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Composition of Diverse Glass Material from the Cathedral of the Assumption of the Blessed Virgin Mary, Dubrovnik, Croatia

Žiga Šmit[1,2*], Ana Franjić[3], Nikolina Topić[4]

[1]*Faculty of Mathematics and Physics, University of Ljubljana, Jadranska ulica 19, 1000 Ljubljana, Slovenia*
[2]*Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[3]*Department of Earth and Environmental Sciences, Division of Geology, Katholieke Universiteit Leuven, Celestijnenlaan 200e, 3001 Leuven, Belgium*
[4]*Independent researcher, Zagreb, Croatia*

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ABSTRACT

The article presents the first archaeometric investigation of the typologically and chronologically diverse assemblage of medieval and post-medieval glass from the Cathedral of the Assumption of the Blessed Virgin Mary in Dubrovnik, Croatia. Sixty samples, comprised of various vessels, lamps, beads, and window glass (*oculi*), and dated between the 12th and 18th century, were analysed with simultaneous PIGE-PIXE methods. The results show that most items were made with the ash of halophytic plants harvested in the Levant, but these can be divided into several compositional subtypes, among which white and common glass are the most numerous. Most glasses can be attributed to the north Italian or Levantine workshops; however, a few analysed samples are of the mixed-alkali type, *façon de Venise*, and Mesopotamian Type I glass. Furthermore, a few distinct samples were made with purer soda sources.
The findings corroborate Dubrovnik's strong cultural and economic links with the Venetian glassmaking tradition and underline the influence and preference of the Mediterranean seafaring trade routes over the continental European ones; an unsurprising fact, considering the status of the Dubrovnik Republic as a stronghold of maritime trade in the period.

1. Introduction

In our historic memory, Dubrovnik is remembered as a free city with extensive political and commercial relations, and a turbulent past. Indeed, soon after its foundation, it first fell under the Byzantine rule (6th–11th century), and then continued to endure many tempestuous events, such as the (unsuccessful) siege by the Arabs in 866–867. Between 1205 and 1358 it was under Venetian sovereignty, but in the 1358 Treaty of Zadar it was proclaimed independent of the Venetian rule. Between 1358 and 1520 Dubrovnik was paying tribute to Croatian-Hungarian kings who guaranteed its protection, and its diplomacy also further secured it against the east, by paying a tribute in golden ducats to Ottoman sultans between 1458 and 1804. At the start of the Napoleonic wars, Dubrovnik first managed to remain neutral, but then lost independence in 1808, and became a part of the Napoleonic Illyrian Provinces from 1810 to 1814. It was then annexed to the Austrian Empire in 1815, following the terms of the Congress in Vienna, and it remained affiliated until the Austro-Hungarian Empire's downfall in 1918.

In the period between 1358 and 1808, Dubrovnik was in essence an independent republic, *Respublica Ragusina*, and its economy, politics and culture were prospering (Foretić, 1980a; Foretić, 1980b; Stulli, 2001). Dubrovnik played an important role in the medieval and post-medieval history of the Mediterranean, the Balkan hinterland and Europe due to its accomplishments in trade, crafts, shipbuilding, and seafaring. A variety of merchandise circulated through Dubrovnik, and both imports and exports were significant sources of income for the city (Foretić, 1980a; Foretić, 1980b). The archival data records the city had its own glass production in the Gothic-Renaissance period (Han, 1981), which suggests a high level of development in the arts and crafts, and, furthermore, that

*Corresponding author. E-mail: ziga.smit@fmf.uni-lj.si

the city was exporting glass via the Mediterranean trading routes, as well as to the Balkan hinterlands.

However, a great natural force majeure during this period – a disastrous earthquake of 1667 – demolished the greater part of the city. During the subsequent reconstruction, many historic buildings needed to be completely rebuilt. Thus, between 1671 and 1713, a new cathedral was built in the place of the former Romanesque Basilica and was devoted to the Assumption of the Blessed Virgin Mary. In 1979 the cathedral was damaged by another earthquake and required a thorough renovation (Horvat-Levaj, 2016). During the reconstruction, systematic archaeological excavations were carried out from 1981 to 1987 inside the cathedral, and outside on the adjoining Bunićeva poljana (Stošić, 1988; Stošić, 1989). The excavations uncovered the nave of the Byzantine Basilica and Romanesque cathedral and unrecorded ancient fortifications (Stošić, 1988; Peković, 1998), and numerous artefacts of diverse typology, provenance, and date, including several hundreds of glass fragments (Stošić, 1989).

2. Materials

The glass found during the excavations in the cathedral is dated from the medieval to post-medieval period (12th–18th century) based on their typology and archaeological context, with most of the artefacts dating to the 16th and 17th century (Figure 1 and Table 1). They comprise several categories: glass beads/rosaries, various types of vessels (beakers, bottles, jars, goblets, tazzas, jugs), lamps, decorative appliqués, and

Figure 1. A selection of samples analysed in this study.

Table 1. List of samples with dating and presumed typological provenance. Compositional types, presumed from the analytical results, are presented in the last column.

Sample	Type	Colour	Date	Provenance by typology	Composition
1	beaker	yellowish	13th–14th century	Levant, S Italy	mixed alkali
2	beaker	greenish	14th–15th century	Italy, Venice, Dubrovnik	*vitrum blanchum*
3	beaker	colourless	15th–16th century	Italy, Venice, Dubrovnik	*vitrum blanchum*
4	beaker	colourless	14th–15th century	Venice, Dubrovnik	high Zr alume catino
5	prunted beaker	amber	14th–15th century	Venice, Dubrovnik	Mesopotamian I
6	gambassini beaker	colourless	14th–15th century	middle Italy, Venice	Mesopotamian I
7	gambassini beaker	greenish	14th–15th century	middle Italy, Venice	*vitrum blanchum*
8	stem goblet	green	12th–13th century	Byzantine (Corinth, south Italy?)	natron
9	stem goblet	turquoise	12th–13th century	Byzantine (Corinth, south Italy?)	natron Foy 2.1
10	stem goblet	purplish	16th century	Venice, Dubrovnik	commune
11	stem goblet	colourless	16th–17th century	Venice, Dubrovnik	*vitrum blanchum*
12	tazza	colourless with b/w decoration	16th–17th century	Venice	*vitrum blanchum*
13	bowl	turquoise	12th–13th century	Corinth, S Italy	mixed alkali
14	bowl	green	12th–13th century	Corinth, S Italy	mixed alkali
15	bowl	red	13th–14th century	Italy, Venice	Mesopotamian I
15	bowl	dark red	13th–14th century	Italy, Venice	Mesopotamian I
16	bowl	colourless	15th–16th century	Italy, Venice, Dubrovnik	Mesopotamian I
17	bowl	colourless	15th–16th century	Italy, Venice, Dubrovnik	commune
18	bowl	colourless purplish	16th century	Italy, Venice, Dubrovnik	*vitrum blanchum*
19	bowl	blue decoration	15th–17th century	Venice, Dubrovnik	commune
19	bowl	colourless	15th–17th century	Venice, Dubrovnik	mixed alkali
20	bowl	turquoise with red, white and blue	16th century	Venice	*vitrum blanchum*
21	bowl	colourless with white decoration	16th century	Venice	commune
22	bowl	colourless	18th century	Bohemia	industrial soda
23	bottle	purple	13th–14th century	Levant, S Italy	commune
24	bottle	bluish	12th–13th century	Italy, Venice, Dubrovnik	natron
25	bottle	bluish	14th –15th century	Italy	high Zr alume catino
26	bottle	green	17th–18th century	W Europe, Italy	commune
27	jar	Co blue	16th century	Italy, Venice	*vitrum blanchum*
28	plate	colourless	15th–16th century	Italy, Venice	high Zr alume catino
29	jug	purplish	16th century	Italy, Venice, Dubrovnik	*vitrum blanchum*
30	handle	colourless with blue decoration	16th century	Venice	*vitrum blanchum*

Table 1. List of samples with dating and presumed typological provenance. Compositional types, presumed from the analytical results, are presented in the last column. (*Continuation*)

Sample	Type	Colour	Date	Provenance by typology	Composition
31	undefined	purple	14th–17th century	Italy, Venice	Mesopotamian I
32	decorative application (?)	colourless	16th–17th century	Venice	*vitrum blanchum*
33	decorative application (?)	colourless	16th–17th century	Venice	*vitrum blanchum*
34	beaker	colourless	Unknown	?	*vitrum blanchum*
35	stem goblet	greyish	16th–17th century	Venice, Dubrovnik	*vitrum blanchum*
36	bottle	colourless	14th–17th century	Italy, Venice, Dubrovnik	commune
37	bottle	colourless	14th–17th century	Italy, Venice, Dubrovnik	*facon de Venise*
38	bottle	greyish	14th–15th century	Italy, Venice	commune
39	undefined	greyish	14th–15th century	Italy, Venice	high Zr alume catino
40	bottle	greenish	17th–18th century	W Europe, Italy	*facon de Venise*
41	lamp	greenish with green decoration	13th–14th century	Venice	commune
42	lamp	greenish with green decoration	13th–14th century	Venice	high Al
43	lamp	colourless	14th century	Venice	*vitrum blanchum*
44	bead	white blue yellow linear decoration	17th century	Venice	*facon de Venise*
45	bead	purple? corroded	17th century	Venice	commune
46	bead	pinkish-yellowish	17th century	Venice	Mesopotamian I
47	bead	Co blue	17th century	Venice	commune
48	bead	Co blue	17th century	Venice	*facon de Venise*
49	bead	green	17th century	Venice	*vitrum blanchum*
50	bead	turquoise	17th century	Venice	cristallo
51	bead	blue with white red linear decoration	17th century	Venice	*vitrum blanchum*
52	bead	colourless	17th century	Venice	*vitrum blanchum*
53	bead	colourless	17th century	Venice	commune
54	bead	Co blue	17th century	Venice	commune
55	oculus	colourless	14th–15th century	Venice, Dubrovnik	*vitrum blanchum*
56	oculus	colourless	14th–15th century	Venice, Dubrovnik	mixed alkali
57	oculus	greyish	15th–16th century	Venice, Dubrovnik	commune
58	oculus	pinkish-yellowish	15th–16th century	Venice, Dubrovnik	commune
59	oculus	turquoise	15th–16th century	Venice, Dubrovnik	commune
60	oculus	colourless	15th–16th century	Venice, Dubrovnik	commune

window glass (*oculi*). Glass from the described assemblage is mostly translucent, and in various colours (greyish, yellow, green, olive-green, blue, blue-green, purple), while some is colourless; furthermore, several samples are opaque (purple-brown, red). It is presumed these items were imported from Venice, the Levant, and Western Europe, and that perhaps some were made in local Dubrovnik workshops.

These objects were produced using diverse techniques: free blowing, mould blowing, and the so-called decorative techniques – *filigrana* and *millefiori*, which also require blowing in the final process. Even though only fragments of these glasses remain, and the stratigraphy is not always reliable, as it was partially disturbed, the physical characteristics necessary to determine the typology and approximate date of the artefacts are still discernible and were further cross-referenced through comparison with known analogies (Table 1; *cf.* Ignatiadou and Antonaras, 2011).

The finds primarily consist of everyday use vessels, which could have been brought from households near the cathedral, as part of rubble material, at the time of the construction of the new building in the second half of the 17th century. The most common are beakers (*moioli* – simple beakers, *gambassini* – with optic blown motifs, *a fili* – with applied threads, *moioli imperlati* or *cieti imperlati* – with applied prunts) and bottles with elongated necks – popular *ingastaras*. Finds of different bowls, a *tazza*, a jug, a jar, a plate, and a basket handle were also retrieved. Archival data reveal that many of these types were locally produced in Dubrovnik: simple beakers (*gotti*), prunted beakers (*gotti gropolosi*), stem goblets, *tazz*e, ornamented and simple bottles with long necks (*gastare*, *ingastarae*), and small jugs (*bochali*) were produced at the beginning of the 16th century in Dubrovnik in the workshop of the Murano glassmaker Johannes Tambarlinus (Han, 1971a; Han, 1971b).

The glass from the cathedral's inventory comprises wine bottles, stem goblets and chalices, which were used during liturgy, as well as biconical lamps of the Islamic or Mosque type, with applied handles for hanging. These glass lamps were an important part of the inventory of the cathedral and were used for illumination of many sacral buildings. The use of glass lamps (*lampe de vitro*) is mentioned in the local archives in the first half of the 15th century, but their origin is not mentioned (Han, 1973; Han, 1975). In the 16th century documents, *candilarchi* and *candile* – night lamps with three handles (*candile di tre maniche*) – are also mentioned (Han, 1974), and all of these correspond in form with some of the finds from the cathedral, although the latter are of a somewhat earlier date.

Several examples of circular window glass (*oculi*) were retrieved during the excavations; Dubrovnik archival records reveal several terms for circular window glass – *oculus*, *ogio*, *logio* and *oziza de vitro* (Han, 1971a) and report that the circular window glass (*vetri tondi*) was produced by Johannes Tambarlinus at the beginning of the 16th century, and that he sold them for the same price as the Venetian-produced ones (Han, 1971b). A considerable amount of stained glass was retrieved during the excavations as well, but these findings will be presented in a separate publication. Window glass was an important part of the cathedral's architecture, having both an ornamental and educational function.

In addition to vessels, biconical lamps, and *oculi*, multicoloured rosary beads, offered as grave goods, and decorative appliques, are also present. In the last quarter of the 16th century, glass beads – very likely of Murano origin – were widely used in the city. The tradesmen of Dubrovnik, together with their Jewish partners, also traded with them in Egypt (Alexandria) and the Levant, mainly in Constantinople. Archival documents mention the trade in beads (*conterie*) and rosaries (Han, 1981). Black, and simple beads (*perle negre*, *perle caravane*) as well as a variety of beaded necklaces (*corona di christallo, corone vitree, corone di pater noster*) are also mentioned in local archival records (Han, 1979, documents 413 and 472; Han, 1981).

Previous analyses of glass from the eastern Adriatic region demonstrated the variability of the chemical composition present during the medieval to post-medieval period (Topić *et al.*, 2016), with plant-ash glass, unsurprisingly, being the most frequent type (Jovanović, 1975; Brill, 1973; Jackson, 2006; Topić *et al.*, 2019**).** Our investigation set out to determine the chemical composition of the glass from the described assemblage, to assess the variability of the glass composition present in religious contexts in Dubrovnik during the period from the 12th to 18th century and compare it to coeval glass found in Europe and the Mediterranean. Furthermore, we hope that this case-study will contribute to, as well as encourage new archaeometric analyses of glass from the eastern Adriatic area, which is still underrepresented in current glass studies.

3. Methods

Sixty samples were analysed with proton-induced X-rays (PIXE) and gamma-rays (PIGE), a combination of methods which we had already successfully applied to the analysis of glass from the Dubrovnik region (Topić *et al.*, 2019). Glass of different colours used in decoration on a few samples were additionally measured, giving 64 measurements in total. Twenty-four elements were analysed for each sample, which, except for Cl and Br, are given in oxide form: Na_2O, MgO, Al_2O_3, SiO_2, SO_3, K_2O, CaO, TiO_2, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO, As_2O_3, Rb_2O, SrO, ZrO_2, SnO_2, Sb_2O_3, PbO, and Bi_2O_3. Phosphorous was not measured, due to the interference of its K-lines with the escape peak of calcium. The measurements were performed at the Tandetron accelerator of the Jožef Stefan Institute in Ljubljana, using a proton beam of 3 MeV nominal energy in air. After passing a 200 nm thick exit window of Si_3N_4 and a 7 mm wide air gap between the exit window and target, the target impact energy was about 2.94 MeV. The X-rays were detected by a Si(Li) X-ray detector positioned 6 cm from the target at an angle of 135º with respect to the beam direction. Accurate values for the two air gaps were obtained from the measurements of elemental targets and simple chemical compounds as well as

Table 2. Oxide concentrations in mass %. Values below detection limits are denoted as bdl. All percentages in the text are also given as mass %.

#	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	Br	Rb_2O	SrO	ZrO_2	SnO_2	Sb_2O_3	PbO	Bi_2O_3
1	12.0	2.20	1.86	71.2	0.78	1.46	2.57	6.18	0.227	0.55	0.89	bdl	0.001	0.003	0.008	0.001	0.002	0.001	0.020	0.023	bdl	0.01	bdl	bdl
2	11.8	2.78	0.99	67.2	0.27	0.88	2.11	13.0	0.090	0.13	0.69	bdl	bdl	0.002	0.008	bdl	0.004	0.002	0.067	0.018	bdl	bdl	0.01	bdl
3	15.6	3.69	1.16	63.8	0.76	0.99	2.24	10.8	0.050	0.32	0.49	bdl	0.002	0.001	0.003	0.007	0.006	0.002	0.078	0.002	bdl	bdl	bdl	bdl
4	12.9	3.10	0.75	67.0	0.64	0.88	2.12	11.3	0.130	0.63	0.38	bdl	bdl	0.009	0.006	0.001	0.005	0.002	0.074	0.042	bdl	bdl	bdl	bdl
5	15.0	3.89	3.23	64.8	0.36	1.16	2.74	6.56	0.135	0.74	1.30	bdl	0.001	0.010	0.008	0.001	0.003	0.001	0.053	0.004	bdl	bdl	bdl	bdl
6	10.2	3.91	3.83	65.6	0.50	1.19	1.23	12.0	0.104	0.31	0.93	bdl	bdl	0.002	0.007	bdl	0.002	0.002	0.096	0.005	bdl	bdl	bdl	bdl
7	12.5	2.95	0.90	66.5	0.35	0.92	2.01	12.9	0.086	0.09	0.66	bdl	bdl	0.004	0.008	bdl	0.005	0.001	0.075	0.018	bdl	bdl	0.01	bdl
8	18.0	1.60	2.55	66.4	0.00	0.97	0.80	7.06	0.165	1.06	1.05	bdl	bdl	0.100	0.006	bdl	0.001	bdl	0.065	0.009	bdl	0.03	0.12	bdl
9	16.0	0.86	2.34	67.4	0.66	1.19	0.62	9.83	0.254	0.02	0.87	bdl	bdl	0.001	0.003	bdl	bdl	0.001	0.019	0.019	bdl	bdl	bdl	bdl
10	14.5	3.09	1.73	63.7	0.47	0.88	3.81	9.17	0.080	1.46	0.81	bdl	0.002	0.010	0.006	bdl	0.005	0.002	0.059	0.003	0.05	bdl	0.15	bdl
11	12.5	2.77	1.38	66.6	0.44	1.05	3.93	10.2	0.051	0.55	0.42	bdl	0.001	0.003	0.002	0.006	0.003	0.002	0.067	bdl	bdl	bdl	0.01	bdl
12	13.6	3.08	1.46	67.7	0.48	0.95	4.25	7.54	0.047	0.47	0.42	bdl	bdl	0.001	0.002	0.004	0.004	0.003	0.061	0.003	bdl	bdl	0.01	bdl
13	15.4	1.57	2.07	67.1	0.00	0.97	1.90	8.36	0.138	0.99	1.03	bdl	bdl	0.084	0.009	bdl	0.002	0.001	0.059	0.011	bdl	0.02	0.35	bdl
14	12.8	1.98	2.02	68.8	0.42	1.06	2.38	8.42	0.134	1.13	0.69	bdl	bdl	0.008	0.003	bdl	0.003	0.001	0.064	0.007	bdl	bdl	0.02	bdl
15	13.3	2.80	2.77	60.2	0.00	0.82	3.16	9.17	0.176	0.82	2.02	bdl	0.020	3.29	0.030	bdl	0.004	bdl	0.072	0.013	0.19	0.04	1.12	bdl
16	12.6	3.13	3.24	67.7	0.32	0.92	2.25	7.58	0.344	0.33	1.52	bdl	bdl	0.008	0.005	bdl	0.002	bdl	0.086	0.017	bdl	bdl	0.03	bdl
17	14.6	2.81	1.71	67.4	0.46	1.02	2.86	7.46	0.081	1.09	0.46	bdl	bdl	0.001	0.003	bdl	0.004	0.002	0.053	0.004	bdl	bdl	bdl	bdl
18	13.8	4.12	0.96	65.7	0.00	0.91	2.58	10.9	0.041	0.29	0.37	bdl	bdl	0.002	0.003	bdl	0.006	0.001	0.094	bdl	0.08	bdl	0.11	bdl
19	15.7	1.83	0.86	69.6	0.61	1.10	2.76	6.87	0.030	0.32	0.29	bdl	bdl	0.006	0.003	0.001	0.004	0.001	0.042	bdl	bdl	bdl	bdl	bdl
20	16.0	3.84	0.66	66.9	0.73	1.03	1.76	8.29	0.032	0.12	0.37	0.008	0.002	0.166	0.003	0.010	0.004	bdl	0.068	bdl	0.04	bdl	0.06	bdl
21	12.6	2.79	1.17	67.3	0.00	1.05	3.30	9.85	0.065	0.74	0.72	bdl	0.001	0.009	0.004	bdl	0.004	0.001	0.077	bdl	0.10	bdl	0.17	bdl
22	17.5	0.37	0.70	69.0	0.87	0.26	0.33	10.8	0.024	0.00	0.06	bdl	bdl	bdl	0.003	bdl	bdl	bdl	0.006	0.002	bdl	bdl	0.03	bdl
23	12.2	2.86	1.41	62.5	0.53	0.82	1.89	12.1	0.102	4.34	1.13	bdl	bdl	0.008	0.010	bdl	0.005	bdl	0.083	0.006	0.02	bdl	0.06	bdl
24	14.4	0.27	1.56	68.3	0.30	0.18	2.41	11.9	0.087	0.03	0.45	bdl	bdl	0.002	0.003	0.020	bdl	0.004	0.014	0.004	bdl	bdl	0.03	bdl
25	12.5	2.99	0.86	66.1	0.47	0.91	2.33	12.7	0.112	0.22	0.63	bdl	bdl	0.015	0.007	0.000	0.007	0.002	0.073	0.035	bdl	bdl	0.01	bdl
26	9.9	2.99	1.95	63.2	0.82	1.11	4.12	13.5	0.113	0.74	1.20	bdl	0.001	0.007	0.006	0.026	0.001	bdl	0.123	0.005	bdl	bdl	0.19	bdl
27	12.2	3.38	1.53	60.8	0.00	0.84	4.03	8.19	0.075	0.41	1.64	0.146	0.047	0.566	0.007	0.24	bdl	bdl	0.066	bdl	2.59	bdl	3.10	0.16
28	11.6	3.22	1.05	67.8	0.54	0.94	2.07	10.9	0.196	1.12	0.50	bdl	bdl	0.001	0.003	0.001	0.005	0.001	0.061	0.051	bdl	0.01	bdl	bdl
29	13.5	3.76	1.24	63.7	0.72	0.92	2.04	12.5	0.068	0.81	0.58	bdl	0.001	0.002	0.006	0.001	0.005	0.001	0.111	0.004	bdl	bdl	bdl	bdl
30	11.8	3.37	1.16	68.2	0.55	0.87	2.37	10.3	0.070	0.61	0.58	bdl	0.002	0.002	0.005	bdl	0.004	0.001	0.097	0.001	bdl	bdl	0.01	bdl
31	10.0	3.29	2.99	63.6	0.54	0.82	2.29	13.6	0.105	1.96	0.63	bdl	bdl	0.004	0.006	bdl	0.005	0.001	0.094	0.011	bdl	bdl	bdl	bdl
32	11.9	2.95	1.06	67.7	0.86	0.91	2.38	11.2	0.067	0.39	0.48	bdl	0.001	0.004	0.020	0.001	0.005	0.002	0.088	0.003	bdl	bdl	bdl	bdl

Table 2. Oxide concentrations in mass %. Values below detection limits are denoted as bdl. All percentages in the text are also given as mass %. (*Continuation*)

#	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	Br	Rb_2O	SrO	ZrO_2	SnO_2	Sb_2O_3	PbO	Bi_2O_3
33	12.4	3.66	1.02	67.2	0.87	0.88	2.27	10.1	0.062	0.63	0.60	0.047	bdl	0.075	0.065	bdl	0.005	0.001	0.075	0.001	bdl	bdl	0.05	bdl
34	12.6	2.82	1.90	66.4	0.57	1.11	3.07	8.98	0.121	1.66	0.65	bdl	bdl	0.006	0.003	bdl	0.003	0.001	0.093	0.005	bdl	bdl	bdl	bdl
35	12.6	3.32	1.39	67.1	0.53	0.97	2.81	9.94	0.072	0.61	0.64	bdl	bdl	0.003	0.004	bdl	0.002	0.001	0.066	0.003	bdl	bdl	0.03	bdl
36	14.7	3.74	1.64	63.5	0.00	0.78	2.72	10.3	0.062	1.28	0.84	bdl	bdl	0.032	0.007	bdl	0.004	0.001	0.076	0.001	0.02	0.03	0.25	bdl
37	13.3	1.77	1.10	65.6	0.46	1.23	4.83	9.23	0.057	1.34	0.81	bdl	bdl	0.017	0.007	0.011	0.003	0.001	0.105	0.001	bdl	0.03	0.06	bdl
38	13.3	3.83	1.48	64.0	0.55	0.81	3.51	9.57	0.066	1.63	0.79	bdl	bdl	0.023	0.005	0.010	0.004	0.003	0.078	0.002	0.14	bdl	0.22	bdl
39	13.3	3.48	0.67	67.2	0.99	0.99	2.31	10.1	0.133	0.38	0.33	bdl	bdl	0.002	0.004	0.001	0.003	0.001	0.065	0.052	bdl	bdl	bdl	bdl
40	9.70	2.63	2.02	65.3	0.00	0.93	5.83	11.0	0.085	0.98	1.17	bdl	bdl	0.015	0.009	0.026	0.002	0.005	0.076	0.003	0.01	0.02	0.20	bdl
41	12.8	2.62	1.93	66.9	0.79	1.00	2.70	8.83	0.122	1.29	0.76	bdl	bdl	0.081	0.005	bdl	0.003	0.001	0.070	0.005	bdl	bdl	0.07	bdl
42	19.4	2.70	6.85	59.1	0.36	1.39	2.52	4.31	0.386	0.68	2.30	bdl	bdl	0.007	0.005	bdl	0.0037	0.0032	0.031	0.012	bdl	bdl	0.004	bdl
43	14.3	3.56	1.10	64.0	0.79	1.06	2.63	10.9	0.093	0.93	0.52	bdl	0.001	0.010	0.005	bdl	0.004	0.001	0.080	0.010	bdl	bdl	0.05	bdl
44	11.3	3.19	1.42	64.0	0.00	0.80	7.49	9.66	0.058	0.69	0.53	bdl	bdl	0.003	0.002	bdl	0.005	0.002	0.076	bdl	0.36	bdl	0.46	bdl
45	14.7	3.13	1.34	65.0	0.00	1.09	1.89	10.7	0.062	1.13	0.79	bdl	0.002	0.006	0.004	bdl	0.003	bdl	0.081	bdl	0.04	bdl	0.07	bdl
46	14.3	3.07	2.89	62.3	0.00	0.50	2.40	13.0	0.078	0.52	0.79	bdl	bdl	0.018	0.015	bdl	0.003	0.002	0.087	0.002	0.01	bdl	0.03	bdl
47	15.3	3.69	1.86	61.9	0.00	1.04	3.45	10.5	0.093	0.36	0.98	0.089	0.028	0.36	0.015	0.18	0.005	0.002	0.074	0.002	bdl	0.03	0.05	0.03
48	13.2	2.74	1.95	66.8	0.00	0.97	5.45	6.98	0.118	0.05	1.07	0.103	0.014	0.017	0.011	0.16	0.007	0.004	0.037	0.005	0.04	bdl	0.10	0.16
49	13.4	3.00	1.46	61.6	0.00	0.91	4.25	10.8	0.066	0.39	1.92	0.025	0.003	1.42	0.008	bdl	0.008	0.001	0.076	0.002	0.13	bdl	0.52	bdl
50	18.8	1.56	0.79	67.7	0.77	1.80	2.99	3.68	0.029	0.01	0.34	bdl	bdl	1.51	0.006	0.030	0.0105	0.0010	0.025	0.001	bdl	bdl	0.024	bdl
51	13.7	3.44	1.40	62.1	0.00	0.80	2.70	9.63	0.076	1.14	1.49	0.057	0.013	0.32	0.004	0.069	0.005	0.003	0.074	bdl	1.33	bdl	1.71	bdl
52	15.4	2.87	0.82	67.8	0.00	1.07	3.42	7.66	0.037	0.30	0.37	bdl	bdl	0.004	0.002	bdl	0.004	0.001	0.056	0.002	0.06	bdl	0.12	bdl
53	12.5	3.53	1.58	64.1	0.00	0.90	3.20	10.5	0.085	0.92	0.84	bdl	bdl	0.021	0.005	bdl	0.007	0.001	0.086	bdl	0.55	bdl	1.22	bdl
54	13.0	3.82	1.22	63.8	0.86	0.88	3.41	10.2	0.068	0.62	0.81	0.25	0.046	0.024	0.004	0.423	0.007	0.001	0.086	0.003	0.12	bdl	0.20	0.16
55	13.2	3.12	1.52	68.3	0.58	0.90	2.21	8.49	0.057	0.96	0.64	bdl	bdl	0.003	0.004	0.004	0.008	0.003	0.059	0.003	bdl	bdl	bdl	bdl
56	13.5	2.38	2.03	67.5	0.00	0.73	2.00	9.11	0.158	0.91	1.00	bdl	0.001	0.32	0.010	bdl	0.002	bdl	0.077	0.005	bdl	bdl	0.29	bdl
57	15.6	3.99	1.79	62.3	0.60	1.25	1.22	10.9	0.128	0.90	1.11	bdl	0.001	0.011	0.004	0.013	0.001	bdl	0.076	0.004	bdl	bdl	0.05	bdl
58	11.9	3.44	1.29	64.0	0.65	0.99	3.03	12.7	0.078	1.07	0.71	bdl	0.001	0.047	0.005	bdl	0.006	bdl	0.095	0.003	0.02	bdl	0.04	bdl
59	11.3	3.04	2.40	64.6	0.46	1.22	3.21	11.6	0.122	0.55	1.33	bdl	0.002	0.006	0.009	0.002	0.003	bdl	0.102	0.001	bdl	bdl	0.07	bdl
60	10.3	3.90	2.15	64.3	0.64	0.78	2.87	12.7	0.102	1.22	0.88	bdl	0.001	0.008	0.005	bdl	0.004	0.003	0.093	0.004	bdl	bdl	0.05	bdl
15	12.4	2.19	3.11	61.1	0.00	0.27	3.14	9.02	0.182	0.78	1.99	bdl	0.014	4.59	0.053	bdl	0.002	bdl	0.068	0.013	0.13	0.03	0.94	bdl
19	14.8	2.58	1.19	68.6	0.54	0.79	2.80	7.20	0.046	0.35	0.70	0.182	0.002	0.015	0.005	0.13	0.004	0.001	0.044	bdl	bdl	bdl	bdl	0.01

from the NIST 620 glass standard. The X-ray detector was equipped with a pinhole filter made of 0.05 mm aluminium foil with a relative opening of 9%. (However, for accurate reproduction of the pinhole transmission function, it had to be assumed that the hole also had an inner rim of smaller thickness). With this set up, it was possible to detect X-rays of the elements between silicon and antimony. Lighter elements were then detected through their characteristic gamma rays, induced by inelastic nuclear scattering. The respective gamma-ray energies were 440 keV for Na, 585 keV for Mg, and 844 and 1014 keV for Al. Among them, the Mg line of 585 keV was the weakest; we regulated the measuring time needed to collect satisfactory results. For a proton current of about 1 nA (which causes an X-ray dead time of up to 7%), the typical measuring time was 20 minutes, resulting in a detection limit of about 0.2% for MgO. We also observed the boron line at 429 keV in the gamma spectra, but it was not detected in the present set of samples; the detection limit for B_2O_3 was around 0.1%. The detection limit for Na_2O was below 50 µg/g, and below 0.1% for Al_2O_3. The detection limit for the X-ray determined-elements was approximately 5–10 µg/g for Z<40, and around 50 µg/g for Z=50, due to lower ionization cross-sections. The method thus cannot detect elements with concentrations below 1 µg/g, accessible by other instruments such as LA-ICP-MS; however, the advantage of this method is that the measuring points can be selected irrespective of the object size and no material is consumed.

Glass samples were cleaned with alcohol before analysis, to facilitate the peeling of the thin corrosion layer present on the surface. In a few cases, where a thick corrosion layer was showing, the measuring points were gently brushed with a small steel ball covered with diamond powder. We therefore believe the measurements were not afflicted by corrosion effects.

During post-processing of the data, the X-ray intensities were obtained by fitting the spectra by applying the XANTHO code (Šmit, 2023), and for the gamma intensities another code developed in the lab (current name GfitFl) was applied. The elemental concentrations were calculated by the procedure that considers the matrix effects (X-ray attenuation and proton stopping) for the X-rays and gamma-rays simultaneously. The elemental concentrations for light elements (Na-Al) were calculated from the gamma intensities according to the surface approximation based on the NIST 620 standard. For normalisation, we used the RBS signal from a gold foil in the chopper, intersecting the proton beam in the vacuum. For control, we inspected the ratio between the RBS signal and the X-ray signal of argon atoms from the air gap between the exit window and target; the variation of this ratio due to fitting errors was below 10%. The concentrations from the X-rays were calculated according to the method of independent physical parameters, and the sum of all oxides was normalised to 100 mass %. For control purposes, the sum of X-ray determined elements was also compared to the apparent concentration of argon atoms in the air. The differences greater than 10% were ascribed to geometrical effects, mainly for sample mis-rotation and surface roughness (Šmit, 2020). The proton impact and X-emission angles were then varied until a 10% agreement was obtained between the two normalisation procedures.

Standards NIST 620 and 621, and BAM S005B were measured as unknown samples to assess precision and accuracy of the instrument. Major concentrations were reproduced with 5% and minor and trace elements within 10–15%.

All results are given as oxides and normalised to 100 mass %, except for chlorine and bromine, which are presented in mass percent element (Table 2). Values below detection limits of the instrument are reported as "bdl" in the data.

4. Results and discussion

The results are presented in Table 2 and are discussed according to the frequency of the glass type in the assemblage, rather than according to the established timeline of distinctive compositional types.

All analysed samples are soda-lime-silica glass, with Na_2O concentrations ranging between 9.7% and 18%, and CaO ranging from 3.68 to 13.6%. Five major compositional glass groups were discerned based on the type of flux used, with further subgroups detected within some of the main groups. In the accompanying figures we use different symbols to represent the typology of the sample, and different colours to denote the date. Some types are represented by a single example.

4.1 Glass types

4.1.1 Halophytic plant ash glass

Most samples are made with plant ash; in most cases, the ash of halophytic plants with K_2O concentration between 2.21 and 3%, and MgO concentrations between 2.5 and 4%, characteristic of Levantine origin, was used (Figure 2).

A higher resolution of the halophytic plant sources is possible by comparing the relative fractions of sodium and potassium oxides (Figure 4); De Raedt (2001) suggested that the samples with low K_2O values were produced using high-quality plant ash – *alume catino* – harvested in the Levant (Verità, 2013). This group in our assemblage comprises glass types originally produced in Venetian workshops (Šmit *et al.*, 2004), which suggests that these are likely original Venetian products.

4.1.2 Mixed-alkali glass

Six glasses, with Na_2O concentrations ranging from 12.0–15.7%, K_2O from 1.90–2.76%, contain MgO in concentrations around 2% (sd=0.28), which indicates a mixture of plant ash and a purer source of alkali. The items belonging to this subtype are dated relatively early (12th–15th century), with only one sample dated to 15th–17th century. In Figure 4, they are located around the high-Na_2O boundary of *vitrum blanchum* I oval.

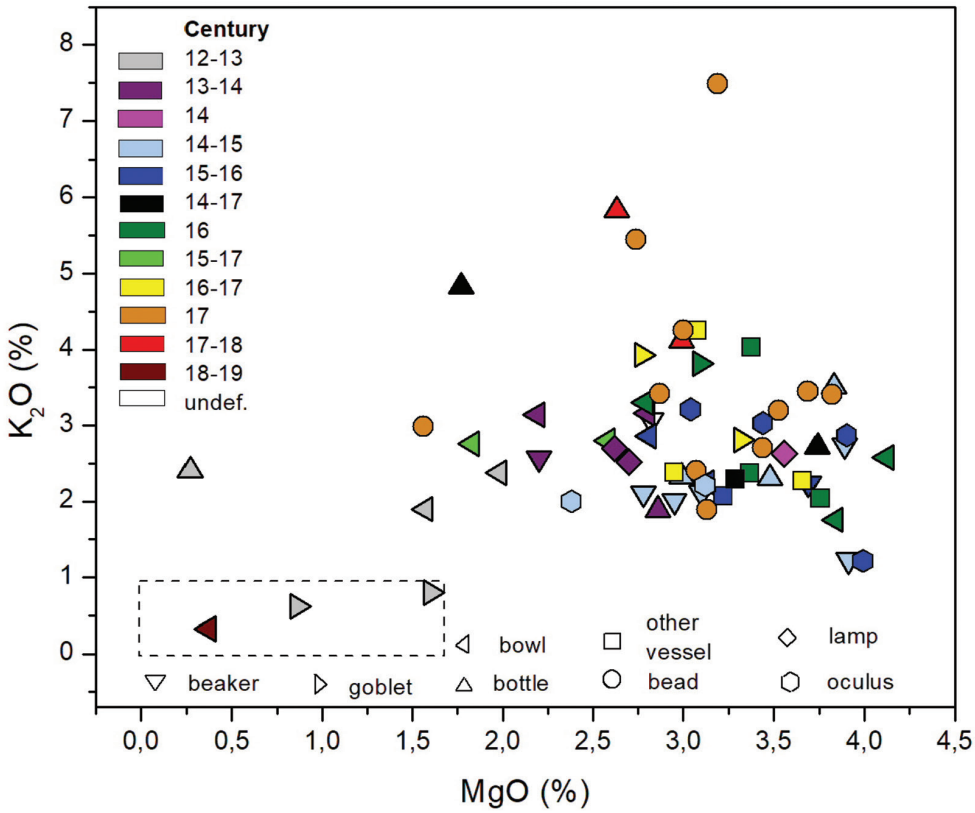

Figure 2. Scatterplot of magnesium and potassium oxides. The rectangle marks the typical natron glass values range.

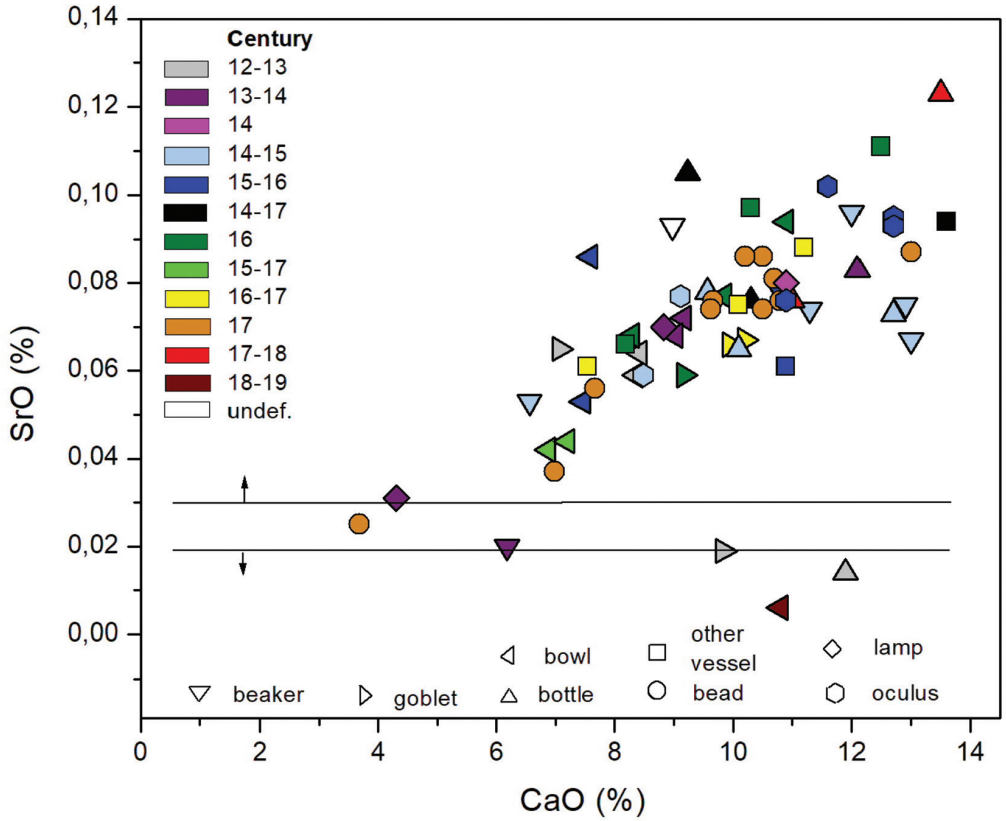

Figure 3. Scatterplot of SrO and CaO. The lines mark areas with SrO below 180 µg/g – characteristic for lime-bearing sands, and above 300 µg/g – typical of plant-ash and coastal sands (Freestone, 2005). Linear correlation of the two oxides in most samples indicates that SrO is related to the CaO source.

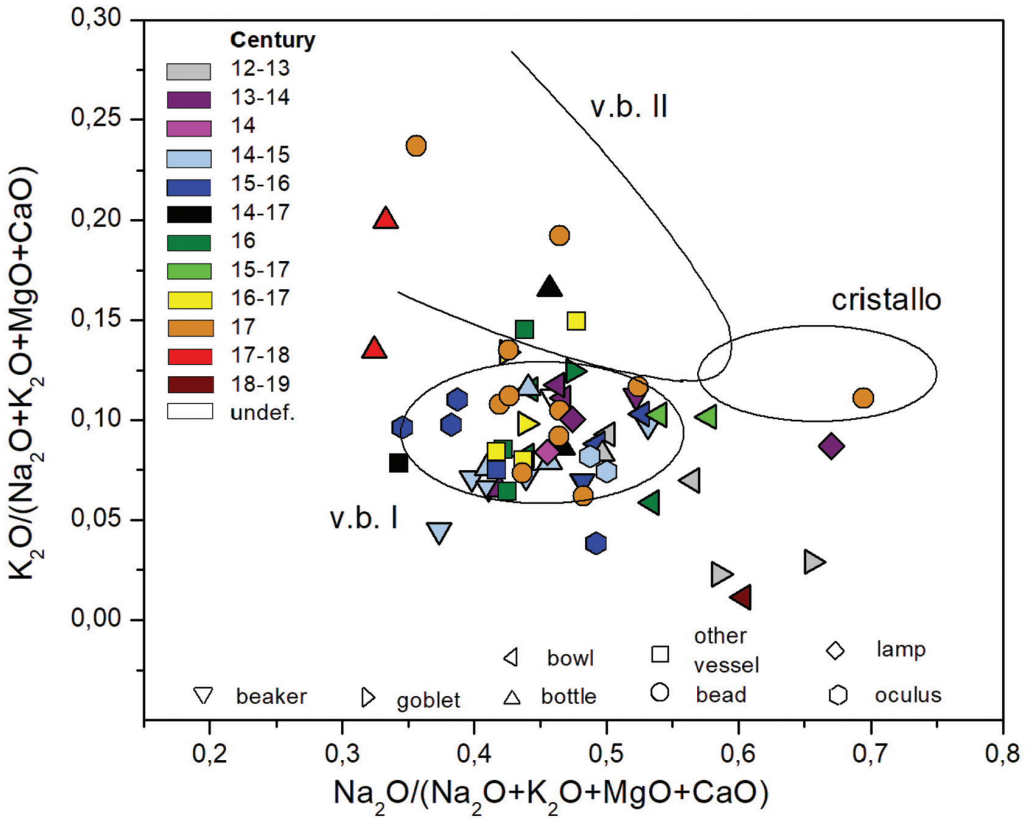

Figure 4. Relative fractions of sodium and potassium oxides with respect to the sum of alkaline and alkali-earth oxides. The boundaries are drawn according to De Raedt *et al.* (2001) and Šmit *et al.* (2009).

4.1.3 Vitrum blanchum II/Façon de Venise

A group of four glasses, with K_2O concentrations between 5 and 7.5%, Na_2O concentrations between 9.7 and 13.3%, and MgO concentrations ranging from 1.8–3.2% were also detected. Higher K_2O, and negative correlation of sodium and potassium oxides indicate use of different alkali source(s). Ash of lesser quality – *barilla* from Spain – was the most probable ingredient for most of these samples (Cagno *et al.*, 2012a).

In our study of glass from the Albanian city of Lezha, we labelled the glasses made with different purity of ashes as *vitrum blanchum* I and II (Šmit *et al.*, 2009) – the presented group corresponds to the *vitrum blanchum II* group, which also encompassed glasses of Venetian provenance.

The puzzling question of whether glass with such a composition can also be of local Venetian production can be explained by the fact that alongside producing large quantities of glass, Venice was also importing glass, as well as raw materials, notably from the Levant (Lane, 1973; Verità, 2013; Occari *et al.*, 2021). The finest example of this type of glass among our inventory is *tazza* (sample no. 12). The group can also be defined as mixed-alkali glass, associated with *façon de Venise* glassmaking.

4.1.4 Natron glass

Two goblets dated to the 12th–13th century have low concentrations of both MgO (<1.6%) and K_2O (<0.8%), which is indicative of natron glass (Figure 2). This is further corroborated by the amounts of alumina (2.34–2.55%), calcium oxide (7.06 9.83%) and iron oxide (0.87–1.05%), which is also typical of the Roman natron-based industry.

One of the goblets contains significant amount of manganese oxide (1.06%), likely used as a decolourant, and furthermore, 0.1% CuO, 0.12% PbO, and 0.03% Sb_2O_3. Cu^{2+} ions colour the sample turquoise green. Glass used to manufacture the other goblet can likely be ascribed to the Foy Série 2.1, according to its characteristic ratios of Al_2O_3/SiO_2=0.038 and TiO_2/Al_2O_3=0.065 (Freestone *et al.*, 2018). This is the most common glass type found in the Balkans during Late Antiquity (Balvanović and Šmit, 2022). Strontium amounts are different for the two natron glasses and indicate the use of different sand sources: the former having 548 µg/g Sr and 70 µg/g Zr, and the latter 159 µg/g and 142 µg/g Zr. High Sr, above 300 µg/g, and low Zr, around 60 µg/g are characteristic of plant ash or coastal sands (the latter used with natron in the production of Roman glasses), whereas Sr levels below 150 µg/g and higher Zr around 160 µg/g denote limestone bearing, inland sand (Degryse *et al.*, 2006; Freestone, 2005; Wedepohl and Baumann, 2000).

Lastly, a 12th–13th century bottle fragment has low MgO (0.27%), but somewhat higher K_2O (2.41%). The concentrations of Na_2O, CaO, alumina and iron oxide are similar to trends in natron glass (14.4%, 11.9%, 1.56%, and 0.45%, respectively); and the elevated K_2O might be a consequence of a recycling event which occurred sometime

in the life history of this object, where contamination with potassium had been imparted by fuel, furnace lining or tools (Paynter and Jackson, 2016; Al Bashaireh *et al.*, 2016).

4.1.5 Industrial soda glass

A bowl dated to the 18th–19th century has very low concentrations of magnesium and potassium oxides (MgO 0.37%, K_2O 0.33%). Furthermore, it has very low alumina, iron oxide, titania, and strontium concentrations (0.7%; 0.06%; 0.02% and 0.01%, respectively). Its chemical composition suggests it was made of industrial soda, which is also concordant with the dating and type of vessel, likely of Bohemian provenance (Figure 3).

4.1.6 Cristallo? glass

Chemical composition of a 17th century milky-blue glass bead, with low magnesia (0.89%), alumina (0.79%) and iron oxide (0.34%) resembles Venetian *cristallo* glass – this glass was made with purified plant ashes, subject to a purifying procedure that increased sodium and decreased calcium oxides, as so in genuine *cristallo*, with the decreased CaO content being compensated by adding mineral limestone (Verità, 2013). It is interesting to note that one of the first descriptions of such purified glass comes from the Dubrovnik archives (Verità, 2013). Furthermore, compositionally similar beads were produced in London and Amsterdam for export to North America, and the plant ashes were purified to a different degree when compared to the Venetian examples (Dussubieux and Karklinks, 2016). Tentative use of purified alkali is thus possible in the studied bead; however, its low CaO content (3.68%) could indicate no mineral lime was added, so the bead is essentially rendering the bead not *cristallo*. The magnesia (MgO) concentrations are also somewhat lower (0.89%) than in the real *cristallo* (1.10–2.35%; *cf.* Verita and Zecchin, 2009, Table 4). Its date could suggest it might belong to a glass type made of purer raw materials and decoloured with As_2O_3, instead of MnO. The bead does contain 0.03% As_2O_3, which could be an impurity related to the colourant, or arsenic oxide was added to reduce the bubbles as the glass was forming; in both cases, perhaps, its low value indicates that the glass was recycled. This glass type (dubbed *Mechelen cristallo* and *Antwerp cristallo*) is also dated to the 17th century in the Low Countries and was produced locally (Van der Linden *et al.*, 2005). In the Mediterranean, it was encountered among the glasses of Lezha (Albania), a city of strong Venetian influence (Šmit *et al.*, 2009). Furthermore, it is interesting to note that such a type of glass is absent in Ljubljana, whose local workshops disappeared before the 17th century (Kos, 2007).

4.2 Impurities related to silica sources

Some of the silica impurities in sand (Al, K, Fe) are important, "accidental" additions which facilitate the quality and stability of glass – this is why coastal sands were preferred for natron glass, as the natron itself is a rather pure substance. In plant ash glass, stabilizer – CaO – is carried over with the flux, which also contains high sodium compounds and

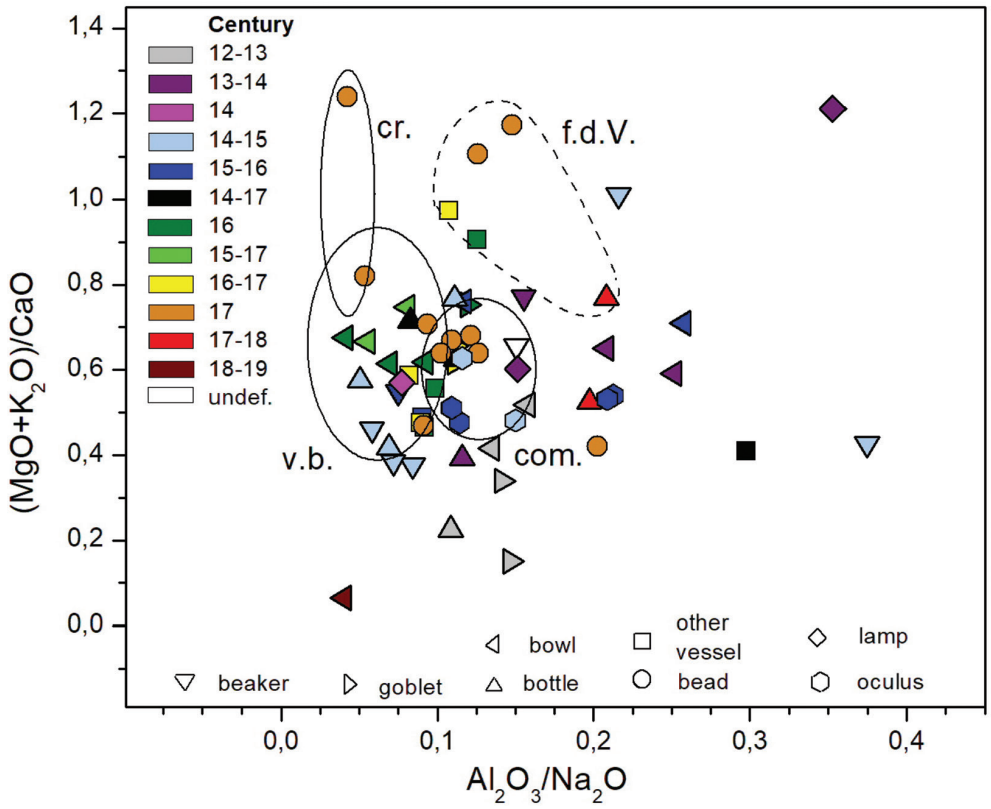

Figure 5. Scatterplot of $(MgO+K_2O)/CaO$ and Al_2O_3/Na_2O ratios. The contours for *vitrum blanchum* (v.b.), *vitrum commune* (com.) and *cristallo* glass are taken from Verità (2013), the contour for *façon de Venise* glass (f.d.V.) was drawn by authors to mark the samples identified in Figure 3.

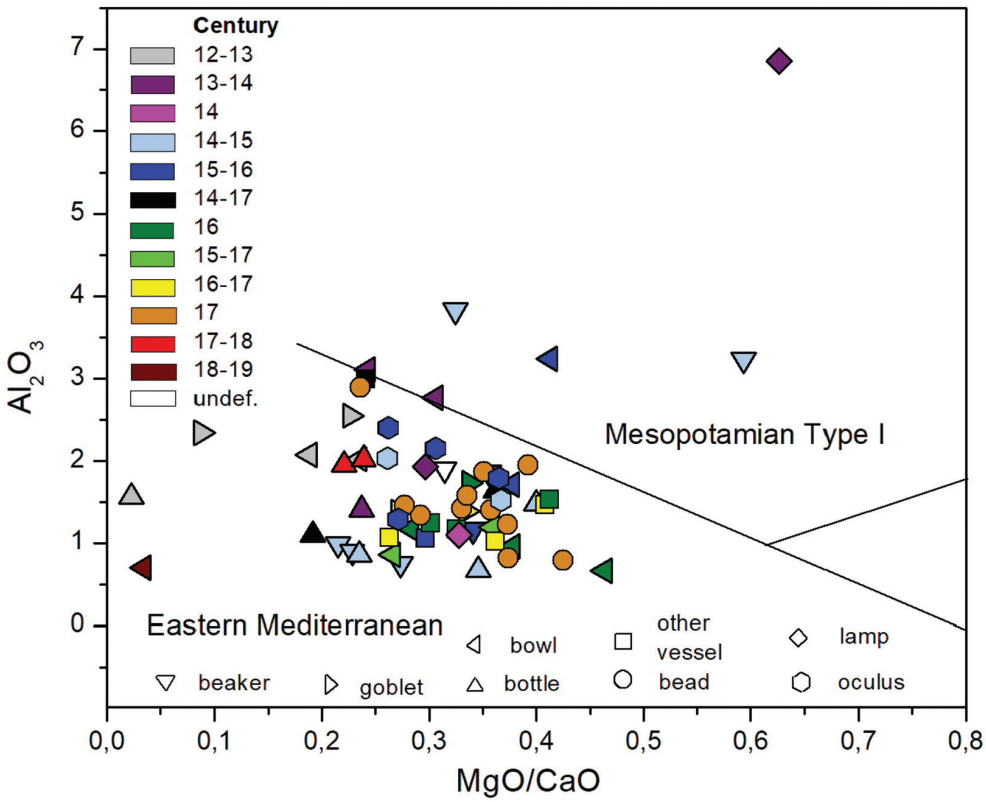

Figure 6. Scatterplot of Al_2O_3 and. MgO/CaO showing the distinction between Mediterranean and Mesopotamian glass. Separation lines according to Phelps *et al.* (2018).

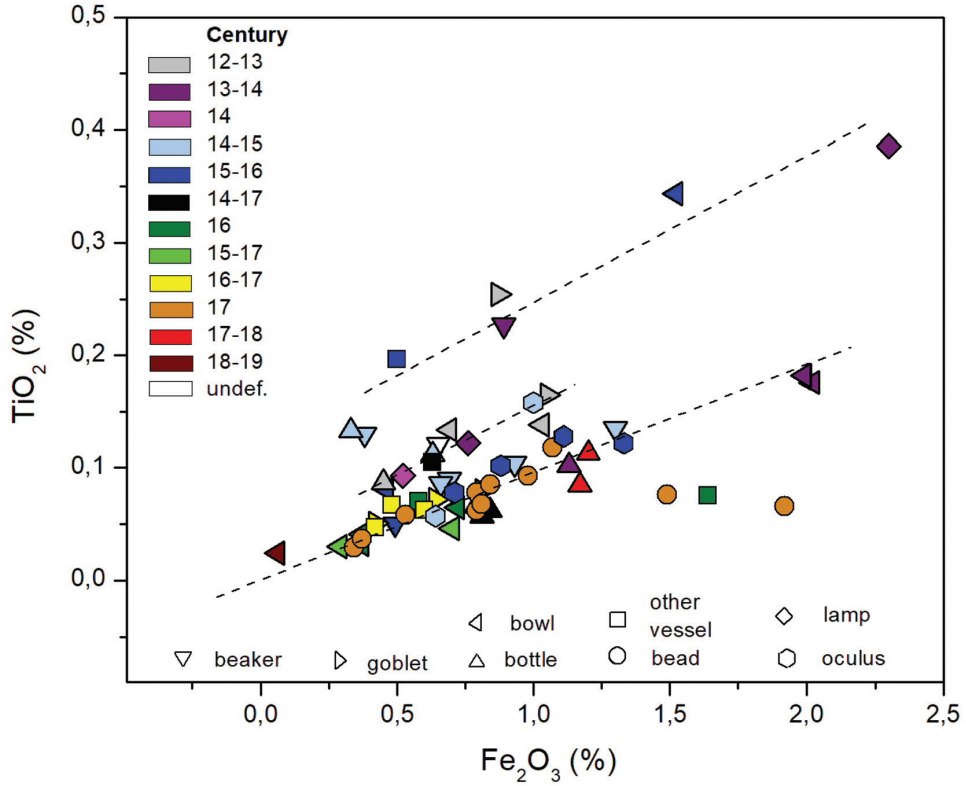

Figure 7. Scatterplot of TiO_2 and Fe_2O_3. Tentative correlation lines suggest potential different silica sources.

other impurities (K, Mg, P, Fe, Mn), so much purer sources of silica can in theory be used in the production of a good quality plant ash glass – this might have been a very pure sand, or, according to several authors, crushed pebbles or mineral sources of silica (McCray, 1998; Freestone, 2005).

Discrimination of siliceous sands is possible by looking at the accompanying trace elements found in the sands, where, for example, Egyptian sands are enriched in heavy elements brought by the Nile, while the Levantine sands are richer in light elements contained in feldspars, such as aluminum oxide (Freestone, 2005; Freestone *et al.*, 2018) and alkali oxides. Further distinctions of the studied assemblage can be made by looking at the differences in the silica source; for example, in his investigations of Venetian glass, Verità (2013) distinguished between white glass (*vitrum blanchum*) and common glass (*vetro commune*) – the latter being characterised by higher amounts of iron oxide (Fe_2O_3>0.6%), alumina (Al_2O_3>1.5%) and manganese oxide (MnO~1.3%), and by a slightly greenish hue (Verità and Zecchin, 2009). With respect to silica, some caution is required, as Al_2O_3, Fe_2O_3, CaO, and TiO_2 are also impurities in plant ash added to the glass batch.

For distinguishing these types of glass within our halophytic plant ash glass samples, a diagram (Figure 5; (MgO+K_2O)/CaO vs. Al_2O_3/Na_2O), with boundaries (ellipses with semi axis length of approximately two standard deviations) reproduced according to Verità (2013), clearly shows the division of the main group into white glass (*vitrum blanchum*) and the less pure common glass (*vetro commune*); the latter being slightly more numerous in the assemblage. The most common types made with *vitrum blanchum* are the 14th to 16h century beakers, bottles, and bowls, while some other objects are slightly older (14th century lamp) or younger (17th century beads). Common glass objects are typologically different: the most numerous finds are window *occuli*, dated from the 15th to 16th century, and 17th century-beads. This subgroup also includes some earlier dated bowls and a lamp (12th–13th century and 13th–14th century, respectively), as well as bottles, produced from this glass type for a long period, from the 13th to 18th century.

The few items belonging to the *vitrum blanchum* II (Figure 4) group are indeed also distinguished according to these ratios, due to the higher amounts of alkalis (Figure 5); these include the items belonging to the 16th–17th century and comprise an elaborately decorated *tazza* with an interwoven blue thread, two glass beads, and a possibly somewhat later-dated bottle (17th–18th century). It is tempting to classify them as glass *à façon de Venise*; however, we cannot exclude Venetian production made of imported raw glass.

Outliers from the four groups identified (Figure 5) are those made of purer alkalis (natron and industrial soda glass), as well as the slightly scattered group of samples within the *vetro commune* group characterised by higher values of alumina (2.77–3.83%), indicating the use of less pure sands in their production. This group comprises two beakers and two bowls (14th–16th century) and a slightly earlier-dated lamp (13th–14th century). Their MgO/CaO vs. Al_2O_3 diagram (Figure 6; reproduced after Phelps *et al.*, 2018, Figure 11) suggests these items were made of Mesopotamian Type I glass. Alongside elevated alumina (2.27%), this glass type is characterised by low CaO (7.07%), and flux ratios of 0.4 MgO/CaO, and 8.67 K_2O/P_2O_5 (Phelps *et al.*, 2018). The objects classified as Mesopotamian have higher alumina concentrations of about 3%, which are still smaller than the alumina concentrations in siliceous sands from Tuscany (Cagno *et al.*, 2010), suggesting that the silica source of these glasses indeed has a different origin. These samples could arguably be further subdivided into two groups, based on the slight differences in CaO, TiO_2, and Fe_2O_3 concentrations – one group having lower CaO, but higher TiO_2 and Fe_2O_3 (6.56–9.17%, 0.13–0.34%, and 1.30–2.02%, respectively), compared to the other (12.0–13.6%, 0.08–0.1%, and 0.79–0.93%, respectively). Finally, it is interesting to note that, although Mesopotamian Type I glasses are predominantly coloured blue with cobalt in the Phelps *et al.* (2018) assemblage, the glasses from our study are mostly colourless with a yellowish, greenish, and brownish tint, and one of the bowls is coloured red (its colour consistency is inhomogeneous, showing different shades of red across the glass).

Another outlier, with high alumina concentrations is a 13th–14th century lamp with 6.85% Al_2O_3 (this value is a mean of two measurements taken several cm apart). It may have originated in Egypt (Schibille, 2022), or even South Asia (Dussubieux *et al.*, 2008; Dussubieux *et al.*, 2010); high alumina glasses also appear in Asia Minor, but these are characterised by about 1% B_2O_3 (Schibille, 2011), which was not detected in this sample.

A 17th century bead and a vessel of undeterminable date are close to the tentative boundary which separates the Mediterranean from Mesopotamian glass. Furthermore, two *oculi* contain higher alumina concentrations (2.15–2.42%) than the typical common glass (Figure 5), but these are made with Mediterranean sands. It is interesting to note that *occuli* were not always made with the purest ingredients; the likely reason for this being, perhaps, that the windows' main function was not as we perceive it in today's contemporary contexts – *i.e.*, providing a view of the outside, but a functional one of allowing the light to illuminate the building's interior.

Differences in titania and iron oxide ratios in Dubrovnik glasses (after Cagno *et al.*, 2012b) also confirm several distinct silica sources (Figure 7), the variability being especially noticeable in the 14th to 15th century material. Furthermore, in Figure 8 we show the dependence of TiO_2/Al_2O_3 vs. Al_2O_3/SiO_2 ratios – this type of diagram was introduced by Schibille *et al.* (2017) and distinctly shows Roman and Late Roman types of glass (Freestone *et al.*, 2018). The majority of Dubrovnik glass in Figure 8 forms a rather compact group comprising about 90% of all samples. Figure 8 also shows the boundaries of common Late Antique glass groups (plotted according to the individual points in Freestone *et al.*, 2018). We can then see that these glasses partly encompass the glass types of Foy 3.2 and 2.1, which originate from Egypt (Schibille *et al.*, 2017; Freestone *et al.*, 2018; Balvanović and Šmit, 2022).

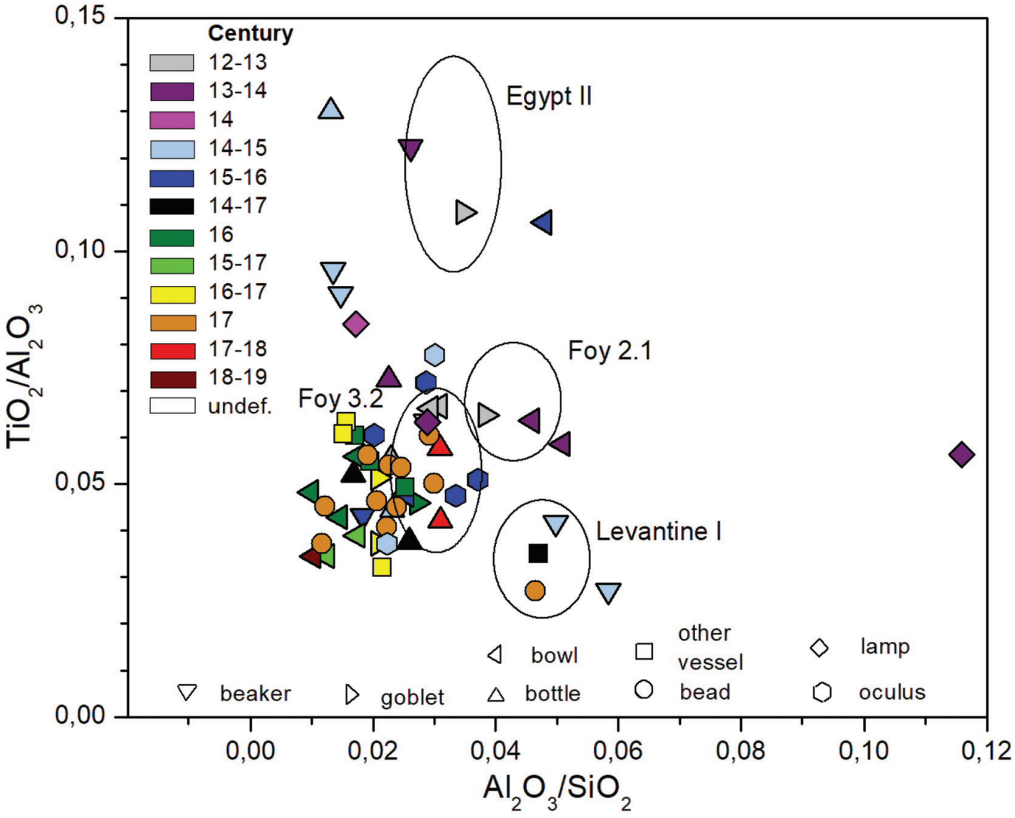

Figure 8. Distribution of glasses according to titania and alumina present in the sand. The Late Antique glass groups of known provenances are shown according to Freestone *et al.* (2018).

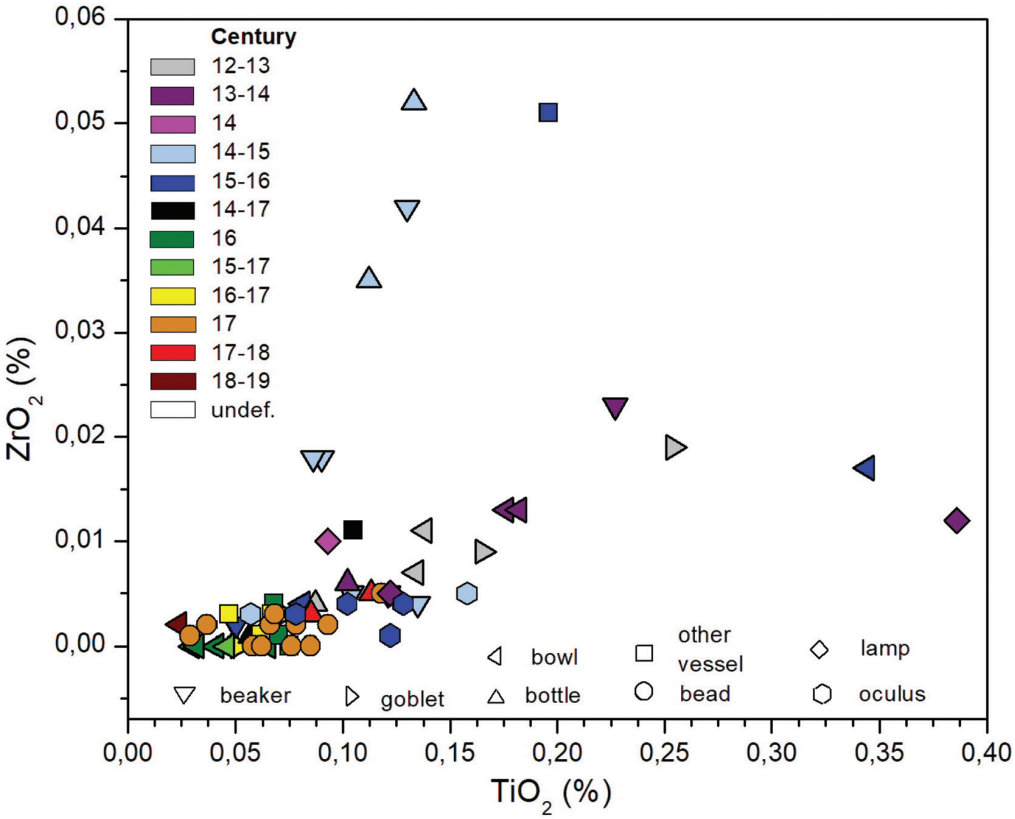

Figure 9. Scatterplot of ZrO_2 and TiO_2. Note the two groups of 14th–15th century beakers and bottles.

According to the chronology of the samples, there is a tentative difference between the Al_2O_3/SiO_2 values below and above 0.02. Samples dated from the 14th to 18th century exhibit higher values, which coincide with known Late Roman groups, while the samples dated to a narrower time frame from the 15th to 17th century have lower values. The prevailing types in the latter group are the 16th century bowls and 17th century beads, including the "*cristallo*" bead of Figures 3 and 4. This indicates that the producers of both types of items did not rely on recycled older glass.

The outliers from these groups comprise a beaker and a goblet (in the Egypt II region), and three objects of different typology from the Levantine glass group.

The results suggest that the silica sources among the sampled glass are rather diverse, implying the breadth of the commercial relations of the Dubrovnik Republic. Even from the point of individual types, two glass sources are clearly seen for the 14th to 15th century beakers, bottles, and bowls – one close to the Levantine and one close to the Egyptian region. Two beakers and a bottle are further characterised by rather high ZrO_2 values (above 300 μg/g; Figure 9). High Zr values are characteristic of sands of Egyptian origin (Weldeab *et al.*, 2002; Shortland *et al.*, 2007).

The Zr level boundary for Venetian imports found in Antwerp was set to 40 μg/g (De Raedt *et al.*, 2001); however, low zirconium values were also observed in the 16th century glass from Ljubljana, which may be indicative of the use of siliceous materials taken from Alpine rivers (Šmit *et al.*, 2005). The situation nevertheless remains complex: as stated by Verità (2013), it is not possible to distinguish between Venetian and Levantine glasses according to their chemical composition; furthermore, Venice also imported sand from Crete and Sicily (Verità, 2013), so the high Zr values might also be present due to imported sand. According to the criteria of Coutinho *et al.* (2017) for original Venetian glass (Al_2O_3<2%, TiO_2<0.07%, ZrO2<40 μg/g), 22 glasses (or 37%) would fall into this category. They include mainly bowls and beads dated after the 16th century.

4.3 Colourants

Only a small number of samples among the assemblage are coloured. Several glasses – mostly beads, one vessel, and some vessel glass's decoration – are coloured blue, and another bowl is coloured red.

The blue-coloured glasses are coloured with cobalt (0.1–0.25%; n=3) and copper oxide (1.4%; n=1), as well as the combination of the two oxides (CoO 0.09–0.15%, CuO 0.3–0.6%; n=3). Cobalt sources can be distinguished by examining the concentrations of impurities found in the complex cobalt ores, such as nickel, arsenic, and zinc (Gratuze *et al.*, 2018; Schibille, 2022). Most cobalt-coloured samples show a positive correlation of cobalt with both nickel and arsenic, with similar ratios of the oxides, which suggests the use of a similar colourant source – likely the cobalt ore from the European Ore Mountains (Erzgebirge or Krušné hory in German and Czech languages, respectively), which is known to have been used in the Late Medieval period, after the 15th century (Giannini *et al.*, 2017; Verità, 2013). Most of these samples are dated to the 17th century, except for a slightly earlier dated jar (16th century), and a more broadly dated bowl (15th–17th century), which has NiO concentrations below the detection limits of the instrument. A bead and linear blue line decoration on a vessel had only insignificant nickel concentrations. The bead, however, does contain significant ZnO concentrations (650 μg/g), which could suggest an Iranian cobalt source (Gratuze, 2013; Gratuze *et al.*, 2018), whereas all other blue samples have ZnO concentrations below 150 μg/g.

The red colour of a 14th–15th century bowl fragment was achieved by cuprite and/or colloidal Cu^+ ions (Noirot *et al.*, 2022). The sample contains elevated iron concentrations, which facilitated copper reduction, and elevated lead, which helped the solubility of copper (Freestone, 1987). Copper was also used in colouring the aqua-blue *cristallo* glass bead, and four further blue samples contain copper in trace amounts. The cristallo sample is free from any additions of lead, antimony, or tin, indicating copper was added to a freshly-made, or carefully-recycled *cristallo* batch. Lastly, a third of the samples (n=20) were either intentionally coloured purple, or decoloured with pyrolusite, while some samples contain low levels of transition metals (Cu, Zn, Sn, Pb), which could signify recycling.

Most samples (n=33) contain some lead, around fifteen samples have increased concentrations of tin and lead oxide, and another seven, of earlier dates (12th–14th century), have trace amounts of antimony alongside tin and lead. These oxides are positively correlated, suggesting they were coming in together, likely as the opacifiers and white and yellow pigments tin oxide, lead antimonate, lead stannate, and lead-tin antimonate. It is interesting to note that in Renaissance glass recipe notebooks (Moretti and Toniato, 2001) it is mentioned that metallic lead used in the production of *Calcina di piombo stagno* (lead and tin calx) originates from Dubrovnik (Moretti and Toniato, 2001). Lastly, the hue of the two amber-coloured glasses was imparted by a carefully controlled reducing atmosphere and the reaction between the iron oxide and sulphur.

5. Conclusions

A variety of diverse glass types, encountered in the Dubrovnik Cathedral, and distinguished by the flux, silica sources, and the colourants, seem to be concordant with trends in Venice – the leading glass producer of the period imported large quantities of the raw materials and glass, mainly from Egypt and Levant (Lane, 1973; Verità, 2013; Occari *et al.*, 2021). Such a situation is also reflected in the Dubrovnik glasses: it is possible to identify glasses from Mesopotamia, Levant, and Egypt; however, a significant number of sources remain undetermined (Table 1, last column, and Figure 10).

Most glasses are made of high-quality *alume catino* ash from the Levantine shores. According to the silica sources, the objects were made of the white glass (*vitrum blanchum*)

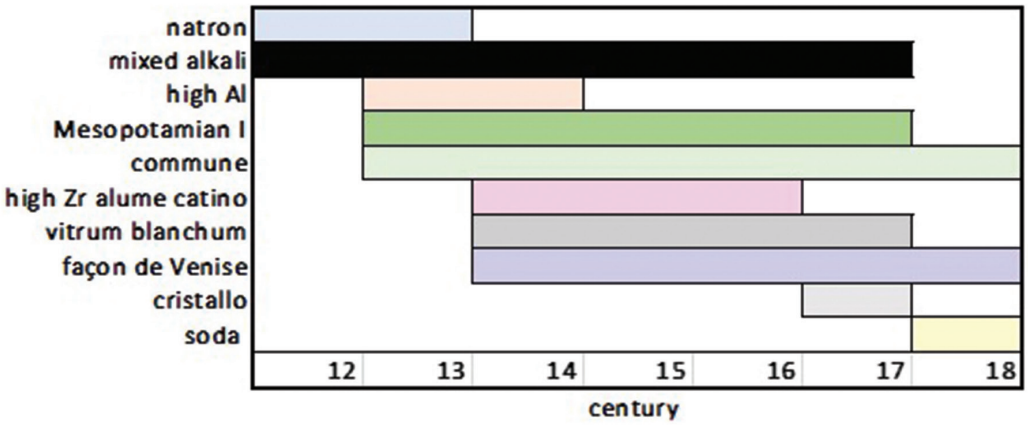

Figure 10. Temporal distribution of identified glass types.

and common glass (*vetro commune*) in approximately equal proportions. Common glass was predominantly used to produce beads and window glass and is present somewhat earlier in the assemblage than the *vitrum blanchum*. Six glasses (about 10% of the assemblage) are made of mixed alkalis, likely composed of less qualitative *barilla* from Spain. These glasses, which typologically include vessels and beads, are also made with an impure silica source – and such a composition generally characterises glass that was made in the Venetian manner (*à façon de Venise*).

As would be expected, natron glass is one of the earliest in the assemblage (12th–13th century), while glass made with industrial soda is the latest (18th century). Mixed alkali glasses appear from the 12th to 15th century, with one outlier sample of a likely later date (15th–17th century). Glasses made with Levantine plant ash cover the widest date range from the 13th to 17th century. Examples dating to the 17th century, when the trade with the Levant slowly subsides, comprise *façon de Venise* (with one example dated more broadly to the 14th–17th century), and the tentative *cristallo* or As_2O_3-decoloured glass. The widest array of compositional types is found in the 16th century, and there does not seem to be a strong correlation between the typology and composition. Some of the shapes, like bottles and bowls, are present throughout the studied time frame (13th–18th century), *oculi* are encountered from the 14th to 15th century, beakers are present from the 13th to 16th century, and stem goblets, decorative appliques, and *tazza* from the 16th to 17th century. On the other hand, lamps do not appear after the 14th century, and beads are dated exclusively to the 17th century.

From the glass composition alone, it is not possible to distinguish between local Dubrovnik production and imports, and further research is needed. The results, however, indicate that Dubrovnik was part of the wide-spread glass trade in the Mediterranean, which connected the Near East with Venice, and other cities on both sides of the Adriatic. Dubrovnik was importing the various sub-types of glass made with *alume catino,* which were produced in different workshops in Venice and other North Italian glassmaking shops, as well as in the Near East.

The overwhelming presence of glass made with fine Levantine ash, from different producers, alongside smaller amounts of glass *à façon de Venise* and glasses from Mesopotamia, as well as no detected desert plant ash, or forest glass from northern Europe, suggests a well-established Venetian influence and the stronger connections of Dubrovnik with the Mediterranean maritime trade than with the northern, continental European glass workshops. The range and variety of the glass compositions present in the assemblage testify to the diversity of glass production between the 12th and 18th century, coinciding with the prosperous era of the Dubrovnik Republic, while the composition diversity found in this assemblage serves as a testimony to the widespread connections and high standing of the Dubrovnik merchants in the trade networks of the Mediterranean. This newly obtained data will hopefully contribute to the slowly growing database of the chemical compositions of eastern Adriatic archaeological and historical glass, which is currently still underrepresented, and will allow for further comparative studies of the production and trade of coeval glasses from the region and beyond.

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References

AL-BASHAIREH, K., AL-MUSTAFA, S., FREESTONE, I. C., and AL HOUSAN, A.Q., 2016. Composition of Byzantine glasses from Umm el Jimal, northeast Jordan: Insights into glass origins and recycling. *Journal of Cultural Heritag*e, 21, 809–818.

BALVANOVIĆ, R., and ŠMIT, Ž., 2022. Emerging Glass Industry Patterns in Late Antiquity Balkans and Beyond: New Analytical Findings on Foy 3.2 and Foy 2.1 Glass Types. *Materials*, 15, 1086. DOI:10.3390/

ma15020403
BRILL, R.H., 1973. The Gnaliæ Wreck: Analyses of Some Glasses. *Journal of Glass Studies*, 15, 93–97.
BRILL, R.H., 1995. Appendix 3: chemical analyses of some glass fragments from Nishapur in the Corning Museum of Art. In J. Kröger, ed. *Nishapur: Glass of the Early Islamic Period*. New York: Metropolitan Museum of Art, pp. 211–233.
CAGNO, S., MENDERA, M., JEFFRIES T., and JANSSENS, K., 2010. Raw materials for medieval to post-medieval Tuscan glassmaking: new insight from LA-ICP-MS analyses. *Journal of Archaeological Science*, 37, 3030–3036.
CAGNO, S., FAVARETTO, L., MENDERA M., IZMER, A., VANHAECKE, F., and JANSSENS, K., 2012a. Evidence of early medieval soda ash glass in the archaeological site of San Genesio (Tuscany). *Journal of Archaeological Science*, 39, 1540–1552.
CAGNO, S., BRONDI BADANO, M., MATHIS, F., STRIVAY, D., and JANSSENS, K., 2012b. Study of medieval glass fragments from Savona (Italy) and their relation with the glass produced in Altare. *Journal of Archaeological Science*, 39, 2191–2197.
COUTINHO, I., MEDICI, T., ALVES, L.C., GRATUZE, B., and VILARIGUES, M., 2017. Provenance studies on *façon-de-Venise* glass excavated in Portugal. *Journal of Archaeological Science – Reports*, 13, 185–198.
DEGRYSE, P., SCHNEIDER, J., HAACK, U., LAUWERS, V., POBLOME, J., WAELKENS, M., and MUCHEZ, P., 2006. Evidence for glass 'recycling' using Pb and Sr isotopic ratios and Sr-mixing lines: the case of early Byzantine Sagalassos. *Journal of Archaeological Science*, 33, 494–501.
DE RAEDT, I., 2001. *Compositions of 16–17th Century Façon-de-Venise Glass Excavated in Antwerp and Neighbouring Cities.* Unpublished thesis (PhD.), University of Antwerp.
DE RAEDT, I., JANSSENS, K., VEECKMAN, J., VINCZE, L., VEKEMANS, B., and JEFFRIES, T.E., 2001. Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16th and 17th century. *Journal of Analytical Atomic Spectrometry*, 16, 1012–1017.
DUSSUBIEUX, L., KUSIMBA, C.M., GOGTE, V., KUSIMBA, S.B., GRATUZE, B., and OKA, R., 2008. The trading of ancient glass beads: New analytical data from South Asian and East African soda-alumina glass beads. *Archaeometry*, 50, 797–821.
DUSSUBIEUX, L., GRATUZE, B., and BLET-LEMARQUAND, M., 2010. Mineral soda alumina glass: occurrence and meaning. *Journal of Archaeological Science*, 37, 1646–1655.
DUSSUBIEUX, L., and KARKLINS, K., 2016. Glass bead production in Europe during the 17th century: Elemental analysis of glass material found in London and Amsterdam. *Journal of Archaeological Science – Reports*, 5, 574–589.
FORETIĆ, V., 1980a. *Povijest Dubrovnika do 1808. I. Od osnutka do 1526.* Zagreb: Nakladni zavod MH.
FORETIĆ, V., 1980b. *Povijest Dubrovnika do 1808. II. Od 1526 do 1808.* Zagreb: Nakladni zavod MH.
FREESTONE, I.C., 1987. Composition and microstructure of early opaque red glass. In: M. Bimson, and I.C. Freestone, eds. *Early Vitreous Materials.* British Museum Occasional Paper, 56, London: British Museum, pp. 173–191.
FREESTONE, I.C., 2005. The Provenance of Ancient Glass through Compositional Analysis. *Materials Research Society Symposium – Proceedings*, 852, OO8.1.1–14.
FREESTONE, I.C., DEGRYSE, P., LANKTON, J., GRATUZE, B., and SCHNEIDER, J., 2018. HIMT, Glass composition and commodity branding in the primary glass industry. In: D. Rosenow, M. Phelps, A. Meeks, and I. Freestone, eds. *Things that Travelled: Mediterranean Glass in the Fist Millennium CE*. London: UCL Press, pp. 159–190.
GIANNINI, R., FREESTONE, I.C., and SHORTLAND, A.J., 2017. European cobalt sources in the production of Chinese *famille rose* porcelain. *Journal of Archaeological Science*, 30, 27–36.
GRATUZE, B., 2013. Provenance analysis of glass artefacts. In: K. Janssens, ed. *Modern methods for analysing archaeological and historical glass.* Chichester: Wiley, pp. 311–344.
GRATUZE, B., PACTAT, I., and SCHIBILLE, N., 2018. Changes in the Signature of Cobalt Colorants in Late Antique and Early Islamic Glass Production. *Minerals*, 8, 255. DOI: 10.3390/min8060225.
HAN, V., 1971a. Arhivske vesti o staklu u Dubrovniku iz XIV I prve polovine XV veka. *Zbornik Muzeja primenjene umetnosti, Beograd*, 15, 41–66.
HAN, V., 1971b. Prilog poznavanju dubrovačkog staklarstva XVI veka, staklo muranskog majstora Đovanija Tambarlina. *Prilozi za književnost, jezik, istoriju i folklor, Beograd*, 37(3–4), 213–225.
HAN, V., 1973. Fifteen and sixteen century trade in glass between Dubrovnik and Turkey. *Balcanica*, 4, 163–178.
HAN, V., 1974. Problèmes relatifs à l'identification de l'ancienne verrerie ragusaine. *Balcanica*, 5, 215–233.
HAN, V., 1975. The origin and style of medieval glass found in the central Balkans. *Journal of Glass Studies*, 17, 114–126.
HAN, V., 1979. Vitroi u srednjovekovnom Dubrovniku, *Zbornik Narodnog muzeja u Beogradu*, 9–10, 455–468.
HAN, V., 1981. Tri veka dubrovačkog staklarstva (XIV–XVI vek). In: *Posebna izdanja Balkanološkog instituta, knjiga 11.* Beograd: Srpska akademija nauka i umetnosti, pp. 295–297.
HORVAT-LEVAJ, K., 2016. The historic interpretation of the Cathedral. In: K. Horvat-Levaj, ed. *The Cathedral of the Assumption of the Virgin in Dubrovnik*. Dubrovnik – Zagreb: Gradska župa Gospe Velike, Institut za povijest umjetnosti, pp. 25–30.
IGNATIADOU, D., and ANTONARAS, A., 2011. *Dictionary of ancient and medieval glassworking – terminology, technology, typology.* Kraljevo: Zavod za zaštitu spomenika kulture Kraljevo, Serbia.
JACKSON, C.M., 2006. Compositional analysis of the Gnalić glass. In: I. Lazar and H. Willmott, eds. *The glass from the Gnalić wreck*. Koper, Piran: Univerza na Primorskem, Znanstveno-raziskovalno središče Koper, Inštitut za dediščino Sredozemlja, Annales, Piran, pp. 87–95.
JOVANOVIĆ, M., 1975. Etudes chimiques du verre médiéval trouvé dans certaines régions de la Yougoslavie. In: *Srednjovekovno staklo na Balkanu (V–XV vek). Verre médiéval aux Balkans (Ve–XVe s.), Recueil des travaux conférence internationale*. Beograd: Balkanološki institut, pp. 219–224.
KOS, M., 2007. *15th and 16th century glass in the collection of the National Museum of Slovenia.* Ljubljana: National Museum of Slovenia.
LANE, F.C. 1973. *Venice, A Maritime Republic.* Baltimore: John Hopkins University Press.
MCCRAY, W.P., 1998. Glassmaking in Renaissance Italy: The Innovation of Venetian Cristallo, *JOM*, 50, 14–19.
MORETTI, C., and TONIATO, T., eds., 2001. *Ricette vetrarie del Rinascimento. Trascrizione da un manoscritto anonimo veneziano.* Venice: Marsilio Editori.
NOIROT, C., CORMIER, L., SCHIBILLE, N., MENGUY, N., TRCERA, N., and FONDA, E., 2022. Comparative investigation of red and orange Roman tesserae: Role of Cu and Pb in colour formation. *Heritage*, 5, 2628–2645. DOI: 10.3390/heritage5030137
OCCARI, V., FREESTONE, I.C., and FENWICK, C., 2021. Raw materials and technology of Medieval Glass from Venice: The Basilica of SS. Maria e Donato in Murano. *Journal of Archaeological Science – Reports*, 37, 102981.
PAYNTER, S., and JACKSON, C., 2016. Re-used Roman rubbish: a thousand years of recycling glass. *European Journal of Postclassical Archaeologies*, 6, 31–52.
PEKOVIĆ, Ž., 1998. *Dubrovnik, Nastanak i razvoj srednjovjekovnoga grada.* Split: Muzej hrvatskih arheoloških spomenika.
PHELPS, M., 2018. Glass supply and trade in early Islamic Ramla: An investigation of the plant ash glass. In: D. Rosenow, M. Phelps, A. Meeks, and I. Freestone, eds. *Things that Travelled: Mediterranean Glass in the First Millennium CE*. London: UCL Press, pp. 236–282.
STOŠIĆ, J., 1988. Prikaz nalaza ispod Katedrale i Bunićeve poljane u Dubrovniku. In: *Arheološka istraživanja u Dubrovniku I dubrovačkom području*. Zagreb: Izdanja Hrvatskog arheološkog društva, 12, pp. 15–38.
SHORTLAND, A., ROGERS, N., and EREMIN, K., 2007. Trace element discriminants between Egyptian and Mesopotamian Late Bronze Age glasses, *Journal of Archaeological Science*, 34, 781–789.
SCHIBILLE, N., 2011. Late Byzantine mineral soda high alumina glasses from Asia Minor: A new primary glass production group. *PloS One*, 6, e18970.
SCHIBILLE, N., STERRETT-KRAUSE, A., and FREESTONE, I.C., 2017. Glass groups, glass supply and recycling in late Roman Carthage.

Archaeological and Anthropological Sciences, 9, 1223–1241.

SCHIBILLE, N., 2022. *Islamic Glass in the Making: Chronological and Geographical Dimensions.* Leuven: Leuven University Press.

STOŠIĆ, J., 1988. *Prikaz nalaza ispod katedrale i Bunićeve poljane u Dubrovniku.* Zahreb: Izdanja Hrvatskog arheološkog društva, 12.

STOŠIĆ, J., 1989. Istraživanja, nalazi i problemi prezentacije pod katedralom i Bunićevom poljanom. In: S. Knežević, ed. *Obnova Dubrovnika 1979–1989.* Dubrovnik: Zavod za obnovu Dubrovnika, pp. 326–335.

STULLI, B., 2001. *Studije iz povijesti Dubrovnika.* Zagreb: Konzor.

ŠMIT, Ž., JANSSENS, K., SCHALM, O., and KOS, M. 2004: Spread of façon-de-Venise glassmaking through central and western Europe. *Nuclear Instruments and Methods in Physics Research B*, 213, 717–722.

ŠMIT, Ž., JANSSENS, K., BULSKA, E., WAGNER, B., KOS, M., and LAZAR, I., 2005. Trace element fingerprinting of façon-de-Venise glass. *Nuclear Instruments and Methods in Physics Research B,* 239, 94–99.

ŠMIT, Ž., STAMATI, F., CIVICI, N., VEVECKA-PRIFTAJ, A., KOS, M., and JEZERŠEK, D., 2009. Analysis of Venetian-type glass fragments from the ancient city of Lezha (Albania). *Nuclear Instruments and Methods in Physics Research B*, 267, 2538–2544.

ŠMIT, Ž., KNIFIC, T., JEZERŠEK, D., and ISTENIČ, J., 2012. Analysis of early medieval glass beads – Glass in the transition period. *Nuclear Instruments and Methods in Physics Research B*, 278, 8–14.

ŠMIT, Ž., 2019. Glass analysis in relation to historical questions. In: N. Palincaş, and C.C Ponta, eds. *Bridging science and heritage in the Balkans: studies in archaeometry, cultural heritage restoration and conservation*. Oxford: Archaeopress, pp. 103–109.

ŠMIT, Ž., 2020. Physics beyond PIXE. *Nuclear Instruments and Methods in Physics Research B*, 477, 13–18.

ŠMIT, Ž., 2023. XANTHO – A simple basic program for fitting X-ray spectra. *Nuclear Instruments and Methods in Physics Research B*, 540, 19–23.

TOPIĆ, N., BOGDANOVIĆ RADOVIĆ, I., FAZINIĆ, S., and SKOKO, Ž., 2016. Analysis of Medieval and Post-medieval glass fragments from the Dubrovnik region, Croatia. *Archaeometry*, 58, 574–592.

TOPIĆ, N., BOGDANOVIĆ RADOVIĆ, I., FAZINIĆ, S., ŠMIT, Ž., SIJARIĆ, M., GUDELJ, L., and BURIĆ, T., 2019. Compositional analysis of Late Medieval glass from the western Balkan and eastern Adriatic hinterland. *Archaeological and Anthropological Sciences*, 11, 2347–2374.

VAN DER LINDEN, V., BULTINCK, E., DE RUYTTER, J., SCHALM, O., JANSSENS, K., DEVOS, W., and TIRI, W., 2005. Compositional analysis of 17–18th century archaeological glass fragments, excavated in Mechelen, Belgium: Comparison with data from neighbouring cities in the Low Countries. *Nuclear Instruments and Methods in Physics Research B*, 239, 100–106.

VERITÀ, M., 2013. Venetian Soda Glass. In: K. Janssens, ed. *Modern Methods for Analysing Archaeological and Historical Glass*. Hoboken: John Wiley & Sons, pp. 515–536.

VERITÀ, M., and ZECCHIN, S., 2009. Thousand years of Venetian glass: The evolution of chemical composition from the origins to the 18th century. In: K. Janssens, ed. *Annales du 17e Congrès de l'Association Internationale pur l'Histoire du Verre (AIHV)*. Antwerp: University Press Antwerp, pp. 602–613.

WEDEPOHL, K.H., and BAUMANN, A., 2009. The Use of Marine Molluscan Shells for Roman Glass and Local Raw Glass Production in the Eifel Area (Western Germany). *Naturwissenschaften*, 87, 129–132.

WELDEAB, S., EMEIS, K.-C., HEMLEBEN, C., and SIEBEL, W., 2002. Provenance of lithogenic surface sediments and pathways of riverine suspended matter in the Eastern Mediterranean Sea: evidence from $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}$ Sr ratios. *Chemical Geology*, 186, 139–149.