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Compositional identification of 6th c. AD glass from the Lower Danube

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ABSTRACT

A group of finds (vessels, raw glass chunks, window panes) from three sites in present-day Bulgaria was selected as representative of the circulation and usage of glass in the Lower Danube region during the 6th c. AD. In total, 79 samples were analysed by EPMA and/or LA-ICP-MS techniques. The data quality was assessed for each analytical run according to the measurement of reference glasses and to pairs of results obtained from representative samples of archaeological glass analysed by both techniques. Combining EPMA and LA-ICP-MS data allowed a sufficiently consistent and unified set of primary results to be formed. As already suggested in an earlier preliminary paper, only a single glass composition was found to dominate the 6th c. contexts in the region. The current study recognises this 6th c. glass from the Lower Danube as identical with the so called 'Serie 2.1.' defined by D. Foy and co-workers (2003) in various assemblages in Southern France and North Africa. The major, minor and trace oxide evidence presented here indicates that this is a distinct primary glass composition, with an iron-rich sub-group tentatively differentiated within the main group. Accordingly, an attempt is made to situate it relative to the other main primary compositions in the region. The proposed interpretation is that the 6th c. glass should not be linked to the HIMT glass despite the nominal similarity between them due to their elevated iron oxide, manganese, and titania concentrations. Instead, a possible link between the geochemical characteristics of the 6th c. glass and an earlier group of manganese decolourised glass, equivalent to 'Serie 3.2.' outlined by D. Foy and co-workers (2003) is suggested. This may imply the use of sand from a broadly identical geological area, hence it is possible that both the 6th c. glass and the manganese decolourised composition are likely to share a common origin.

1. Introduction

A substantial amount of analytical work on Roman and late antique glass has been carried out during the last decades demonstrating the utility of a growing range of scientific methods (Janssens, 2013) and a sustained scholarly interest in this research field, from some of the earliest key works (e.g. Sayre and Smith, 1961) to the most recent contributions (e.g. Keller et al., 2014). Numerous archaeological and compositional findings gave ground to the leading and widely accepted understanding about the glass industry as being structured in two distinct stages for most of the first millennium AD — primary glass making and secondary glass working (Freestone et al., 2002; Foy and Nenna, 2001). Locating the primary glass production installations in the Eastern Mediterranean is based on direct archaeological evidence (e.g. Gorin-Rosen, 2000; Tal et al., 2004; Nenna, 2008). At the same time, analytical research implies the possible existence of such primary centres in the Western parts of the Mediterranean as well (Brems et al., 2012), as indicated by historical sources (Freestone, 2008).

The fundamentals of present-day multidisciplinary studies, in the case of Roman and late antique glass, mostly consist of defining particular groups within the broader category of low magnesia soda–lime–silica glass composition. Distinguished by their specific chemical makeup such groups reveal the variability of raw materials (i.e. sand) and diversity of recipes used in the primary glass production centres. The possibility to unequivocally identify certain groups at the sites of their manufacture (e.g. Levantine I glass — Freestone et al., 2008b), or, based on distinct geological settings, to point to wider regions as potential places of origin for other groups (e.g. HIMT glass — Freestone et al., 2005; Nenna, 2014) allows the provenance of glass found in various contexts in the Mediterranean and beyond to be traced. Several primary groups established in the literature so far (Freestone, 2005; Foy et al., 2003) are most often used as reference points when compositional affinities of particular glass assemblages are studied (or 'quasi-reference' groups: Rehren and Freestone, 2014, 76). However, the growing body of available analytical data apparently demonstrates that the variability, even within relatively narrow ranges of values for most of the oxides, may result in sub-groups, intermediate, or blurred compositions. This is due to the complex character of the factors which determine the chemical makeup of Roman and late antique glass (see also Rehren,

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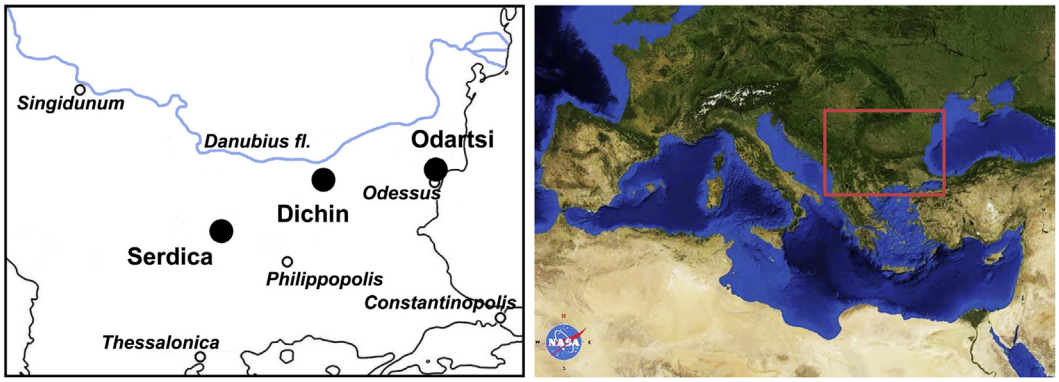

Fig. 1. Location of the fortified settlements near modern Dichin and Odartsi, and the Roman town of Serdica in the Northern part of the Balkans. After Dinchev et al. (2009).

2000). Defining such sub-divisions and their affiliations to the well-recognised major primary compositions is one of the recent foci in the analytical study of glass. In this way, modified nomenclatures and respective interpretations are often introduced (e.g. Foster and Jackson, 2009; Ceglia et al., in press), posing the overall challenge of how to maintain a consistent terminology, and how to correlate discussions of formal compositional groupings with a substantial, up-to-date, archaeologically meaningful enquiry.

The present paper aims to outline a particular glass composition with such 'intermediate' characteristics which, at the same time, stands out as a consistent group in terms of its archaeological and chronological features, and also seems to be the quantitatively prevailing one in the Lower Danube region at the end of antiquity. Discussing the 6th c. glass finds from present day Bulgaria in respect to some of the known main primary compositions is an attempt to find their analogies elsewhere and, on the other hand, to situate them against other contrasting groups. Furthermore, certain general questions are addressed considering the principles for defining and differentiating glass groups and subgroups, and the interpretative meaning of this patterning.

2. Archaeological background

The 6th century is a turbulent period in the history of the Balkan provinces of the Empire. The territories at the Lower Danube border (Fig. 1) have been intensively attacked by different ethnic groups in the preceding centuries and in the beginning of the Migration period. During the 6th c., substantial changes of the population structure, settlement patterns and economy of the region are driven partly by the massive invasions of Avars and Slavs, and, on the other hand, by internal socio-cultural processes at the margins of the Empire. The reign of Justinian I (527–565) demonstrates the intention of the state to maintain control over the Lower Danube (Whitby, 2001), including a possible centralisation of supplies to the region through the establishment of the *quaestura exercitus*, a new and especially designed administrative unit (Torbatov, 1997). However, the end of the 6th–early 7th c. marks the decline and archaeologically well attested final abandonment of most of the late antique settlements in the region (Dinchev et al., 2009).

Three sites provided glass vessel assemblages for the current study (Fig. 1). The fortified settlement near the present village of Dichin is situated in central North Bulgaria. The excavations there were conducted in the framework of a joint British-Bulgarian project exploring transformations towards the end of antiquity on the Lower Danube (Poulter, 2007). Founded at the beginning of the 5th c., the semi-urban settlement is relatively prosperous during its first main period of occupation until ca. AD 490. After a fire followed by a hiatus of nearly half a century, the settlement is partly rebuilt; this 6th c. phase is dated ca. AD 540–580 (Dinchev et al., 2009). A decrease of the quality of construction, of access to imported goods, and an overall decline are evident during this second main phase of occupation, relative to the 5th c. phase. Matching changes are attested in the glass vessel assemblage from Dichin (Cholakova, 2009), and confirmed by a shift in the glass composition during the 6th c. (Rehren and Cholakova, 2014).

The site near the present village Odartsi in Northeast Bulgaria is a fortified semi-urban settlement similar in many aspects to Dichin. Extensive fieldwork done by a Polish-Bulgarian joint project (Kurnatowska and Mamzer, 2007) revealed a complex history of the locality, with most intense late antique habitation during the 6th c. (Dončeva-Petkova and Torbatov, 2001). The end of this phase is marked by a devastating fire, probably around AD 610 (Torbatov, 2002), and most of the studied glass assemblage can be tentatively dated to that time.

Since ancient Serdica lies beneath the modern city of Sofia, the archaeological research there is mainly performed as rescue work. During one of the most recent campaigns a large area in the centre of the Roman and late antique town was excavated (Ivanov, in press). Glass fragments, well dated to the 6th c. in terms of their context of discovery and/or morpho-typology were selected for the present analysis in an attempt to complement the data obtained from the Dichin and Odartsi assemblages.

3. Materials and methods

3.1. Selection of the glass fragments

The analytical work presented in this paper was done on 78 glass fragments from Dichin, Odartsi, and Serdica (Appendix A). In total, 79 sets of sample measurements are reported here, since a chunk of raw glass is represented by two separate results due to the relatively higher degree of heterogeneity of this piece (samples SER 22(1) and SER 22(2), Appendix A). Initially, the samples from Dichin were studied as part of the research on the entire site assemblage (Rehren and Cholakova, 2014). Through a repeated and integrated refinement of the compositional, morpho-typological, and contextual data (the '*va-et-vient*' way of research, Foy et al., 2003, 80), a specific group of fragments (respectively, samples) was outlined; it is believed that this group is representative of the repertoire of glass used at the site during the period ca. AD 540–580, although some of the finds have been assigned to contexts of earlier date. Remarkably, only a single chemical composition and a single vessel type (Isings 111) are attested in the layers securely dated to the second phase of Dichin,[1] as opposed to the compositional and

[1] This conclusion is based on the results from the Bulgarian-excavated part of the site (Dinchev et al. 2009); see Appendix A.

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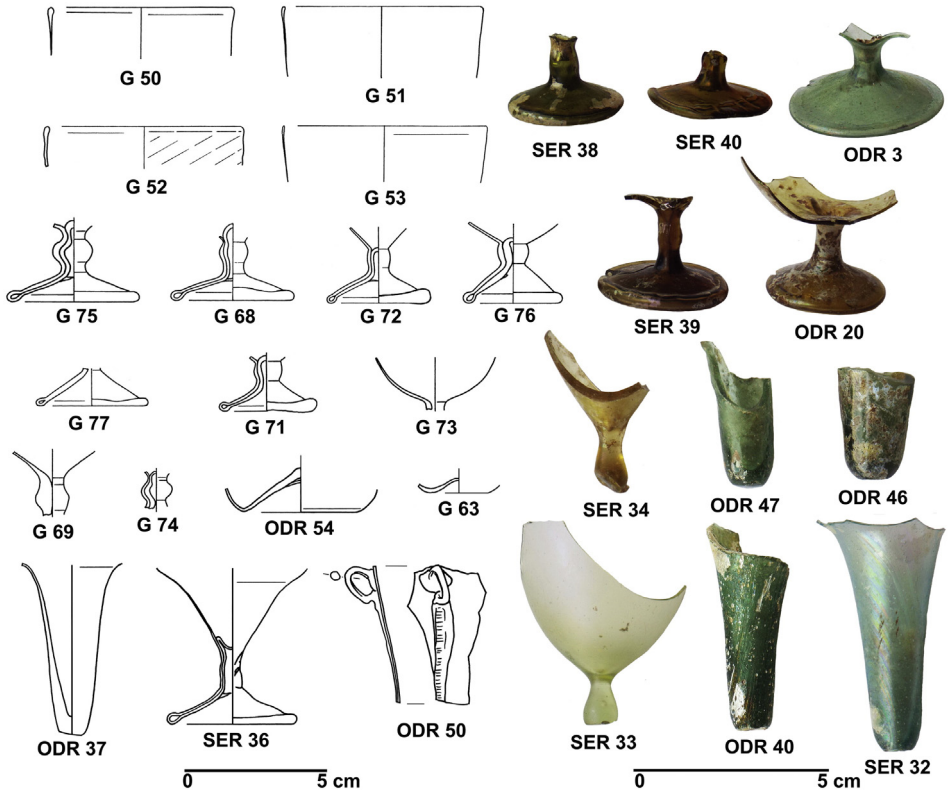

Fig. 2. Vessel shapes generally representative for the 6th c. contexts of Dichin, Odartsi, and Serdica (after Cholakova, 2009 and unpublished); indicated sample numbers correspond to the data in Appendix A.

morphological diversity of the glass finds from the first, i.e. the 5th c. phase of the settlement. Therefore, an initial working hypothesis of a significant shift in glass circulation and usage in the 6th c. (Rehren and Cholakova, 2014) was further explored in the assemblage from Odartsi. As pointed out earlier, nearly all of the glass from this site seems to reflect the pattern of consumption in the late 6th–very beginning of the 7th c. AD, and the analyses confirmed that almost all the Odartsi samples belong to the same composition as the 6th c. group from Dichin. Finally, the targeted sampling of the Serdica assemblage attested the correlation between a particular vessel morphology mostly typical for the 6th c. contexts (Isings 111, lamps), and the composition concerned, as well as adding further evidence from the analyses of raw glass chunks. The functional distribution within the whole set of sampled fragments is as follows: four unworked chunks (represented by five analyses), three window panes, and 71 vessels (Fig. 2). Furthermore, 53 out of 71 vessels belong to various sub-types of the stemmed goblets Isings 111 (Isings, 1957). The remaining 18 fragments are reconstructed mostly as oil lamps of different types, with only two exceptions (a vessel handle and a flask neck, possibly both belonging to the functional category of tableware).

The unifying characteristics of the outlined group of 6th c. vessels mainly consist of the standardised techniques of their manufacture — use of pontil, fire-rounded rims, no engraving or any other decoration added, except two examples of optic-blowing. Interestingly, the colour range of the fragments is not constant and a variety of tints are observed: from nearly colourless or weakly blue-green to very intense shades of dark green and dark yellow (Fig. 2). Most probably the majority of the vessels in this group were used as lighting devices, similarly to many other contemporaneous finds from the Balkans (Olczak, 1995; Băjenaru and Bâltâc, 2000–2001; Drauschke and Greiff, 2010) and the Mediterranean (Foy, 2011, Fig. 12). In fact, this can be seen as a significant shift in the usage pattern of glassware in the Early Byzantine period (Cholakova, 2014a). It is believed that the selection of finds from Dichin, Odartsi and Serdica is fairly representative for the overall circulation and use of glass during the 6th c. in the broader Lower Danube region. In terms of morpho-typology these examples belong to an interregional and commonly produced vessel repertoire of late antique glasswork. However, their manufacture in local and regional secondary ateliers in the Balkans seems most probable, when various indications are taken into account, such as the working quality of individual finds and evidence for local workshops.

3.2. Analytical techniques and data handling

The 79 selected samples were analysed using EPMA and LA-ICP-MS techniques. The sample preparation of the polished cross sections and the EPMA measurements were done over several years in the Wolfson Archaeological Science Laboratories at the UCL Institute of Archaeology, using a JEOL 8100 electron microprobe, following the established laboratory procedures (comparable to the procedures described in Freestone et al., 2008b). The instrumental settings were as follows: 15 kV accelerating voltage, beam current of 50 nA, analysed area of approximately 150 μm^2, at magnification 800×. Typically, the measurement time was 60 s on peaks and, respectively, 20 s on backgrounds either side of the peak, with certain variations for some of the elements analysed. The LA-ICP-MS analyses were carried out at the Institute de Recherche sur les Archéomatériaux (IRAMAT), Centre Ernest Babelon, CNRS, in Orléans, in two separate runs. A Nd:YAG pulsed laser, with Ar carrier gas was used, coupled with an Element XR mass spectrometer, Thermofisher Instruments (Gratuze, 2013; B. Gratuze pers. comm.), operated at 266 nm at a quadrupled frequency in the ultraviolet region (VG UV-Microprobe laser system), using 6 to 8 Hz laser pulse frequency. The measurements were performed partly on polished sections used for EPMA analysis, and partly on lose fragments. The procedure consisted of 20 s time for pre-ablation, followed by 50 s for analysis as point scanning, regular blank runs, and other routine practises. The calculations of the concentrations were done according to an established analytical protocol (Gratuze, 2013, Smirniou and Rehren, 2013).

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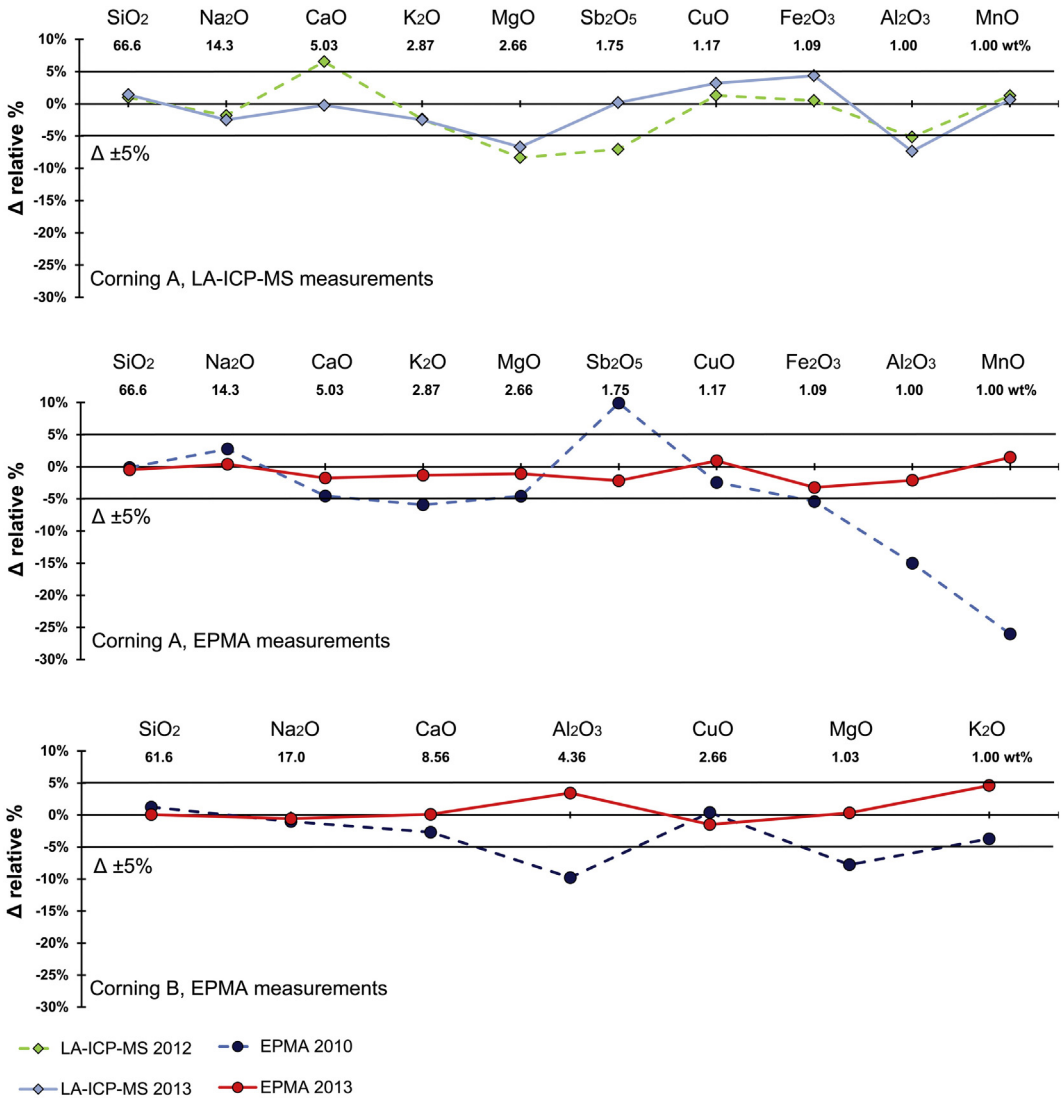

Fig. 3. Comparison of the trueness of the LA-ICP-MS and EPMA analytical runs expressed as relative difference (Δ relative) from the accepted reference values of Corning A and B glass standards (major oxides in descending order of their concentrations, using data from Vicenzi et al., 2002, Table 1). Full data and relative standard deviation calculations are given in Appendix B (1). The graphs illustrate the extent of agreement between the measurements of Corning A and Corning B produced as part of each analytical run and the accepted values of the reference glasses. For major oxides, trueness within approximate limits of ± 5% Δ relative is achievable for both EPMA and LA-ICP-MS analyses. In cases when Δ relative significantly exceeds these limits (e.g. EPMA 2010 run) a selective use and additional refinement of the data were preferred.

Both types of measurements were conducted on 27 samples, another 40 samples were analysed by LA-ICP-MS only, and the remaining 12 samples by EPMA only, a total of four analytical runs for the two techniques.[2] A detailed study was done of the inter-method comparability based on the data from the standard measurements (Corning A and B archaeological reference glasses) and on the paired data from actual samples analysed twice by both methods (similar to the approach reported in Lankton et al., 2014). A summarised overview of the results obtained on the reference glasses within each analytical run and the correlation of the actual sample measurements is given in Fig. 3 and Appendix B (1, 2). The main implication is that the data obtained by both techniques, within a particular range of concentrations, can be successfully combined in order to achieve a sufficiently consistent and unified set of primary results. For certain minor oxides measured on representative actual samples the agreement between both methods is good enough so that the LA-ICP-MS and EPMA results can be seen as interchangeable (strength of correlation for TiO_2, MgO, and Fe_2O_3 expressed as R^2 is >0.96, and for MnO R^2 is >0.88; Appendix B (2)). Therefore, for such oxides the LA-ICP-MS results are preferred in those cases when the EPMA measurements look problematic (e.g. the EPMA 2010 run). However, some of the major oxides (Al_2O_3, CaO) have lower extent of accordance between the EPMA and LA-ICP-MS values obtained on archaeological samples, despite the overall plausible measurement results for the reference glasses for most of the analytical runs, or, despite the empirical corrections applied to bring the data in line with the standards (Appendix B (1)). The preferred solution here is to use such results mostly as indicative only and to avoid taking them as leading evidence in the interpretation.

4. Results

Representative analytical data is reported in Appendix A, including all the details of combining the LA-ICP-MS and EPMA results and their processing for refinement; the averaged concentrations are presented in Table 1. Overall, the soda content varies within a wide range of approximately 15 to 20 wt.%, with a tendency for the samples higher in iron oxide to have lower soda. Alumina and lime also have generally broad distribution, from nearly 2 to over 3 wt.% for Al_2O_3, and about

[2] This time-fragmented layout of the analytical work was a result of various constraining factors such as access to the materials for sampling, availability of the analytical instruments, etc.

Table 1
Average concentrations of major, minor and selected trace oxides in the 6th c. samples from Dichin, Odartsi and Serdica; combined EPMA and LA-ICP-MS data (details are given in Appendix A). The results are presented separately for the main compositional group and for the iron-rich sub-group, as well as a general average of all the samples for comparison with the published values of 'Serie 2.1' (Foy et al., 2003, Annexe 2).

	Wt.%							ppm				
	SiO_2	Na_2O	Al_2O_3	CaO	K_2O	MgO	Fe_2O_3	P_2O_5	Cl	SO_3[a]	TiO_2	MnO
6th c. composition	66.1	17.7	2.52	7.97	0.69	1.10	0.98	1478	0.82	0.34	0.15	1.37
SD (n = 50)	1.0	1.1	0.24	0.58	0.12	0.14	0.15	452	0.08		0.02	0.37
6th c. Fe-rich sub-group	65.2	17.8	2.82	7.61	0.78	1.16	1.83	1846	0.79	0.35	0.15	1.04
SD (n = 29)	0.9	1.1	0.22	0.54	0.08	0.12	0.56	530	0.06		0.02	0.33
total average	65.8	17.8	2.63	7.84	0.73	1.12	1.29	1613	0.81	0.35	0.15	1.25
SD (n = 79)	1.0	1.1	0.28	0.59	0.12	0.13	0.55	511	0.08		0.02	0.39
'Serie 2.1.' Foy et al., 2003	64.5	18.5	2.54	7.78	0.79	1.23	1.35	1800			0.16	1.60

ppm	ZrO_2	Cr_2O_3	HfO_2	Nb_2O_3	Y_2O_3	La_2O_3	CeO_2	PrO_2	Nd_2O_3
6th c. composition	112	26	2	3	9	10	17	2	9
SD (n = 50)	16	13	0	1	1	1	2	0	1
6th c. Fe-rich sub-group	116	25	2	3	12	13	18	3	12
SD (n = 29)	16	2	1	1	2	3	2	1	2
total average	114	26	2	3	10	11	18	2	10
SD (n = 79)	16	11	0	1	2	2	2	1	2

ppm	NiO	As_2O_3	Li_2O	Rb_2O	BaO	SrO	V_2O_5	B_2O_3	Sb_2O_3	CoO	CuO	ZnO	SnO_2	PbO
6th c. composition	18	6	10	9	320	831	54	498	186	12	95	30	34	137
SD (n = 50)	6	1	9	3	45	88	9	54	135	6	99	8	31	84
6th c. Fe-rich sub-group	29	14	7	10	278	777	75	497	122	24	113	43	26	198
SD (n = 29)	8	6	6	1	32	74	21	35	70	7	28	8	8	76
total average	22	9	9	9	305	812	61	498	164	16	101	34	31	158
SD (n = 79)	8	5	8	3	46	87	17	48	120	9	82	10	26	86

[a] No sufficiently representative data is available to calculate the standard deviation for SO_3; the average values are indicative only.

6.7 to 9.7 wt.% for CaO. As another relatively clear trend, higher alumina levels are typical for the iron-rich samples. Potash has more constant concentrations, approximately 0.5 to 1 wt.%, and the same can be observed for titania which varies within 0.11 and 0.19 wt.%, with a single exception of a higher (0.24 wt.%) content. The results for magnesia are somewhat elevated, approximately 0.9 to 1.5 wt.%, compared to more common mineral soda glass compositions; this is one of the characteristics for all the samples in the analysed 6th c. group. Iron oxide demonstrates similarly higher values of nearly 0.8 to 3.5 wt.% and a separation of the samples in two sub-clusters with a slight gap between them at about 1.2 wt.% Fe_2O_3. The same division in two sub-groups is evident for certain trace oxides (NiO, As_2O_3, V_2O_5), which have higher ranges for the samples with elevated iron oxide. However, such a separation is not seen in the titania concentrations which have a relatively narrow range, as pointed out above, and which are not correlated with iron oxide. Manganese has a wide spread of concentrations, from 0.2 to nearly 2 wt.%, but typical values are higher than 0.7 wt.%. Interestingly, strontium oxide is above the expected levels for common natron glass (e.g. Freestone et al., 2003, Fig. 3), with an average of about 800 ppm and reaching concentrations of approximately 1000 ppm in individual samples.

5. Discussion

As stated previously, the main objective of the present study is to characterise a particular glass composition which, according to the chronology and distribution of the finds, during the 6th c. AD seems to be the dominant one in the Lower Danube region. The analyses demonstrate that this composition is similar to a certain extent to the glass produced in the earlier Roman tradition although it has elevated concentrations for most of the impurities introduced with the glassmaking sand. Using the average composition of late Roman blue-green glass from Foster and Jackson (2009, Table 4) as a reference, this similarity provided the basis for its preliminary definition as 'dirtier Roman blue-green glass' (Rehren and Cholakova, 2014, 90, Fig. 11.10). A subsequent refinement of the data shows that the 6th c. glass from the Lower Danube is in fact consistent with the broadly contemporary compositional group attested in Southern France and Northern Africa and named 'Serie 2.1.' (Foy et al., 2003). This identification becomes evident when the main components are juxtaposed (Table 1). It is further confirmed by the high concentrations of strontium oxide which seems to be of diagnostic importance for this group. The average SrO values of 'Serie 2.1.' is nearly 790 ppm (669 ppm Sr, Foy et al., 2003, Annexe 2), compared to 812 ppm for the glasses analysed here, while other late antique glass groups have typically less than about 600 ppm SrO (<c 500 ppm Sr, Freestone et al., 2003, Fig. 3). Furthermore, the similarity in chronology and morpho-typological range of the vessels in 'Serie 2.1.' (Foy et al., 2003, Fig. 11) provide additional arguments to draw an archaeologically meaningful parallel between the finds from the Mediterranean and those from the Lower Danube. A closer assessment of the data obtained from the 6th c. Balkan materials allows a sub-group with elevated iron oxide concentrations to be separated within the main glass composition (Table 1). However, a more detailed discussion of this sub-group is beyond the objectives of the present paper.

Taking as a starting point the recognition of the 6th c. glass from the Lower Danube as identical with the 'Serie 2.1.' from the Western Mediterranean, a concise discussion of the present results in respect to the other main glass groups found in the region is a necessary part of the interpretation. The plot of alumina and lime concentrations (Fig. 4) illustrates the position of the 6th c. samples relative to the two main compositional groups of the 5th c. in the Lower Danube — HIMT glass (Rehren and Cholakova, 2010) and a manganese decolourised composition[3] neatly matching 'Serie 3.2.' as defined by Foy and co-workers (2003). It does not seem probable to explain this 'intermediate' position of the 6th c. glass simply as an effect of mixing and recycling of the earlier glasses. In fact, an attempt to find arguments for possible links and affiliations of the 6th c. glass to any of the earlier groups, based on such blurred pattern only, may not be quite conclusive. Even though, the 6th c. glass seems closer to the manganese decolourised group rather than to the HIMT cluster. This observation stands in

[3] The preliminary definition for this composition was 'cleaner Roman blue-green glass' (Rehren and Cholakova, 2014, 9-, Fig. 11.10). In addition to the parallel with 'Serie 3.2.' from Southern France, analogies of this group are attested elsewhere in the Mediterranean and beyond (Gallo et al. 2014, AQ/3; Foster and Jackson, 2010, Group 2).

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contrast to the understanding that 'Serie 2.1' is a variety of HIMT composition (as seen for example in Foster and Jackson, 2009; Jackson and Foster, 2014, 8; however, recently opposed by Ceglia et al., in press).

Trace oxide data provide further very useful insight into the question of the relationships between the compositional groups (Fig. 5). Here the gap between the HIMT samples from the Lower Danube region and the 6th c. glass is evident. At the same time, a nearly complete overlap between the latter and the manganese decolourised composition of the 5th c. points to probable links between the geochemistry of glassmaking sands used for the production of these two groups. This hypothesis corroborates the preliminary observation made about the Dichin assemblage that the 6th c. glass and the earlier manganese decolourised glasses form a broad continuum with positively correlated minor oxide levels (Rehren and Cholakova, 2014). Interestingly, the trace oxide pattern of the iron-rich sub-group seems to place these glasses even further away from the HIMT cluster, apparently excluding their explanation as a result of mixing HIMT cullet with the main 6th c. glass, e.g. due to recycling. In fact, the peculiarity of this sub-group consists mostly in the lack of correlation between iron oxide and titania (Fig. 6). An identical trend is seen in 'Serie 2.1.' from the Western Mediterranean (Foy et al., 2003, Annexe 2), reinforcing a possible implication that the sub-group in the 6th c. glass from the Lower Danube is not only a regional phenomenon.

A comparison of some of the diagnostic oxides for the 6th c. glass (Fe_2O_3, MgO, and TiO_2) confirms its identification as a separate primary glass group with close similarity to the 5th c. manganese decolourised composition in the Lower Danube (Fig. 7, left graph), once again implying the use of sand from a broadly identical geological area (even with a possible internal zoning resulting in compositional fluctuations between the melting episodes over time), and which differs fundamentally from the raw materials of the HIMT glass production. When the same comparison is made for the respective groups from Southern France and Britain (Fig. 7, right graph) the overall pattern is still very similar, especially for the samples from the Western Mediterranean. Nevertheless, differences and a certain blurring of the groups are also evident, not at least because of the chronologically more complex perspective.

It has to be clearly said, that even if the main 6th c. glass group appears to fully match the manganese decolourised composition, i.e. 'Serie 3.2.' in Fig. 7, there are many other compositional criteria that keep both groups apart as discrete clusters (e.g. alumina and lime concentrations (Fig. 4), or their levels of manganese), so they can be recognised as probably linked but still different primary compositions. A particular argument for distinguishing between both groups is the positive correlation between strontium oxide and manganese in the

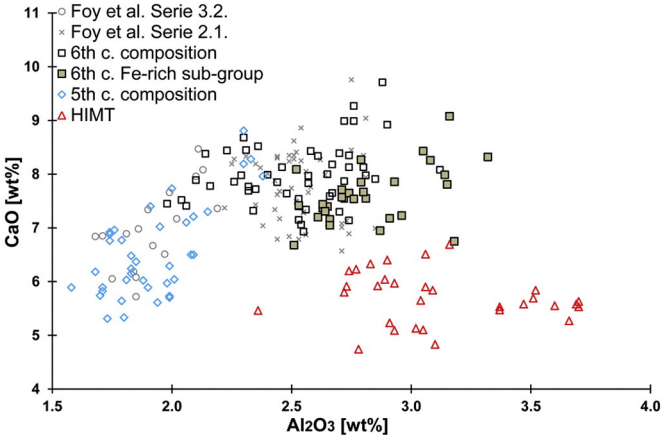

Fig. 4. Alumina vs lime concentrations of the 6th c. glass from the Lower Danube compared to the HIMT and the 5th c. manganese decolourised compositions from the same region (refined data from Rehren and Cholakova, 2010; Rehren and Cholakova, 2014, present work, and unpublished), and to the respective compositions from the Mediterranean. Data from Foy et al. (2003).

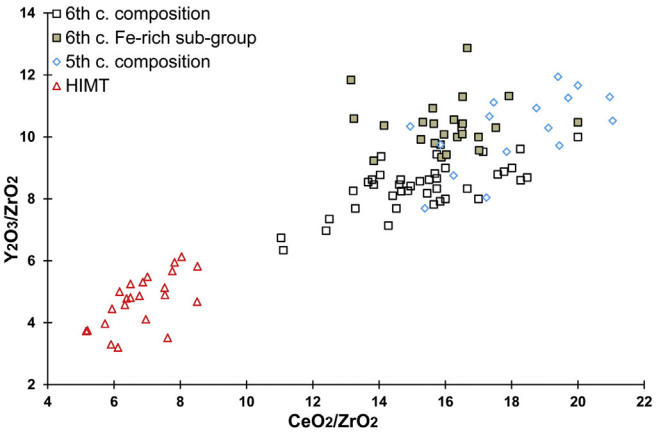

Fig. 5. Trace oxide ratios in the samples from Dichin, Odartsi and Serdica analysed by LA-ICP-MS: a comparison of the 6th c. glass and the earlier HIMT and manganese decolourised compositions (data from present work and unpublished).

6th c. glass which is not characteristic of the 5th c. manganese decolourised composition (Fig. 8). As pointed out, the average concentration of 800 ppm SrO in the 6th c. glass is above the common levels for natron glass suggesting the likely presence of an additional source of SrO, along with the well-known sand impurities (i.e. lime and seashells). The correlation of SrO and MnO levels indicates that the manganese containing additive most probably introduced certain amounts of strontium oxide to the glass melt, as already proposed elsewhere (Gallo et al., 2013, Fig. 8b). Manganese-rich minerals with significant amounts of strontium are known (e.g. strontiomelane with approximately 9–13 wt.% SrO — Meisser et al., 1999), and could have been used by the glass producers as recipe ingredient in the 6th c. The absence of such correlation in the compositions preceding the 6th c. glass in the Lower Danube marks certain changes in raw material supplies and technology of production towards the end of antiquity.

6. Conclusion

Analytical work done on a representative group of 6th c. AD glasses (vessels, window panes, and chunks) found at three sites in present-day Bulgaria allows a specific composition to be outlined. Based on the archaeological evidence, this composition is considered as the predominant one in the region at the end of antiquity. It is characterised by an overall increased content of minor oxides which was the reason for its preliminary definition as 'dirtier Roman blue-green' in the Dichin glass

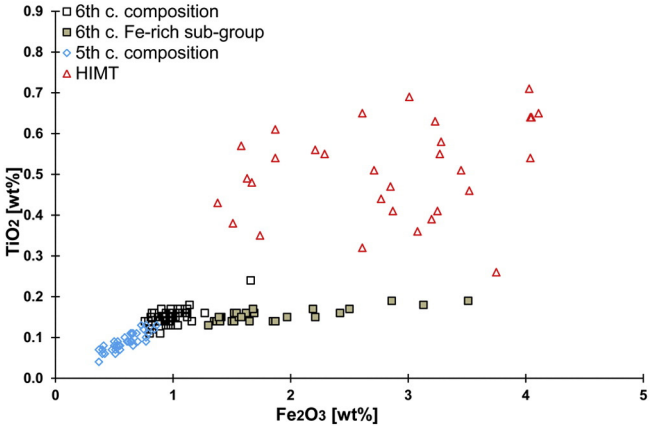

Fig. 6. Iron oxide vs titania concentrations of the 6th c. glass from the Lower Danube compared to the HIMT and the 5th c. manganese decolourised compositions from the same region (refined data from Rehren and Cholakova (2010); Rehren and Cholakova (2014), present work, and unpublished).

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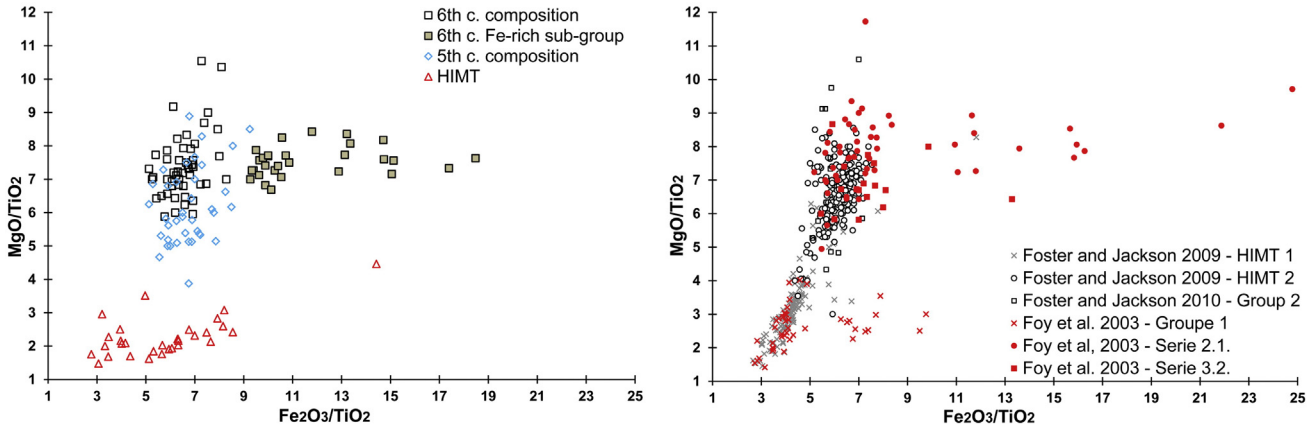

Fig. 7. Combined results for iron oxide, magnesia, and titania for the 6th c. glass from the Lower Danube, juxtaposed with earlier HIMT and manganese decolourised compositions from the same region (left graph; refined data from Rehren and Cholakova, 2010; Rehren and Cholakova, 2014, present work, and unpublished), and the same comparison for the respective major reference glass groups (right graph; data from Foy et al., 2003; Foster and Jackson, 2009; Foster and Jackson, 2010).

assemblage, evolving out of the 'cleaner Roman blue-green' glasses of the earlier periods (Rehren and Cholakova, 2014).

The present study identifies the 6th c. glass from the Lower Danube as a distinct composition, identical with 'Serie 2.1.' as described by Foy et al. (2003), but not linked to the HIMT group despite its elevated iron oxide content. This is based on the logic of geochemical evidence and implies a particular interpretative meaning. It is generally acknowledged that the different primary glass groups correspond to different locations of production. Defining their compositional relationships and affinities, and recognising gradual shifts or clear gaps between the groups are essential tools of provenancing and for reconstructing the dynamics of the primary glass making industry of the first millennium AD. Certain compositional separations may reflect deliberate changes of the location of production, different choices of raw materials and/or their supplies, recipes, or even modifications in the organisation and/or ownership of the manufacturing. Another type of patterning could be driven only by the internal geological heterogeneity of sand deposits within a single area. Additionally, beyond the stage of primary glass making, phenomena such as cullet recycling and mixing would contribute to an even more complex picture of compositional grouping.

Based on the present data, the 6th c. glass may be associated through its geochemical characteristics with the earlier manganese decolourised group (identical with 'Serie 3.2.' of Foy et al., 2003). Therefore, as a working hypothesis, these two compositions can be considered related to each other in terms of their origin (hence, separately from the HIMT glass; discussing the provenance of any of these compositional groups remains beyond the scope of this paper). At the same time, a range of features, including the levels of added manganese, indicates that the two main compositions of the 5th and 6th centuries, respectively, in the region still have to be differentiated as separate primary groups, and not simply seen as a single geochemical continuum evolving over time. At this stage, the reasons for defining the cluster of iron-rich samples as a sub-group within the 6th c. glass, rather than a separate group in its own right, lie mostly in the understanding that it is due to a deterioration of the quality of the glassmaking sand, possibly within the same locality. However, a technological explanation may well be possible, and more data is needed to address in details the question of this sub-group.

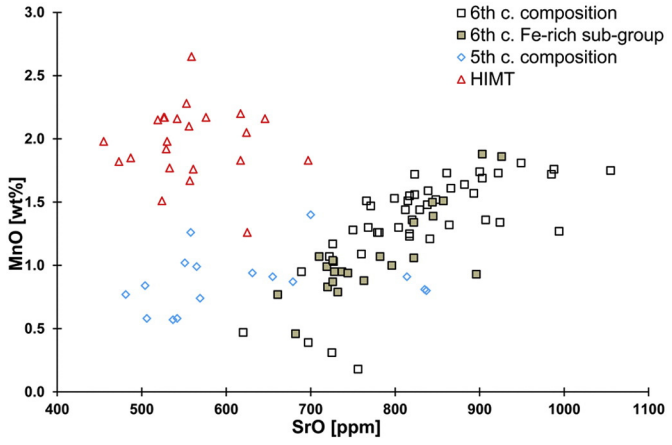

Fig. 8. Strontium oxide vs manganese concentrations in the samples from Dichin, Odartsi and Serdica analysed by LA-ICP-MS: a comparison of the 6th c. glass and the earlier HIMT and manganese decolourised compositions (data from present work and unpublished).

Certain other aspects of the 6th c. glass remain outside the present summarised discussion, for example the evidence for recycling in these glasses, or, the significance of the group in terms of its archaeological interpretation. An overview of the geographical distribution of this composition and its equivalents or possible analogies in the Balkans (e.g. Drauschke and Greiff, 2010) and far afield (e.g. Freestone et al., 2008a; Ceglia et al. in press) is also beyond the limits of this paper, as well as the key question of how this group should be placed in the discourse on the currently recognised ranges of HIMT glass.

However, it is hoped that the data presented here and the suggested explanations contribute to a better understanding of the existing variations in glass group terminology (Rehren and Freestone, 2014) and its interpretative reading.

Considering the broader long-term perspectives of glass studies, it may seem beneficial not only to achieve a coherent nomenclature of the compositional groups but also to progress from the formal labelling of data. A promising way forward would be an attentive examining of the technological phenomena behind the data in the context of the socio-cultural and economic processes of Late Antiquity (e.g. Cholakova, 2014b).

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Appendices A–B. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jasrep.2015.08.009.

References

Băjenaru, C., Bâltâc, A., 2000–2001. Depozitul de candele din sticlă descoperit la bazilica episcopală de la Histria. Pontica 33–34, 469–513.

Brems, D., Degryse, P., Hasendoncks, F., Gimeno, D., Silvestri, A., Vassilieva, E., Luypaers, S., Honings, J., 2012. Western Mediterranean sand deposits as a raw material for Roman glass production. J. Archaeol. Sci. 39, 2897–2907.

Ceglia, A., Cosyns, P., Nys, K., Terryn, H., Thienpont, H., Meulebroeck, W., 2015. Late Antique glass distribution and consumption in Cyprus: a chemical study. J. Archaeol. Sci. http://dx.doi.org/10.1016/j.jas.2015.06.009 (in press).

Cholakova, A., 2009. Glass vessels from Gradishteto. In: Dinchev, V., Kuzmanov, G., Vladkova, P., Cholakova, A., Popova, T. (Eds.), Bulgarian-British Archaeological Excavations of Gradishteto Near the Village of Dichin, Veliko Tarnovo region, 1996–2003 — The Results of the Bulgarian Team. Excavation and Res. 39. National Institute of Archaeology — Bulgarian Academy of Sciences, Sofia, pp. 257–307 (in Bulgarian).

Cholakova, A., 2014a. Composition, distribution, and use of glass in the 6th c. AD in the Lower Danube region: recognising changes – understanding the change. Interdisciplinary Studies of Ancient Materials From the Mediterranean. International Conference, Nicosia, 17–19 September 2014, University of Cyprus (Abstracts, p. 12. http://www.eurocyinnovations.com/narnia-portal/wp-content/uploads/2014/02/NARNIA-conference-programme-and-abstracts.pdf).

Cholakova, A., 2014b. Networks of distribution at the margins of the Empire – late antique glass vessels from the Lower Danube region. In: Kassianidou, V., Dikomitou-Eliadou, M. (Eds.), The NARNIA Project: Integrating Approaches to Ancient Material Studies. Nicosia: The NARNIA project and the Archaeological Research Unit. University of Cyprus, Nicoasia, pp. 94–104 http://www.eurocyinnovations.com/narnia-portal/wp-content/uploads/2015/02/The-Narnia-Project-EBOOK-RGB-144ppi.pdf.

Dinchev, V., Kuzmanov, G., Vladkova, P., Cholakova, A., Popova, T., 2009. Bulgarian-British Archaeological Excavations of Gradishteto Near the Village of Dichin, Veliko Tarnovo region, 1996–2003 — The Results of the Bulgarian Team. Excavation and Res. 39. National Institute of Archaeology — Bulgarian Academy of Sciences, Sofia (in Bulgarian).

Dončeva-Petkova, L., Torbatov, S., 2001. Zur Chronologie der Architektur der spätrömischen Befestigung und frühbyzantinischen Siedlung bei Odărci (Provinz Skythien). In: Wendel, M. (Ed.), Karasura: Untersuchungen zur Geschichte und Kultur des alten Thrakien. I. 15 Jahre Ausgrabungen in Karasura, Internationales Symposium Čirpan/Bulgarien 1996. Beier & Beran, Weissbach, pp. 237–245.

Drauschke, J., Greiff, S., 2010. Chemical aspects of Byzantine glass from Caričin Grad/Iustiniana Prima (Serbia). In: Drauschke, J., Keller, D. (Eds.), Glass in Byzantium — Production, Usage. Analyses. RGZM, Mainz, pp. 25–46.

Foster, H., Jackson, C., 2009. The composition of 'naturally coloured' late Roman vessel glass from Britain and the implications for models of glass production and supply. J. Archaeol. Sci. 36, 189–204.

Foster, H., Jackson, C., 2010. The composition of late Romano-British colourless glass: glass production and consumption. J. Archaeol. Sci. 37, 3068–3080.

Foy, D., 2011. Les porte-méche des lampes en verre de l'Antiquité tardive. Provence historique, Hommages à Jean Guyon LXI fasc. 243–244, janvier-juin 2011, 207–239.

Foy, D., Nenna, M.-D., 2001. Tout feu, tout sable: Mille ans de verre antique dans le Midi de la France. Musées de Marseille-Édisud, Marseille.

Foy, D., Picon, M., Vichy, M., Thirion-Merle, V., 2003. Caractérisation des verres de l'Antiquité tardive en Méditerranée occidentale: l'émergence de nouveaux courants commerciaux. In: Foy, D., Nenna, M.-D. (Eds.), Échanges et commerce du verre dans le monde antique: actes du colloque de l'Association Française pour l'archéologie du verre, Aix-en-Provence et Marseille, 7–9 juin 2001. Éditions Monique Mergoil, Montagnac, pp. 41–78.

Freestone, I., 2005. The provenance of ancient glass through compositional analysis. In: Vandiver, P., Mass, J., Murray, A. (Eds.), Material Issues in Art and Archaeology VII. Materials Research Society Symposium Proceedings 852.Materials Research Society, Warrendale, PA, pp. OO8.1.1–OO8.14

Freestone, I., 2008. Pliny on Roman Glassmaking. In: Martinón-Torres, M., Rehren, Th. (Eds.), Archaeology, History and Science — Integrating Approaches to Ancient Materials. Left Coast Press, Walnut Creek, CA, pp. 77–100.

Freestone, I., Ponting, M., Hughes, M., 2002. The origins of Byzantine glass from Maroni Petrera, Cyprus. Archaeometry 44, 257–272.

Freestone, I., Wolf, S., Thirlwall, M., 2005. The production of HIMT glass: elemental and isotopic evidence. Annales du 16e Congrès de l'Association Internationale pour l'Histoire du Verre, London 2003. AIHV, Nottingham, pp. 153–157.

Freestone, I., Hughes, M., Stapleton, C., 2008a. The composition and production of Anglo-Saxon glass. In: Evison, V., Marzinzik, S., Freestone, I., Hughes, M., Stapleton, C. (Eds.), Catalogue of Anglo-Saxon glass in the British Museum. British Museum Research Publications 167. British Museum, London, pp. 29–46.

Freestone, I., Jackson-Tal, R., Tal, O., 2008b. Raw glass and the production of glass vessels at Late Byzantine Apollonia — Arsuf, Israel. J. Glass Stud. 50, 67–80.

Freestone, I., Leslie, K., Thirlwall, M., 2003. Strontium isotopes in the investigation of early glass production: Byzantine and early Islamic glass from the Near East. Archaeometry 45, 19–32.

Gallo, F., Silvestri, A., Molin, G., 2013. Glass from the Archaeological Museum of Adria (North-East Italy): new insights into Early Roman production technologies. J. Archaeol. Sci. 40, 2589–2605.

Gallo, F., Marcante, A., Silvestri, A., Molin, G., 2014. The glass of the 'Cassa delle Bestie Ferite': a first systematic archaeometric study on Late Roman vessels from Aquileia. J. Archaeol. Sci. 41, 7–20.

Gorin-Rosen, Y., 2000. The ancient glass industry in Israel: summary of the finds and new discoveries. In: Nenna, M.-D. (Ed.), La route du Verre: ateliers primaires et secondaires de verriers du seconde millénaire av. J.-C. au Moyen Âge. Travaux de la Maison de l'Orient. vol. 33, pp. 49–63.

Gratuze, B., 2013. Glass characterisation using laser ablation inductively coupled plasma mass spectrometry methods. In: Janssens, K. (Ed.), Modern Methods for Analysing Archaeological and Historical Glass 1. John Wiley and Sons Ltd, Chichester, pp. 201–232.

Isings, C., 1957. Roman Glass From Dated Finds. Archaeologica Traiectina 2. J. B. Wolters, Groningen/Djakarta.

Ivanov, M., 2015. Serdica (I–VI c. AD). Main results of archaeological excavations 2010–2012 in Sofia. In: Fingarova, G. (Ed.), Serdica–Sredec–Sofia: Urban Reinventions Through Three Millennia. International Conference Held in Vienna 27–29 January 2011 (in press).

Jackson, C., Foster, H., 2014. The last Roman glass in Britain: recycling at the periphery of the empire. In: Keller, D., Price, J., Jackson, C. (Eds.), Neighbours and Successors of Rome: Traditions of Glass Production and Use in Europe and the Middle East in the Later 1st Millennium AD. Oxbow Books, Oxford, pp. 6–14.

Janssens, K. (Ed.), 2013. Modern Methods for Analysing Archaeological and Historical Glass. John Wiley and Sons Ltd, Chichester (2 volumes).

Keller, D., Price, J., Jackson, C. (Eds.), 2014. Neighbours and Successors of Rome: Traditions of Glass Production and Use in Europe and the Middle East in the Later 1st Millennium AD. Oxbow Books, Oxford.

Kurnatowska, Z., Mamzer, H., 2007. Ergebnisse und Erfahrungen aus den polnischen Untersuchungen in Starmen und Odartsi. In: Henning, J. (Ed.), Post-Roman towns, trade and settlements. Byzantium, Pliska and the Balkans Vol. 2. De Gruyter, Berlin–New York, pp. 527–542.

Lankton, J., Gratuze, B., Cholakova, A., Freestone, I., Phelps, M., Rehren, Th., 2014. Glass chemical analysis: assessing the new heterarchy. 40th International Symposium on Archaeometry ISA 2014, May 19–23, 2014, Los Angeles, California, pp. 81–82 (Program and Abstract Book).

Meisser, N., Perseil, E.-A., Brugger, J., Chiappero, P.-J., 1999. Strontiomelane, $SrMn^{4+}{}_6Mn^{3+}{}_2O_{16}$, a new mineral species of the cryptomelane group from St. Marcel — Praborna, Aosta Valley, Italy. Can. Mineral. 37, 673–678.

Nenna, M.-D., 2008. Nouveaux acquis sur la production et la commerce du verre antique entre Orient et Occident. Zeitschrift für Schweizerische Archäologie und Kunstgeschichte 65, 61–66.

Nenna, M.-D., 2014. Egyptian glass abroad. HIMT glass and its markets. In: Keller, D., Price, J., Jackson, C. (Eds.), Neighbours and Successors of Rome: Traditions of Glass Production and Use in Europe and the Middle East in the Later 1st Millennium AD. Oxbow Books, Oxford, pp. 177–193.

Olczak, J., 1995. Szkło rzymskie z terenu Komendatury w Novae. Novensia 8, 15–86.

Poulter, A., 2007. The transition to late Antiquity on the Lower Danube: the city, a fort and the countryside. In: Poulter, A. (Ed.), The Transition to Late Antiquity on the Danube and Beyond. Proceedings of the British Academy 141. Oxford University Press, Oxford, pp. 51–97.

Rehren, Th., 2000. Rationales in Old World base glass compositions. J. Archaeol. Sci. 27, 1225–1234.

Rehren, Th., Cholakova, A., 2010. The Early Byzantine HIMT glass from Dichin, Northern Bulgaria. Interdisciplinary Stud. (Sofia) 22–23, 81–96.

Rehren, Th., Cholakova, A., 2014. Glass supply and consumption in the late Roman and early Byzantine site Dichin, northern Bulgaria. In: Keller, D., Price, J., Jackson, C. (Eds.), Neighbours and Successors of Rome: Traditions of Glass Production and Use in Europe and the Middle East in the Later 1st Millennium AD. Oxbow Books, Oxford, pp. 83–94.

Rehren, Th., Freestone, I., 2014. Pattern in glass use in the Roman and Byzantine Worlds: a report on current research at the Institute of Archaeology and UCL Qatar. Archaeol. Int. 17, 74–78, DOI: http://dx.doi.org/http://dx.doi.org/10.5334/ai.1718.

Sayre, E.V., Smith, R.W., 1961. Compositional categories of ancient glass. Science 133, 1824–1826.

Smirniou, M., Rehren, Th., 2013. Shades of blue — cobalt–copper coloured blue glass from New Kingdom Egypt and the Mycenaean world: a matter of production or colourant source? J. Archaeol. Sci. 40, 4731–4743.

Tal, O., Jackson-Tal, R., Freestone, I., 2004. New evidence of the production of raw glass at late Byzantine Apollonia-Arsuf, Israel. J. Glass Stud. 46, 51–66.

Torbatov, S., 1997. Quaestura exercitus: Moesia Secunda and Scythia under Justinian. Archaeol. Bulgarica 1 (3), 78–87.

Torbatov, S., 2002. Coin Circulation in the Hill-top Settlement Near Odartsi (310 BC–AD 610). Faber, Veliko Tarnovo (in Bulgarian).

Vicenzi, E., Eggins, S., Logan, A., Wysoczanski, R., 2002. Microbeam characterization of Corning archaeological reference glasses: new additions to the Smithsonian Microbeam Standard Collection. Journal of Research of the National Institute of Standards and Technology 107, 719–727.

Whitby, M., 2001. The Balkans and Greece 420–602. In: Cameron, A., Ward-Perkins, B., Whitby, M. (Eds.), The Cambridge Ancient History. Late Antiquity: Empire and Successors, AD 425–600 Volume 14. University Press, Cambridge, pp. 701–730.

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