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Composition of 6th–1st century BC glass of core-formed vessels from the North Black Sea region

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ABSTRACT

The composition of 38 samples of core-formed vessels from the State Historical Museum (Moscow) was studied using SEM-EDS and LA-ICP-MS techniques. Most of them were unearthed in North Pontic Greek colonies. Most studied vessels are likely made of Levantine glass. However, the composition of glass of the Mediterranean group I vessels is not absolutely homogeneous, slightly differing for the earlier and the later types. It could imply that either the glassmaking centres supplying workshops manufacturing core-formed containers changed the location within the Levantine region or some modifications in the production technology occurred over the 5th century BC. A slight difference in the composition of blue and yellow glass could suggest a specialisation in the production of some colours, namely blue glass coloured with cobalt – a mineral colourant not universally available. Two samples likely originated from Egyptian (or Italian) glassmaking centres. One of them is dated to the late 6th century BC, implying the early use of low-Al glass by workshops manufacturing core-formed containers. Some peculiarities of the composition and repartition of glass of the Mediterranean Group II possibly suggest the existence in the Hellenistic period of various production centres for such vessels, supplying them to the "western" and "eastern" regions of the ancient world.

KEYWORDS

core-formed vessels, North Black Sea region, origin of glass, SEM-EDS, LA-ICP-MS

INTRODUCTION

Core-formed glass vessels–containers for perfumed oils made of strongly coloured glass and imitating Greek ceramic forms–were widespread in the Mediterranean from the Levant to Spain from the mid-/late 6th century BC to the turn of the 1st century AD. They were also imported to continental Europe and the Greek colonies of the North Pontic region. It is likely that the style appeared in the Mediterranean under the influence of Mesopotamian craftsmen working in the Eastern Mediterranean, probably on Rhodes.[1] Donald Harden singled out three chronological groups of core-formed vessels – Mediterranean I (further– MG I, mid-6th–early 4th century AD), Mediterranean II (MG II, 4th–early 3rd century BC),

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[1]Harden (1981); McClellan (1984).

and Mediterranean III (MG III, 3rd–late 1st century BC) – and later this typo-chronological system was developed by David Grose[2] and Murray McClellan,[3] who created their detailed chronology. The distribution of finds as well as the archaeological evidence for the production of core-formed vessels points to the existence of the workshops on the island of Rhodes all over the period of the popularity of the style.[4] If for the vessels of the Mediterranean group I Eastern Aegean, first of all, Rhodes seems to be the main production centre, the distribution pattern of the MG II indicates that by the 4th century BC Rhodes ceased to be an important place of their manufacturing. The majority of finds of the MG II originated from the Greek mainland (possibly they were produced in Thessaly and Macedonia) and central or southern Italy.[5] It is likely that Cyprus played a key role in the production of MG III containers; some of them could also have originated from Punic workshops.[6] In terms of the chemical composition of glass, almost all the vessels of the MG I analysed so far, including the specimens from Rhodes, their eventual production place, represent a homogeneous group featuring close similarity with the later materials of Levantine origin. The composition of the finds of MG II is more heterogeneous; it is likely that the vessels of MG II were made using glass of Levantine as well as Egyptian or, possibly, Italian origin.[7] The glass of MG III is represented by isolated samples analysed so far, the composition of which is rather close to the Egyptian glass.[8] It suggests that the workshops produced core-formed vessels using the imported raw glass,[9] raising questions on the primary origin and distribution of glass in the production places of the core-formed vessels themselves in dynamics throughout the entire period of the existence of the style.

Our study undertaken for the core-formed vessels from the collection of the State Historical Museum in Moscow (Russia) aims at more detailed analysis of the chemical composition of MG I vessels, with respect to their chronology within the group developed by McClellan,[10] as well as chemical characterisation of some new samples of MG II and III, extending the already existing database and comparing the results with the published data from the Mediterranean and the Pontic region. Our dataset also allows some observations regarding the colouring of glass, shedding light on the details of the *chaîne opératoire* of the manufacturing of this exceptional kind of antiquities.

[2]Grose (1989).

[3]McClellan (1984).

[4]McClellan (1984); Grose (1989); Triantafyllidis (2003); Arletti et al. (2015).

[5]McClellan (1984).

[6]McClellan (1984); Cosyns, Nys (2010).

[7]Shortland and Schroeder (2009); Arletti et al. (2010, 2011, 2012); Panighello et al. (2012); Reade et al. (2015); Blomme et al. (2017); Oikonomou et al. (2018); Oikonomou (2018).

[8]Panighello et al. (2012); Lončarić and Costa (2023).

[9]Ibid.

[10]McClellan (1984).

MATERIALS AND METHODS

The chemical composition of 38 samples of glass, taken from 24 core-formed vessels (Table 1), has been studied with SEM-EDS and LA-ICP-MS methods. Most of them were unearthed in the Greek colonies found in the North Black Sea region (Fig. 1). The provenance of more than a third of vessels is unknown, although it is likely that they also came from the North Pontic littoral (Figs 2 and 3).

Most finds with known context are concentrated on the Taman Peninsula, in the eastern part of the Bosporan Kingdom, known as Asian Bosporus. Three alabastra (samples Ke-1–5) were unearthed in the city necropolis of Kepoi situated on the eastern shore of Taman Bay, 3 km from Phanagoria – the capital of Asian Bosporus. The excavations of the necropolis, which yielded more than 400 burial complexes dated from the 6th century BC to the 4th century AD, were undertaken in 1957–1978 by the expedition of the Institute of Archaeology RAS and the State Historical Museum under the direction of N. I. Sokolsky and N. P. Sorokina.[11] The core-formed vessels were found in well-dated burials containing ceramic imports, including black glazed ware, and weaponry.

Two finds, an alabastron and an unguentarium (SHM-29 and 30), were unearthed in the graves of the Tuzla necropolis excavated by V. V. Shkorpil, the director of the Kerch Museum, in 1911. The necropolis is situated in the northwestern part of the Taman Peninsula, near Cape Tuzla on the shore of the Kerch Strait. Their chronology cannot be refined by the archaeological context.[12]

Two graves of a necropolis are related to the Greek settlements named Suvorov's Phanagoria 1 and 2 (*Suvorovskaya Phanagoria 1* and *2*), while they were situated near a fortress named Phanagoria built in the 18th century under the direction of General Alexander Suvorov. Two burials investigated in 1951 by T. V. Blavatskaya, in the framework of a project of the Sind expedition, which was working in the eastern part of the Bosporan Kingdom, yielded an alabastron and an aryballos (SHM-47a-b and 48).[13]

A small fragment of a core-formed vessel, most probably an amphoriskos (*SHM-42a,b),* was discovered at the Greek settlement Golubitskaya 2, also at the Taman peninsula (excavations of the State Historical Museum led by D.V. Zhuravlev in 2007). The finding was excavated in the layers of the 4th–3rd century BC, disturbed by ploughing. While the earliest materials from the settlement are dated to the second quarter of the 6th century BC, an earlier date for the glass fragment, indeterminate typologically, cannot be excluded.

Two vessels are related to the Tauric region. An amphoriskos (*SHM-41a,b)* came from the modern city of Kerch, antique Pantikapaion, the capital of the Bosporan

[11]Lomtadze and Rumyantseva (2024).

[12]Rumyantseva and Lomtadze (2025).

[13]Blavatsky (1957) 118.

Table 1. Summary of the analyzed vessels from the collection of the State Historical Museum

Group	Sample	Vessel form	Glass colour	Provenance	Collection and inventory number	Type after McClellan (1984)	Date of the type after McClellan (1984) and by the archaeological context	Reference to the figure
Mediterranean group I (early generation)	SHM-3	alabastron, décor	white	Kerch, collection of V. I. Sizov	SHM 51921, Б981/25	II.A.VI	525–450 BC	Fig. 2: 5
	SHM-4	alabastron, body	blue					
	SHM-5	alabastron, décor	yellow					
	SHM-14	amphoriskos, body	white	Unknown provenance. Transferred from the People's Comissariat of Internal Affairs in 1936 (probably a confiscated private collection)	SHM 78444, Б501/146	II.C.I	last third of the 6th century BC	Fig. 2: 1
	SHM-18a	amphoriskos, décor	white	Kherson region, Olbia (?), transferred by Archaeological commission in 1888, the 'collection of Block', in the museum from 10.01.1890	SHM 19316, B4/10	II.C.IV	1st quarter of the 5th century BC or slightly later	Fig. 2: 3
	SHM-18b	amphoriskos, body	blue					
	Ke-3	alabastron, body	blue	Kepoi, grave 69	SHM 97998, Б1288/14	II.A.VIII (gen 3)	last quarter of the 6th–1st half of the 5th century BC. After the context-2nd quarter of the 5th century BC	Fig. 2: 6
	Ke-4	alabastron, décor	yellow					
	SHM-29	alabastron, décor	blue	Tuzla necropolis, grave 98/53	SHM 49472, Б99/54	II.A.VIII (gen 1, 2)	525–475 BC	Fig. 2: 4
	SHM-37	amphoriskos, body	blue	Tuzla necropolis, grave 113/68	SHM 49472, Б99/44	II.C.IV	late 6th–1st quarter of the 5th century BC	Fig. 2: 2
	SHM-48	aryballos, body	blue	Suvorovskaya Phanagoria, grave 2	SHM 83813, Б902/73	II.D.II	mid-6th-1st half of the 5th century BC (after the context -2nd quarter of the 5th century BC)	Fig. 2: 7

(continued)

Table 1. Continued

Group	Sample	Vessel form	Glass colour	Provenance	Collection and inventory number	Type after McClellan (1984)	Date of the type after McClellan (1984) and by the archaeological context	Reference to the figure
Mediterranean group I ('classical' forms)	SHM-1	alabastron, décor	white	Kherson region, Olbia (?), buying at the antique market in 1891	SHM 23425, Б8/16	II.A.XII (gen 2)	5th century BC (most probably 2nd quarter)	Fig. 2: 12
	SHM-2	alabastron, body	brown					
	SHM-6	alabastron, body	red	Unknown provenance. Transferred from the People's Comissariat of Internal Affairs in 1936 (probably a confiscated private collection)	SHM 78444, Б501/137	II.A.XIII (gen 2)	2nd half of the 5th century BC	Fig. 2: 14
	SHM-7	alabastron, décor	yellow					
	SHM-8	alabastron, décor	purple	-"-	SHM 78444, Б501/139	II.A.IV (division 1)	500–450 BC	Fig. 2: 10
	SHM-9	alabastron, body	white					
	SHM-10	aryballos, décor	yellow	-"-	SHM 78444, Б501/144	II.D. IV (gen 2)	1st half of the 5th century BC	Fig. 2: 8
	SHM-12a	amphoriskos, body	reddish brown	-"-	SHM 78444, Б501/145	II.C.VII (gen 2, 3)	after 480 BC; 2nd–3rd quarter of the 5th century BC	Fig.2: 9
	SHM-12b	amphoriskos, décor	yellow					
	SHM-16a	amphoriskos, body	blue					
	SHM-16b	amphoriskos, décor	turquoise					
	SHM-17	aryballos, body	blue	-"-	SHM 78444, Б501/168	II.D. IV (gen 2)	1st half of the 5th century BC	–
	Ke-1	alabastron, décor	yellow	Kepoi, grave 140	SHM 97998, Б1288/191	II.A.XI (gen 3)	475–450 (440–450) BC. After the context-turn of the	Fig. 2: 15

(continued)

Table 1. Continued

Group	Sample	Vessel form	Glass colour	Provenance	Collection and inventory number	Type after McClellan (1984)	Date of the type after McClellan (1984) and by the archaeological context	Reference to the figure
	Ke-2	alabastron, body	blue				1st/2nd quarters of the 5th century BC	
	Ke-5	alabastron, décor	yellow	Kepoi, grave 29	SHM 96629, Б1112/84	II.A.XIV	2nd half of the 5th century BC (after the context-no later than 460–450 BC)	Fig. 2: 13
	SHM-47a	alabastron, body	white	Suvorovskaya Phanagoria, grave 1	SHM 83813, Б902/66	II.A.IV (division 1)	500–450 BC; after the context-2nd quarter of the 5th century BC	–
	SHM-47b	alabastron, décor	purple					
	SHM-49	alabastron,body	white	Tauric region, Kerch, necropolis of Myrmekion, grave No. 45. Excavations by F. I. Gross, 1888	SHM 62998, Б37/24	II.A.IV (division 1)	500–450 BC (after the context-late 6th-early 5th century BC)	Fig. 2: 11
Indefinite (MG I or II)	SHM-42a	vessel, décor	yellow	Taman peninsula, Settlement Golubitskaya 2. Excavations by D. Zhuravlev, 2007, № 128	SHM 113457/128, Б2076/128	–	Found in the layers of the 4th–3rd centuries BC disturbed by plowing)	Fig. 2: 16
	SHM-42b	vessel, body	blue					
Mediterranean group II	SHM-19	amphoriskos, body	brown	Unknown provenance. Northern Pontic region? Collection of A. S. Uvarov	SHM 54791, Б605-619	III.B.II (gen 1)	2nd half of the 4th-mid-3rd century BC	Fig. 3: 2
	SHM-30	unguentarium, body	blue	Tuzla necropolis, disturbed grave	SHM 49472, Б99/42	IV.C.II	mid-3rd-late 3rd century BC (possibly up to the 1st century BC)	Fig. 3: 4
	SHM-31	alabastron,body	black'	Kherson region, Olbia, necropolis, excavations by Yu. Kulakovskiy, 1900. In the museum from 1902	SHM 40711, Б15/220	III.A.III	2nd half of the 4th century BC	Fig. 3: 5
	SHM-38	alabastron, body	blue	Kerch, bought in 1891	SHM 24009, B47/1	III.A.I (Harden, form 7; Grose, form II:1)	second half of the 4th-early 3rd century BC	Fig. 3: 1
	SHM-41a	amphoriskos, body	blue	Tauric region, Kerch, necropolis of Pantikapaion,	SHM 54746, Б624/83	III.B.1 (?)	4th century BC (?)	Fig. 3: 3

(continued)

Table 1. Continued

Group	Sample	Vessel form	Glass colour	Provenance	Collection and inventory number	Type after McClellan (1984)	Date of the type after McClellan (1984) and by the archaeological context	Reference to the figure
	SHM-41b	amphoriskos, décor	yellow	excavations of 1862, in "brick grave on the mount Mithridates". From Rumyantsevskiy museum				
Mediterranean group III	SHM-32	alabastron, body	blue	Kherson region, Olbia, necropolis, excavations by Yu. Kulakovskiy, 1900. In the museum from 1902	SHM 40711, Б15/221	IV.A.III	1st half of the 1st century BC (after Harden, 1981-3rd-late 1st century BC)	Fig. 3: 6

SHM - State Historical Museum.
gen - generation.

Kingdom. It was found during excavations of the necropolis in 1862, in the "brick grave on the mount Mithridates". There is no information about other inventory items from this grave.

One more vessel from Bosporus – an alabastron (SHM-49)–was discovered in the necropolis of Myrmekion, grave 45, with a black-figure lekythos dated to the late 6th – early 5th century BC and a black glazed plate *(patera)*, by F. I. Gross in 1888 (unpublished). The remains of this Greek city are situated in the eastern part of Kerch, 4 km east of the ancient Pantikapaion, on the shore of the Kerch Strait.

Two alabastra (*SHM-31* and *32*) come from Olbia (actually the village of Parutino on the right bank of the Bug estuary, Ochakov district of the Nikolaev region, Ukraine), excavations by Yu. A. Kulakovsky in 1900. The information about the graves containing these vessels and their inventory is absent to date.

The exact provenance of the following vessels studied is unknown. An alabastron, likely from Olbia (*SHM-1* and *2*), was bought at an antique market, possibly in Ochakov or Odessa, in 1891. The second vessel from Olbia *(SHM-18 a,b)* got into the State Historical Museum from the Imperial Archaeological Commission in 1888 and was previously in a private collection.

A series of vessels was purchased in Kerch. One of them, an alabastron *(SHM-3-5)* from the collection of V. I. Sizov, a member of the Moscow Archaeological Society and, further, the first academic secretary of the State Historical Museum, who donated a part of his collection to the museum before its official opening in 1883. The glass vessels of the "silicate group" were transferred to the museum later, in 1919. A large alabastron *(SHM-38)* was bought in Kerch in 1891.

The provenance of an amphoriskos *(SHM-19)* from the collection of Count A. S. Uvarov, head of the Moscow Archaeological Society and one of the founders of the State Historical Museum, is unknown; apparently it also comes from the North Black Sea region. It was transferred to the museum in 1924 as part of a collection from the famous Uvarov's estate in Porechye in the vicinity of Moscow.

A series of core-formed vessels *(SHM-6-17)*, also of unknown provenance, got into the museum in 1936 from the People's Commissariat of Internal Affairs *(NKVD)*, notorious for its activities during the years of Stalinist repressions. Apparently, it's a part of antiquities confiscated from a former private collection(s). Judging by the other items in this collection, it is likely that they also were excavated in the North Black Sea region.

Given that the majority of vessels are of undetermined provenance and the archaeological context of most finds is unknown, they were classified and dated upon the chronological system by M. McClellan.[14] Some vessels (mostly from the necropoleis of the Taman Peninsula) can also be independently dated upon other inventory items from the burials. The dates determined upon McClellan's chronology

[14] McClellan (1984).

Fig. 1. The places of origin of the core-formed vessels sampled (archaeological sites and points of acquisition). 1–4: excavations and acquisitions before 1917. 1: Olbia; 2: Kerch/Pantikapaion necropolis; 3: Mirmekion; 4: Tuzla necropolis; 5: Suvorovskaya Phanagoria; 6: Kepoi; 7: Golubitskaya

Fig. 2. Core-formed vessels, subjected to the analyses. 1–7: Mediterranean group I, early generation; 8–15: Mediterranean group I, "classical" forms; 16: indefinite group. For details, see Table 1. ©State Historical Museum, Institute of Archaeology RAS

Fig. 3. Core-formed vessels of the Mediterranean groups II and III, subjected to the analyses. For details, see Table 1. ©State Historical Museum, Institute of Archaeology RAS

and the archaeological context corroborate quite well (Table 1; see also the publications of dated complexes with core-formed vessels from Taman).[15]

Most studied glass, 29 samples, belongs to the Mediterranean group I, dated by M. McClellan from the mid-6th to 5th century BC (Fig. 2).[16] One of the goals of the study was to trace a possible difference in the composition of the earlier and the later vessels of this rather representative group. For this purpose, the composition of glass of alabastra and amphoriskoi of the first generations (11 samples), dating to the late 6th–early/first half of the 5th centuries BC, were considered separately and compared with the composition of the other MG I vessels. The chronological division of the MG I vessels is certainly very arbitrary; its goal is only to identify possible trends in the change of composition, if any. Six samples belong to the Mediterranean group II (4th to early 3rd century BC), and one to the Mediterranean group III (third to first centuries BC) (Fig. 3).

The typologically indeterminate vessel fragment from Golubitskaya (SHM-42a,b, Fig. 2.16) could belong either to MG I or MG II as regards the décor type and the context of finding. It is dated to the 4th–3rd centuries BC but could contain the materials of earlier periods (see above).

SEM-EDS

SEM-EDS analyses were carried out in the Scientific Research Centre “Wear Resistance” of the National Research University “Moscow Power Engineering Institute” (Moscow). The samples were mounted in epoxy resin, polished on the cross-sections to a 1 μm diamond suspension finish, and coated with carbon. Major and some minor elements were analysed using a Tescan Mira LMU scanning electron microscope with an attached energy dispersive spectrometer X-Max 50 (Oxford Instruments). The samples were analysed at an electron beam current of 1.7 nA and an accelerating voltage of 20 kV for a counting live time of 140 seconds. The EDS data were quantified using INCA Oxford Instruments software. The accuracy and precision of the results were checked by analysing the Corning Museum of Glass A, B, and C standards at the beginning of every analytical run (Table 2). For each sample, random areas of approximately 0.1 mm^2 were analysed. The results totalled between 98 and 102%; they are reported as original analytical totals without normalisation. The mean values of four or five separate measurements (excluding strongly deviating data points) are reported. The results are presented as weight oxides (with the exclusion of chlorine), with oxygen calculated by stoichiometry (Table 3). The analytical precision as indicated by the relative standard deviation (SD) is better than 4% for elements in concentrations from 1 wt% and better than 10% for the majority of elements in concentrations between

Table 2. SEM-EDS analyses of glass standards (wt%), compared with reported values after Vincenzi et al. (2002) and Adlington (2017)

Standard	Compound	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	SnO_2	Sb_2O_5	BaO	PbO
CMG A	Mean, $n = 5$	14.33	2.62	0.92	65.65	0.12	0.16	0.09	2.92	4.94	0.83	1.06	1.12	0.17	1.23	0.31	1.78	0.49	0.11
	Recommended	14.30	2.66	1.00	66.56	0.0847	0.14	0.09	2.87	5.03	0.79	1.00	1.09	0.17	1.17	0.19	1.75	0.46	0.08
	Std	0.11	0.04	0.03	0.43	0.01	0.01	0.01	0.02	0.04	0.03	0.02	0.03	0.04	0.03	0.04	0.07	0.04	0.04
	Std, %	0.77	1.53	3.26	0.65	8.33	6.25	11.11	0.68	0.81	3.61	1.89	2.68	23.53	2.44	12.90	3.93	8.16	36.36
CMG B	Mean, $n = 5$	16.94	1.01	4.35	61.10	0.82	0.57	0.17	1.07	8.60	0.13	0.25	0.35	0.04	2.85	0.24	0.42	0.05	0.59
	Recommended	17.00	1.03	4.36	61.55	0.82	0.49	0.16	1.00	8.56	0.089	0.25	0.34	0.046	2.66	0.0241	0.46	0.077	0.61
	Std	0.18	0.02	0.04	0.12	0.02	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.04	0.04	0.04	0.07	0.02	0.07
	Std, %	1.06	1.98	0.92	0.20	2.44	1.75	5.88	1.87	0.12	15.38	8.00	5.71	100.00	1.40	16.67	16.67	40.00	11.86
CMG C	Mean, $n = 5$	1.09	2.68	0.89	34.35	0.00	0.20	0.17	2.86	4.90	0.88	0.00	0.33	0.18	1.11	0.34	0.00	12.17	36.85
	Recommended	1.07	2.76	0.87	34.87	0.068	0.10	0.10	2.84	5.07	0.79	0.0011	0.34	0.18	1.13	0.19	0.0001	11.40	36.70
	Std	0.03	0.04	0.03	0.07	0.00	0.09	0.01	0.02	0.03	0.08	0.01	0.03	0.02	0.03	0.06	0.00	0.05	0.16
	Std, %	2.75	1.49	3.37	0.20	-	45.00	5.88	0.70	0.61	9.09	-	9.09	11.11	2.70	17.65	-	0.41	0.43

[15] Lomtadze and Rumyantseva (2024, 2026); Rumyantseva and Lomtadze (2025).

[16] McClellan (1984).

Table 3. SEM-EDS data for the glass of core-formed vessels from the collection of the State Historical Museum, in wt%

Group	Sample	Colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	Sb_2O_5	BaO	PbO
Mediterranean group I (early generation)	SHM-3	white	16.00	0.38	1.86	64.14	<0.10	<0.20	1.20	0.29	4.52	0.11	<0.10	0.41	<0.10	<0.10	10.22	<0.10	<0.10
	SHM-4	blue	17.18	0.50	2.30	69.69	<0.10	<0.20	1.35	0.31	7.07	<0.10	<0.10	0.47	0.13	<0.10	0.46	<0.10	<0.10
	SHM-5	yellow	13.95	0.29	1.63	60.98	<0.10	<0.20	1.05	0.26	4.06	<0.10	<0.10	0.96	<0.10	<0.10	1.91	<0.10	13.41
	SHM-14	white	14.90	0.50	0.43	71.84	<0.10	0.21	1.03	0.17	7.59	<0.10	<0.10	0.25	<0.10	<0.10	2.21	<0.10	<0.10
	SHM-18a	white	15.49	0.44	2.33	63.29	<0.10	0.22	1.08	0.36	7.79	<0.10	<0.10	0.39	<0.10	<0.10	4.54	<0.10	3.02
	SHM-18b	blue	18.03	0.46	2.48	67.80	<0.10	0.33	1.15	0.39	7.57	<0.10	<0.10	0.58	<0.10	<0.10	<0.20	<0.10	0.33
	Ke-3	blue	16.34	0.64	2.33	68.01	<0.10	0.21	1.10	0.36	9.59	<0.10	<0.10	0.87	0.10	0.17	<0.20	<0.10	<0.10
	Ke-4	yellow	13.02	0.47	1.71	52.06	<0.10	<0.20	0.96	0.32	7.00	<0.10	<0.10	1.09	0.01	0.11	2.49	<0.10	19.89
	SHM-29	blue	17.55	0.64	2.36	65.30	<0.10	0.29	1.05	0.57	9.60	<0.10	<0.10	0.79	<0.10	<0.10	0.52	<0.10	0.18
	SHM-37	blue	14.08	0.55	2.55	70.10	<0.10	<0.20	0.97	0.37	9.49	<0.10	<0.10	0.57	<0.10	<0.10	0.25	<0.10	0.11
	SHM-48	blue	15.99	0.43	2.16	70.49	<0.10	0.29	0.74	0.47	6.63	<0.10	<0.10	1.88	<0.10	0.43	<0.20	<0.10	<0.10
Mediterranean group I (‘classical’ forms)	SHM-1	white	16.26	0.46	2.29	66.08	<0.10	0.24	1.17	0.56	8.61	<0.10	0.18	0.51	<0.10	<0.10	2.56	<0.10	<0.10
	SHM-2	brown	16.64	0.46	2.32	65.65	<0.10	0.21	1.25	0.58	8.93	<0.10	2.05	0.50	<0.10	<0.10	<0.20	0.13	<0.10
	SHM-6	red	16.70	0.68	2.65	61.63	0.14	0.43	0.96	0.73	11.71	0.12	<0.10	2.23	<0.10	0.55	0.20	<0.10	0.48
	SHM-7	yellow	14.04	0.45	2.20	60.02	<0.10	0.37	0.61	0.55	6.58	<0.10	<0.10	0.97	<0.10	<0.10	0.96	<0.10	12.34
	SHM-8	purple	16.74	0.50	2.51	68.52	<0.10	0.36	0.70	0.58	6.87	<0.10	1.77	0.61	<0.10	<0.10	0.23	0.21	<0.10
	SHM-9	white	16.39	0.43	2.44	67.70	<0.10	0.40	0.72	0.53	6.65	<0.10	0.26	0.41	<0.10	<0.10	3.41	<0.10	<0.10
	SHM-10	yellow	13.48	0.46	1.96	55.62	<0.10	0.44	0.43	0.46	5.02	<0.10	<0.10	0.91	<0.10	<0.10	1.42	<0.10	18.44
	SHM-12a	reddish brown	16.64	0.53	2.39	69.17	<0.10	0.27	0.81	0.56	6.28	<0.10	<0.10	2.03	<0.10	0.29	<0.20	<0.10	0.12
	SHM-12b	yellow	13.15	0.43	1.95	58.97	<0.10	0.29	0.64	0.48	4.85	<0.10	<0.10	1.46	<0.10	<0.10	1.45	<0.10	14.93
	SHM-16a	blue	16.94	0.50	2.33	69.56	<0.10	0.29	0.90	0.57	6.53	<0.10	<0.10	1.40	<0.10	0.20	<0.20	<0.10	0.11
	SHM-16b	turquoise	16.07	0.48	2.26	65.95	<0.10	0.31	0.80	0.52	7.27	<0.10	<0.10	0.37	<0.10	1.88	2.73	<0.10	0.11
	SHM-17	blue	17.44	0.67	2.51	62.06	<0.10	0.45	0.92	0.70	10.23	<0.10	0.10	3.33	<0.10	0.25	<0.20	<0.10	0.38
	Ke-1	yellow	11.71	0.50	1.88	55.07	<0.10	0.22	0.89	0.40	5.50	<0.10	<0.10	1.36	<0.10	<0.10	1.98	<0.10	19.32
	Ke-2	blue	15.38	0.67	2.55	69.71	<0.10	<0.20	1.05	0.58	7.50	<0.10	<0.10	1.48	<0.10	0.14	<0.20	<0.10	<0.10
	Ke-5	yellow	11.88	0.34	1.77	54.74	<0.10	0.21	0.90	0.27	6.00	<0.10	<0.10	1.91	<0.10	0.30	1.91	<0.10	18.41
	SHM-47a	white	16.47	0.50	2.55	66.63	<0.10	0.43	0.79	0.42	8.76	<0.10	<0.10	0.42	<0.10	<0.10	2.58	<0.10	<0.10

(continued)

Table 3. Continued

Group	Sample	Colour	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	Sb_2O_5	BaO	PbO
	SHM-47b	purple	16.70	0.53	2.59	66.90	<0.10	0.43	0.70	0.51	8.90	<0.10	1.83	0.40	<0.10	<0.10	<0.20	0.20	<0.10
	SHM-49	white	15.38	0.45	2.54	69.57	<0.10	0.22	1.00	0.37	7.88	<0.10	<0.10	0.36	<0.10	<0.10	2.01	<0.10	<0.10
Indefinite (MG I or II)	SHM-42a	yellow	13.04	0.31	1.87	56.81	<0.10	0.29	0.93	0.35	5.46	<0.10	<0.10	1.47	<0.10	<0.10	2.11	<0.10	15.99
	SHM-42b	blue	17.73	0.39	2.36	68.18	<0.10	0.30	1.03	0.52	6.95	<0.10	<0.10	0.83	<0.10	<0.10	<0.20	<0.10	0.58
Mediterranean group II	SHM-19	brown	17.70	0.76	2.27	69.97	<0.10	<0.20	1.28	0.82	5.64	<0.10	<0.10	0.37	<0.10	<0.10	<0.20	<0.10	<0.10
	SHM-30	blue	14.79	1.10	2.16	67.42	0.16	<0.20	0.93	1.48	9.07	<0.10	0.89	0.73	<0.10	<0.10	<0.20	<0.10	0.13
	SHM-31	black'	19.12	0.61	2.39	65.40	<0.10	0.24	1.17	0.86	7.57	<0.10	0.35	0.99	0.13	0.16	<0.20	<0.10	0.22
	SHM-38	blue	16.10	0.76	4.14	72.20	<0.10	<0.20	0.75	0.32	1.88	0.32	<0.10	2.02	<0.10	0.13	<0.20	<0.10	<0.10
	SHM-41a	blue	18.39	0.69	2.37	63.39	0.14	0.61	0.67	0.96	8.63	<0.10	0.66	1.56	0.14	0.41	<0.20	<0.10	0.21
	SHM-41b	yellow	16.58	0.63	1.94	58.06	<0.10	0.49	0.83	0.35	5.42	<0.10	<0.10	0.97	<0.10	<0.10	1.62	<0.10	11.81
Mediterranean group III	SHM-32	blue	19.10	0.67	2.35	64.23	<0.10	0.34	0.89	0.72	8.50	<0.10	1.14	1.07	<0.10	0.13	<0.20	<0.10	0.10

0.1 and 1 wt%; the accuracy was generally better than 5% for the former and 10% for the latter. Due to the SEM-EDS limitations, the data demonstrate poor precision and accuracy for chlorine (CMG C), as well as for phosphorus (CMG C), sulphur (CMG B, C), titanium (CMG B), cobalt (CMG A), tin (CMG A, B, C), antimony (CMG B), and lead oxides (CMG A, B) at low concentrations. For these oxides, as well as for all elements at concentrations up to 0.1 wt%, only LA-ICP-MS data will be considered.

Backscattered electron microphotographs of calcium antimonate crystals and their composition and distribution maps of elements were performed using a Tescan Mira LMS scanning electron microscope coupled with EDS X-max 80 (Oxford Instruments) in the Common Use Centre "Geoanalyst", Institute of Geology and Geochemistry of the Ural Branch of RAS (Yekaterinburg) at an electron beam current of 0.8 nA and accelerating voltage of 20 kV. The data were quantified using AZTEC 3.1 Oxford Instruments software.

LA-ICP-MS

The trace and minor element concentrations were measured using the LA-ICP-MS technique performed with a Perkin Elmer NexION 300S Inductively Coupled Plasma Mass Spectrometer, equipped with an ESI NWR 213 laser ablation sampling device, in the Common Use Centre "Geoanalyst," Institute of Geology and Geochemistry of the Ural Branch of RAS (Yekaterinburg). For LA-ICP-MS measurements, the same samples mounted in epoxy resin as those used for SEM-EDS were used. The laser ablation system parameters: laser beam energy–10.5–11.5 J cm^{-2}, the repetition rate of the laser–10 Hz, laser beam diameter – 50 µm, carrier gas: He (400 mL min^{-1}), the analytical time–50 s, and the blank time–20 s. The ICP-MS parameters were as follows: the sample was flushed by 1.1–1.2 L min^{-1} of argon carrier gas, ICP RF power–1,500 W, dwell time–10 ms per isotope element, the number of scan cycles–1, and the number of replicates–250. The length of the connecting tube between the mass spectrometer and laser ablation system was 1.5 m. The data were quantified using GLITTER V4.4 software. SiO_2 was used as an internal standard; NIST 610–for the calibration procedure, and NIST SRM 612–as an external standard to calculate the reproducibility and accuracy. NIST 610 and 612 were measured after every 10–12 sample measurements (Table 4). The mean values for 3–4 measurements for each studied sample, excluding deviating data points, are given as the results (Table 5).

RESULTS AND DISCUSSION

Base glass composition

For the examination of the base composition of glass and primary raw materials used for its production, it was reduced and normalised to 100% without lead and antimony – technological additives introduced into the glass

Table 4. LA-ICP-MS analyses of glass standards (in ppm), compared with reported values

Element	NIST 610				NIST 612			
	Mean, $n = 18$	std	std, %	Published value*	Mean, $n = 6$	std	std, %	Published value*
Li	486	17.5	3.6	482.2	36.5	2.82	7.72	41.54
Be	460	13.9	3.0	460.7	35.9	1.81	5.06	37.74
B	358	11.5	3.2	357.6	40.0	0.90	2.26	34.73
P	339	46.1	13.6	342.5	69.6	9.85	14.15	55.16
Sc	451	11.5	2.6	450	36.8	0.37	1.00	39.1
Ti	477	14.2	3.0	476	44.3	3.92	8.85	48.11
V	444	9.4	2.1	444	43.1	0.51	1.18	38.2
Cr	389	12.0	3.1	388	44.4	5.58	12.58	39.88
Mn	436	16.2	3.7	436.4	41.4	1.61	3.88	38.43
Fe	453	19.0	4.2	453.1	55.3	5.14	9.29	56.33
Co	387	13.3	3.4	388	35.6	0.89	2.49	33
Ni	413	19.9	4.8	415	36.5	2.04	5.59	34.5
Cu	429	16.6	3.9	432.9	38.0	4.84	12.72	36.71
Zn	429	40.6	9.5	429.3	43.9	4.44	10.13	37.92
Ga	431	16.6	3.9	431	37.7	0.87	2.30	35.9
Ge	430	10.7	2.5	431	43.7	3.26	7.45	34.64
As	318	12.3	3.8	317.6	42.8	2.90	6.78	37.33
Se	115	24.2	21.1	112	21.3	5.14	24.08	
Rb	429	8.5	2.0	430	31.5	1.54	4.89	32.2
Sr	523	12.9	2.5	525	80.8	5.09	6.30	79.3
Y	488	8.5	1.7	490	33.1	1.13	3.42	41.2
Zr	490	11.8	2.4	490	36.5	1.40	3.84	42.1
Nb	510	10.1	2.0	512	41.3	1.34	3.25	42.3
Mo	394	6.5	1.7	396.1	39.0	2.85	7.29	38.3
Ag	239	6.3	2.6	239.4	26.1	1.19	4.54	21.92
Cd	259	9.9	3.8	260.9	40.1	3.89	9.71	28.32
In	439	11.8	2.7	439.8	42.9	1.09	2.54	42.93
Sn	389	13.0	3.4	390	37.9	1.86	4.90	37.96
Sb	380	24.2	6.4	388.3	41.8	2.44	5.84	38.44
Te	300	13.7	4.6	302	40.1	1.18	2.95	30.9
Cs	360	8.9	2.5	361	41.3	1.79	4.34	42.2
Ba	446	16.1	3.6	446	40.2	1.76	4.38	38.8
La	438	14.1	3.2	440	31.0	0.67	2.16	35.8
Ce	446	14.1	3.2	446	37.3	1.47	3.95	39.2
Pr	467	12.1	2.6	468	35.1	0.98	2.79	39
Nd	453	14.2	3.1	454	30.2	0.67	2.21	36.3
Sm	462	12.9	2.8	463	34.0	0.73	2.15	38
Eu	451	10.6	2.4	452	35.0	1.51	4.31	35.9
Gd	450	16.2	3.6	450	29.8	0.90	3.02	37.4

(continued)

Table 4. Continued

Element	NIST 610				NIST 612			
	Mean, $n = 18$	std	std, %	Published value*	Mean, $n = 6$	std	std, %	Published value*
Tb	442	11.3	2.6	442	29.8	0.72	2.42	35.92
Dy	453	11.6	2.6	453	30.7	1.34	4.36	36.7
Ho	475	11.2	2.4	475	34.3	0.67	1.95	40.1
Er	463	10.7	2.3	463	34.3	1.09	3.17	38.8
Tm	454	9.8	2.1	454	33.7	0.90	2.66	37.55
Yb	479	14.2	3.0	479	34.8	1.23	3.54	40.5
Lu	466	10.6	2.3	467	33.3	1.05	3.16	38.7
Hf	457	11.7	2.6	458	33.6	1.28	3.80	38.5
Ta	490	10.2	2.1	490.6	37.4	1.23	3.28	40.5
W	434	12.8	2.9	434.5	43.7	1.93	4.42	39.55
Tl	61.0	2.3	3.8	61.3	19.8	1.38	6.96	15.07
Pb	395	88.2	22.3	419.1	45.4	2.61	5.74	38.96
Bi	372	14.5	3.9	373.8	43.7	2.37	5.43	29.84
Th	482	14.3	3.0	481	35.4	1.14	3.23	39.5
U	487	12.9	2.6	487	42.7	2.33	5.46	39.1

*After Normann et al. (1996).

batch during the colouring process and present in some samples in rather high concentrations.[17] The concentration of other technological additives – iron, copper, manganese, etc. – is moderate, and it does not significantly influence the base composition of glass. All studied glass is of the soda-lime-silica type, with MgO and K_2O concentrations up to 1.1 and 1.5 wt%, respectively. It suggests that the glass was melted using natron as a flux.[18] The term "natron" refers to minerals rich in sodium carbonate, derived from evaporite deposits of alkaline lakes, most probably Egyptian.[19] The use of natron glass is typical for manufacturing core-formed vessels of the Mediterranean groups I–III.[20]

Most glasses of all chronological groups (MG I–III), more precisely, 36 of 38 samples studied, belong to a homogeneous compositional group (Fig. 4A) with average values of 17 wt% Na_2O, 2.4 wt% Al_2O_3, 69 wt% SiO_2, 7.8 wt% CaO, and low concentrations of TiO_2 (averagely 0.07 wt%). This group is close to the glass of MG I, and the majority of MG II samples analysed so far originated from Italy, mainland Greece, Rhodes, the northeastern Pontic littoral (Georgia), and Asia Minor (Central Turkey).[21] Such composition is also typical for most Iron Age glass objects of synchronous periods from Western and Central Europe.[22] In terms of trace elements, these samples feature high content of Sr (>300 ppm) and low levels of zirconium (up to 48 ppm in normalised composition), strongly correlated with Hf ($R^2 = 0.97$), with a Zr/Hf ratio between 36 and 45, typical for zircons derived from granites.[23] High strontium and low zirconium content are typical for the glass made using Mediterranean coastal sands containing aragonite coming from molluscan shells, a source of lime in the glassmaking production. Such compositions were attested for the glass of Levantine origin, and for the Mediterranean core-formed vessels, the conclusion on the origin of glass from the Syro-Palestinian littoral has been supported by the isotopic composition of Sr and Nd.[24] Worth noting that the thorium to zirconium and lanthanum to titanium ratios (1,000(Th/Zr) – from 16 to 26, La/TiO_2 – from 56 to 112)

[17]See Panighello et al. (2012).

[18]Sayre and Smith (1961); Brill (1970).

[19]Rolland and Venclová (2021), with the references therein.

[20]Shortland and Schroeder (2009); Arletti et al. (2010, 2011, 2012); Panighello et al. (2012); Reade et al. (2015); Blomme et al. (2016, 2017); Oikonomou et al. (2018); Oikonomou (2018).

[21]Shortland and Shroeder (2009); Arletti et al. (2010, 2011, 2012); Panighello et al. (2012); Reade et al. (2015); Blomme et al. (2016, 2017); Oikonomou et al. (2018); Oikonomou (2018).

[22]Gratuze (2009); Purowski et al. (2020); Šmit et al. (2020); Rolland and Venclová (2021).

[23]Blomme et al. (2017) with references therein.

[24]Freestone et al. (2003a); Freestone (2006); Degryse and Schneider (2008); Panighello et al. (2012); Blomme et al. (2017); Rolland and Venclová (2021).

Table 5. LA-ICP-MS data for the glass of core-formed vessels from the collection of the State Historical Museum, in ppm (P_2O_5, TiO_2-in wt%)

Group	Sample	Colour	Li	Be	B	P	P_2O_5	Sc	Ti	TiO_2	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd
Mediterranean group I (early generation)	SHM-3	white	1.92	0.28	62.8	150	0.03	1.37	421	0.07	5.80	11.5	71.0	2,472	2.94	3.09	165	11.1	1.97	0.82	14.8	BDL	4.71	304	4.88	35.2	1.42	0.33	0.74	0.19
	SHM-4	blue	2.35	0.23	54.5	126	0.03	1.37	364	0.06	5.06	13.9	91.5	2,918	901	3.78	184	40.8	3.77	1.14	3.57	BDL	5.69	461	6.37	34.4	1.38	0.34	BDL	BDL
	SHM-5	yellow	2.02	0.34	53.4	108	0.02	1.26	397	0.07	5.35	11.6	65.9	5,908	10.9	3.24	217	9.30	1.74	0.55	109	BDL	4.01	262	4.35	31.9	1.34	0.15	14.39	0.32
	SHM-14	white	2.95	0.13	119	137	0.03	2.33	325	0.05	5.89	19.4	599	1,906	1.32	3.38	10.6	9.22	0.70	0.60	6.56	BDL	2.28	284	5.11	49.7	1.09	0.38	0.13	0.22
	SHM-18a	white	4.09	0.23	118	180	0.04	2.50	338	0.06	5.90	20.7	91.3	2,998	74.2	5.01	153	14.8	2.74	0.76	34.1	BDL	6.88	441	6.31	32.1	1.38	0.29	4.91	BDL
	SHM-18b	blue	4.20	0.22	112	129	0.03	2.28	307	0.05	4.78	19.3	82.3	3,944	517	4.15	206	37.2	3.60	0.88	4.35	BDL	5.95	394	5.57	27.7	1.22	0.39	0.54	0.16
	Ke-3	blue	2.12	0.14	132	154	0.04	1.47	315	0.05	6.65	14.5	112	6,614	803	4.52	1,312	143	5.78	0.97	7.94	BDL	5.52	531	6.57	27.1	1.16	0.47	0.43	0.34
	Ke-4	yellow	2.11	BDL	50.9	131	0.03	1.15	325	0.05	6.00	11.8	90.1	6,988	18.2	4.94	640	13.8	1.70	0.55	169	BDL	4.64	392	5.12	23.6	1.09	0.22	47.3	0.46
	SHM-29	blue	3.97	0.29	91.5	209	0.05	1.46	408	0.07	7.96	16.6	424	4,964	531	5.67	631	73.2	4.15	0.91	8.05	BDL	7.64	428	6.20	39.8	2.04	0.44	0.57	0.20
	SHM-37	blue	7.29	0.21	168	141	0.03	1.28	318	0.05	5.97	19.2	118	3,736	578	4.16	414	56.1	4.15	0.94	5.04	BDL	5.93	586	7.11	32.3	1.24	BDL	0.22	BDL
	SHM-48	blue	2.19	0.14	67.5	140	0.03	1.41	391	0.07	6.20	14.3	83.7	12,335	476	4.68	2,994	36.6	4.34	1.84	5.98	BDL	7.22	391	5.31	34.8	1.26	0.70	0.44	0.25
Mediterranean group I ('classical' forms)	SHM-1	white	2.77	0.27	126	135	0.03	1.23	309	0.05	7.45	11.3	822	2,058	1.23	2.97	9.41	7.84	2.19	0.56	3.34	BDL	8.19	510	6.45	29.3	1.11	0.36	0.24	0.15
	SHM-2	brown	3.91	0.50	132	166	0.04	1.25	324	0.05	45.8	12.8	14,016	2,970	14.4	10.5	177	43.9	2.85	1.02	2.30	BDL	7.43	623	7.90	30.7	1.21	1.40	0.43	BDL
	SHM-6	red	4.27	0.52	145	428	0.10	2.01	724	0.12	17.4	23.3	727	17,400	29.4	12.4	3,738	155	3.57	0.82	22.6	BDL	10.1	479	7.64	47.2	2.74	0.76	1.26	0.36
	SHM-7	yellow	2.71	BDL	66.7	180	0.04	1.30	429	0.07	8.52	15.0	99.4	7,495	1.44	6.12	276	8.03	2.39	0.52	48.6	BDL	9.10	433	6.18	37.8	1.51	0.56	19.9	BDL
	SHM-8	purple	3.06	0.38	200	223	0.05	1.37	361	0.06	25.8	16.5	11,820	4,423	13.9	7.67	80.5	12.1	2.64	1.84	3.74	BDL	7.78	485	7.10	35.4	1.31	1.78	BDL	0.47
	SHM-9	white	3.48	0.31	188	184	0.04	1.33	354	0.06	11.6	14.3	1,696	3,042	5.16	3.89	52.7	7.39	2.58	0.77	6.65	BDL	8.06	407	6.56	33.6	1.39	0.77	0.20	0.20
	SHM-10	yellow	2.36	0.41	52.0	147	0.03	1.16	344	0.06	12.9	12.3	80.4	6,538	1.66	7.71	230	6.92	1.94	BDL	5.09	BDL	7.76	329	5.01	35.3	1.23	0.59	25.5	BDL
	SHM-12a	reddish brown	2.56	0.37	111	189	0.04	1.34	489	0.08	7.46	17.1	91.8	14,000	169	3.79	2,779	95.6	5.32	1.26	6.72	BDL	7.24	373	5.70	44.5	1.66	2.51	1.59	0.52
	SHM-12b	yellow	2.07	0.64	89.4	172	0.04	1.09	396	0.07	8.96	14.0	77.1	10,441	3.20	6.45	270	10.1	1.78	BDL	5.37	BDL	5.95	299	4.56	34.5	1.35	1.08	9.54	BDL
	SHM-16a	blue	3.87	0.16	94.0	188	0.04	2.34	323	0.05	6.70	19.8	264	7,749	104	3.31	1,314	63.7	4.10	1.25	5.51	BDL	8.32	356	5.29	32.1	1.21	1.35	0.16	BDL
	SHM-16b	turquoise	2.78	BDL	102	180	0.04	2.42	342	0.06	6.29	19.9	110	2,349	4.70	7.37	11,789	26.2	2.21	0.86	35.6	BDL	7.93	352	5.63	33.4	1.26	0.67	2.73	0.15
	SHM-17	blue	4.43	0.46	134	371	0.08	2.85	534	0.09	14.5	28.4	667	21,763	19.7	9.59	1,950	33.7	3.11	1.00	9.16	BDL	9.47	421	6.86	42.5	2.12	0.92	0.66	BDL
	Ke-1	yellow	2.48	BDL	118	150	0.03	1.30	398	0.07	11.2	10.9	88.6	9,260	2.75	7.86	439	20.9	1.95	0.63	50.2	BDL	6.55	320	4.64	27.9	1.35	1.11	33.2	0.39
	Ke-2	blue	2.98	0.28	163	185	0.04	1.53	427	0.07	9.68	16.7	116	9,138	263	4.47	967	137	5.59	1.49	4.37	BDL	8.83	409	5.54	32.5	1.52	1.90	0.49	0.29
	Ke-5	yellow	1.99	0.25	62.4	130	0.03	1.32	448	0.07	7.15	13.8	134	11,358	4.75	7.53	3,159	20.7	1.93	0.69	10.5	BDL	5.29	328	4.94	27.3	1.50	0.21	13.6	BDL
	SHM-47a	white	2.91	0.73	102	127	0.03	1.56	364	0.06	7.84	11.9	184	2,660	1.40	3.54	40.3	8.93	2.41	0.96	3.82	BDL	6.20	445	6.43	29.5	1.50	0.47	BDL	0.87
	SHM-47b	purple	2.23	0.34	95	159	0.04	1.57	365	0.06	32.7	15.3	12,433	2,595	14.1	5.88	63.7	14.2	2.83	1.00	2.21	BDL	6.92	561	7.47	30.6	1.34	1.52	0.15	0.47
	SHM-49	white	2.27	0.29	115	127	0.03	1.60	337	0.06	6.22	20.1	141	2,399	1.22	2.89	4.69	9.41	2.39	0.76	4.15	BDL	6.59	472	5.80	29.9	1.22	0.44	BDL	BDL
Indefinite (MG I or II)	SHM-42a	yellow	2.07	0.22	159	125	0.03	1.04	265	0.04	6.23	12.6	80.9	5,449	113	3.44	448	24.5	4.10	0.97	9.00	BDL	6.33	343	4.55	24.5	1.00	0.74	7.73	0.16
	SHM-42b	blue	3.78	0.35	193	143	0.03	1.26	303	0.05	7.20	14.9	89.1	5,581	155	3.49	609	34.9	5.94	1.29	4.73	BDL	7.85	409	5.23	28.3	1.15	1.00	1.03	BDL

(continued)

Table 5. Continued

Group	Sample	Colour	Li	Be	B	P	P_2O_5	Sc	Ti	TiO_2	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd
Mediterranean group II	SHM-19	brown	2.81	0.35	148	254	0.06	2.55	434	0.07	8.97	20.8	95.4	2,479	1.31	3.01	8.53	8.60	2.54	0.70	1.67	BDL	11.2	370	5.43	34.1	1.62	0.71	BDL	0.17
	SHM-30	blue	4.34	0.29	213	499	0.11	1.46	398	0.07	15.4	18.9	6,412	5,274	359	20.4	801	42.5	3.78	3.31	8.52	BDL	13.6	590	6.40	34.9	1.50	4.49	15.5	0.79
	SHM-31	black'	3.32	0.50	124	322	0.07	1.53	452	0.08	17.4	19.8	2,470	6,846	1,083	103.4	1,316	400	7.45	19.31	25.0	8.29	10.9	425	6.38	41.1	1.66	1.22	0.40	1.24
	SHM-38	blue	8.13	0.65	217	196	0.04	4.70	2,128	0.35	33.5	56.5	231	13,270	514	50.3	1,021	41.9	5.21	5.28	8.63	BDL	6.74	137	8.45	68.5	5.35	0.81	0.16	0.33
	SHM-41a	blue	3.85	0.36	99.6	437	0.10	1.68	546	0.09	18.9	21.1	4,729	9,363	853	94.3	3,017	79.6	4.06	2.46	18.1	BDL	11.8	443	6.15	38.8	2.02	3.12	0.37	0.22
	SHM-41b	yellow	2.55	0.21	115	194	0.04	1.16	326	0.05	8.58	13.4	1,020	6,563	199	25.4	669	23.9	2.31	1.07	132.0	BDL	6.57	354	4.57	25.2	1.27	0.76	17.3	0.18
Mediterranean group III	SHM-32	blue	2.87	BDL	147	324	0.07	1.61	364	0.06	22.1	19.2	7,997	8,438	433	20.3	1,091	114	3.84	3.47	5.06	BDL	8.18	583	6.31	33.0	1.41	4.52	0.50	BDL

Group	Sample	Colour	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U
Mediterranean group I (early generation)	SHM-3	white	0.09	5.35	73,262	BDL	0.09	154	4.63	8.41	1.12	4.16	1.01	0.28	0.84	0.14	0.99	0.22	0.54	0.08	0.43	0.09	0.85	0.15	0.11	BDL	86.7	0.03	0.78	1.42
	SHM-4	blue	0.17	0.44	3,429	BDL	0.07	191	5.18	9.54	1.35	5.05	1.22	0.37	0.96	0.18	1.12	0.27	0.68	0.09	0.55	0.09	0.87	0.10	0.09	BDL	118	0.11	0.79	1.41
	SHM-5	yellow	BDL	1.03	25,433	BDL	0.07	135	3.95	7.43	0.94	3.65	0.92	0.24	0.75	0.12	0.72	0.16	0.47	0.07	0.44	0.06	0.79	0.09	0.04	BDL	82,337	46.0	0.67	1.21
	SHM-14	white	0.01	0.48	24,775	BDL	0.05	40.6	5.06	5.44	1.07	4.21	0.82	0.21	0.86	0.10	0.80	0.16	0.42	0.06	0.37	0.07	1.19	0.09	0.04	BDL	25.7	BDL	0.53	4.22
	SHM-18a	white	0.04	0.69	33,009	BDL	0.09	173	5.01	9.79	1.27	5.03	1.10	0.37	0.97	0.14	1.13	0.22	0.58	0.12	0.50	0.13	0.85	0.11	0.04	BDL	25,236	18.7	0.69	1.82
	SHM-18b	blue	0.06	0.38	1,800	BDL	0.08	161	4.39	8.60	1.08	4.48	0.94	0.28	0.86	0.15	0.96	0.19	0.56	0.09	0.40	0.08	0.76	BDL	0.04	BDL	1,744	1.18	0.63	1.80
	Ke-3	blue	0.29	15.04	1,917	BDL	0.06	173	5.34	10.6	1.30	5.18	1.12	0.35	1.03	0.15	1.12	0.22	0.62	0.08	0.56	0.09	0.64	0.07	0.03	BDL	457	0.30	0.65	1.76
	Ke-4	yellow	0.02	1.91	15,337	BDL	0.05	124	3.98	7.19	0.98	3.80	0.91	0.27	0.71	0.12	0.84	0.18	0.48	0.07	0.42	0.06	0.58	0.07	0.13	BDL	164,527	92.5	0.52	1.05
	SHM-29	blue	0.28	5.39	4,870	BDL	0.10	175	5.51	10.2	1.33	4.97	1.16	0.35	0.92	0.14	1.04	0.21	0.65	0.09	0.46	0.09	1.00	0.13	0.08	BDL	2,018	1.51	0.85	2.35
	SHM-37	blue	0.12	3.54	1,769	BDL	0.08	196	5.94	11.0	1.45	5.77	1.38	0.42	1.21	0.16	1.22	0.25	0.77	0.12	0.62	0.13	0.82	0.09	0.15	BDL	473	0.27	0.77	1.55
	SHM-48	blue	0.16	1.34	156	BDL	0.10	160	4.45	9.02	1.09	4.26	1.03	0.34	0.82	0.14	1.07	0.20	0.58	0.09	0.51	0.08	0.85	0.09	0.10	BDL	348	0.07	0.68	2.69
Mediterranean group I ('classical' forms)	SHM-1	white	0.01	0.34	16,397	BDL	0.08	230	5.45	10.3	1.36	5.53	1.16	0.34	1.07	0.17	1.23	0.24	0.66	0.10	0.59	0.09	0.75	0.08	0.03	BDL	116	0.03	0.69	1.80
	SHM-2	brown	0.09	1.11	533	1.32	0.07	1,170	5.73	10.2	1.37	5.62	1.33	0.35	1.14	0.20	1.27	0.29	0.71	0.11	0.69	0.11	0.77	0.08	0.15	0.18	643	0.04	0.69	1.72
	SHM-6	red	2.47	316	1,925	BDL	0.19	203	6.88	12.4	1.51	5.86	1.33	0.41	0.98	0.18	1.25	0.25	0.75	0.10	0.60	0.10	1.16	0.19	0.08	BDL	4,086	0.22	1.12	2.45
	SHM-7	yellow	BDL	0.79	8,942	BDL	0.10	180	5.27	9.38	1.23	5.31	1.21	0.35	1.05	0.15	1.10	0.23	0.58	0.09	0.62	0.10	0.93	0.11	0.07	BDL	107,523	2.23	0.75	2.95
	SHM-8	purple	0.02	0.48	2,369	BDL	0.09	1,599	5.64	9.54	1.23	5.45	1.26	0.36	1.09	0.18	1.31	0.25	0.67	0.11	0.68	0.08	0.89	0.11	0.16	BDL	7.83	0.01	0.84	2.69
	SHM-9	white	0.02	0.36	22,970	BDL	0.09	328	5.57	9.99	1.32	5.40	1.20	0.36	1.12	0.17	1.12	0.22	0.63	0.10	0.52	0.08	0.79	0.12	0.07	BDL	21.3	0.01	0.74	2.80
	SHM-10	yellow	0.02	3.65	9,969	BDL	0.06	153	4.23	8.05	0.97	4.32	1.04	0.29	0.72	0.12	0.85	0.18	0.48	0.08	0.48	0.06	0.88	0.07	0.04	BDL	157,584	0.30	0.78	3.25
	SHM-12a	reddish brown	0.17	1.01	201	BDL	0.08	176	5.08	9.42	1.14	4.61	1.04	0.27	0.82	0.13	0.85	0.19	0.64	0.09	0.54	0.08	1.12	0.06	0.06	BDL	1,584	0.07	0.81	2.60
	SHM-12b	yellow	0.02	0.94	11,931	BDL	0.05	137	3.85	7.36	0.94	3.75	0.89	0.28	0.71	0.11	0.80	0.16	0.52	0.07	0.35	0.06	1.14	0.09	0.04	0.06	128,018	0.24	0.68	2.14
	SHM-16a	blue	0.14	2.81	982	BDL	0.05	168	4.49	8.93	1.10	4.29	1.16	0.36	0.92	0.15	0.88	0.19	0.68	0.07	0.50	0.08	0.70	0.12	0.03	0.15	112	0.04	0.65	1.61
	SHM-16b	turquoise	0.33	26.7	16,566	BDL	0.09	153	4.44	8.51	1.06	4.38	0.93	0.27	0.86	0.13	1.02	0.22	0.61	0.08	0.52	0.07	0.81	0.11	0.07	0.10	333	0.25	0.67	1.84
	SHM-17	blue	0.21	44.1	815	BDL	0.24	179	5.85	10.9	1.39	5.28	1.09	0.42	1.20	0.21	1.12	0.33	0.56	0.15	0.58	0.17	1.06	0.33	0.27	BDL	2,704	0.17	1.03	2.68
	Ke-1	yellow	0.03	0.99	16,346	BDL	0.08	135	3.97	7.92	0.93	3.77	0.95	0.26	0.63	0.11	0.79	0.17	0.45	0.07	0.42	0.06	0.74	0.08	0.04	BDL	158,445	2.26	0.60	1.41

(continued)

Table 5. Continued

Group	Sample	Colour	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U
	Ke-2	blue	0.28	1.16	1,565	BDL	0.11	174	4.87	9.65	1.22	4.64	1.00	0.33	0.90	0.13	0.96	0.21	0.48	0.08	0.54	0.07	0.82	0.08	0.13	BDL	1,869	0.04	0.73	1.87
	Ke-5	yellow	0.12	12.2	16,577	BDL	0.08	133	4.36	8.51	1.04	4.05	0.86	0.27	0.75	0.12	0.84	0.19	0.51	0.07	0.45	0.06	0.69	0.09	0.06	BDL	134,264	0.27	0.67	1.50
	SHM-47a	white	0.13	2.27	18,723	BDL	0.09	185	5.60	10.7	1.46	5.19	1.25	0.45	1.04	0.21	1.23	0.27	0.78	0.18	0.61	0.12	0.75	0.10	0.26	BDL	43.2	0.10	0.75	3.66
	SHM-47b	purple	0.09	0.55	22.8	BDL	0.11	1,690	5.90	10.9	1.47	5.52	1.30	0.43	1.21	0.20	1.23	0.32	0.81	0.15	0.82	0.13	0.71	0.11	0.14	BDL	5.22	0.05	0.78	3.96
	SHM-49	white	0.03	0.30	14,680	BDL	0.10	198	5.00	10.6	1.37	4.91	1.13	0.39	0.97	0.15	0.99	0.21	0.58	0.09	0.56	0.15	0.76	0.31	0.02	BDL	54.2	0.05	0.81	2.84
Indefinite (MG I or II)	SHM-42a	yellow	0.04	0.32	3,979	BDL	0.05	149	3.76	7.56	0.94	3.58	0.84	0.28	0.66	0.11	0.75	0.15	0.46	0.06	0.42	0.05	0.61	0.06	0.05	0.06	31,825	0.33	0.55	1.91
	SHM-42b	blue	0.06	0.33	710	BDL	0.08	179	4.54	9.11	1.12	4.53	0.98	0.31	0.88	0.12	0.88	0.19	0.52	0.07	0.48	0.08	0.72	0.06	0.05	BDL	4,858	0.06	0.64	2.41
Mediterranean group II	SHM-19	brown	BDL	0.40	5.52	BDL	0.10	163	4.48	8.92	1.08	4.53	0.98	0.33	0.83	0.13	0.93	0.16	0.49	0.09	0.46	0.09	0.83	0.11	0.11	BDL	31.9	0.00	0.65	1.49
	SHM-30	blue	1.17	66.2	1,278	BDL	0.11	202	5.41	10.4	1.34	5.09	1.11	0.37	0.96	0.15	1.07	0.22	0.63	0.09	0.58	0.08	0.88	0.09	0.10	BDL	1,202	0.10	0.80	1.05
	SHM-31	black'	20.6	149	723	BDL	0.12	219	5.18	9.96	1.23	4.96	1.14	0.36	1.02	0.15	1.03	0.26	0.56	0.08	0.59	0.08	1.08	0.10	0.13	BDL	1,595	0.15	0.88	1.45
	SHM-38	blue	2.36	14.2	6.10	BDL	0.21	100	8.20	18.0	2.19	8.00	1.82	0.49	1.43	0.24	1.52	0.33	0.94	0.14	0.87	0.14	1.64	0.36	0.35	BDL	163	0.04	2.42	3.45
	SHM-41a	blue	1.91	32.1	311	BDL	0.14	197	5.48	10.6	1.33	5.09	1.02	0.32	0.93	0.15	0.95	0.21	0.62	0.08	0.59	0.08	0.97	0.12	0.37	BDL	827	0.45	0.88	1.71
	SHM-41b	yellow	0.63	6.68	9,097	1.02	0.08	150	3.90	7.82	0.99	3.80	0.82	0.26	0.73	0.09	0.73	0.15	0.48	0.07	0.35	0.05	0.63	0.08	0.08	BDL	80,251	42.5	0.58	2.61
Mediterranean group III	SHM-32	blue	2.40	394	3.08	BDL	0.07	251	5.25	9.90	1.28	4.91	1.16	0.37	1.02	0.14	1.00	0.23	0.62	0.09	0.56	0.08	0.73	0.13	0.21	BDL	412	0.03	0.70	1.19

BDL-Below detection limit

for the glass of this group match perfectly those calculated by Schibille[25] for the late Byzantine-early Islamic glass from Tyre and Apollonia, made using Syro-Palestinian sands.

Ti/Nd to Zr/Hf ratios allowed distinguishing glass melted using different sources of sand for Epirotic MG II and III vessels[26] – the groups A and B of different primary origin. On the diagram the samples of MG II and III of the data set under consideration practically overlap the gap between the Epirotic groups A and B (Fig. 4B), and the glass of the group MG I corresponds to both of them. The most evident reason could be some analytical inconsistency between the assemblages studied; nevertheless, it would be intriguing to examine these ratios using an expanded dataset. Different sources of raw materials used in the production of North Pontic and Epirotic vessels cannot be excluded either.

Oikonomou[27] noticed a tendency to negative correlation between SiO_2 and the total of Al_2O_3+Fe_2O_3+CaO content, with higher silica concentration and lower amount of the sum of silica-related elements in the glass of later vessels, having thus a "cleaner" composition. In the sample set studied regarding compositions reduced and normalised to 100%, there is no clear distinction between the earlier and the later glass – it does not seem that for the production of later glass, purer sands were used (Fig. 4C). Most samples of the homogeneous "Levantine" group of MG I and II are characterised by SiO_2 content between 66 and 73 wt% and Al_2O_3+Fe_2O_3+CaO amount between 7.6 and 13 wt%. Lower silica content is attested for two samples of MG I (SHM-6 and 17) of red and blue colours due to higher lime but also to the elevated iron content; the latter is likely related to the colouring agents. The single sample of MG III unguentarium (SHM-32) features slightly lower silica content than typical for the dataset.

Panighello et al.[28] stated for Italian assemblages that the glass of vessels of the Mediterranean groups II and III tends to have slightly higher MgO, K_2O, and P_2O_5 content than earlier MG I glass. This trend is also attested for the Levantine compositional group of the studied dataset, especially for potassium and phosphorus content. Moreover, within the MG I assemblage, K_2O concentrations tend to be slightly lower in the glass of vessels of earlier generations of the late 6th–early/mid-5th centuries BC than in the glass of "classical" types of the 5th century BC (Fig. 5), according to the chronology by M. McClellan.[29] The sample SHM-49, formally assigned to the 'classical' group of MG I vessels (the type II.A.IV, early generation, after M. McClellan – see the Table 1) but dating to the late 6th–early 5th century BC after the burial context, is closer compositionally to the earlier part of the MG I samples, confirming the significance of this feature. This difference could be due to multiple sources of silica used as raw materials, containing minor

[25]Schibille (2022) 118, Fig. 36.

[26]Oikonomou (2018).

[27]Oikonomou (2018).

[28]Panighello et al. (2012).

[29]McClellan (1984).

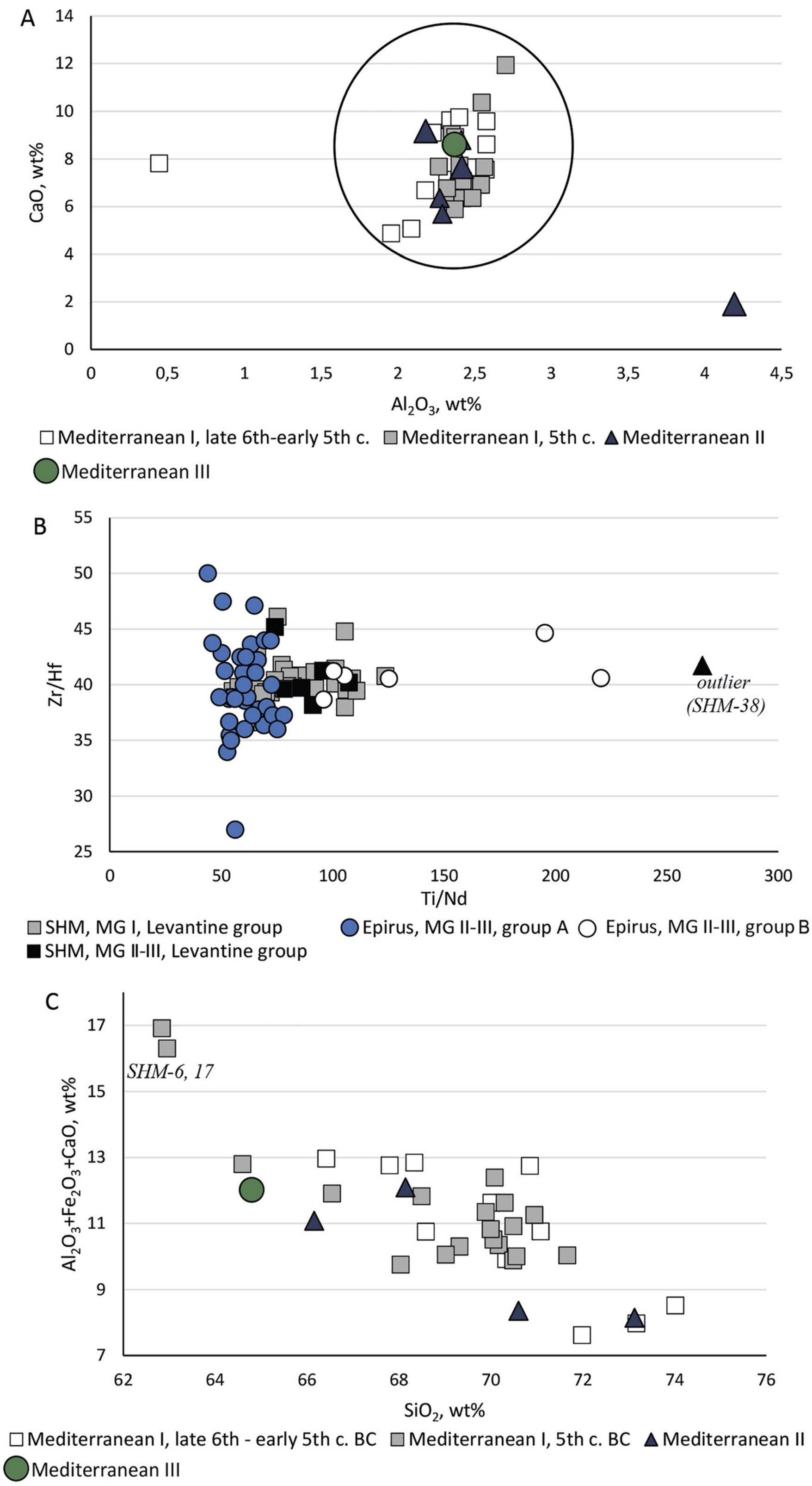

Fig. 4. Core-formed vessels from the State Historical Museum. Silica-related elements' content and ratios. SEM-EDS data in wt% (reduced and normalised to 100% without antimony and lead); Ti, Zr, Nd, Hf – LA-ICP-MS data
Epirus glass composition (B). Data after Oikonomou (2018) table 4

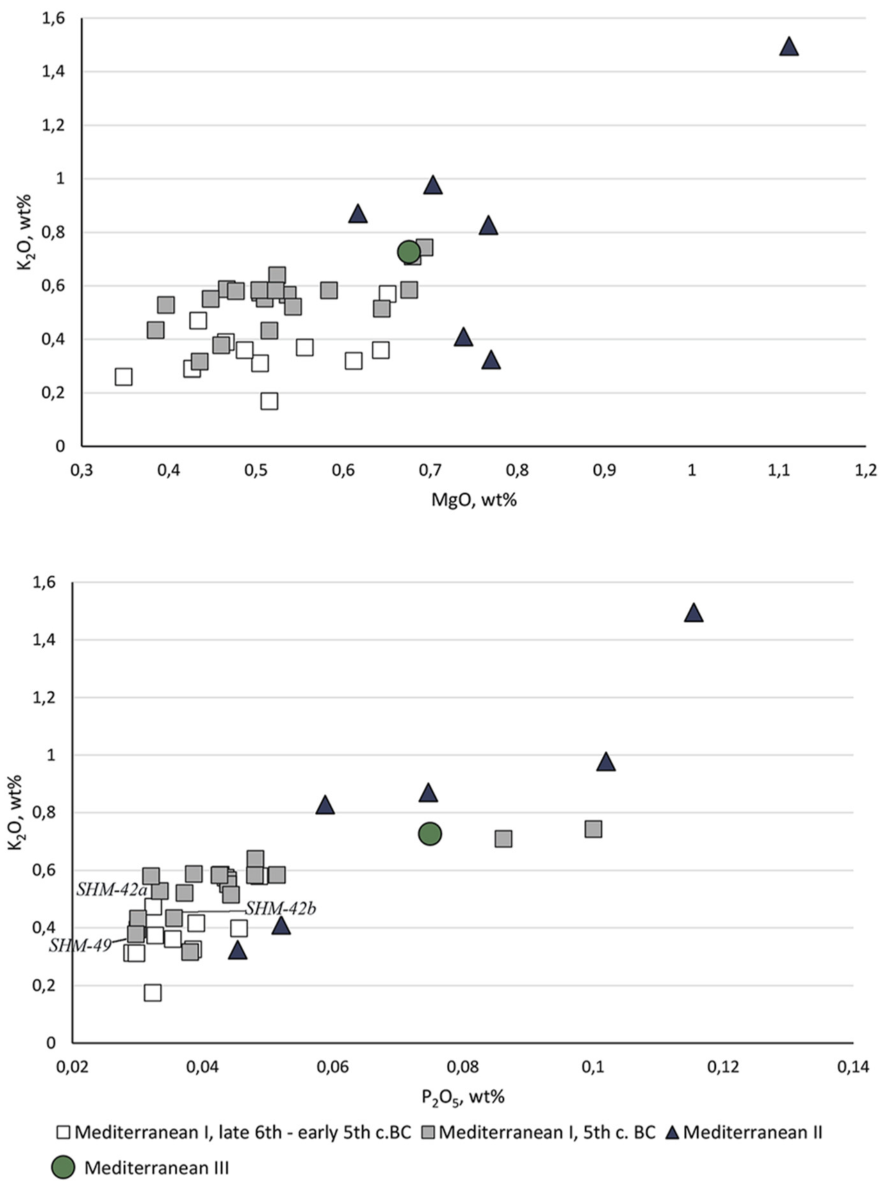

Fig. 5. Magnesium, phosphorus, and potassium content and ratios in the glass of core-formed vessels from the State Historical Museum (data reduced and normalised to 100% without antimony and lead). MgO, K_2O – SEM-EDS data, P_2O_5 – LA-ICP-MS data

concentrations of magnesium and potassium oxides;[30] bone fragments attested by Brill in Belus sand[31] could also introduce trace concentrations of phosphorus, always attested in natron glass. But more likely, it is related to the technological changes in the glass working over time. The concentrations of magnesium, potassium, and phosphorus oxides slightly increase in the glass batch in the course of continuous melting.[32] The latter suggestion is supported by a slight difference in the chlorine content: in the glass of early generations of MG I it is averagely slightly higher than in "classical" types. Chlorine volatilises during melting; thus, its higher concentrations suggest a shorter melting period.[33] The difference in the soda content, which also could be influenced by the duration of the melting period,[34] is not evident for the glass of early and "classical" MG I vessels; for most samples of MG II and the sample of MG III it is slightly higher, also suggesting possible technological changes (Fig. 6).

For the glass of later periods, the levels of magnesium, potassium, and phosphorus slightly elevated due to fuel ash contamination could suggest the recycling of glass cullet.[35]

[30]Foy et al. (2003) 79.

[31]Brill (1999) 479; Henderson (2013) 60.

[32]Paynter (2008); Schibille et al. (2012); Freestone (2015) 30.

[33]Freestone and Stapleton (2015).

[34]Freestone and Stapleton (2015); Freestone (2015).

[35]Freestone (2015).

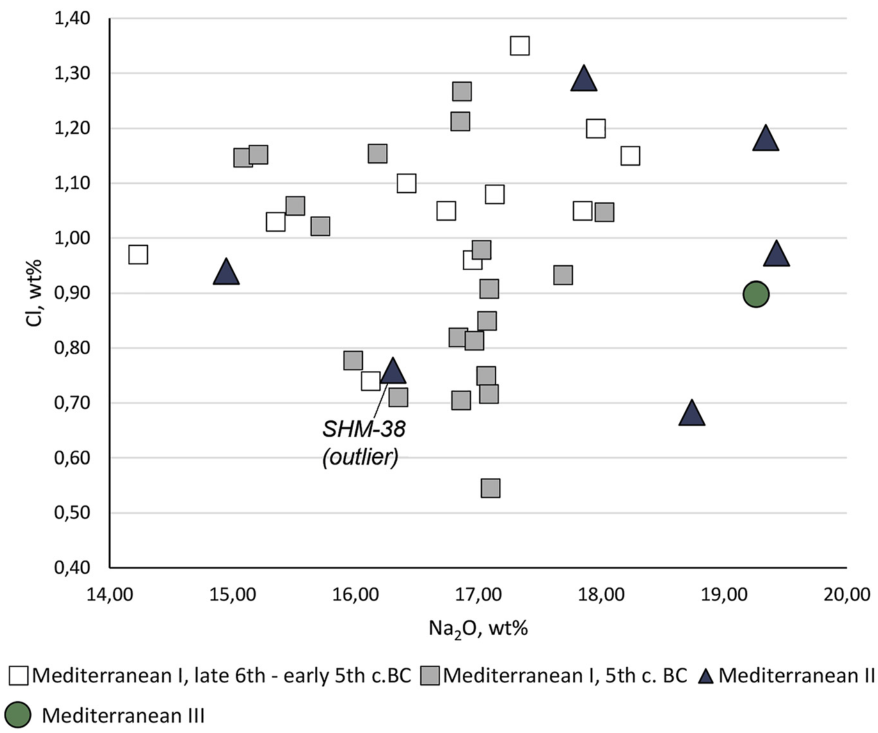

Fig. 6. Soda and chlorine content and ratio in the glass of core-formed vessels from the State Historical Museum (data reduced and normalized to 100% without antimony and lead). SEM-EDS data

This practice is well attested beginning from Roman times.[36] For the period under discussion, it was assumed for the manufacturing of glass beads.[37] Although this possibility cannot be ruled out for core-formed vessels, it is difficult to trace it for coloured glass. One of the most spectacular recycling markers is elevated levels of high transition metals when they are not related to the colouring.[38] In the data set studied it is attested for some samples (for example, copper concentration >100 ppm in yellow and white glass). Nevertheless, the glass contamination in the course of the decoration process cannot be excluded.[39] Although recycling events could have taken place, generally this practice was hardly widespread, while the limited volumes of glass, mostly strongly coloured, produced and circulated in this period did not imply its collecting for recycling.

The group of seven samples with higher phosphate and potassium content (>0.58 wt% P_2O_5 and >0.73 wt% K_2O) includes amphoriskoi and alabastra of MG II and III of black, brown and blue colours (SHM-19b, 41a, 30–32), as well as a sample of red colour (SHM-6). It was previously stated that the red glass often contains higher concentrations of these elements.[40] Schibille et al. assumed that they were introduced to the glass during the colouring process, potentially due to the use of fuel ash as a reducing agent.[41] Only one sample belongs to a vessel of MG I group (SHM-17, an aryballos of blue glass).

Two samples of the Mediterranean group II (SHM-38 and 41b) are close in P_2O_5 and K_2O concentrations to the glass of MG I. One of them (SHM-38) is high-alumina glass, likely of another (probably Egyptian) origin (see below). The second one is a thread of yellow glass decorating an amphoriskos (SHM-41b). The blue glass of its body (SHM-41a) is higher in phosphorus and potassium content, it belongs to the group with higher phosphate and potassium level, suggesting the difference in the technology or duration of colouring of blue and yellow glass.

The typologically indeterminate fragment from Golubitskaya (SHM-42a, b) found in the layers of the 4th–3rd centuries BC, possibly containing earlier materials, matches compositionally the samples of MG I rather than MG II, and is thus possibly related to an earlier horizon of the settlement.

The difference in silica, natron, and iron content, attested for the glass of Mediterranean I and II vessels from Gordion in Central Turkey,[42] is not observed for the sample set of the State Historical Museum.

Two samples differ considerably from the main group (Fig. 4). One of them is a sample of white opaque glass of an amphoriskos of the Mediterranean group I (SHM-14), which belongs to the early generation of MG I, dating to the

[36]Foy (2003); Freestone (2015).

[37]Oikonomou et al. (2018), with the references therein.

[38]Freestone (2015), with the references therein.

[39]See, for example, Rehren et al. (2018).

[40]Henderson (1991); Nenna and Gratuze (2009); Schibille et al. (2012).

[41]Schibille et al. (2012).

[42]Reade et al. (2015).

last third of the 6th century BC. It features the lowest concentrations in the dataset of Al_2O_3 (0.43 wt%), Fe_2O_3 (0.25 wt%), K_2O (0.17 wt%), Rb (2.27 ppm), and Ba (40.6 ppm), suggesting another origin of primary glass. The content of Sr (292 ppm in composition reduced and normalised to 100%) is slightly lower than the threshold determined for the glass in which molluscan shells are the source of lime (300 ppm);[43] the concentration of Zr is moderate (51.2 ppm), but it is slightly higher than in the samples of MG I in the dataset considered. Among the vessels of the Mediterranean group I, the glass with low (<1 wt%) content of Al_2O_3 is extremely scarce. One of them, belonging to a black alabastron, was excavated in Pichvnary (Georgia); it also has low potassium, strontium, and rubidium levels, likely suggesting a common primary origin of glass of both vessels (Shortland and Schroeder, 2009, sample P4bl). Unlike the vessel studied, the glass from Pichvnary belongs to a "classical" 5th century BC form; thus, this compositional glass type, although very scarce, seems to have been used during a long time span. One more vessel made of low-Al glass, featuring also close trace elements pattern, has been identified in the necropolis Volna 1, also in the North Black Sea region. It is an aryballos dating to the 1st half of the 5th century BC.[44] One low-Al, low-K sample is from Sicily; Arletti et al. attribute it to the Mediterranean group I (MZ-09b);[45] nevertheless, it differs by higher titanium content, and there is no information about its trace element composition.

At least the majority of vessels of MG I (if not all of them) are thought to be fabricated at Rhodes.[46] In this context it is worth noting that three of four vessels of MG I, made of low-Al glass, were excavated in the North Black Sea region. It could suggest the existence of separate, possibly small-scale workshops using raw glass of non-Levantine origin. Core-formed vessels from them reached the North Black Sea region, but they are not known by now in the Western Mediterranean.

A greater variability in terms of chemical composition has been found for beads as opposed to core-formed vessels in the archaic and classical periods,[47] and the glass featuring low Al, Sr, and Ba content is more frequent among the glass of beads. Beads made of glass featuring close composition (low-Al, Ti, Zr and Sr) have been attributed to Type I by Lü et al.[48] Most finds of this glass type were found in Italy and Central Europe, which allowed the scholars to assume its Italian origin. Most adornments are dated from the 8th to before the 6th century BC.[49] Recently a series of beads made of low-Al, low-Ba glass has been identified in the contexts of the 6th century BC in Bilsk in the Ukrainian forest steppe, situated 500 km from the Black Sea littoral. They belong to the chronological horizon somewhat earlier than the earliest core-formed vessels.[50] The core-formed containers from the North Pontic region made of low-Al glass discussed here are dated to the late 6th–5th century BC, i.e., to the period when the production of beads from such glass seems to have already ceased. If the glass of this type has Italian origin, the distribution of low-Al core-formed vessels of MG I looks surprising. None of them were found in Italy, and three findings were excavated in the North Black Sea region.

In the Hellenistic period the glass with relatively low alumina, strontium, and barium content together with high zirconium level is known among core-formed vessels of MG II and III in Italy and Greece.[51] Compared to the SHM-14 sample, they feature an averagely higher level of alumina (usually >1 wt% Al_2O_3), as well as of titanium, zirconium, and barium. Close compositions are also known among the glass of Celtic adornments–beads and bracelets, especially for the mid-3rd to early 2nd century AD.[52] The glass of these published samples is associated with Egyptian production, according to high Zr and low Sr levels, previously linked to carbonates derived from limestone of inland origin, in contrast to the high-Sr low-Zr source of lime, suggesting the presence in the glass of aragonite deriving from the molluscan shells of beach sands.[53] Previously scholars also suggested their possible origin from Italian glassmaking centres.[54] Recently the glass of close composition has also been identified among the beads from Scythian barrows of the Lower Dniester region, dated to the second half of the 4th century BC.[55]

The glass of an alabastron of the Mediterranean group II (SHM-38) has high alumina (4.14 wt% Al_2O_3) and titanium (0.32 wt% TiO_2) concentrations along with low calcium content (1.88 wt% CaO). In terms of trace element composition, it also features the lowest Sr level (137 ppm), along with the highest in the dataset Zr (69 ppm) and rather low Ba (101 ppm) concentrations. Glass with a high zirconium content and low levels of strontium has been previously associated with Egyptian glassmaking sands.[56] High titanium level is also typical for the Egyptian sands.[57] Concentrations of zirconium and barium comparable to

[43]Degryse and Schneider (2008).

[44]Rumyantseva et al. (forthcoming).

[45]Arletti et al. (2012).

[46]McClellan (1984); Grose (1989).

[47]Lončarić and Costa (2023).

[48]Lü et al. (2021).

[49]See the references in Lü et al. (2021).

[50]Kolesnychenko et al. (2024).

[51]Arletti et al. (2011); Panighello et al. (2012); Oikonomou et al. (2018): Satricum A group; Oikonomou (2018): Cas-4 and 20; Lü et al. (2021): Type III.

[52]Rolland and Venclová (2021) 124, with references therein; Lü et al. (2021): Type III.

[53]Freestone et al. (2003a); Nenna and Gratuze (2009); Panighello et al. (2012); Rolland and Venclová (2021); Lü et al. (2021).

[54]Oikonomou et al. (2018); Oikonomou (2018).

[55]Rumyantseva et al. (2025).

[56]Rolland and Venclová (2021) with references therein; see also above.

[57]Foy et al. (2003).

those in the sample SHM-38 have been attested for the glass from the workshop in Tebtynis (Egypt) of the 3rd–2nd centuries BC.[58] It was suggested that high-Al, high-Zr, low-Sr glass from the La Tène sites has Egyptian origin.[59] In the blue glass coloured with cobalt, elevated alumina content could be due to the source of the colourant. The association of these elements in glass could point to the use of cobaltiferous alums, most probably Egyptian.[60] Nevertheless, the glass coloured with cobalt from this source seems to disappear by the mid-7th century BC.[61] Moreover, in the glass coloured with cobalt derived from alums, the concentrations of magnesium, manganese, nickel and zinc are usually higher than in the sample SHM-38.[62] The alabastron itself, made of high-alumina glass (SHM-38, Harden, group 2, form 7; Grose, form II:2), was probably manufactured in Italy.[63]

Such composition has not been previously identified among core-formed vessels from the European sites and Asia Minor, but it is known among Celtic glass jewellery.[64] A glass of a single core-formed vessel featuring similar composition has been identified in a burial mound of Gospitalny in Kerch (Eastern Crimea), dated to the mid/3rd quarter of the 4th century BC. Although the vessel type is undetermined, the date of the context suggests that it belongs to the Mediterranean group II.[65]

Chemical composition and the glass colour

For the main group of glass of likely Levantine origin, a slight difference has been identified in the concentration of lime in blue and yellow glass, the number of samples of which is the most representative in the dataset. In the composition reduced and normalised to 100% without antimony and lead, yellow glass tends to have lower concentrations of lime than blue glass (Fig. 7), which could be explained by the difference in sand composition. It could indicate that the glass of these two colours originates from different primary workshops, and it was melted using compositionally close but slightly differing raw materials (sand), perhaps originating from different locations of the same region. The specialisation in the production of glass of certain colours – namely, blue and red – has been previously suggested for the Egyptian Late Bronze Age workshops.[66] The specialisation of the glassmaking centres of the 1st millennium BC, like in earlier periods, could have been related to the peculiarities of colouring of blue glass using cobalt, a colourant originating from cobalt-bearing ores, which are not universally available. This suggestion is also supported by the general compositional difference in glass of different colours used for the manufacturing of the same vessels (see below). White glass would tend to have averagely

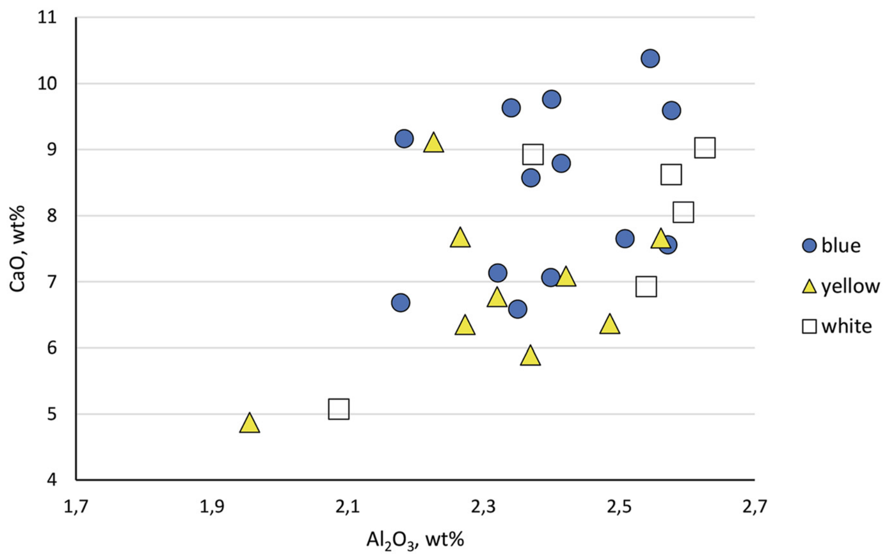

Fig. 7. Glass of the core-formed vessels from the collection of the State Historical Museum, lime to alumina ratios. SEM-EDS data. Data reduced and normalised to 100% without Sb and Pb

[58] Nenna and Gratuze (2009)199, 204; Fig. 4.

[59] Rolland and Venclová (2021) 124.

[60] Gratuze and Picon (2005); Henderson (2013).

[61] Gratuze and Picon (2005).

[62] Ibid.

[63] Arveiller-Dulong and Nenna (2000) Cat. No 47–48.

[64] Rolland and Venclová (2021).

[65] Rukavishnikova et al. (2022); Rumyantseva et al. (2022).

[66] Smirniou and Rehren (2011).

higher alumina and, probably, lime concentrations within the group (compared first of all to the yellow glass), with the exception of one sample; nevertheless, they are represented by only six samples generally.

In the dataset studied there are eight pairs, a triple, and a tetrad of samples taken from the same vessels – the body and the decor. In terms of flux- and silica-related elements, the composition of white and purple glass of alabastra is absolutely identical for the base and the decor in both cases (SHM-8 and 9; SHM-47a and 47b), differing in the concentration of colouring and opacifying agents, first of all – manganese and antimony. It suggests that the same glass batch was coloured in white and purple at the secondary production stage – likely at the workshop, where the vessels were manufactured (Fig. 8A).[67] It also means that for the formation of calcium antimonate crystals responsible for the white opaque colour (Fig. 9), no additional calcium was required–it was enough that it was contained in the glass-making sand.[68] The glass of an alabastron with a brown body and a white trail of décor (SHM-1, 2) features the same similarity in the composition (Fig. 8B), also suggesting that the base raw glass was coloured in brown (with manganese, see below) and white (using antimony) in a secondary workshop.

Blue and yellow glass (four vessels of MG I and II – Ke-1 and 2; Ke-3 and 4; SHM-41a and b; SHM-42a and b) differ in base compounds, especially in soda, alumina, and lime concentrations (Fig. 10A, Table 3). It suggests that the glass of at least one colour should have been imported already coloured to the workshop producing the core-formed vessels. The same difference is also attested for the couple of red and yellow glasses (SHM-6 and 7); on the diagram (Fig. 10B) it is especially evident for CaO content (11.94 wt% in SHM-6, 7.66 wt% in SHM-7; Na_2O–17.03 and 16.35 wt%, Al_2O_3–2.70 and 2.56 wt% in composition reduced and normalised to 100% without Sb_2O_5 and PbO). For the latter vessel the difference partly could be due to the contamination of the red glass by fuel ash possibly added as a reducing agent (see above), but it does not explain the higher sodium content in the yellow glass and so the significant difference in lime concentration.

For one object (SHM-3, 4, 5), the glass of three colours–blue, white, and yellow–has been analysed. The difference in the composition of white and yellow glass is not significant, while the blue glass differs significantly from them (Fig. 10C).

An amphoriskos of MG I is made using glass of four colours. Its body is made of blue glass, coloured with copper. The cobalt content is low (104 ppm); it does not seem to be added intentionally (see below). The body of blue glass is covered with a layer of reddish-brown glass, and the vessel is decorated with yellow and turquoise glass threads. Although the base glass of this vessel cannot be related to a single glass batch, it is rather homogeneous (especially of blue and turquoise colours), differing essentially in soda and lime concentrations (Tables 3 and 5, SHM-12a, 12b, 16a, 16b). The highest lime content is attested for the turquoise glass, where it could have been related to the colouring process (see below). More observations are needed to draw more confident conclusions in this case.

[67]For the methodological description, see Cholakova et al. (2017).

[68]Freestone and Stapleton (2015).

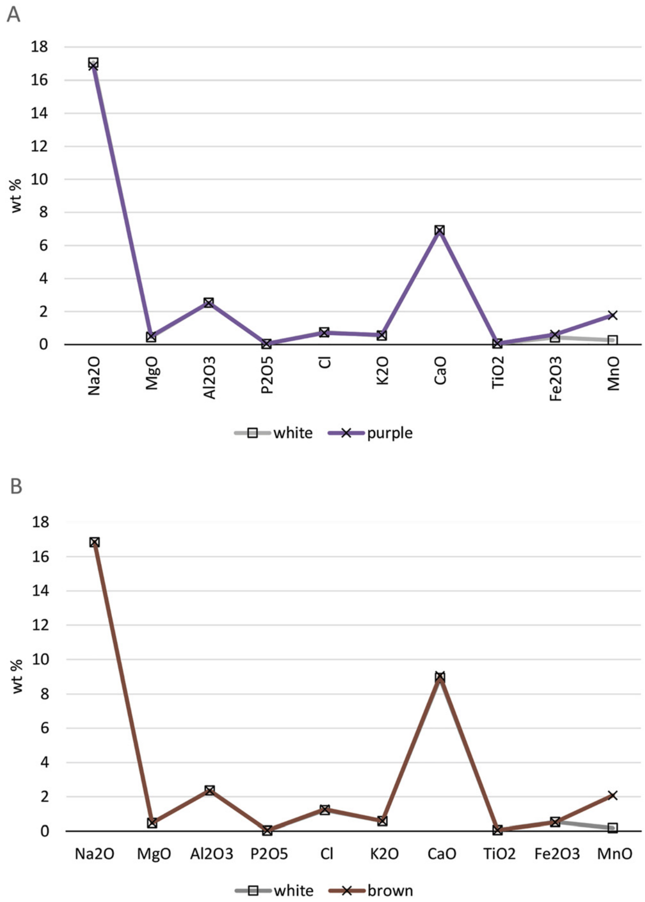

Fig. 8. The concentration of the selected elements in the glass of different colours combined in the same vessel. Data reduced and normalised to 100% without Sb and Pb
P_2O_5, TiO_2 -LA-ICP-MS data; the other compounds - SEM-EDS data
A: alabastron of white glass decorated with a purple trail (SHM-8, 9); B: alabastron of brown glass decorated with a white trail (SHM-1, 2)

Colourants and opacifiers

Glass of the core-formed vessels from the collection studied is represented by 14 samples of blue glass, seven samples of white, nine of yellow, two of purple and brown, and one of turquoise, red, reddish-brown, and "black" (greenish-brown on the chip) glass.

Blue colour is used essentially for manufacturing vessel bodies. Ten of them are of MG I (including six samples of the vessels of early generations), three of MG II (including the high-Al alabastron, probably of Egyptian origin), and one of MG III. All the samples of blue glass contain variable concentrations of cobalt and copper (Fig. 11), responsible for the blue colour of the vessel bodies. Cobalt, a mineral colourant, can be associated in glass with copper, manganese, arsenic, iron, zinc, nickel, alumina, antimony and some

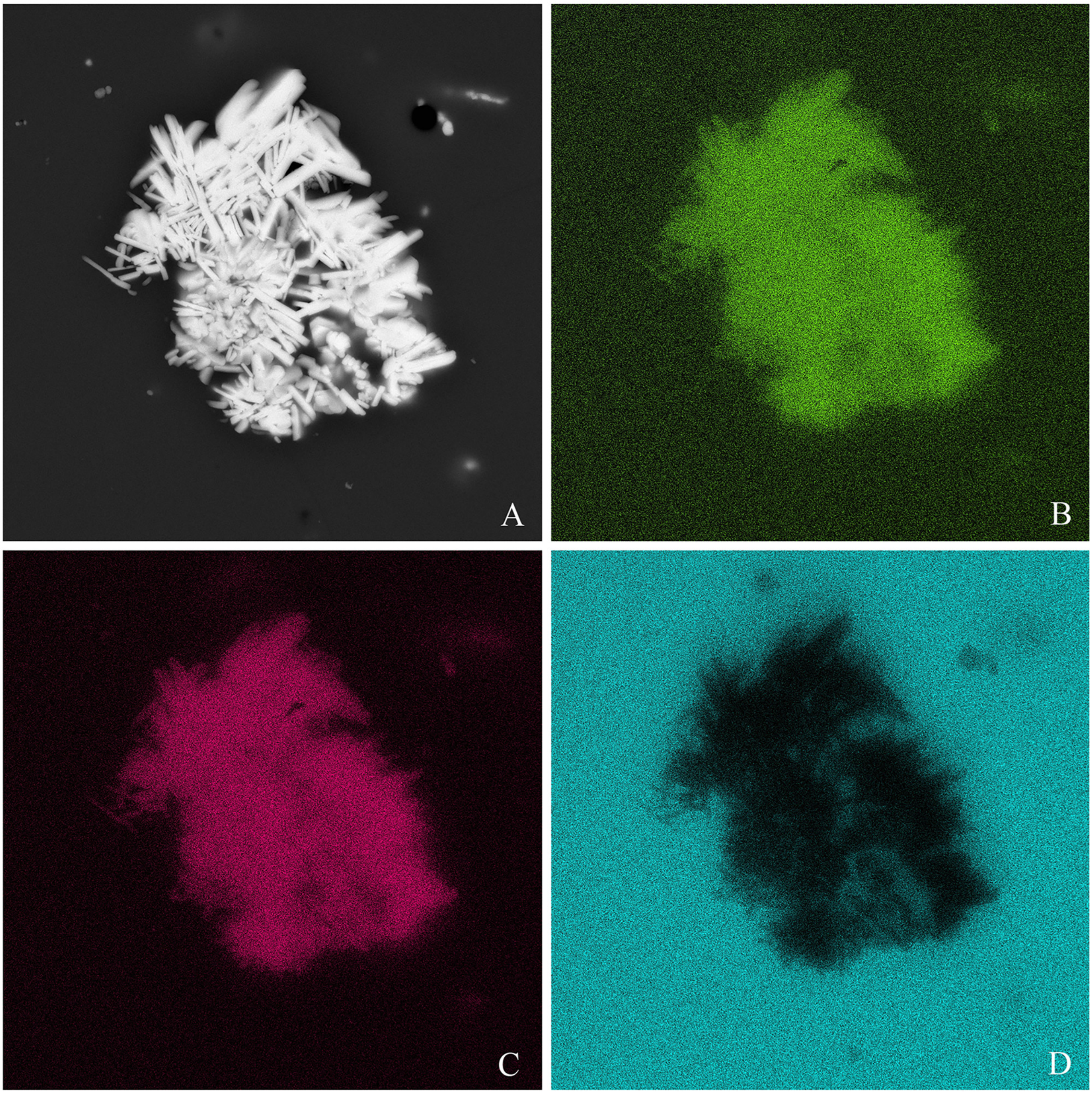

Fig. 9. Calcium antimonate crystal in a sample of opaque white glass (SHM-1). A backscattered electron microphotograph (A); distribution maps of Ca, Sb, and Si repartition (B–D)

other elements;[69] at the same time, most of them could enter the glass not only as impurities characterising the cobalt source but also as independent colourants and decolourizers or silica-related elements.[70]

Published data on the Mediterranean core-formed vessels as well as on the Iron Age glass of the mid-/late 1st millennium BC show the significant variability of cobalt colourants, which could reflect either the contemporaneous exploitation of different cobalt-bearing ores or a small-scale exploitation of a large cobalt mine with different types of cobalt ores.[71] Nevertheless, the dataset under consideration seems to demonstrate some possible chronological changes. The glass of the earlier forms of the Mediterranean group I features higher concentrations of cobalt than the later vessels of "classical" MG I types (Fig. 11). All the glass of the MG I vessels is low in manganese (up to 667 ppm, and in most

[69] Henderson (2013) 69.

[70] Gratuze et al. (2018) with the references therein.

[71] Gratuze et al. (2018) with the references therein; Oikonomou et al. (2018); Rolland and Venclová (2021).

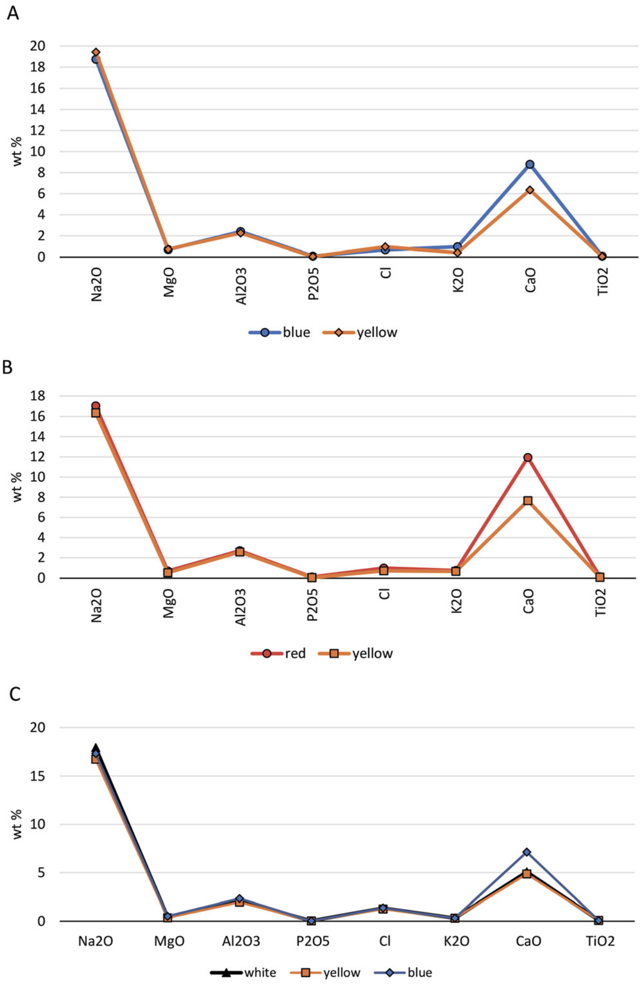

Fig. 10. **The concentration of the selected elements in the glass of different colours combined in the same vessel. Data reduced and normalised to 100% without Sb and Pb**
P_2O_5, TiO_2 - LA-ICP-MS data; the other compounds - SEM-EDS data
A: SHM-41a, 41b Na_2O – 18.74 and 19.43 wt%; Al_2O_3 – 2.41 and 2.27 wt%; CaO – 8.79 and 6.35 wt%; B: SHM-6, 7 (Na_2O – 17.03 and 16.35 wt%, Al_2O_3 – 2.70 and 2.56 wt%; CaO – 11.94 wt% and 7.66 wt%); C: SHM-3, 4, 5 (Na_2O – 17.96, 17.34 and 16.74 wt%; Al_2O_3 – 2.09, 2.32 and 4.87 wt%; CaO – 5.07, 7.13 and 4.87 wt%)

samples, it is lower than 250 ppm, corresponding to the natural level in glassmaking raw materials)[72] and nickel concentrations (below 10 ppm). In the glass of MG II and III vessels, Mn is higher (0.66–1.14 wt% MnO, with the exception of the high-Al glass), which is in good agreement with the previously published data, demonstrating variable levels of Mn for MG II vessels as well as for another group of Hellenistic (La Tene) glass.[73] Ni content is also higher in the MG II and III samples, featuring the correlation between Co and Ni. It could suggest the change of a cobalt source in this period. Iron, copper, antimony, and lead concentrations are variable. The correlation between Fe, Cu, Co, and Zn, attested for the Mediterranean group I by Panighello et al.,[74] is absent in the dataset under consideration.

The 'black' glass of an MG II alabastron, greenish-brown on the chip, contains a high concentration of cobalt (1083 ppm), accompanied by elevated iron, copper, manganese, nickel, zinc, and arsenic levels, as well as elevated tin, antimony, and lead. Thus, it is close in composition to the blue glass of the dataset studied. It is not evident whether the resulting colour was desirable or turned out accidentally when coloured in blue. Only this sample in the data set contains traces of indium (20 ppm), previously attested in different Co/In ratios in late antique, Islamic, and European blue glass of the Mediaeval period.[75] It could suggest another source of cobalt. Only in this sample of the dataset are determinable traces of selenium (8.3 ppm) present, probably also related to the source of colourant.

The composition of yellow glass, used for decoration of eight MG I samples (including two glasses of vessels of the earlier generation) and one of MG II, is very homogeneous. Lead antimonate, $Pb_2Sb_2O_7$, is responsible for the colour and opacity of glass, and, as was suggested earlier, Pb was added in a strong excess,[76] varying between 11.8 and 19.9 wt%. In contrast to the previous study by Panighello et al.,[77] iron, which features elevated concentrations and seems to be related to a colouring agent, is not correlated with antimony and lead. The samples of yellow glass contain variable amounts of arsenic, probably also related to the colouring agent;[78] nevertheless, it is not correlated with Sb, Fe, and Pb. The highest concentrations of As, more than 100 ppm, are attested in two samples of glass of the early generation of MG I, as well as in the unique sample of MG II yellow glass. It could imply the changes that have occurred over time in the sources of colouring agents. All samples of yellow glass also contain elevated copper levels, which could be either related to the colourant source[79] or the result of contamination by an instrument during decoration.[80] It is also present in previously published compositions of yellow glass.[81] Cobalt in concentrations exceeding 100 ppm in two cases could have originated from the blue glass of the same vessels.

White and turquoise opaque glasses (seven and one sample of MG I) owe their opacity (and also the colour, for

[72] Schibille et al. (2017).
[73] Oikonomou et al. (2018); Oikonomou (2018); Rolland and Venclová (2021) with the references.
[74] Panighello et al. (2012).
[75] Gratuze et al. (2018).
[76] Panighello et al. (2012).
[77] Ibid.
[78] Dillis et al. (2019).
[79] Dillis and Degryse (2022).
[80] Rehren et al. (2018).
[81] Panighello et al. (2012).

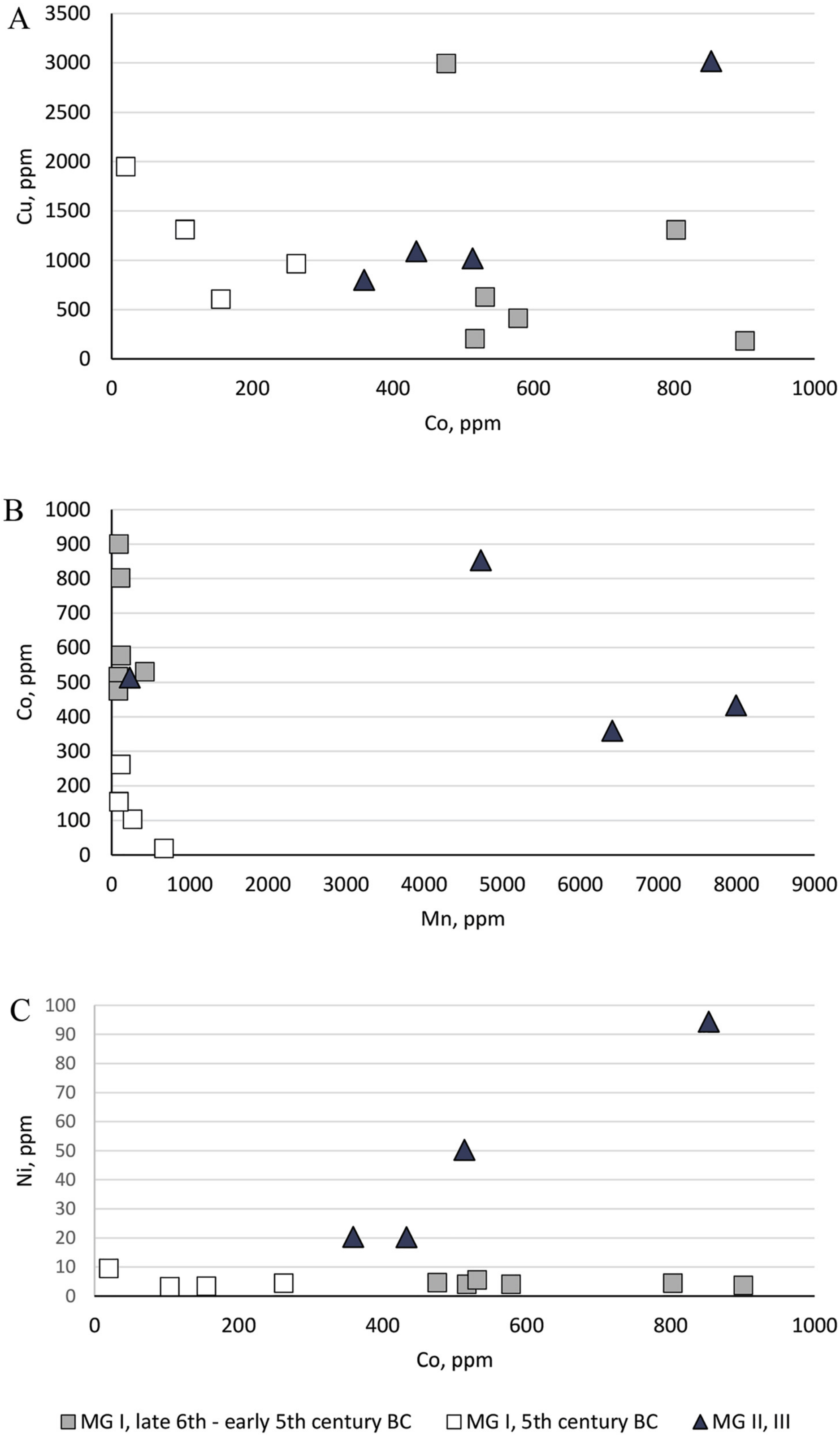

Fig. 11. Blue glass. Cobalt, copper, manganese, and nickel concentrations and ratios. LA-ICP-MS data (in ppm); Fe_2O_3 – SEM-EDS data (in wt%)

the white glass) to the presence of crystals of calcium antimonate.[82] The turquoise glass is coloured with copper, and low Sn content does not suggest the use of metal scrap as a source of copper (Ibid.). At the same time, elevated As content (35 ppm) and possibly Zn (26 ppm) should be related either to the copper colourant, possibly deriving from the metallurgical waste[83] or to the antimony source.[84] While the concentration of lime in white glass does not exceed its content in the glass of the "Levantine" group of the other colours, especially the one used for the purple décor of alabastra, which seems to be made using the same base glass (see above), it appears that no additional lime was used for the colour formation. The antimony could have been added to the batch in the form of stibnite or antimony oxide.[85] White glass is variable in lead, possibly deriving from the antimony source.[86] Elevated manganese content in three samples (SHM-1, 9, 14) is more difficult to explain; possibly the glass could have been contaminated with instruments used for the glass of different colours in the course of decoration: two of these vessels are made of white and purple glass.[87]

Purple glass used for the decoration of two alabastra of MG I is due to the addition of manganese. The source of colourant is characterised by elevated concentrations of barium and vanadium (and, possibly, Sr and slightly elevated Co), originating from the Mn-bearing ores.[88] The brown body of an alabastron (SHM-2, MG I) also contains manganese in a high concentration (2.05 wt%), also accompanied by Ba, V, Sr, and, possibly, Zn and Co. The ion Mn^{3+} can be responsible for the various glass colours from wine red to purple and brown.[89] In ancient glass iron is often responsible for the brown colour; nevertheless, in the sample SHM-2 its content is low (0.5 wt%), suggesting its origin from the glassmaking sand.

The red glass of an alabastron of MG I is coloured with copper, likely accompanied by Sn, Zn, and a slightly elevated concentration of As. The source of colourant could have been metal scrap or metallurgical waste.[90] Iron in high concentration should have acted as a reducing agent, necessary for the colour formation in red opaque glass; the lead content is unusually low for the Iron Age red glass.[91] In comparison with the other MG I samples, the red glass features also slightly elevated magnesium, potassium, and phosphorus levels, generally typical for red glass and probably related to the peculiarities of colouring,[92] as well as slightly higher titanium and zirconium concentrations.

The sample of reddish-brown glass (SHM-12a), covering the blue body of an amphoriskos, is also coloured with copper and contains elevated iron and low lead levels. At the same time, the level of tin, antimony, and arsenic is lower than in the red glass of the alabastron SHM-6, suggesting another source of colourant was used.

Conclusion

The results of our study are generally consistent with previously published data on the composition of core-formed vessels, which were excavated essentially in the European part of the Mediterranean basin but also in Asia Minor. Most core-formed vessels from the collection of the State Historical Museum are made of glass of likely Levantine origin in the workshops using imported raw glass from the Syro-Palestinian region. Nevertheless, the glass composition of the Mediterranean group I vessels is not absolutely homogeneous. The glass of the earliest types of the late 6th–early 5th century BC differs from the later vessels by slightly lower potassium concentration. It could imply that either the glassmaking centres supplying the workshops manufacturing core-formed vessels changed the location within the Levantine region in that period, or some modifications have taken place in the production technology. As regards blue glass, the difference between earlier and later forms has also been traced in the colouring technology.

A slight difference in the composition of blue and yellow could suggest their origin from different glassmaking centres operated within the same region, raising the issue of their specialisation in the production of glass of some colours in the Iron Age. First of all, it could concern the blue glass coloured with cobalt – the colourant that is not universally available. At the same time, the base composition of white and purple glass taken from the same vessels is absolutely identical, implying the colouring of glass in the secondary workshops manufacturing the vessels and eventually supporting the hypothesis about their separate production suggested by McClellan and Grose.[93]

Although the vast majority of vessels of the Mediterranean group I are made using the Levantine glass, a limited amount of raw glass of a different origin (most probably Egyptian or Italian) was supplied to the glassworking (Rhodian or located in another area) workshops making core-formed vessels from the late 6th century BC. Most likely that the three findings of non-Levantine low-Al glass known by now are related to the Black Sea region (Pichvnary, Volna 1 and the unknown North Pontic (?) site).

Some changes in the production technology previously attested by Panighello et al. (2012) occurred in the time of transition from the Mediterranean I to the Mediterranean II

82 Panighello et al. (2012).
83 Freestone et al. (2003b).
84 Dillis and Degryse (2022).
85 Freestone and Stapleton (2015).
86 Dillis et al. (2019); Dillis and Degryse (2022).
87 Rehren et al. (2018).
88 Freestone et al. (2018, 2023).
89 Galibin (2001) 38.
90 Freestone et al. (2003b).
91 Henderson (1991); Freestone et al. (2003b).
92 Nenna and Gratuze (2009); Schibille et al. (2012).
93 McClellan (1984); Grose (1989).

group, reflected in the base composition of the Levantine glass and, evidently, in the source of cobalt colourant. At the same time, not all the features of chemical composition, previously attested for the core-formed vessels, are observed for the dataset studied. This heterogeneity, possibly reflecting slight differences in the location of raw materials' sources and in the production technology not yet fully unified, likely supports the existence of various production regions for the core-formed vessels of the MG II and III.

High-alumina glass, probably of Egyptian origin, attested for glass adornments from the European sites of the Hellenistic period, was identified for core-formed vessels of the MG II only twice for the findings from the Black Sea region. Such vessels are not known at the European sites. At the same time, core-formed containers made of low alumina, probably also Egyptian (or Italian) glass, were attested only in Western Europe (in Italy and Greece). By now, they are absent in the North Pontic region and Asia Minor (Gordion) (Reade et al., 2015). It could be due, first of all, to a very limited dataset of the studied glass of the Mediterranean groups II and III from the Black Sea littoral. The dataset from Gordion is more representative; nevertheless, low-Al Egyptian glass is also absent here. It's worth noting that the Greek cities of the North Black Sea littoral, the majority of which were founded by colonists from Asia Minor, always maintained stable economic and cultural relations with this region. Archaeologically it is reflected in numerous imports from this region. Thus, it is very tempting to suggest the existence of multiple production centres supplying core-formed glass containers to "western" and "eastern" regions of the ancient world, although actually this suggestion is very speculative.

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