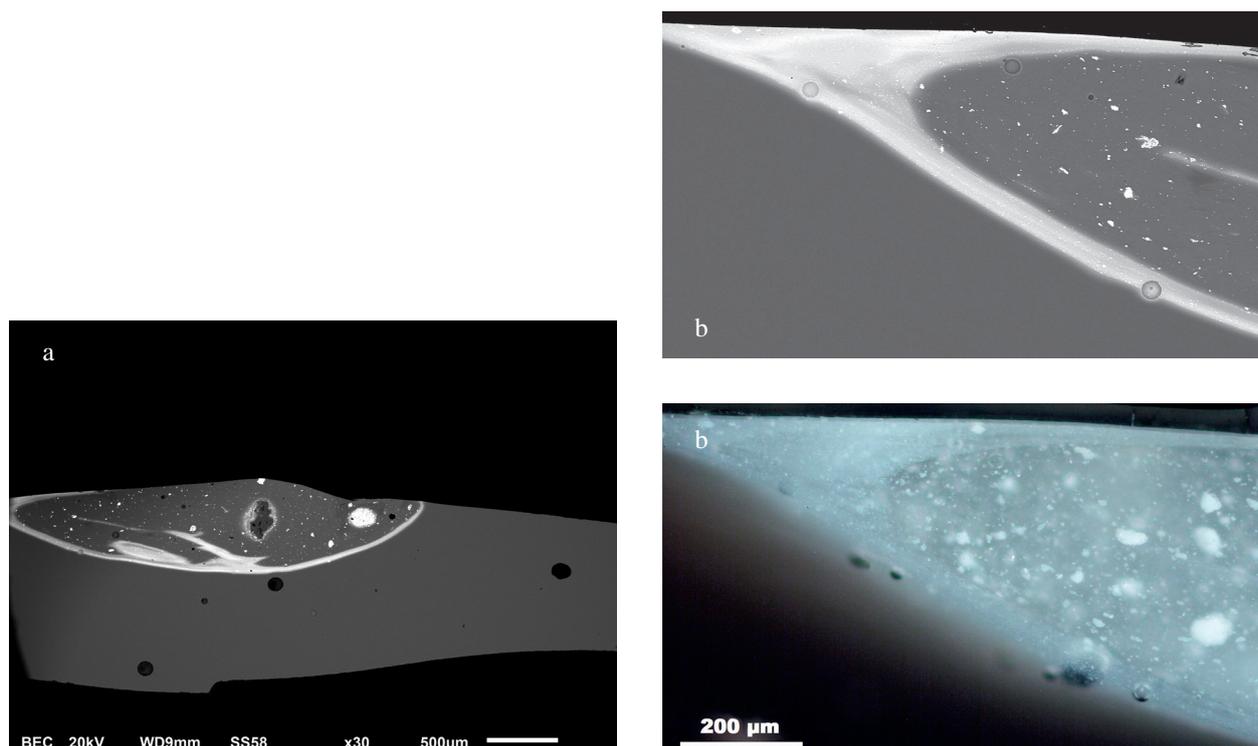


Fig. 8. Cross section through fragment BRN 1-13. Note the homogenous body (mid grey) and the white trail marvered into the body (white, upper part, with discrete bright white particles and clusters of tin oxide). SEM-BSE image (a; scale bar is 0.5 mm). Close-up of the left corner of the trail as OM micrograph and as SEM-BSE image showing that the glass is not fully opacified and only the external layer of the trail is rich in tin and lead oxides (b; scale bar is 0.2 mm)

Сл. 8. Пресек кроз фрагменту BRN 1-13. Уочавају се хомогено тело (средње сива) и бела ниш створљена са телом посуде (бела, горњи део, са дискретним светлим белим честицама и кластерима оксида калаја). SEM-BSE слика (a; размера је 0,5 mm). Детаљ левој угла беле ниши као OM микрограф слика и као SEM-BSE слика показује да стакло није потпуно непрозирно и да је само спољашњи слој ниши бојати оксидима олова и калаја (b; размера је 0,2 mm)

Texture of the purple glass

Vessel glass is often considered very homogenous, due to the nature of glass as a melt which solidified without crystallisation. The purple area of fragment BRN 1-13 is an example of such a very homogenous glass (Fig. 8a, b). However, all other sampled purple glasses are not entirely homogenous in their texture, but in cross section appear striated with slightly lighter stripes or layers within the predominantly mid-grey²¹ matrix (Fig. 9a, b). These stripes are due to different concentrations of metal oxides in the different layers, with increased lead and tin content in the lighter parts. At higher magnification, discrete particles rich in lead and tin oxide become visible within some of the light striations (Fig. 9b). Among the six fragments studied microscopically,

this is particularly pronounced in the purple areas of BRN 1-04, 1-09, and 1-14b. BRN 1-05 and 1-07 are less clearly layered, while only BRN 1-13 appears entirely homogenous in the purple glass. There is no correlation between the presence and intensity of layering and the compositional subgrouping; two of the striped fragments belong to Purple 1 subgroup (i.e. samples BRN 1-14b.p, 1-05.p), and three to Purple 2 subgroup (i.e. samples BRN 1-04.p, 1-09.p, and 1-07.p).

²¹ The grey shade refers to the appearance in the SEM-BSE images, which highlight compositional differences. Lighter shades represent higher concentrations of elements with a higher atomic number, such as heavy metals.

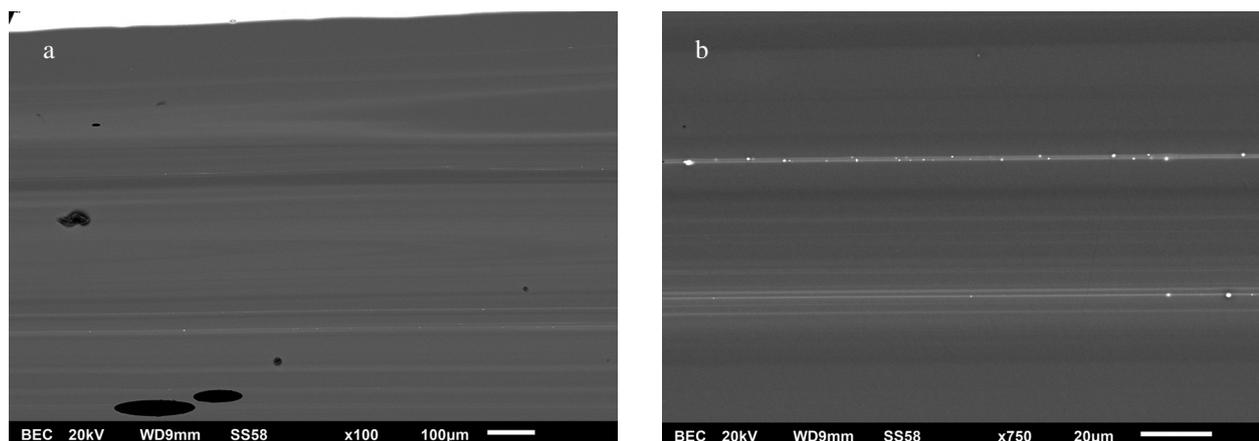


Fig. 9. Partial cross section through fragment BRN 1-04, showing the striation in the purple body. Different shades of grey represent different compositions, with higher levels of lead and tin oxide showing as lighter tones. Air bubbles appear black (lower left corner), while the upper edge of the image shows the beginning of the bright white layer on top of the purple body. SEM-BSE image (a; scale bar is 0.1 mm). Close-up of the same fragment, showing details of the striation in the purple body. The bright white particles are very rich in lead. SEM-BSE image (b; scale bar is 0.02 mm)

Сл. 9. Делимичан пресек кроз фрагмент BRN 1-04 показује пругасте трајеве на пурпурној позадини. Различите сенке сиве боје представљају различити хемијски састав, са вишим вредностима оксида олова и калаја који су приказани у светлијим тоновима. Ваздушни мехурићи се појављују у црној боји (доњи леви угао), док горња ивица слике приказује почетак светлој белој слоја на површини пурпурне основе. SEM-BSE слика (a; размера је 0,1 mm). Кружни план истој фрагменту показује детаље пругастих елемената у пурпурној основи. Светле беле честице су веома бојате оловом. SEM-BSE слика (b; размера је 0,02 mm)

The triplicate LA-ICPMS analyses of almost all analysed fragments also show this strong and relatively unusual pattern of compositional heterogeneity, indicating that the molten glass was not very well mixed, and contaminated with some white glass, as demonstrated by the elevated tin and lead content (see below).

The white decoration

The trails of opaque white glass were clearly applied on the outer surface of the purple vessels, as is common for this type of decoration which goes back to the first core-formed glass vessels dating to the Late Bronze Age, and continued to be used through the Hellenistic and Roman to Late Antique periods, into the Islamic period and even into early modern Western Europe²². Typically, the trailed decoration was then combed and marvered into the body glass, making a flush and smooth overall surface and feathered design²³.

While the vessels studied here fall into the group of vessels commonly referred to as ‘marvered’, it is noteworthy that in several of the Braničevo fragments this marvering appears not to have been done fully in each case, with some of the white trails left standing

proud of the purple glass surface (Fig. 10a, b; Fig. 11).

In other areas, however, the white glass appears fully pressed into the purple glass, as one would expect from properly marvered glass. The marvered working is recognisable in some cross sections, from the sloping boundary between the two glass types, and the dislocation of the striations in the purple glass (Fig. 12; see also Fig. 8).

As already mentioned, the LA-ICPMS data suggests that the white glass is compositionally quite heterogeneous (see Appendix), and this is also evident from the SEM imaging, in particular if the contrast is adjusted to reveal these differences (Fig. 13a, b, c). In SEM-BSE images, the white glass also appears white due to its high lead and tin content, in a similar contrast to the optical appearance (cf. Fig. 6b). Closer inspection

²² An extraordinary example of marvered combed decoration from Western Europe, late 16th – beginning of the 17th c. in Patin et al. 2017.

²³ For instance, see kohl bottles from the al-Sabah Collection, dated to the 12th–13th c. in Carboni 2001, 304–305, Cat. No 80.



Fig. 10. Examples of white decoration trailed onto the wall surface but not marvered into the body – wall fragment of a bottle (a) and rim fragment of a flask (?) Cat. No 14 (b); width of each image c 3–4 cm

Сл. 10. Примерци беле декорације на површини посуде који нису сипољени са шелом посуде – фрагменти шела боце (a) и фрагменти обода мале боце? Cat. No 14 (b); ширина сваке слике износи око 3–4 cm

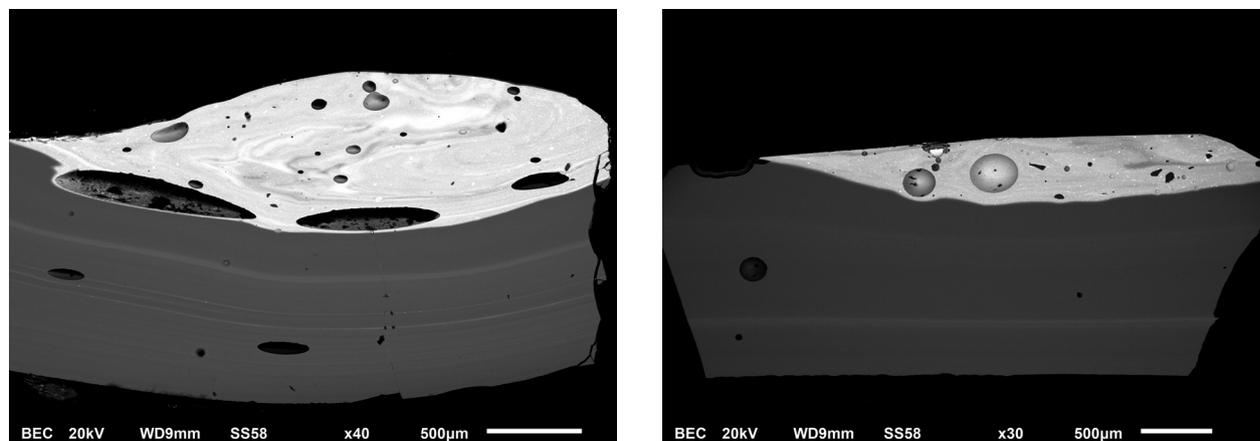


Fig. 11. Cross section through fragment BRN 1-07, with an incompletely marvered white thread overlaying the purple glass body (mid-grey). Air bubbles appear black. Note the internal heterogeneity of the white glass, and the elongated air bubbles trapped between the white and purple glass showing the incomplete bonding of the two glasses. SEM-BSE image; scale bar is 0.5 mm

Fig. 12. Cross section through fragment BRN 1-05. The tapering of the white colour shows how the white glass has been marvered into the purple body. SEM-BSE image; scale bar is 0.5 mm

Сл. 11. Пресек кроз фрагмент BRN 1-07, са непуно сипољеном и ушиснутом белом нишом која покрива цурпурно шело посуде (средње сива). Ваздушни мехурићи су црни. Обратите пажњу на унутрашњу хетерогеност белој стакла и издужене мехуриће „заробљене“ између белој и цурпурној стакла који указују на непуно сипање ове две врсте стакла; SEM-BSE слика; размера је 0,5 mm

Сл. 12. Пресек кроз фрагмент BRN 1-05. Исцртавање беле боје показује како је бело стакло ушисано у цурпурну основу; SEM-BSE слика; размера је 0,5 mm

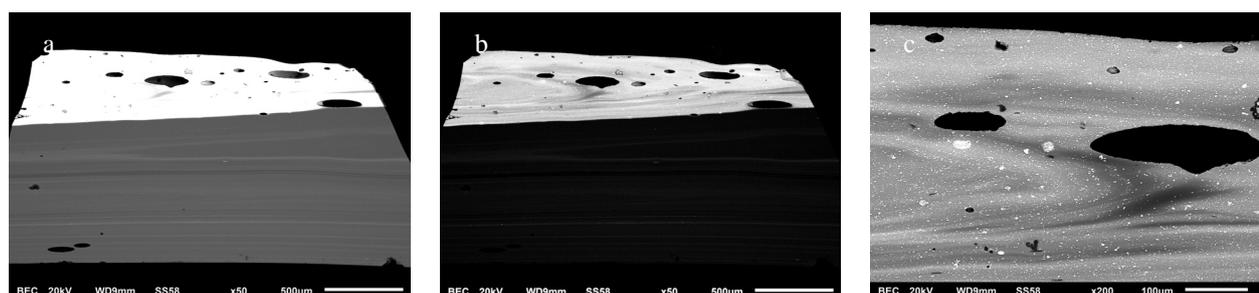


Fig. 13. Cross section through fragment BRN 1-04, at normal contrast setting showing the lead-rich white layer on top of purple (mid-grey, striated). Note the equally elongated air bubbles (black) in the white and purple glass, indicating that the vessel was possibly further inflated after the white decoration had been applied. SEM-BSE image (a; scale bar is 0.5 mm). The same area with the contrast setting to show the heterogeneity of the lead-rich opaque white layer on top of the purple glass (almost black, striation faintly visible). SEM-BSE image (b; scale bar is 0.5 mm). Close-up of the same area showing the internal structure within the white layer with parts of the glass having a much lower lead content (dark grey), and discrete particles and clusters of tin oxide (white) acting as an opacifier. SEM-BSE image (c; scale bar is 0.1 mm)

Сл. 13. Пресек кроз фрагмент BRN 1-04. При нормалном подешавању контраста уочава се слој белог стакла бољаш оловом на пурпурној основи (средње сива, пругастии пратови). Уочавају се једнако издужени ваздушни мехурићи (црна боја) и у белом и у пурпурном стаклу, који наводе на помисао да је посуда поново дувана након што је бела декорација аплицирана; SEM-BSE слика (a; размера је 0,5 mm). Исти део са контрастним подешавањем показује хетерогеност непрозирног белог слоја бољашо оловом на пурпурној основи (скоро црна, пругастии елементи једва видљив); SEM-BSE слика (b; размера је 0,5 mm). Увећање овог дела показује структуру белог слоја са деловима стакла који имају знатно нижи ниво олова (шамносива), и дискретне честице и класстере оксида калаја (бело), који се користии да би се постигла непрозирност; SEM-BSE слика (c; размера је 0,1 mm)

and respective SEM-EDS measurements demonstrate that the white glass has variable quantities of tin and lead oxides resulting in a swirled or *schlieren* appearance typical of incomplete mixing of two viscous liquids. Higher magnification shows the individual discrete particles and bigger clusters of particles of tin oxide which give opacity to the glass, and their uneven distribution in a matrix which is also very variably saturated with lead oxide.

The white thread in fragment BRN 1-13 is unusual in that it seems to consist mostly of a thin lead-rich outer layer surrounding a core of weakly coloured glass which is only partly opacified with relatively big particles of tin oxide and, according to the EDS data, contains hardly any lead oxide (see Fig. 8b). Thus, the texture of the white area of fragment BRN 1-13 provides further evidence of the heterogeneity of the opaque white glass.

DISCUSSION

Several aspects of the results presented here can be discussed that are informative for the understanding and archaeological interpretation of this unique assem-

blage. Firstly, there is the question of how the different glass compositions relate to each other, and what this tells us about the working practices of the producers of these vessels. Secondly, there is the question of the origin of the base glass and the nature of the colorants used to produce these colourful objects. Finally, we will briefly discuss how this assemblage compares compositionally to other analysed marvered vessels with white trails.

The working practices of the vessel producers

The assemblage consists of three chemically distinct glasses, namely the two subgroups of the translucent purple – Purple 1 and 2 – and the opaque white glass. The compositional difference between Purple 1 and 2 is only small, but for several oxides and trace elements it is clearly bigger than the variability within each subgroup, indicating that they are indeed two separate subdivisions of the purple glass. On balance, the base chemical makeup of Purple 1 and Purple 2, their colorations, as well as the technique of vessel decoration bind the two subgroups together. Importantly, the opaque white glass on the two purple glasses does not separate

into two clearly distinct subgroups, but appears to be chemically consistent, regardless of whether it is applied on Purple 1 or Purple 2. Thus, the white glass was taken from one and the same stock, even if the purple glass is slightly different. One can, therefore, argue that all vessels were probably made in the same workshop, with Purple 1 and Purple 2 representing two different stocks, batches or pots of molten glass, while the opaque white trails, used much more sparingly and in smaller amounts than the purple, were from the same batch for both production series of purple vessels.

Important differences between the two purple subgroups are observed in their trace element patterns, particularly in the levels of tin and lead oxide contamination (see Fig. 4), where Purple 2 has noticeably higher levels. We argue that the presence of these elements indicates some contamination of the batch by the white glass, possibly by incidental inclusion of white glass pieces (wasters?), or/and perhaps during the working process when the same tools were used to retrieve hot glass and combine it with the purple paraison when forming the vessels. Such a hypothetical explanation is further corroborated by the contamination of the opaque white glass of fragment BRN 1-09. Its adulteration with stripes of purple glass (see Fig. 6) represents the opposite effect of the same working practice, i.e. a certain amount of purple glass was accidentally admixed into the white batch. As mentioned above, Purple 2 subgroup features higher SnO₂ and PbO values than Purple 1, and this peculiarity once again confirms the differentiation of the two subgroups, possibly caused by variations of the secondary glass working operations. Nevertheless, the seemingly different trends for the Sn/Pb ratios in the two subgroups (see Fig. 4) should be taken with caution since the calculated higher average lead oxide levels in Purple 1 samples may well result from the internal heterogeneity of some of them²⁴.

At the same time, Purple 2 has an intriguing pattern of relatively high contamination with antimony oxide (around 290 ppm on average compared to only c 75 ppm in Purple 1); the white glass, in contrast, has even less antimony, with only about 15 ppm Sb₂O₃ (see Fig. 7), close to the natural background concentration of this oxide in glassmaking raw materials²⁵. The copper content is variable but also higher (at trace oxide level) in the analysed purple fragments than in the white glass, and this pattern is overall indicative of a further source of contamination of the purple batches. Increased levels of elements which can affect the colour of the glass (e.g. copper, cobalt, antimony, etc.), which are,

however, significantly lower than those of purposely used additives, have long been recognised to denote contamination of raw glass with cullet containing small amounts of coloured fragments²⁶. Accordingly, we interpret the current data as evidence of the addition of certain amounts of cullet glass, particularly in the purple melts. Such mixing could have taken place either at the stage of primary glass making, or in the secondary glass workshop where the actual vessel manufacture took place, or possibly even at both stages of production²⁷.

An even more detailed insight into this practice of cullet re-melting can be inferred from the differences at trace element level between Purple 1 and Purple 2. Samples of the Purple 2 subgroup feature the highest boron concentrations in this assemblage which set them apart from the other purple glass and the white glass (Fig. 14). Traces of boron are usually present in the raw materials used in glass making but such an abrupt increase of B₂O₃ concentrations as seen in Purple 2 (even if still being at trace oxide level) could indicate an additional source of this element in the glass melt. High-boron glasses of the Middle Byzantine period, approximately contemporaneous with the vessel assemblage from Braničevo, form a well distinguishable category of various chemical compositions, which is likely related to specific raw materials from Western Anatolia²⁸. Recently, a particular link between these compositions and manufacture of 10th–12th c. Byzantine glass bracelets has been proposed²⁹. As suggested above, the cullet inclusion in the purple batches seems quite probable, and the increased B₂O₃ levels in Purple 2 allow further hypothesizing that at least a certain part of that reused glass was of high-boron composition. This, in turn, could be interpreted as evidence for an

²⁴ The heterogeneity of Purple 1 subgroup is particularly pronounced for the PbO content of samples BRN 1-05 and BRN 1-11. The coefficient of variation between the triple individual PbO measurements for the Purple 1 samples typically ranges between c 6% and 27%, while for samples BRN 1-05 and BRN 1-11 it is 57% and 103%, respectively. The highest PbO level is nearly 8000 ppm, measured on BRN 1-05, and the lowest individual measurement on the same sample is c 1000 ppm.

²⁵ Brems, Degryse 2014, 79; Jackson 2005, 764; Rehren, Brüggler 2015, and literature therein.

²⁶ Jackson 1996; Freestone 2015, 34–36.

²⁷ Recycling of cullet and discarded glass is considered an intrinsic feature of Islamic glass production – cf. Jenkins 1986, 3; Freestone 2002, 76.

²⁸ Brill 2005, 215–219; Rehren et al. 2015, 276–277.

²⁹ Swan et al. 2018, 228 and literature therein.

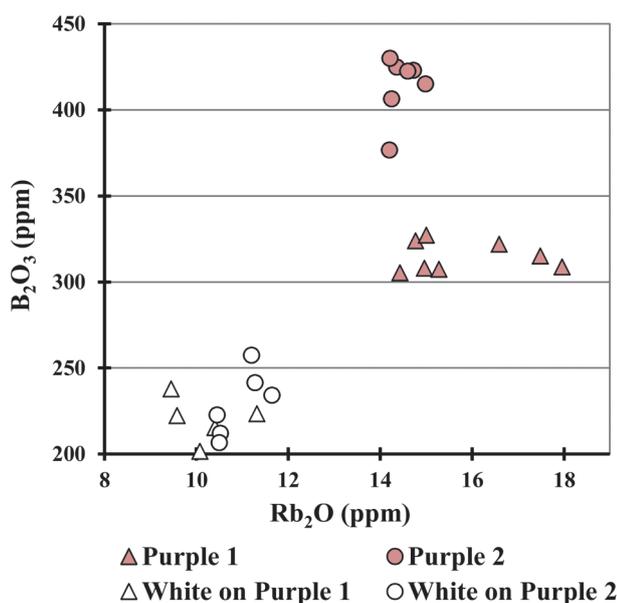


Fig. 14. The rubidium oxide (Rb_2O) and boron oxide (B_2O_3) contents of the purple glasses are higher than those of the opaque white glass, with a further increase of B_2O_3 in the Purple 2 subgroup which is tentatively explained as resulting from the addition of cullet of high-boron composition in the Purple 2 batch. LA-ICPMS data from B. Gratuze, IRAMAT

Сл. 14. Вредности оксида рубидијума (Rb_2O) и борона (B_2O_3) више су у пурпурном стаклу него у непрозирном белом стаклу, са даљим увећањем B_2O_3 у подгрупи Пурпур 2, што је условно објашњено као резултат догађања стаклене отпаде са високом концентрацијом борона у прешајању подгрупе Пурпур 2. LA-ICPMS подаци од Б. Грагуза, IRAMAT

unselective and possibly ad hoc recycling practice which could have taken place in the workshop of the vessel manufacturers, causing minor compositional variations between the different batches of purple glass.

Overall, we interpret the chemical composition of the Braničevo assemblage to indicate that the analysed vessels were made in two separate production events, but most likely in the same workshop which used slightly different batches of purple glass. This could have been either on two different days, or even at the same time, using two separate pots of molten glass from which glass blowers worked side-by-side. It is noteworthy that it seems that a single stock of white glass was used during both production episodes. From the trace element concentrations we recognise the incorporation of some cullet containing certain amounts of copper in the purple batches, and antimony and boron in the Purple 2 batch in particular. Such an indiscriminate recycling could indicate relatively unsophisticated production practices, as is further corroborated by the reciprocal contamination of the purple and white batches, possibly resulting from not too attentive or skilful tool manipulation by the craftsmen when applying the vessel decoration.

Finally, when comparing the purple compositional subgroups and vessel shapes, it is evident that the bottles and the analysed bigger bowl are made of Purple 2 glass, while the smaller bowls and flasks are Purple 1 (see Appendix). The correlation between glass compositions and vessel shapes within a single set, likely manufactured in a single workshop, provides an

intriguing glimpse at the organisation of the craftsmen. It seems possible that relatively standard series of uniform vessels were made from a single batch – e.g. bottles with handles made of Purple 2 glass only – either by a single (specialised?) glassblower, or by several craftsmen simultaneously implementing identical production tasks.

The origin of the glass, and its colouration

The composition and provenance of Islamic glass from the late 1st and early 2nd millennium AD has been the subject of numerous studies³⁰, which provide a sound body of comparative data against which to juxtapose the composition of the vessels from Braničevo. In this way, it is possible to broadly specify the production region from which the glass used for the manufacture of the set originated. Such an attribution, however, would only locate the production of the raw glass itself, and does not imply that the vessels as objects were necessarily manufactured in the same region. This is due to the organisation of the medieval Near Eastern glass industry which was likely divided into technologically, and possibly also spatially, separate stages of glass making and glass working³¹.

As mentioned earlier, the analysed purple and white samples generally match the common Islamic soda

³⁰ Most recently Phelps 2017; Henderson et al. 2016; and Swan et al. 2017, 110–114, and references therein.

³¹ Whitehouse 2009, 506–507.

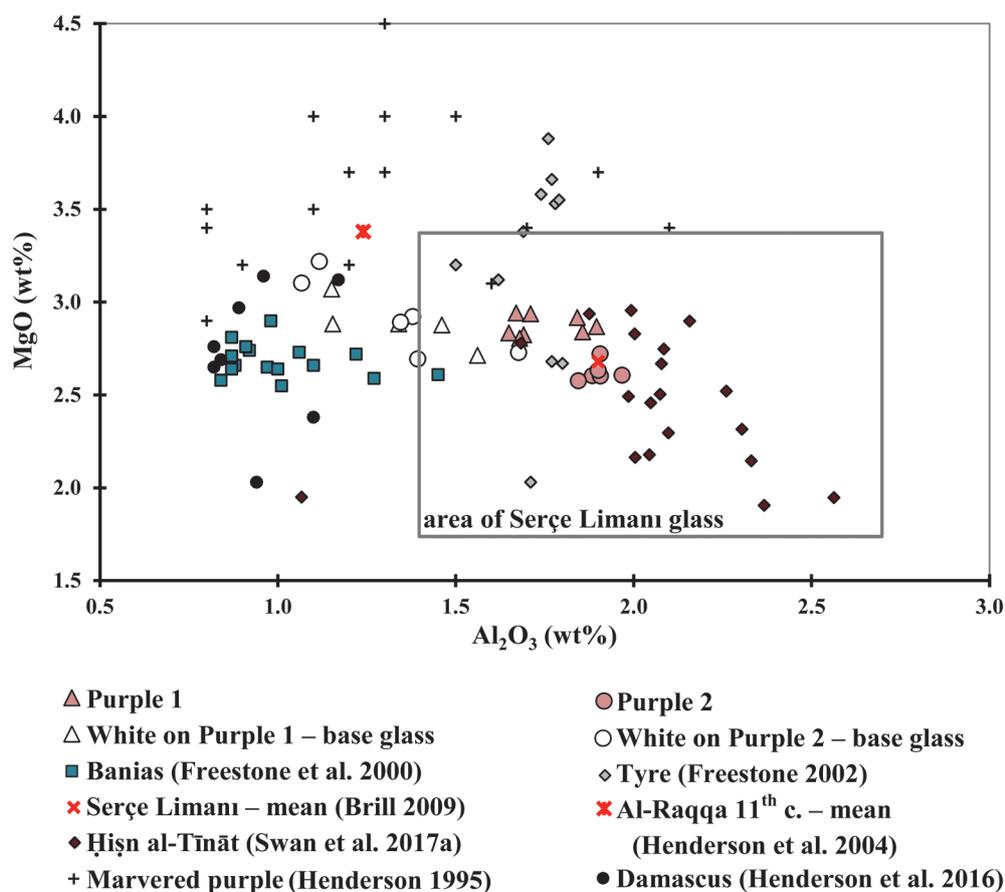


Fig. 15. The alumina (Al_2O_3) and magnesia (MgO) contents of the Braničevo glasses (the opaque white glass recalculated to represent the base composition – see footnote 32) compared to published analytical data for selected glass groups from the Levant. The samples of purple glass decorated with marvered threads in the Ashmolean Museum (data from Henderson 1995) have generally higher magnesia and do not seem to form a defined cluster

Сл. 15. Вредности оксида алуминијума (Al_2O_3) и магнезијума (MgO) у стаклу из Браничеве (вредности за непрозирно бело стакло су модификоване – види нап. 32) у поређењу са публикованим аналитичким подацима за издвојене групе стакла са Левантиа. Узорци пурпурног стакла украшени аплицираним нишима у музеју Ешмолијен (подаци из: Henderson 1995) имају генерално виши ниво магнезијум-оксида и не представљају дефинисану групу

plant-ash glass composition, as could also be expected on the basis of the stylistic features of the vessels. Among the several major regions known to have produced glass in the early 2nd millennium AD Byzantine and Near Eastern Islamic worlds³², the Levantine coast and the adjacent territories seem to provide the closest compositional parallels of the Braničevo assemblage. It is beyond the scope of this paper to present a thorough comparison of the Braničevo samples with the known glass makeup from this region, not least because of the variable extent of compatibility between the available literature data. Nevertheless, some general

compositional affiliations are outlined below, based on two diagnostic major oxides.

A scatter graph of the alumina and magnesia levels in the present samples shows how they relate to some of the published analytical sets from the Levantine

³² These regions include Egypt, the Levantine coast, Mesopotamia and Iran, and Western Anatolia, with the latter two being ruled out based on their specific trace element pattern. The differentiation between glass of Egyptian and Levantine origin is less clear-cut, and for now better understood for earlier mineral natron glasses than for medieval plant-ash glasses.

region, broadly dated to c 10th–12th/14th c. AD (Fig. 15). Since the added tin and lead oxides in the opaque Braničevo samples significantly distort the original composition of the raw glass, the values for all the white glass in this plot are recalculated in order to make them consistent with the rest of the data (see Table 1)³³.

As expected, the Purple 1 and Purple 2 subgroups form a tight single cluster featuring relatively high alumina concentrations. As mentioned above, we tentatively interpret the internal differentiation of this cluster as a result of minor variations between the two batches and glass mixing which have no significance in regard to glass provenancing. Remarkably, the recalculated base composition of the opaque white samples has lower alumina and, on average, slightly higher magnesia than the purple glass. Such Al₂O₃ values (mean c 1.3 wt%) associate the base glass of the Braničevo decoration with the composition found in chunk glass samples from a secondary production site in Baniyas (Northern Israel) dated to the 10th/11th–13th c. AD³⁴. Samples of 12th–14th c. vessel glass from Damascus (Syria), broadly from the same inland Levantine region, also display comparable alumina and magnesia levels³⁵.

In contrast, the purple samples from Braničevo fall into the area of the Serçe Limanı glass – a vast shipwreck assemblage of vessels, cullet and raw chunks of Levantine/Syrian provenance, found off the South-Western Anatolian coast of Turkey, near Rhodes, and dated to the third decade of the 11th c. AD³⁶. These glasses have generally higher alumina and also more variable magnesia levels. A similar trend of negative correlation of Al₂O₃ and MgO is seen in a late 10th – early 12th c. assemblage of glass bracelets from Hisn al-Tīnāt (Turkey), at the North-Western edge of the Levantine coast³⁷. The samples from the large primary glass production furnaces excavated in Tyre (Lebanon) on the Levantine coast and tentatively dated to the 10th–11th c. should also be mentioned here, despite their broader range of MgO, since a common regional origin of the Tyre composition and the Serçe Limanı glass can possibly be recognised³⁸.

Such a summarised overview of the compositional analogies of the Braničevo samples confirms the differentiation of the opaque white and the purple glasses in terms of their base chemical makeup, and may suggest that they possibly come from different production zones within the broader Levantine region. This would imply that the workshop where the vessel set was manufactured procured its raw materials from more than one source. Nevertheless, provenancing plant-ash glass on

the basis of major oxides only may not be entirely straightforward or conclusive because of the variability of the plant ash component³⁹ as well as due to the dynamic connections and exchange of raw materials which likely existed between the different production centres within the Levant and beyond⁴⁰. Some isotope studies, for example, suggested that the Baniyas glass was probably produced, like the Tyre glass, on the Mediterranean coast instead of in the inland Levant, but these two littoral production centres used plant ashes procured from different areas⁴¹. Furthermore, on the basis of isotope data, a common origin of the plant ash used in Tyre and the North Syrian production centre at al-Raqqā has been proposed⁴².

Apparently, complex phenomena of technological and economic interactions developed between the glass production regions in the medieval Levant and on a wider geographical scale. In this context, a secondary workshop, such as the one that manufactured the Braničevo vessels, could probably have been supplied with raw glass, cullet and possibly even prefabricated opacified glass (see below) from various sources. Therefore, associating its production with a particular primary production centre within the Levant may not be plausible at the present stage of research.

Regarding the colouration of the analysed samples, it was previously mentioned that the purple colour is

³³ This recalculation excluded SnO₂ and PbO, and the remaining composition was re-cast to 100% to represent the base glass used to produce the opaque white composition, similar to the approach of 'reduced composition' in Brill 2009, 482 and the references therein.

³⁴ Freestone et al. 2000, 69, Table 2; Freestone 2006, 203. Note that Samples 49 and 54 from Freestone et al. 2000 are not included in Fig. 15 as they do not match the main cluster of Baniyas glass.

³⁵ Henderson et al. 2016, 144.

³⁶ Brill 2009, 479–492. The outlined area in Fig. 15 includes the samples of the main group of Serçe Limanı glass, without the samples with extreme Al₂O₃ and MgO values.

³⁷ Swan et al. 2018, plant-ash glass of Group 1, 222–223.

³⁸ Freestone 2002, 73–77 and the references therein; Brill 2009, 480. Note that Sample 5 from Tyre in Freestone 2002 is not included in Fig. 15 as it is supposed to be an outlier.

³⁹ Freestone 2006, 205, 212; Degryse et al. 2010, 83.

⁴⁰ Henderson et al. 2009, 426.

⁴¹ Degryse et al. 2010, 89.

⁴² Freestone et al. 2009, 44–45; for al-Raqqā glass see Henderson et al. 2004. The plant-ash glass of subtype 1 found at the Tell Fukhkhar site in 11th c. AD al-Raqqā has, on average, slightly higher MgO than the Braničevo samples (Fig. 15).

caused by higher levels of manganese oxide⁴³. Besides the intentionally added MnO, there are higher strontium, barium and iron contents in the purple compositions, with Fe₂O₃ particularly higher in Purple 2. Rather than weakening our argument for a close chemical similarity to the Levantine glasses which typically have lower levels of these elements, we argue that these differences are a direct consequence of the added manganese mineral. This is most clearly argued for barium, the concentration of which in the purple glass is closely correlated with the manganese concentrations, reflecting the known geological correlation of the two elements in barium-containing manganese minerals. However, the added Mn-bearing material was possibly a mixture of different minerals, some rich in manganese, others rich in iron (and possibly also titanium and aluminium), which accordingly increased the iron oxide content of the purple glasses even though no direct Mn–Fe correlation can be identified⁴⁴.

The opaque white glass of the Braničevo vessels is produced by adding tin and lead oxide to common transparent and, most probably, decolourised or slightly tinted base glass. The opacity and the white colour result from the minute tin oxide particles dispersed in the glass, while lead is typically dissolved in the glass matrix, helping to lower the range of temperatures at which glass is sufficiently soft to be shaped⁴⁵. Such particular working properties of the opaque white glass, even if probably not deliberately sought, were certainly necessary when the soft threads were applied onto the vessel walls and dragged up to form the festoon pattern, while at the same time the purple vessel itself had to be kept stable and not deformed by the contact with the viscous white glass.

The analytical study of Islamic marvered vessels by J. Henderson found the same additives in the opaque white thread decorations⁴⁶. Furthermore, an identical production technology of mixing base plant-ash soda-lime-silica glass with tin and lead oxides is recognised in pre-fritted tin white enamels of the later Islamic glasses of the 13th–14th c⁴⁷. A comparison of these data and the Braničevo samples demonstrates that all opaque white decorations have similar levels of SnO₂ and PbO, with the Braničevo samples featuring generally lower tin oxide concentrations (Fig. 16). Interestingly, the trend of a pronounced heterogeneity of the glass and incomplete mixing of the additives mentioned above is also noticed in some tin white enamel samples⁴⁸.

Previous research suggested that opaque glass production possibly formed a more specialised section

of the Islamic glass industry because of the particular knowledge and skills required regarding the opacifying technology⁴⁹. Hypothetically, this includes the distribution of prefabricated coloured glass as raw material to secondary workshops. The differences between the base composition of the purple and the opaque white samples from Braničevo could be interpreted as an indirect corroboration of such a hypothesis. At the least, these differences rule out the possibility that both colours were produced in the glass blowers' atelier using one and the same starting batch of common base glass. It seems plausible that the white glass was brought as readymade raw material to the glass blowers' workshop and was used there without further compositional modifications (apart from the contamination with purple glass) in the two separate production events of Purple 1 and Purple 2 vessel manufacture.

Comparison with other Islamic marvered vessels

The extent of published analytical data on Islamic marvered glasses available from the literature is relatively limited. The most comprehensive research is the already mentioned study by J. Henderson⁵⁰, who presents compositional analyses of 26 different objects

⁴³ It is suggested that manganese was added in Islamic plant-ash glasses already at the primary stage of production in order to improve their colour and texture, and this addition may not have been according to a strictly controlled recipe (Freestone 2002, 76). However, it is not clear whether higher manganese concentrations used to obtain purple glass colour were added during the primary glass making, or at the stage of secondary glass working. Significantly, the dark purple colour of marvered vessels is presumed to be characteristic of Syrian workshops (Carboni 2001, 305), further supporting the proposed Levantine origin of the glass of the Braničevo vessels.

⁴⁴ Cf. Henderson 1995, 37.

⁴⁵ Previous studies on Islamic white enamels have demonstrated that the significant levels of lead oxide facilitate lower softening temperatures of the enamel, while also providing an increased opacity effect due to the complex processes of tin particles recrystallisation – see Freestone, Stapleton 1998, 126; Salvant et al. 2016, 10.

⁴⁶ Henderson 1995, Table 2.

⁴⁷ Freestone, Stapleton 1998, 125, 126–127, Table 3; Wypyski 2010, 113. However, certain compositional differences between opaque white marvered decoration and white enamels are also noted – Henderson 1995, 40–41.

⁴⁸ Freestone, Stapleton 1998, 125.

⁴⁹ Henderson 1995, 40.

⁵⁰ Henderson 1995.

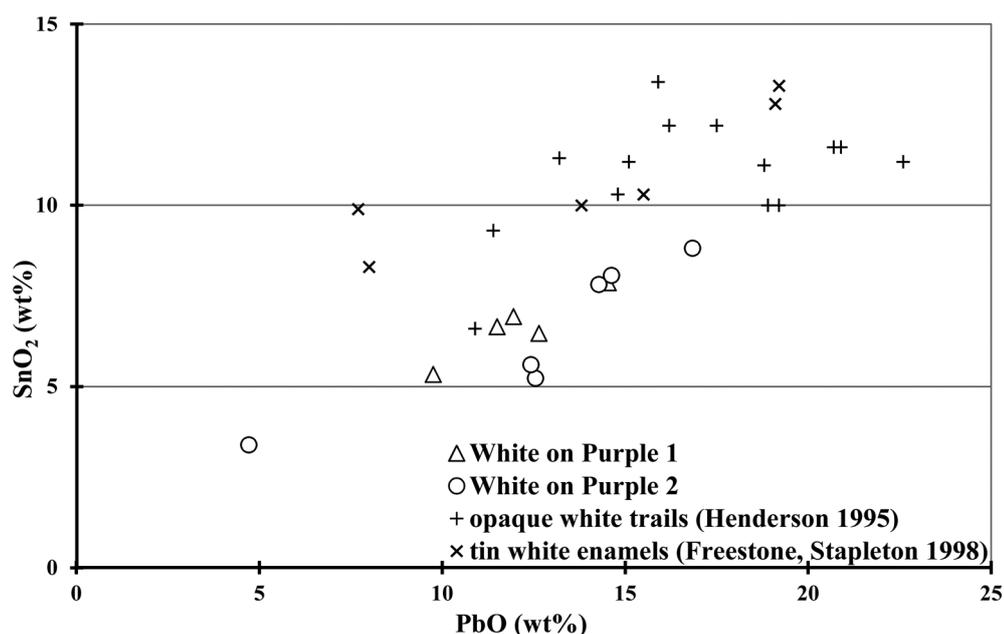


Fig. 16. The lead oxide (PbO) and tin oxide (SnO₂) levels in the opaque white glass are similar to the values found in the marvered white threads of the Islamic glass in the Ashmolean Museum (data from Henderson 1995) and in the tin white enamel decoration of the Islamic vessels in the British Museum (data from Freestone, Stapleton 1998). Note the lower SnO₂ content of the present samples; the tight positive correlation of the two additives in the Braničevo glasses strongly suggests that they come from a single batch, as opposed to the more dispersed pattern of the Ashmolean and British Museum datasets obtained from vessels of diverse origins

Сл. 16. Вредности оксида олова (PbO) и калаја (SnO₂) у непрозирном белом стаклу сличне су вредностима нађеним у аплицираним белим нишима у исламском стаклу у музеју Ешмолијен (подаци из: Henderson 1995) и у калајнобелој емајлираној декорацији исламских посуда у Британском музеју (подаци из: Freestone, Stapleton 1998). Обраћајући пажњу на нижи ниво SnO₂ у присућним узорцима; чврста позитивна корелација два додатака оксида у стаклу из Браничева доказ је да постоји из јединствене смесе, насупротив друкчијем обрасцу у сетовима података добијених код посуда које имају различито порекло

from the Ashmolean Museum's collection, including 13 opaque white trails and 16 transparent purple bodies. The majority of these finds come from Fustat (Egypt) but unfortunately lack clear archaeological context and dating⁵¹. Five samples of white-marvered and threaded glass fragments of brown colour are published among the analysed finds from the Monastery of Wadi al-Tūr in Sinai (Egypt), typically of a post 10th c. AD date⁵². Finally, a fragmented white-marvered vessel of reddish brown colour excavated at Pergamon (Turkey) is dated to the 12th–13th c. AD⁵³.

Significantly, there is no compositional match between these published samples and the glass of the vessel bodies from Braničevo, even though the decoration and stylistic features of the objects define all of them as belonging to the group of marvered Islamic glass.

The vessels in the Ashmolean collection have generally higher magnesia levels which are comparable, for instance, to the 11th c. AD plant-ash glass found in Northern Syria (Fig. 15)⁵⁴. Furthermore, the Ashmolean samples of purple vessel glass demonstrate a wide compositional range, not forming a clearly defined

⁵¹ Allan 1995, 7–9.

⁵² Kato et al. 2010, minor type III, 1393, Figs 2q, 2r.

⁵³ Rehren et al. 2015, sample PER062, Fig. 2f (the label in the figure wrongly attributes this sample to the plant ash glass group of Pergamon; it in fact belongs to the HBA1 / High Boron Alumina group, see Table 2, p. 270).

⁵⁴ Cf. Henderson et al. 2004, Table 3, Fig. 3 – the 11th c. AD Tell Fukhkh plant-ash glass of subtype 1.

cluster, as opposed to the tight grouping of the Braničevo purple glasses. On the other hand, the samples from Sinai have a particular chemical pattern which resembles glasses of Egyptian provenance (e.g. elevated titania associated with a combination of higher alumina values and relatively low concentrations of lime), which distinctly sets them apart from the common Levantine glass makeup. In this respect, the Pergamon example is similar to the samples from Sinai but also features considerably elevated alumina ($\text{Al}_2\text{O}_3 > 8\text{wt}\%$) and high boron levels, indicating yet another production origin of the raw glass used in Islamic marvered vessel production.

This diversity of chemical glass compositions found across a fairly small and unsystematic database of available analytical results is not surprising, given that the manufacture of vessels with marvered trails is associated with different wider regions (e.g. Egypt and Syria⁵⁵) and particular cities (e.g. Jerusalem⁵⁶). It seems possible that, in fact, the Islamic marvered glass represents an inter-regional phenomenon of shared and replicated aesthetic trends and fashion, rather than production of a specific artisanal centre which could be characterised by a distinct chemical glass composition.

Such a complex and non-centralised model, probably with its own dynamics over time, tentatively reconstructed on the basis of glass chemistry, is also confirmed by the diversity of techniques of applying the trails. As previously mentioned, the decoration of the Braničevo vessels does not seem to be fully marvered in all areas, as usually seen with such objects⁵⁷. The smear-like strokes of some of the festoons are not compatible with the typical technique of marvered trails⁵⁸. This suggests that the glass blowers probably tried to imitate, with their supplies of raw materials and at their level of proficiency, the appearance of the fashionable ornamentation without being closely familiar with the genuine ways of creating combed patterns.

CONCLUSION

The studied set from Braničevo is unique in terms of the extent of the assemblage and the securely-dated archaeological context, and for the first time offering the opportunity for a detailed chemical characterisation. Even if stylistically homogenous, the assemblage forms two distinct though compositionally closely related groups of purple glass, linked further by the opaque white glass, indicating their origin from the same workshop but from different batches and production

events. Both batches of purple glass have evidence of recycling in the base glass, and differ in the amount of added manganese, the purple colorant. They also have clear evidence of contamination with traces of the opaque white glass. The base compositions of the purple and the opaque white glasses are likely of Levantine origin. Nevertheless, such a provenancing does not necessarily indicate that the vessels themselves were manufactured in the Levant because of the division of the glass industry into primary glass making and secondary glass working stages.

For now, there are still not sufficiently large numbers of samples analysed for firm conclusions to be drawn, but apparently the marvered glasses do not form a consistent production group. The diversity of the glass compositions attested so far should not be unexpected if the popularity of the fashion had triggered the spread of this ornamental style and its further imitations in numerous workshops across the Islamic Near East – workshops which could have procured glass from various regions, hence with different chemical compositions. Nevertheless, the possibility of a more standardised production of the opaque white glass and its distribution as prefabricated raw material for the secondary glass workshops should not be ignored.

Further data from analytical research and thorough artefact studies would help to identify possible correlations between the chronologies, regions of distribution, vessel shapes, decoration techniques and glass chemistry within the apparently broader and diverse group of Islamic marvered vessels.

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⁵⁵ Carboni 2001, 305, 309, Cat. No 82.

⁵⁶ Brosh 2017, 305.

⁵⁷ See footnote 23.

⁵⁸ Cf. Carboni 2001, 291.

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ХЕМИЈСКИ САСТАВ И ТЕКСТУРА СЕТА СТАКЛЕНИХ ПОСУДА УКРАШЕНИХ АПЛИЦИРАНИМ НИТИМА (12. ВЕК) ИЗ БРАНИЧЕВА (СРБИЈА)

Кључне речи. – исламско стакло, декорација аплицираним стакленим нитима, Браничево, Србија, 12. век, LA-ICPMS, SEM-EDS, pXRF.

Стаклене посуде интензивних боја, украшене аплицираним нитима, представљају широко распрострањену и популарну, али слабо изучавану групу висококвалитетног стакленог посуђа средњовековног исламског порекла. У раду су дати детаљни хемијски и микроструктурни подаци за пурпурне стаклене посуде украшене непрозирним белим нитима, које су откривене у сету током ископавања на локалитету Браничево – Мали град. Фрагментоване посуде потичу из затвореног контекста, из слоја рушења Куће 4, који је, захваљујући осталим археолошким налазима, пре свега примерцима новца, датован у средину / другу половину 12. века.

Међу фрагментима је издвојено најмање 16 различитих посуда, и то шест малих здела, две велике зделе, три веће и две мале боце, и три посуде које су са резервом одређене као мале боце. Петнаест фрагмената од најмање 9 различитих посуда анализирано је методом масене спектрометрије са индукованом куплованом плазмом путем ласерске аблације (LA-ICPMS). Неколико уломака из ове групе издвојено је за анализу оптичким микроскопом и скенирајућим електронским микроскопом са енергетски дисперзивном спектрометријом (SEM-EDS), коришћењем детектора повратно расутих електрона (SEM-BSE) за снимање. Осим мерења у оквиру поменутог сета посуда, вршена су и мерења на око 30 других уломака пурпурног стакла, и то преносним рендгенским флуоресцентним спектрометром (pXRF), како би се потврдило издвајање хемијских подгрупа у читавом сету.

Резултати показују да је пурпурна основа посуда израђена од стакла на бази $\text{Na}_2\text{O} - \text{CaO} - \text{SiO}_2$ са биљним пепелом. Пурпурна боја добијена је захваљујући високим садржајима манган-оксида, који је намерно додат за потребе бојења стакла. Овакав став одговара типично исламском стаклу са биљним пепелом, а стилски типовима и декорацији посуда исламског порекла. У сету из Браничева идентификоване су две хемијске подгрупе – Пурпур 1 и Пурпур 2, са благим разликама у садржају главних оксида и елемената у траговима. Непрозрачно бело стакло, од којег су израђене аплициране нити, има сличну основну композицију као и пурпурно

стакло. Међутим, додавање оксида калаја и олова основном саставу овог стакла обезбедило је његову непрозирност и белу боју. У ове две подгрупе пурпурног, манганом бојеног стакла није уочена разлика у саставу белог стакла које је коришћено за израду декоративних нити на свим посудама у сету, што значи да оно вероватно има јединствено порекло.

У оба случаја (пурпурна основа, бела декорација) стакло је хетерогено и у микроструктури већине узорака видљиве су линије или слојеви који представљају различиту концентрацију оксида метала, као и дискретне честице богате оксидима олова и калаја. Оваква хетерогеност означава непотпуно мешање растопљеног стакла, вероватно рециклирање отпада, и по свој прилици контаминацију стакла алаткама коришћеним приликом израде посуда.

Хемијски састав посуда из браничевског сета показује да су оне израђене током две производна процеса, највероватније у истој радионици, у којој су коришћене незнатно различите смесе пурпурног стакла (Пурпур 1 и Пурпур 2). Када је реч о белом стаклу, очигледно је да је једна залиха коришћена током оба процеса. Поређењем подгрупа пурпурног стакла са формама посуда, утврђено је да су велике боце и већа здела израђене од стакла подгрупе Пурпур 2, док мање зделе и мале боце припадају подгрупи Пурпур 1.

Основна композиција пурпурног и непрозирног белог стакла вероватно је левантског порекла. То нужно не значи да су и саме посуде израђене на Леванту, будући да је познато да је производња стакла обухватала две гране – примарну израду сировог стакла и секундарну израду финалних производа. Поређењем састава наших примерака са објављеним подацима о хемијском саставу исламског левантског стакла потврђена је разлика у основној композицији пурпурног и белог непрозирног стакла, што указује на то да сировина потиче из две различите продукцијске зоне унутар левантске области. Наши резултати показују да је радионица у којој су посуде прављене набављала сировину из више од једног изворишта и да је могла бити снабдевена готовим непрозирним стаклом и, вероватно, разноврсним стакленим отпадом.

Appendix. Average values for the main oxides and trace compounds of the individual Braničevo glass samples, as determined by LA-ICPMS, and the average of eight separate analyses of Corning A compared to the published values for this reference glass, for references see footnote 14.

Vessel shapes and catalogue numbers from Spasić-Đurić, Jovanović in this volume

Прилој. Просечне вредности главних оксида и једињења у шрафовима у узорцима из Браничева, утјановљене методом LA-ICPMS, и просечне вредности осам различитих анализа Corning A, које су ујоређене са публикованим вредностима за ово референтно стакло; за референце види нај. 14. Форме посуда и каталошки бројеви преузети су из: Спасић-Ђурић, Јовановић у овом броју Старицара

sample	vessel / Cat. No	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	P ₂ O ₅	Cl
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Purple 1									
BRN 1-03	bowl Cat. No 1 - rim fragment	67.1	1.68	12.6	2.35	9.1	2.94	0.31	0.69
BRN 1-01.p	bowl Cat. No 2 - wall fragment	67.3	1.71	12.5	2.24	9.2	2.94	0.31	0.70
BRN 1-15.p	bowl Cat. No 3 - rim fragment	67.8	1.65	12.2	2.31	9.2	2.83	0.31	0.64
BRN 1-05.p	cup Cat. No 6 - wall fragment	67.0	1.86	12.1	2.15	9.2	2.92	0.29	0.73
BRN 1-11.p	flask Cat. No 12 - wall fragment	67.3	1.90	12.0	2.23	9.2	2.87	0.30	0.70
BRN 1-12	flask Cat. No 12 - wall fragment	67.5	1.84	12.0	2.27	9.1	2.84	0.31	0.68
BRN 1-14b.p	? flask Cat. No 14 - wall fragment	67.7	1.69	12.3	2.23	9.1	2.82	0.30	0.79
BRN 1-14a	? flask Cat. No 14 - wall fragment	67.6	1.67	12.3	2.18	9.1	2.80	0.29	0.77
Purple 2									
BRN 1-13.p	bowl Cat. No 8 - wall fragment	67.0	1.88	12.8	1.95	8.8	2.58	0.27	0.77
BRN 1-06	bottle Cat. No 9 - loose handle fragment	66.8	1.91	13.0	1.95	8.7	2.63	0.27	0.76
BRN 1-08	bottle Cat. No 9 - wall fragment	66.7	1.91	13.0	1.89	8.7	2.61	0.26	0.76
BRN 1-07.p	bottle Cat. No 9 - wall fragment	66.5	1.84	12.9	1.89	8.8	2.72	0.27	0.76
BRN 1-09.p	bottle Cat. No 10 - wall fragment	66.8	1.90	13.0	1.93	8.7	2.60	0.26	0.77
BRN 1-10	bottle - neck fragment	66.6	1.97	12.8	1.93	8.6	2.48	0.26	0.79
BRN 1-04.p	? bowl - wall fragment	66.5	1.90	13.1	1.85	8.8	2.60	0.26	0.78
White on Purple 1									
BRN 1-01.w	Cat. No 2	55.1	1.04	8.6	1.80	6.7	2.23	0.21	0.56
BRN 1-15.w	Cat. No 3	57.8	1.26	9.5	1.66	6.1	2.19	0.25	0.71
BRN 1-05.w	Cat. No 6	59.0	1.19	8.8	1.77	6.3	2.35	0.22	0.66
BRN 1-11.w	Cat. No 12	59.4	0.98	9.9	1.87	7.9	2.60	0.26	0.71
BRN 1-14b.w	Cat. No 14	58.2	0.93	8.9	1.74	7.0	2.33	0.23	0.65
White on Purple 2									
BRN 1-13.w	Cat. No 8	64.8	1.54	10.5	2.03	7.9	2.50	0.31	0.82
BRN 1-07.w	Cat. No 9	55.0	1.04	8.6	1.69	6.7	2.23	0.21	0.58
BRN 1-09.w(i)	Cat. No 10 - white area	53.9	1.03	7.9	1.63	6.0	2.00	0.24	0.55
BRN 1-09.w(ii)	Cat. No 10 - pink area	58.3	0.92	8.9	2.01	7.2	2.64	0.25	0.77
BRN 1-09.w(iii)	Cat. No 10 - pink-purple area	58.5	0.87	8.8	2.01	7.1	2.54	0.26	0.70
BRN 1-04.w	? bowl	55.5	1.07	8.5	1.75	6.8	2.27	0.21	0.55
Braničevo set - means									
Purple 1		67.4	1.75	12.2	2.25	9.1	2.87	0.30	0.71
Purple 2		66.7	1.90	12.9	1.91	8.7	2.60	0.26	0.77
White		57.8	1.08	9.0	1.81	6.9	2.35	0.24	0.66
Corning A measured									
mean (n=8)		66.9	0.91	13.9	2.84	5.67	2.46	0.11	0.13
standard deviation (st dev)		0.21	0.03	0.10	0.02	0.05	0.06	42.52	0.01
Corning A published									
difference absolute		0.4	-0.09	-0.4	-0.03	0.64	-0.20	-161	0.04
difference relative		0.6%	-8.9%	-2.5%	-1.1%	13%	-7.4%	-12%	43%

sample	TiO ₂	Fe ₂ O ₃	Li ₂ O	B ₂ O ₃	Rb ₂ O	SrO	BaO	V ₂ O ₅	Cr ₂ O ₃	ZrO ₂	MnO	CoO
	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	wt%	ppm
Purple 1												
BRN 1-03	0.085	0.69	18	327	15	671	1506	26	22	55	2.09	6
BRN 1-01.p	0.086	0.68	21	324	15	681	1362	26	22	56	1.97	6
BRN 1-15.p	0.087	0.67	16	307	15	697	1460	26	17	58	1.95	6
BRN 1-05.p	0.095	0.80	21	322	17	669	1512	28	24	60	2.10	7
BRN 1-11.p	0.100	0.81	25	309	18	682	1556	29	23	64	2.11	7
BRN 1-12	0.097	0.77	23	315	17	682	1615	28	22	62	2.11	7
BRN 1-14b.p	0.088	0.69	17	308	15	692	1314	26	19	58	1.85	6
BRN 1-14a	0.089	0.71	18	305	14	680	1462	27	20	58	1.98	7
Purple 2												
BRN 1-13.p	0.099	1.03	25	406	14	691	1593	31	22	67	2.18	15
BRN 1-06	0.099	1.04	23	423	15	673	1564	31	22	65	2.20	14
BRN 1-08	0.098	1.06	22	430	14	675	1605	31	22	67	2.25	14
BRN 1-07.p	0.095	0.97	25	377	14	679	1764	30	22	63	2.46	10
BRN 1-09.p	0.098	1.07	23	425	14	670	1480	31	21	66	2.16	14
BRN 1-10	0.103	1.18	27	423	15	684	1550	33	26	71	2.25	14
BRN 1-04.p	0.099	1.08	26	415	15	666	1272	31	24	67	2.00	12
White on Purple 1												
BRN 1-01.w	0.060	0.47	9	215	10	462	183	18	17	37	0.56	13
BRN 1-15.w	0.069	0.46	2	201	10	375	207	19	9	39	0.78	6
BRN 1-05.w	0.059	0.41	2	223	11	396	227	18	13	36	0.80	6
BRN 1-11.w	0.060	0.42	11	238	9	551	196	19	14	43	0.66	6
BRN 1-14b.w	0.057	0.39	4	222	10	481	189	18	8	39	0.52	6
White on Purple 2												
BRN 1-13.w	0.082	0.52	5	234	12	505	286	20	11	47	0.70	6
BRN 1-07.w	0.058	0.51	0	223	10	450	188	18	11	39	0.54	10
BRN 1-09.w(i)	0.050	0.40	0	207	10	389	136	17	9	33	0.41	7
BRN 1-09.w(ii)	0.054	0.37	0	257	11	474	178	17	9	37	0.55	5
BRN 1-09.w(iii)	0.055	0.38	0	241	11	468	177	17	10	36	0.54	5
BRN 1-04.w	0.061	0.47	6	212	11	465	181	18	13	38	0.56	12
Braničevo set - means												
Purple 1	0.091	0.73	20	315	16	682	1473	27	21	59	2.02	7
Purple 2	0.099	1.06	25	414	14	677	1547	31	23	67	2.21	13
White	0.060	0.44	4	225	11	456	195	18	11	39	0.60	8
Corning A measured												
mean (n=8)	0.76	1.13	110	2091	96	1028	4518	65	30	51	1.02	1717
st dev	0.01	0.02	2	44	0.8	6	61	0.9	0.7	0.8	0.02	23
Corn A publ	0.79	1.09	100	2000	100	1000	4600	60	30	50	1.00	1700
difference abs.	-0.03	0.04	10	91	-4	28	-82	5	0	1	0.02	17
difference rel.	-3.7%	3.2%	9.9%	4.5%	-3.6%	2.8%	-1.8%	8.0%	1.5%	1.2%	1.7%	1.0%

sample	NiO	CuO	ZnO	As ₂ O ₃	Ag	SnO ₂	Sb ₂ O ₃	PbO	Bi	Y ₂ O ₃	La ₂ O ₃	CeO ₂	Nd ₂ O ₃
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Purple 1													
BRN 1-03	16	203	62	18	1	342	69	719	1	7.3	6.9	12.4	6.2
BRN 1-01.p	16	304	63	17	3	330	67	716	1	7.5	7.0	12.6	6.4
BRN 1-15.p	16	200	62	16	1	324	68	670	1	7.7	7.8	13.9	6.8
BRN 1-05.p	17	852	70	20	8	552	85	3113	2	7.8	7.6	13.7	6.9
BRN 1-11.p	18	630	77	21	2	405	76	1779	2	8.4	8.3	15.0	7.2
BRN 1-12	17	466	66	20	3	353	75	1074	1	8.1	8.0	14.5	7.1
BRN 1-14b.p	16	419	74	17	2	352	68	1011	1	7.8	7.6	13.7	6.8
BRN 1-14a	15	1070	65	19	3	468	83	1584	2	7.6	7.6	13.7	6.5
Purple 2													
BRN 1-13.p	16	366	82	24	2	724	271	2254	3	8.1	7.9	14.1	6.9
BRN 1-06	17	365	82	23	2	765	268	2264	4	7.8	7.5	13.6	6.8
BRN 1-08	16	396	84	24	2	860	293	2549	4	8.0	7.5	13.5	6.7
BRN 1-07.p	16	446	79	25	2	909	225	2838	5	7.9	7.3	13.5	6.7
BRN 1-09.p	16	421	84	23	2	1048	294	3204	5	7.9	7.4	13.4	6.5
BRN 1-10	17	535	92	27	2	1589	383	4372	7	8.2	7.7	14.0	6.9
BRN 1-04.p	17	819	98	21	3	1410	311	5450	7	7.9	7.4	13.3	6.7
White on Purple 1													
BRN 1-01.w	39	304	45	62	25	78620	24	145338	253	4.5	4.6	8.3	4.2
BRN 1-15.w	29	238	31	50	23	64650	14	126428	212	6.0	5.7	10.1	5.2
BRN 1-05.w	31	336	33	48	27	66486	3	114960	494	5.1	5.3	9.2	4.8
BRN 1-11.w	31	217	44	34	16	53328	8	97529	260	5.3	5.7	9.8	4.7
BRN 1-14b.w	35	193	40	60	29	69259	7	119492	276	4.8	5.6	9.6	4.5
White on Purple 2													
BRN 1-13.w	21	152	37	15	7	33942	17	47127	108	6.7	6.8	11.7	6.0
BRN 1-07.w	39	380	42	47	29	80655	21	146235	324	4.9	5.3	8.9	4.4
BRN 1-09.w(i)	40	358	39	36	33	88142	21	168402	400	4.1	5.3	9.2	4.2
BRN 1-09.w(ii)	29	692	37	40	31	52277	41	125452	290	4.4	5.6	9.6	4.5
BRN 1-09.w(iii)	31	683	38	37	29	56055	50	124235	290	4.3	5.6	9.9	4.4
BRN 1-04.w	37	319	44	57	29	78135	21	142784	263	4.8	4.8	8.5	4.3
Braničevo set - means													
Purple 1	17	518	67	19	3	391	74	1333	2	7.8	7.6	13.7	6.8
Purple 2	17	478	86	24	2	1043	292	3276	5	7.9	7.5	13.6	6.8
White	33	352	39	44	25	65595	21	123453	288	5.0	5.5	9.5	4.7
Corning A measured													
mean (n=8)	229	11559	542	32	15	1681	16350	615	8.65	0.72	0.41	0.30	0.15
st dev	3	143	8	1.2	0.5	13	184	9	0.1	0.01	0.02	0.00	0.01
Corn A publ	200	11700	440	—	19	1900	15770	730	—	—	—	—	—
difference abs.	29	-141	102	—	-4	-219	580	-115	—	—	—	—	—
difference rel.	15%	-1.2%	23%	—	-19%	-12%	3.7%	-16%	—	—	—	—	—