Chemical characterization of glass beads from the necropolis of Dren-Delyan (6th–4th century BC), Southwest Bulgaria

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Abstract. The glass beads from the Dren-Delyan necropolis are found in burial complexes dated as from the end of the 6th century BC until the first half of the 4th century BC. The purpose of this study is to obtain data on the chemical composition of the glass and the technology of its production. LA-ICP-MS and SEM-EDS analyses were conducted.

The analysed glass beads are classified as a low-magnesium type (LMG), and only one of the samples is determined as high-magnesium glass (HMG). The yellow colour of the glass is due to crystals of lead antimonate incorporated into the glass matrix. The green colour of the beads is a result of interaction of added copper and lead in the glass mixture, in presence of iron and chromium. Dark blue samples are coloured by additives with cobalt, copper and lower iron content. Light blue colouration of opaque glass beads is due to high copper content, along with the presence of iron. The colouring agent of a transparent light blue bead is FeO in amount up to 0.25 wt%. The brown colour is associated with high iron content. Two different opacifiers were used for the production of opaque glass beads – antimony and tin, either individually or together. The decolourising agent is antimony without the involvement of manganese. Based on the results of the studied glass beads, we assume at least four types of raw material mixtures for their production. Comparison of the obtained results and published data about similar ancient glass findings was made.

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INTRODUCTION

The glass beads from the Dren-Delyan necropolis, Southwest Bulgaria, discovered in 2011 and excavated in 2012, are some of the oldest chemically analysed glass findings from the territory of modern Bulgaria. They were found in burial complexes dated as from the end of the 6th century BC until the first half of the 4th century BC. The detailed description of the archaeological context and the wide variety of their colour, shapes and decoration were a subject of the first stage of our study. These results were presented by Mihaylov and Tzankova (2017). In this paper, for the first time, we provide data on an LA-ICP-MS study of the main oxides and trace elements in the glass and, also, results from SEM-EDS analyses conducted on the not completely

molten particles in the glass matrix. The obtained results were used to define the chemical types of the glass, colour additives, decolourising agents and opacifiers in the studied samples. The comparison of our results with published data about similar ancient glass findings has allowed us to draw conclusions about the specific raw material used and also about its possible geographic location.

ARCHAEOLOGICAL SETTING

The necropolis of Dren-Delyan was discovered in 2011. Most of the fieldwork was conducted in 2012 (Mihaylov, 2014). It is located in south-western Bulgaria (Fig. 1), between the villages of Dren and Delyan (Mihaylov and Tzankova, 2017). Three par-

Fig. 1. Location and aerial photography of the Dren-Delyan necropolis. The cartographic base is from <https://www.arcgis.com>.

allel northeast-southwest rows of crushed stone and slabs were revealed directly below the turf at the foot of an east-facing inclination of the Konyavska Planina Mountain. Forty burial structures have been excavated (Fig. 2). Their combined length is about 400 m, covering an area of over 6575 m².

Two phases of use of the necropolis can be discerned. The first dates back to the Early Iron Age (from the end of the 11th to the beginning of the 8th century BC), and the second dates to the Late Iron Age (from the 6th to the first half of the 4th century BC). During the first phase, the deceased were cremated along with their personal belongings. The personal adornments included beads of bone. Glass beads from this early phase have not been found. Even if there had been glass originally, the probability of it surviving cremation is slim, with the pyre temperature reaching over 1000 °C. During the second phase, most of the graves and ritual features were built of stone (Fig. 2). Grave goods con-

sisted mainly of weapons, jewellery, pottery, parts of horse gear and insignia. Beads are the dominant element of the jewellery and the majority are made of glass. Amber and unworked amber beads are less common.

The glass beads were usually found on the ground or between the stones without a recognisable arrangement (Fig. 2). Some beads clearly went through the funerary pyre, while others were added during the burial or related activities. In most cases, the beads were placed during the rites accompanying the burial. Often, beads were found under the fill of small stones, covering the top of the burial structures, and between the medium and larger stones covering the structures related to the burial (Fig. 2). From this setting, more than 100 glass beads were collected. Most of them are complete and sufficiently preserved to reconstruct their shape and size. Many glass bead fragments were also recovered, but their size and shape did not allow us to determine the original number of beads. Considering the great number of fragments, they are probably not fewer than the intact beads (Mihaylov, 2014).

MATERIALS AND METHODOLOGY

Materials

The glass beads from the Dren-Delyan necropolis greatly vary in shape, colour, pattern, transparency, size, weight and specific gravity (SG). They are semi-transparent, translucent or opaque. Melon-shaped, globular, cylindrical, annular and sub-triangular annular glass beads of different colours have been studied. Some of them belong to “eye glass” beads, with three or four eyes painted with several colours on their surfaces. Typological and physical properties of the eleven representative beads, from over a hundred samples, are shown in Table 1.

Fig. 2. Archaeological setting of the studied glass beads, Dren-Delyan necropolis. The sizes of individual images are different. The entire section of the necropolis is 300 m long.

Table 1
Typological types of the studied glass beads

Lab. code	Description	Picture		Size (mm) h-d1-d2	Weight (g)	SG
B	Globular-shaped, bead dark green glass bead, with four beige spherical sectors, intact, opaque.			15.3-19.7-19.0	5.976	2.30
159	Fragment of melon-shaped black glass bead, opaque.			8.1-8.9-6.7	0.598	2.45
1182	Globular shaped bead, dark orange glass, bubbly, intact, translucent.			6.4-10.3-10.2	0.826	2.43
Dark orange	Cylindrical bead, dark-orange glass, bubbly, intact, translucent.			3.7-6.8-6.5	0.168	2.27
1168	Melon-shaped bead, with five grooves, light-blue glass, intact, translucent.			13.4-19.8-20.3	6.298	2.48
1219	Melon-shaped bead, with seven grooves, dark-blue glass, intact, translucent.			12.3-20.8-20.5	5.740	2.39
1181	Globular-shaped bead, orange-yellow glass, with four pairs of stratified eyes composed of alternating white and dark-blue, intact, opaque.			8.3-10.5-11.2	1.292	2.57
1198	Globular-shaped bead, light-blue glass, with four pairs of stratified eyes composed of alternating white and dark-blue, intact, opaque.			7.2-8.4-8.5	0.616	2.35
1247	Cylindrical bead, dark-brown glass with four stratified eyes composed of alternating white and brown, intact, opaque.			10.3-15.0-16.4	3.082	2.51
White	Globular-shaped bead, white glass, intact, opaque.			5.9-8.6-5.5	0.452	2.32
EB3	Sub-triangular annular dark-green-brownish bead, with three stratified eyes (opaque white, blue and light-green glass) and three yellow spherical mini-beads, opaque.			2.7-7.6-6.7	0.162	2.38

Table 2

LA-ICP-MS analyses of glass beads from the Dren-Delyan necropolis: chemical types, main oxides (wt%) and trace elements (ppm)

HMG			LMG																				
Chem. type	Si (Al)-Na (K)-Ca (Mg)	Si-Na-Ca, Mg	Si-Na-Ca (Si-Pb-Na-Ca for glass bead 1181)																	Si (Al)-Na-Ca			
Picture
Lab. code	B	159	1182	Dark orange	1168 light-blue	1219 dark-blue	1181 yellow	1181 blue	1181 white	1198 light-blue	1198 white	1198 dark-blue	1247 brown	1247 white	White	EB3 dark-green	EB3 blue	EB3 white	EB3 yellow				
wt %	an. 1	an. 2	an. 3	an. 4	an. 5	an. 6	an. 7	an. 8	an. 9	an. 10	an. 11	an. 12	an. 13	an. 14	an. 15	an. 16	an. 17	an. 18	an. 19	an. 20			
SiO ₂	59.16	76.98	62.63	66.81	69.75	67.21	69.50	62.06	70.17	68.74	70.81	69.70	70.59	67.34	68.80	67.28	65.15	66.61	66.79	66.00			
TiO ₂	0.34	0.10	0.26	0.12	0.05	0.07	0.06	0.05	0.05	0.06	0.05	0.06	0.06	0.07	0.06	0.06	0.06	0.06	0.05	0.05			
Al ₂ O ₃	5.15	0.39	1.75	0.63	2.24	2.27	2.59	1.23	2.20	2.01	2.26	2.09	2.42	0.52	0.50	1.46	3.02	3.15	3.25	3.03			
FeO	1.35	0.19	11.02	0.28	0.22	0.26	0.43	0.86	2.17	0.40	0.28	0.37	0.79	3.21	0.32	0.25	1.23	0.60	0.25	0.30			
MnO	0.05	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.08	0.35	0.02	0.01	0.01			
MgO	2.96	0.42	2.40	0.73	0.46	0.58	0.44	0.38	0.34	0.39	0.39	0.51	0.41	0.63	0.59	0.61	0.50	0.54	0.42	0.47			
CaO	8.71	8.39	4.03	11.62	8.40	11.13	8.54	5.37	6.29	7.49	6.94	8.71	7.38	8.62	9.69	12.18	9.16	8.57	8.44	9.6			
Na ₂ O	14.49	12.16	14.88	18.93	17.48	17.23	15.77	13.88	15.63	16.32	16.75	16.56	15.88	17.63	17.87	18.33	17.52	17.62	17.07	17.08			
K ₂ O	4.37	1.22	1.49	0.12	0.40	0.43	0.45	0.48	1.02	0.96	0.64	0.84	0.73	0.21	0.25	0.25	0.56	0.72	0.60	0.52			
P ₂ O ₅	1.13	0.03	0.11	0.04	0.04	0.05	0.04	0.03	0.05	0.06	0.03	0.04	0.03	0.09	0.08	0.05	0.05	0.06	0.05	0.03			
SO ₃	0.01	0.01	0.10	0.01	0.01	0.36	0.28	0.05	0.05	0.01	0.69	0.10	0.29	0.58	0.42	0.22	0.05	0.92	0.01	0.53			
ppm																							
Cu	13725.6	35.70	80.49	2.58	5.84	10.57	358.18	149.13	2183.1	678.81	9723.1	194.66	2106.6	34.57	28.91	47.51	7618.1	522.61	57.68	380.50			
Zn	75.06	6.85	381.54	4.99	8.76	7.40	70.25	10.02	752.99	22.31	143.73	53.51	194.87	12.50	14.30	8.74	556.64	93.98	15.52	14.31			
Co	7.15	0.77	1.63	1.06	5.65	1.10	747.54	4.47	1157.9	8.16	15.93	10.26	3939.1	15.20	1.76	1.21	208.53	679.37	2.03	1.55			
Sn	195.2	5.04	1.45	1.53	1.42	175.06	1.56	73.88	4.35	8.33	241.21	13.36	6.18	5.13	2.43	2.82	172.14	3.16	1.44	2.24			
Sb	1.27	<0.76	28.03	1.42	34.58	4904.4	2754.4	8999.09	4250.1	34942.1	13914	83062.8	5249.9	555.9	68751	30515.32	3880.4	9586.2	35958	7679.95			
Pb	337.9	469.1	3.84	4.35	18.14	30.09	519.21	138488	7971.3	70703.4	132.01	452.79	176.86	178.7	142.26	1967.82	1748.0	14836	1652.5	19865.1			
Ba	207.3	33.73	52.91	49.59	190.0	194.46	216.72	108.60	195.34	232.65	229.78	292.66	212.27	40.77	125.49	165.08	191.95	250.54	252.61	224.16			
Sr	370.5	305.4	170.89	576.6	514.3	594.75	495.85	249.67	356.08	400.17	439.65	534.64	444.68	362.1	404.92	568.41	474.70	540.95	492.15	533.96			
Ni	73.69	10.75	15.45	9.27	9.43	9.09	10.58	9.01	22.68	8.64	39.00	8.74	15.48	23.28	9.89	8.48	39.08	9.31	9.70	29.55			
Sc	6.53	4.15	3.98	3.48	4.34	3.97	4.07	3.30	2.94	3.45	4.25	3.92	3.74	3.70	4.00	3.30	3.98	3.70	4.20	10.84			
V	27.89	5.42	27.17	7.90	4.43	7.23	5.72	5.36	6.97	5.78	4.67	5.79	5.52	11.16	6.08	6.99	12.70	5.83	4.58	3.44			
Cr	39.33	16.79	30.22	18.92	21.35	17.33	19.59	15.41	14.86	15.73	17.70	17.30	18.05	19.16	18.12	16.56	21.69	17.51	19.66	53.36			

Table 2 (continued)

Ga	5.70	2.27	4.19	2.04	2.74	2.55	5.32	1.81	15.51	2.05	2.40	2.65	7.18	2.16	2.04	2.04	3.38	4.36	2.86	6.18
As	9.15	3.39	35.50	3.11	3.92	10.14	6.39	28.60	19.69	24.13	36.57	15.39	13.67	4.90	20.89	12.91	59.54	14.02	15.58	19.99
Rb	26.92	4.50	23.95	1.75	6.90	6.74	9.33	5.21	11.67	11.74	13.38	12.90	12.11	1.98	2.73	3.93	8.48	9.69	9.47	9.59
Zr	76.57	124.1	126.20	202.7	35.97	66.79	30.91	33.89	34.36	36.57	33.40	49.71	35.10	77.69	70.22	62.22	45.56	40.64	29.94	37.51
Mo	2.68	2.77	5.73	3.07	3.97	<2.75	2.89	2.25	2.78	3.10	3.21	3.31	3.40	2.80	3.03	2.91	2.95	2.65	3.09	7.12
Ag	2.12	9.61	0.31	<0.33	<0.50	31.94	<0.37	10.89	1.53	4.26	1.64	0.64	0.75	0.32	<0.46	0.47	5.16	5.18	0.96	68.46
Cs	0.57	<0.08	0.62	<0.10	<0.13	0.13	<0.14	<0.09	0.11	0.14	0.53	0.27	0.40	0.11	<0.10	0.09	0.13	<0.12	<0.12	<0.33
La	13.62	4.43	12.81	5.33	6.35	7.76	6.73	5.30	5.66	9.97	7.83	15.93	6.64	6.04	13.52	9.41	6.70	7.90	10.02	6.90
Ce	27.95	6.37	25.85	7.85	10.84	12.29	11.64	7.12	9.59	10.78	11.24	11.28	10.77	7.72	7.22	9.62	10.22	12.52	10.96	10.58
Pr	3.13	1.15	2.91	1.16	1.56	1.70	1.47	0.93	1.26	1.48	1.60	1.54	1.41	1.28	1.30	1.49	1.53	1.70	1.42	1.44
Nd	12.35	3.19	11.01	4.94	6.29	7.05	6.26	3.48	5.19	4.37	5.81	6.55	6.00	5.82	5.41	5.60	5.90	7.36	5.98	7.34
Sm	2.64	0.77	2.05	1.15	1.32	1.46	1.35	0.83	1.05	0.73	1.40	1.46	1.27	1.08	0.76	1.08	1.32	1.15	1.41	1.53
Eu	0.60	<0.20	0.26	<0.22	0.40	0.41	0.41	<0.17	0.35	0.33	0.34	0.40	0.35	0.32	0.24	0.26	0.44	0.30	0.39	0.50
Gd	2.00	0.85	1.76	0.96	0.92	1.66	1.42	1.00	1.09	1.15	1.07	1.09	1.25	1.18	0.95	1.26	1.07	1.73	1.09	2.03
Tb	0.32	0.14	0.20	<0.13	0.22	0.24	0.16	0.08	0.14	0.19	0.17	0.19	0.18	0.18	0.14	0.17	0.20	0.15	0.18	0.21
Dy	2.17	0.88	1.68	0.73	1.12	1.38	1.14	0.48	0.87	1.07	1.12	1.31	1.16	0.95	1.12	0.99	1.10	1.41	1.11	1.11
Ho	0.43	0.11	0.27	0.19	0.23	0.31	0.27	0.17	0.20	0.24	0.20	0.26	0.19	0.17	0.15	0.22	0.23	0.26	0.28	0.27
Er	1.16	0.45	0.83	0.45	0.52	0.72	0.64	0.45	0.39	0.48	0.61	0.80	0.50	0.63	0.52	0.72	0.58	0.47	0.66	1.04
Tm	0.18	<0.10	0.11	0.07	0.11	0.10	<0.09	<0.06	0.08	<0.09	0.09	<0.10	0.10	0.08	<0.06	0.11	<0.09	0.11	<0.12	<0.23
Yb	1.52	0.64	0.96	0.54	0.73	0.66	0.74	0.54	0.53	<0.43	0.64	0.65	0.59	0.55	0.55	0.56	0.68	<0.58	0.60	1.28
Lu	0.17	0.08	0.12	0.10	<0.11	0.10	0.08	<0.06	<0.07	0.13	<0.10	0.12	<0.10	0.08	<0.09	<0.09	0.10	0.08	<0.08	<0.15
Hf	1.87	2.96	2.96	4.75	0.86	1.62	0.73	0.94	0.90	0.74	1.10	1.18	0.93	1.87	1.67	1.59	1.05	0.98	0.61	1.25
Ta	0.52	0.15	0.41	0.18	<0.14	<0.12	<0.10	<0.07	<0.09	0.10	<0.10	<0.11	<0.11	0.10	<0.11	0.10	<0.11	<0.11	0.12	<0.26
Pt	0.33	<0.22	<0.19	<0.21	0.34	<0.34	<0.35	<0.19	<0.24	<0.28	0.35	<0.15	<0.30	0.25	0.26	<0.24	0.22	<0.30	<0.26	0.780
Au	0.41	<0.29	<0.28	<0.34	0.40	<0.29	<0.29	<0.25	<0.26	<0.37	0.33	0.38	<0.33	0.26	<0.36	<0.32	0.47	<0.21	0.31	1.15
Bi	0.22	<0.08	<0.10	<0.13	<0.14	<0.23	0.38	9.23	0.32	4.92	0.26	0.30	<0.31	0.11	0.10	1.45	1.13	1.20	0.47	3.74
Th	3.75	0.64	4.54	0.66	0.62	0.76	0.75	0.65	0.76	0.72	0.83	0.81	0.82	0.65	0.61	0.73	0.76	0.79	0.75	0.96
U	1.56	1.59	2.67	3.07	1.13	1.64	1.56	3.09	0.92	2.24	0.93	1.26	0.93	0.79	0.88	1.14	0.87	1.03	0.72	0.63

Methodology

Surface observations on the beads and elemental composition of both the glass matrix and the not completely molten relicts of the raw material were made with a scanning electron microscope JEOL JSM6010PLUS/LA, equipped with coupled energy X-ray dispersion spectroscopy (EDS) at the University of Mining and Geology “St. Ivan Rilski” – Sofia. The SEM-EDS analyses were performed with energy resolution of 128 eV in a low-vacuum mode, JEOL software. The low-vacuum mode offers easy observation of the non-conductive materials, without pre-treatment. Measurements were taken from flat polished areas on the surfaces of the samples under the following conditions: low-vacuum pressure (30 Pa); accelerating voltage (15 kV); limitation (0.5%); time of collection (90 seconds); and single-point spot size (70 μm). The not completely molten relicts from the raw material provide information about the type of opacifiers, colour additives and decolourising agents. These elements, however, are below the detection limits of the SEM-EDS apparatus in homogenised portions of the glass mass.

The LA-ICP-MS system of the Geological Institute, Bulgarian Academy of Sciences, was also used. It consists of 193 nm ArF excimer laser (ATLEX-SI, Germany), linked with ELAN DRC-e ICP-MS instrument (Perkin Elmer, Canada). The analyses were performed on 35 μm ablation pits. External standardisation on NIST glass standard SRM-610 allowed linear drift correction of the spectrometer and provided the measurements of relative element concentrations. Element concentrations were transformed into true values by internal standardisation (*i.e.*, the known concentration of the elements determined by SEM-EDS in our case) through the Sills program for data reduction. The high level of sensitivity of LA-ICP-MS provided detailed information about the trace elements in the studied glass beads and the ability to compare them to the glasses from different geographic areas.

RESULTS

The results from the chemical analyses of eleven representative glass beads are shown in Table 2. The samples are grouped according to the chemical type of the glass and the level of magnesium content. The chemical composition of the polychrome beads is presented with several analyses. Each one of them corresponds to the different glass colour of the samples.

The examined glass beads differ substantially in their chemical composition from one another. The

content of the main oxides in their glass matrix composition varies as follows: SiO_2 (59.16–70.81 wt%); Al_2O_3 (0.52–5.15 wt%); MgO (0.38–2.96 wt%); CaO (4.03–11.62 wt%); Na_2O (13.88–18.93 wt%); K_2O (0.12–4.37 wt%) (see Table 2 – an. 1, an. 3–8, an. 11, an. 14, an. 16, an. 17). The concentration of Pb has a wide range of values and reaches up to 138,488 ppm (14.92 wt% PbO) in sample 1181 (Table 2). The content of phosphorus in glass bead B (1.13 wt%) is much higher than in all other examined beads (Table 2).

All studied glass samples are semi-transparent or opaque (Table 1). Semi-transparent samples 159, 1182, as well as the specimen designated as Dark orange, are full of gas bubbles. The tin content in them is of very low values (Table 2). In opaque samples 1181, 1198, EB3 and bead B, the tin content reaches values up to 73.88 ppm, 241.21 ppm, 172.14 ppm and 195.20 ppm, respectively (Table 2). Almost all studied beads, except for three of them (samples 159, 1182 and green bead B), contain high antimony levels (Table 2).

Not completely molten particles with high reflectivity were observed during the SEM investigation of the glasses (see Figs 3–9). They are relict residues from the raw material. Their composition is rich in chemical elements and compounds, which determine the physical properties of the glass.

The white decoration glass in beads 1247, 1181 and EB3 is full of relicts (see Figs 3–6) with very high antimony content (Sb_2O_3) up to 57.42 wt% in bead 1181 (Table 3) and they also contain a substance from the glass matrix.

Not completely molten particles in opaque glass matrix of beads 1198, 1247, EB3 and bead B (Fig. 3a, Figs 7, 8) are characterized by their high antimony and tin content. These particles in samples 1198 and EB3 are enriched in antimony, with contents as follows: sample 1198 – 26.65 wt%, and sample EB3 – 66.71 wt% (see Table 4, Fig. 8a, c). In sample 1247, except antimony in an amount of 46.47 wt%, tin was also found up to 4.02 wt% (Table 4, Fig. 8b). Relicts from the raw material observed in the glass matrix of bead B contain only tin without antimony (Table 4, Fig. 8d–e).

The studied glass beads differ from each other in colour and hue. A very high content of lead and antimony and relatively high iron content was measured in opaque yellow glass bead 1181. Analyses 1181-3-001 and 1181-3-002 (Table 5, Figs 7e, 9) represent the chemical composition of the partially molten solid particles with impurity from the glass matrix. Analysis 1181-5-002 (Table 5, Figs 7f, 9) presents the chemical composition of such almost completely preserved particle with PbO/ Sb_2O_3 ratio

Fig. 3. SEM photo of not completely molten particles dispersed in the glass of the studied beads: a) bead 1247, analyses 1247-4-001–1247-4-010; b) bead 1181, analyses from 1181-2-001 to 1181-2-007; c) bead 1181, analyses from 1181-4-001 to 1181-4-003; d) bead EB3, analyses from EB3-4-001 to EB3-4-003.

of 1.38, which is typical for the stoichiometry of lead antimonate $\text{Pb}_2\text{Sb}_2\text{O}_7$.

The dark blue glass beads are rich in cobalt, in association with copper and lower iron content. In bead 1219, the following values for these pigments were measured: Co – 747.54 ppm (0.10 wt% CoO); Cu – 358.18 ppm (0.05 wt% CuO); and FeO – 0.43 wt% (Table 2). In the dark blue glass of bead 1181, the concentration values for the same pigments are as follows: Co – 1157.9 ppm (0.15 wt% CoO); Cu – 2183.1 ppm (0.27 wt% CuO); and FeO – 2.17 wt% (Table 2). The dark blue glass decoration of bead 1198 contains 3939.1 ppm of Co (0.50 wt% CoO); 2106.6 ppm of Cu (0.26 wt% CuO) and 0.79 wt% of FeO (Table 2). The following values for the same pigments were detected in the dark blue glass of bead EB3: Co – 679.37 ppm (0.09 wt% CoO); Cu – 522.61 ppm (0.07 wt% CuO); and FeO – 0.60 wt% (Table 2).

In the opaque glass with the light blue colouration of bead 1198, high copper (9723.10 ppm; 1.22 wt% CuO) content was found along with the presence of iron (0.28 wt% FeO) and almost complete absence of cobalt (Table 2).

The presence of FeO (0.26 wt%) was detected in the transparent light blue bead 1168 (Table 2).

In the green glass of bead B, a large amount of copper (13,725.6 ppm; 1.72 wt% CuO) was measured, along with elevated contents of FeO (1.35 wt%), Cr (39.33 ppm) and Pb (337.9 ppm; PbO – 0.04 wt%) (Table 2). The concentration levels of these pigments in the green glass composition of bead EB3 are also high: 7618.1 ppm Cu (0.95 wt% CuO); 1.23 wt% FeO; 208.53 ppm Co (0.03 wt% CoO); 1748.0 ppm Pb (0.19 wt%) (Table 2). The high zinc content in bead EB3 (556.64 ppm Zn; 0.07 wt% ZnO) is most likely a lead companion in the feed-stock. High iron content (3.21 wt%) was detected

Fig. 4. Compositional charts of not completely molten particles in the white decoration glass of sample 1247: a) analysis 1247-4-005; b) analysis 1247-4-006; c) analysis 1247-4-007; d) analysis 1247-4-008; e) analysis 1247-4-010.

Fig. 5. Compositional charts of not completely molten particles in the white decoration glass of sample 1181: a) analysis 1181-2-007; b) analysis 1181-4-001.

Fig. 6. Compositional charts of not completely molten particles in the white decoration glass of sample EB3-4: a) analysis EB3-4-001; b) analysis EB3-4-002.

Fig. 7. SEM image of not completely molten particles dispersed in the glass of the studied beads: *a*) bead 1198, analyses from 1198-1-001 to 1198-1-006; *b*) bead EB3 overview; *c*) bead EB3, analyses from EB3-5-001 to EB3-5-008; *d*) bead B, analyses from B-1-001 to B-1-006; *e*) bead 1181, analyses 1181-3-001 and 1181-3-002; *f*) bead 1181, analyses 1181-5-001 and 1181-5-002.

Fig. 8. Compositional charts of not completely molten particles in the bulk glass matrix used as opacifying agents in the studied samples: *a)* bead 1198, analysis 1198-1-006; *b)* bead 1247, analysis 1247-4-010; *c)* bead EB3, analysis EB3-5-005; *d)* bead B, analysis B-1-004; *e)* bead B, analysis B-1-006.

Fig. 9. Compositional charts of not completely molten particles in the opaque yellow glass bead 1181: a) analysis 1181-3-001; b) analysis 1181-3-002; c) analysis 1181-5-002.

Table 3

SEM-EDS analyses (in wt% of oxides) of not completely molten particles in the white glass of the studied samples used as decolourizing agents

Sample	Analysis	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Cl	K ₂ O	FeO	SnO ₂	Sb ₂ O ₃	PbO
1247	1247-4-005	13.42	0.74	0.75	54.22	1.02	1.30	–	0.80	1.69	23.07	–
	1247-4-006	14.76	0.71	0.79	57.01	0.42	0.93	–	–	1.55	23.84	–
	1247-4-007	9.93	0.60	0.72	45.29	–	0.80	–	–	1.88	40.78	–
	1247-4-008	12.16	0.66	0.55	45.99	–	0.74	–	–	2.24	37.67	–
1181	1181-2-007	10.84	0.56	1.91	53.27	–	0.58	–	0.76	–	27.06	5.05
	1181-4-001	4.20	–	1.59	30.90	–	–	–	–	–	57.42	5.89
	1181-4-002	7.58	–	1.88	43.00	–	–	–	–	–	47.54	–
EB3	EB3-4-001	3.45	–	3.37	46.86	–	0.77	–	–	1.59	31.28	11.67
	EB3-4-002	3.35	0.44	3.28	44.06	–	0.59	–	1.20	1.24	34.01	10.83

Table 4

SEM-EDS analyses (in wt% of oxides) of not completely molten particles in the bulk glass matrix of the studied samples used as opacifying agents

Sample	Analysis	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	Cl	K ₂ O	FeO	SnO ₂	Sb ₂ O ₃	CuO
1198	1198-1-006 blue glass	15.23	0.64	2.84	48.02	0.69	2.39	1.02	0.40	–	26.65	1.01
1247	1247-4-010 brown	5.27	0.49	1.49	40.65	–	0.53	1.08	–	4.02	46.47	–
EB3	EB3-5-005 green glass	1.35	0.46	2.59	27.70	0.28	0.91	–	–	–	66.71	–
B	B-1-004 green glass	2.25	0.89	6.77	19.60	–	–	–	2.50	67.69	–	–
B	B-1-006 green glass	–	–	5.58	16.24	–	–	–	–	78.18	–	–

Table 5

SEM-EDS analyses (in wt% of oxides) of not completely molten particles in the opaque yellow glass bead 1181

Bead 1181	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Sb ₂ O ₅	PbO
1181-3-001	1.62	0.82	37.93	4.09	19.33	36.20
1181-3-002	1.88	–	20.34	3.48	28.38	45.93
1181-5-002	1.31	–	5.25	6.92	36.17	49.81

in the chemical composition of the brown-coloured glass in bead 1247 (Table 2).

DISCUSSION

Based on the results obtained from the alkali composition, all examined beads (Table 2), except for one (bead B), are low-magnesium glass (LMG), with a content of K₂O and MgO ≤ 1.5 wt% (Sayre and Smith, 1961, 1967). The alkali source for LMG in the ancient world is natron. The bead B differs from all other studied beads with its higher content of magnesium (MgO – 2.96 wt%), potassium (K₂O – 4.37 wt%) and phosphorus (P₂O₃ – 1.13 wt%). Glasses with values of 2–6% MgO and 0.5–4% K₂O are high-magnesium glasses (HMG) and their production involved plant ashes as an alkali source (Sayre and Smith, 1961; Henderson, 1989; Henderson *et al.*, 2010; Conte *et al.*, 2016). The amount of phosphorus content in the ancient glass is very informative about the type of raw material (Henderson, 1985; Galibin, 2001). Plants contain phosphorus and it remains in their ashes. Phosphorus is included in the composition of the finished glass, although in the process of glass production a sig-

nificant part of it can evaporate (Henderson, 1985; Galibin, 2001). The flux is added to the silica in order to reduce significantly its melting temperature, from 1700 °C to about 700–900 °C, so that the finished melt becomes less viscous and easier to process (Henderson, 1985; Kuleff, 2012).

According to Galibin (2001), the Na₂O/K₂O ratio is also indicative of the alkaline source used. The ratio Na₂O/K₂O < 7.5 and the value of K₂O ≥ 1.5% suggest the use of plant ash as a flux in the glass production, while the ratio Na₂O/K₂O > 7.5 refers to the use of natron as an alkaline source. The black-coloured sample 159 differs from other studied LMG glasses with its high content of MgO (2.40%) and K₂O (1.49%), but it has a chemical composition close to natron-based glass with Na₂O/K₂O > 7.5 (Table 6), nevertheless.

About 800 BC, the chemical composition of soda-lime glasses changed from HMG to LMG due to a change in the use of raw material (Sayre and Smith, 1967; Henderson, 1985). The studied HMG bead B is dated, according to the archaeological setting, as 6th–4th century BC. At this period the plant ash-based glass production is reduced. Plant-ash glasses produced in Central Asia and the Middle East continued to occur until the first millennium

Table 6

Chemical types of the glass beads, $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio, supposed flux and quartz sand with different purity used for their production

Chemical type	Lab. code	$\text{Na}_2\text{O}/\text{K}_2\text{O}$	LMG or HMG	Supposed flux and quartz sand with different purity
Si-Na-Ca	1182	157.75	LMG	Natron and refined sand.
	Dark orange	43.7		
	1168	40.07		
	1219	35.04		
	1181	28.92		
	1198	26.17		
	1247	83.95		
	White	73.32		
Si (Al)-Na-Ca	EB3	31.29	LMG	Natron and unrefined sand with a high level of feldspars or clay.
Si-Na-Ca, Mg	159	9.99		Natron and dark sand rich in magnetite.
Si (Al)-Na (K)-Ca (Mg)	B	3.32	HMG	Ashes from salt-tolerant plants as an alkali source.

BC and the first millennium AD (Brill, 1987, 1989; Dikshit, 1964).

Based on the content of main oxides in the studied samples and according to Galibin (2001), the glasses which the different beads are made of can be classified into four chemical types: 1) Si-Na-Ca; 2) Si (Al)-Na-Ca; 3) Si-Na-Ca, Mg; and 4) Si (Al)-Na (K)-Ca (Mg) (Tables 2, 6). These types are a result of different raw material used for their production.

The difference between Si-Na-Ca, Si (Al)-Na-Ca and Si-Na-Ca, Mg-types depends mainly on the purity of the used quartz sand. In the production of Si-Na-Ca-type beads, well-washed and almost pure quartz sand was used. The increased content of Al_2O_3 in a bead from the chemical type Si (Al)-Na-Ca indicates the use of quartz sand with high feldspars or clay content (Matson, 1951; Henderson, 1985; Galibin, 2001). Aluminium is among the main components of the glass. The introduction of 3–4% Al_2O_3 into the glass increases its mechanical strength to pressure and impact, as well as its hardness (Kuleff, 2012). Aluminium oxide requires higher temperatures in the furnace, as well as more time to clarify the glass (Henderson, 1985; Kuleff, 2012). The chemical type Si-Na-Ca, Mg is due to the use of quartz sand rich in magnetite as raw material (Conte *et al.*, 2016).

The quartz sand is the component that was used in the largest amount in glass production. Thus, it is logical to assume that each primary glass workshop used a source of quartz sand situated nearest to it. From this point of view, we assume that the

three studied chemical types of LMG glass – Si-Na-Ca, Si (Al)-Na-Ca, and Si-Na-Ca, Mg-types (Table 6) – were produced in three different primary glass workshops. Probably, the HMG glass, of which the studied bead B is made, is a product of a fourth primary glass workshop that had preserved the tradition of high-magnesium glass production.

The source of calcium for the production of the studied glass samples is not dolomitic sandstone or dolomite, because the values of calcium do not correlate with the magnesium values (Table 2). The probable source of calcium is the inclusion of shell fragments in the sand used (Henderson, 1985). The main role of the calcium oxide in prehistoric glass production was to reduce weathering in glasses and to serve as a stabilizer (Henderson, 1985).

There is a positive correlation between MgO and K_2O (Table 2). This correlation indicates that MgO was probably introduced with K_2O in the primary raw materials used to prepare the glasses (Henderson, 1985).

The black colour of the bead 159 is due to the rich in magnetite sand used. The content of iron is very high – 11.02 wt% (Table 2). Magnesium is a very common impurity in the mineral magnetite, along with Zn, Cr, Ti, V and Al. This is probably the reason for the increased content of MgO (2.40 wt%) in the composition of bead 159 (Table 2).

The most commonly used decolourizing agents in glass production in the ancient world were MnO and Sb_2O_3 , together or separately, which are capable of oxidizing the iron and thus discolouring the glass (Kuleff, 2012). The high antimony content and the

absence of manganese in the compositions of not completely molten particles in the white decoration glass of the studied samples 1247, 1181 and EB3 (Table 2, Table 3) show that antimony was used as a decolourizing agent without the involvement of manganese. Colourless glasses in the Near East, which were produced in the period from the 7th century BC to the late 1st century BC, were mainly decolourized by antimony (Sayre and Smith, 1967; Henderson, 1985). The change in glass decolourants in which the manganese oxide appears to replace antimony took place slightly earlier, in the 2nd–1st century BC (Henderson and Warren, 1983; Henderson, 1985).

Opacity in the ancient glass can be due to both a large number of gas bubbles and the involvement of antimony- and tin-bearing chemicals, which sometimes form a compound with lead (Henderson, 1985). The results of the SEM-EDS analyses presented in Table 4 and Figure 8 allow us to conclude that, in the opaque samples 1198 and EB3, antimony or antimony-based compounds were the opacifying agents, for sample 1247 – antimony and small amounts of tin, while for the bead B the opacity was obtained only by the addition of tin oxide, in the absence of antimony.

In order to define the source of tin in the glass, it is necessary to pay attention to the possibility of tin introduction into the glass matrix by adding bronze. According to the presented in Table 2 analyses (an. 1, an. 8, an. 11, an. 17), the increased content of tin is accompanied by increased copper content in the samples, but they are not with close proportions to those of copper and tin in the bronze alloy. As is evident from analyses B-1-004 and B-1-006 of the bead B (Table 4), almost pure cassiterite is observed as small impurities in the opaque glass matrix and without any copper or lead content. Because of these facts, we suppose that, in the studied bead B, the tin is introduced consciously and separately from the copper.

Some of the earliest tin-opacified studied glasses are from Celtic Europe and they are dated as the 2nd–1st century BC (Henderson and Warren, 1983), Western China – 5th–3rd century BC (Li *et al.*, 2014) and from Chotin, Slovakia – 7th–5th century BC (Conte *et al.*, 2016). The latter beads are the plant-ash based, with content of Sn in the amount of 139–150 ppm in an almost complete absence of antimony (Conte *et al.*, 2016). These data show that the studied glass bead B found in the necropolis of Dren-Delyan is one of the oldest chemically investigated tin-opacified glass beads found so far.

The chemical composition of almost totally conserved heterogeneities found in opaque yellow

glass bead 1181 (Table 5, Figs 7f, 9), with PbO/Sb₂O₅ ratio 1.38, is typical for the stoichiometry of lead antimonate Pb₂Sb₂O₇, and allows us to assume that the yellow colour in bead 1181 was obtained by the combination of lead and antimony in the presence of iron. Molina *et al.* (2014) established that lead antimonate particles are stable in glass up to operating temperatures in the range of 900–1000 °C before converting to white calcium antimonate, and a small number of impurities, such as iron, zinc and tin, improve their stability (Molina *et al.*, 2014). The content of lead in the yellow glass matrix of bead 1181 is of very high level (see Table 2), up to 138,488 ppm (14.92 wt% PbO). This high value of lead gives us reason to assume that crystals of lead antimonate were added to the batch, along with another lead-bearing phase. For opaque yellow glass bead 1181, the antimony is both a yellowing and an opacifying agent. Crystals of lead antimonate (Pb₂Sb₂O₇) are responsible for the colour and opacity of opaque yellow glass from the Late Bronze Age (Henderson, 1985, p. 285; Duckworth *et al.*, 2012, p. 2146). The widespread use of lead in polychrome glass as a yellow colouring agent made it an additional glass-forming component together with sodium from natron (Galibin, 2001). An example of that is bead 1181 (Si-Pb-Na-Ca).

As is evident from the chemical compositions of the dark blue glass in samples 1219, 1181, 1198 and EB3 (Table 2), the dark blue colour is a result of the combination of cobalt (the main colouring agent), copper and a small amount of iron. In these samples, there is also some correlation between arsenic and nickel values, although they are significantly lower than the above-mentioned ones (Table 2). The addition of copper in the glass production stains the glass light to medium blue in colour (Henderson, 1985, p. 282; Mass *et al.*, 2002, p. 76; Duckworth *et al.*, 2012, p. 2146).

The colouring agent of the transparent light blue bead 1168 is FeO, in amount of 0.26 wt% (Table 2).

The green colour of the studied beads EB3 and B is a result of the interaction in the glass mixture of added copper, lead, iron and chromium (Table 2). The involvement of copper in its oxidized form (CuO) as a glass colourant led to turquoise colour in the finished glass and the presence of lead oxide produces a green instead of a blue colour (Henderson, 1985, p. 282; Mass *et al.*, 2002, p. 76; Duckworth *et al.*, 2012, p. 2146; Weyl, 2016, pp. 154–163). According to Galibin (2001), chromium in the glass mass may be either green or yellow pigment, depending on the valency of the chromium: Cr³⁺ ion stains the glass green and the anions CrO₃⁻¹ and Cr₂O₇⁻² are found in yellow-orange glasses.

The brown colour in bead 1247 is associated with the high iron content ($\text{FeO} - 3.21 \text{ wt\%}$, see Table 2). At this stage of investigation, we have not studied the valency of iron giving this coloration. The use of iron oxide in the form of Fe_2O_3 for brown glass dyeing began in the 6th century BC in the sodium glass (Galibin, 2001).

COMPARISON OF THE GLASS BEADS FROM THE DREN-DELYAN NECROPOLIS WITH PUBLISHED DATA FOR GLASS FINDS DATED TO THE SAME HISTORICAL PERIOD

Among the other chemically studied glass finds from Bulgaria, only the glass beads from the necropolis of Apollonia Pontica – 5th–3rd Century BC (Lyubomirova *et al.*, 2014) are close in their pre-dating to the samples that are the object of this study. The available chemical investigations of glass finds from Bulgaria mainly refer to findings from the Medieval, Roman and Early Byzantine periods (Detcheva *et al.*, 2010; Detcheva *et al.*, 2012; Georgieva *et al.*, 2010; Kirov *et al.*, 2006; Kuleff and Djingova, 1994; Kuleff and Djingova, 1999; Lesigyarski *et al.*, 2013; Rehren and Cholakova, 2010). From this point of view, the glass beads from Dren-Delyan necropolis are the most ancient chemically investigated glass beads found in Bulgaria up to now (Mihaylov and Tzankova, 2017).

In order to draw conclusions about the possible geographic location of specific raw material sources, we compared our results to the published data for glass artefacts from the same historical period. Biplot compositional charts for the glass beads found in Dren-Delyan necropolis are presented at Fig. 10a–c. In these charts, the beads are labelled not only by their lab codes but by their chemical types also. A comparison of analyzed samples and published data for glass artifacts from Apollonia Pontica necropolis in Bulgaria (Lyubomirova *et al.*,

2014), Pichvnari necropolis in Georgia (Shortland and Schroeder, 2009), Pydna and Methoni in Pieria Greece (Blomme *et al.*, 2017) and from Rhodes (Rehren *et al.*, 2003) is given in Fig. 11.

As is evident from Fig. 11a, b, the obtained data for the studied natron-based Si-Na-Ca and Si(Al)-Na-Ca glass beads (Table 2, 6) are very close in their chemical composition to published data about glass artifacts found in Pichvnari necropolis, Georgia (Shortland and Schroeder, 2009) and Methoni, Greece (Blomme *et al.*, 2017). Moreover, comparing chemical analyzes, it was found that the chemical composition of opaque yellow bead 1181 (Table 2) almost completely matches the analyzes data of some glass artefacts found in Pichvnari necropolis, Georgia (Shortland and Schroeder, 2009, p. 955, samples Pic16b, Pic.21b and Pic28b) and Northern Italy (Arletti *et al.*, 2009, pp. 5–6, sample IG4y). The dark brown bead 1247 from the Dren-Delyan necropolis (Table 2) has a similar composition to the black natron based beads from the Pichvnari necropolis, Georgia (Shortland and Schroeder, 2009, p. 955, an. Pic39).

Compared to the glass beads from the necropolis of Apollonia Pontica (Lyubomirova *et al.*, 2014), samples from the Dren-Delyan necropolis are more diverse in term of their shape, colour, pattern, variations in the values of the main oxides and trace elements. They are HMG and LMG, and are subdivided into four chemical types. The reported glass artefacts from the necropolis of Apollonia Pontica are all LMG and they are classified into two groups (Lyubomirova *et al.*, 2014). The beads from the above-mentioned two necropoles are similar in the pigments used for the yellow- and the blue-coloured glasses, although in different concentrations. The lead content in the yellow glass from the Dren-Delyan necropolis (see Table 2, an. 8) is several times higher than that reported for the yellow glass of Apollonia Pontica, $\text{PbO} - \text{up to } 5.56 \text{ wt\%}$ (Lyubomirova *et al.*, 2014). Glass bead with a chemical

Fig. 10. Biplot compositional charts for the analysed glass beads from the Dren-Delyan necropolis: a) Al_2O_3 vs CaO ; b) MgO vs Al_2O_3 ; c) MgO vs K_2O .

Fig. 11. Comparative charts of Al_2O_3 vs CaO , MgO vs Al_2O_3 and MgO vs K_2O for the studied samples and published data for glass finds from the same historical period. *a*) Comparison with glass artefacts from the Apollonia Pontica necropolis, Bulgaria, 5th–3rd c. BC (Lyubomirova *et al.*, 2014) and Pichvnari necropolis in Georgia, ~5th century BC (Shortland and Schroeder, 2009); *b*) Comparison with glass finds from Pydna and Methoni in Pieria, Greece, 8th–4th c. BC (Blomme *et al.*, 2017); *c*) Comparison with glass from Rhodes, 2nd c. BC (Rehren *et al.*, 2003).

composition close to this of bead EB3 with Al_2O_3 over 3.00 wt% and CaO around 9 wt% (Table 2) and low potassium content has been described from Apollonia Pontica, Bulgaria (Lyubomirova *et al.*, 2014).

The chemical similarity between natron-based Si-Na-Ca and Si(Al)-Na-Ca glass beads from the Dren-Delyan necropolis and some glass artefacts from Apollonia Pontica, Bulgaria (Lyubomirova *et al.*, 2014), Pichvnari necropolis in Georgia (Shortland and Schroeder, 2009), Pieria necropolis in Greece (Blomme *et al.*, 2017) and Rhodes (Fig. 11) suggests the same sources of raw material for their primary glass production. In Hellenistic Rhodes, no evidence for a furnace structure has been found, but a large quantity of waste raw glass has been analysed from there (Rehren *et al.*, 2003). The unsuitability

of sand raw materials from the island indicates that there were no first millennium BC primary glass factories (Blomme *et al.*, 2017). The Syro-Palestinian region is the most likely primary production place of this glass (Blomme *et al.*, 2017).

The chemical composition of the black Si-Na-Ca, Mg glass bead 159 from the Dren-Delyan necropolis is almost identical to the reported data for black glass artefacts from Bologna, Italy (9th–7th c. BC) with supposed Egypt origin (Conte *et al.*, 2016, pp. 506, 509). They are rich in iron, with a high level of Na_2O (average 16.2%), low K_2O (average 1.3%) and P_2O_5 , and very low CaO (average 2.8%) content.

The Si(Al)-Na(K)-Ca(Mg) dark green bead with beige decoration (bead B) contains Al_2O_3 (5.15 wt%), CaO (8.71 wt%), K_2O (4.37 wt%), MgO (2.96 wt%) and Sn (195.2 ppm) (Table 2). The chemical com-

Fig. 12. Al_2O_3 vs K_2O of the studied glass bead B (in green colour) applied on the comparative chart of Henderson *et al.* (2018).

position of this plant-ash-based glass bead strongly differs in the percentages of main oxides from the glass composition of the South Asian and the East African glass beads, where the most common type of glass, in general, is high-aluminium (Al_2O_3) soda glass with moderate lime (CaO) and potash, and low-magnesium (MgO) (Lankton and Dussubieux, 2006; Dussubieux *et al.*, 2008). The comparative chart for aluminium versus potassium (Henderson *et al.*, 2018) with added values for bead B in green colour (Fig. 12) shows that bead B has similar chemical features to the glass artefacts from Central Asia, where plant-ash-based glass composition includes Al_2O_3 (2.2–9.5 wt%), CaO (6.0–8.1 wt%), K_2O (4.1–5.4 wt%), MgO (1.9–3.8 wt%) – Henderson *et al.* (2018) and SnO (0.5 wt% – Henderson *et al.*, 2018, p. 92, an. PAG C AS). It is most likely that bead B comes from Central Asia as far as the Gorna Struma region due to the contacts of the Achaemenian Empire with the Thracian tribes. This is documented (including contacts between Persians and tribes inhabiting the Struma region) by ancient Greek authors.

The chemical composition of the studied bead B is very close to the plant-ash-based glass beads from Bara, Pakistan. Bara is 7 km SW from Peshawar near the ancient Pushkatavi and the archaeological finds are from the 2nd c. BC to the 2nd c. AD (Dussubieux and Gratuze, 2003). The values of the main oxides in glass finds from Bara indicate the use of raw material with a close or equal chemical composition to those of the studied glass bead B, and the presence of tin in its role as an opacifier agent testifies to a similar technology of production (Dussubieux and Gratuze, 2003, p. 321).

CONCLUSIONS

The glass beads found in the Dren-Delyan necropolis are extremely different from each other in their shape, colour, pattern, typology and chemical composition. Variations in the concentrations of the main oxides and trace elements are an indication of the use of different types of raw materials and different manufacturing procedures. The obtained compositions of the studied glass beads allowed us to classify them, except one, as low-magnesium glass (LMG) produced with natron as a flux. The only exception is a high-magnesium glass (HMG) produced by different flux raw – ashes from salt-tolerant plants.

The yellow colour of the glass bead 1181 is due to the presence of lead antimonate crystals in the glass matrix. The green colour (beads EB3 and B) is a result of an interaction between added copper and lead in the presence of iron and chromium in the glass mixture. Colouring agents for the dark blue-coloured glass beads are cobalt, copper and lower iron content. The light blue colour of sample 1198 is due to the high copper content, along with the presence of iron. The colouring agent of transparent light blue bead 1168 is FeO , in amount up to 0.25 wt%. The high iron content in the composition of sample 1247 stains it in brown colour.

Two different opacifiers were used for the production of opaque glass beads: antimony and tin, either individually or together. The decolourizing agent is antimony, without the involvement of manganese.

Based on the presented results of the studied glass beads of the Dren-Delyan necropolis, we assume at least four types of raw material mixtures for their production. They differ mainly in the type of flux and purity of quartz sand used. Three of them contain natron as a flux and sand of different composition: refined sand, unrefined sand with a high level of feldspars or clay and dark sand of high iron content. In the fourth raw material mixtures, the ash from a salt-tolerant plant is used as an alkali source (Table 6). The comparison of the chemical composition of the studied beads with published data on glass finds from the same historical period allows us to assume three geographically different areas for their primary glass production: the Syro-Palestinian region, Egypt and Central Asia.

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