Raw materials and technology of Medieval Glass from Venice: the Basilica of SS. Maria e Donato in Murano

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Veronica Occari*, Ian C. Freestone, Corisande Fenwick

6 UCL Institute of Archaeology, 31-34 Gordon Square, London WC1H 0PY, UK

8 *Corresponding author: <u>veronica.occari.16@ucl.ac.uk</u> (V. Occari)

10 Abstract: Assemblages of medieval glass from Venice, the leading glassmaking centre in Europe, are 11 rarely accessible for analysis. Here we present electron microprobe analyses of sixty-one glass vessels 12 dated to between the 12th and 15th centuries from the island of Murano, which from the late 13th century 13 was the centre of glass production in the city. All appear to have used the same type of soda ash, with 14 similar levels of soda, magnesia, potash and phosphate and this is likely to have originated in the 15 Levant. The alumina, iron and titanium contents suggest that three different silica sources have been 16 used for the glass. Comparison with the available data from Venice and elsewhere in northern Italy 17 suggests that the assemblage may include material made on the island. Furthermore, there are 18 similarities with glass from the Levant and Egypt raising the possibility that raw glass from several 19 regions may be represented. However, records indicate that Venice imported sand as well as raw 20 glass from the Levant, which remains a possibility in the present case.

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Keywords: Medieval glass technology; Venetian glass; Levantine plant ash glass; Egyptian plant ash
 glass

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1. Introduction

27 The city of Venice rose to become the leading producer of glass in the European Renaissance 28 $(15^{\text{th}}-17^{\text{th}} \text{ centuries})$ and its products were exported across the world (Tait 1979). Documentary 29 evidence in the Venetian Archives suggests a more-or-less uninterrupted tradition of glassworking 30 from at least the tenth century, and certainly by the mid-thirteenth century Venice was importing raw 31 materials such as sand and ash from the eastern Mediterranean, indicating that her artisans were 32 manufacturing raw glass at that time (Zecchin, 1990:175, 1987:5). However, the origins of this 33 industry are still not fully understood. The remains of a glass workshop on the nearby island of 34 Torcello in the seventh century has been considered as early evidence of a Venetian glass industry 35 (Leciejewicz, 2002, 2000; Leciejewicz et al., 1977; Tait, 1979) but the presence of mosaic tesserae in 36 the workshop (Tabaczinska, 1968) places it with workshops excavated elsewhere in Italy where the 37 activity was based upon the recycling of old Roman natron glass (Bertini et al., 2020; Schibille and 38 Freestone, 2013; Silvestri and Marcante, 2011). The comment by Tait (op. cit.: 9) that "distressingly 39 little has survived to support....an unbroken history of Venetian glassmaking from Roman times"

40 remains true.

41 Venetian glass was a soda-lime-silica type, based upon fusing the ashes of halophytic plants 42 with silica. This is the technology adopted across the Middle East following the demise of the natron 43 tradition in the 9th century (Phelps *et al.*, 2016; Schibille *et al.*, 2019). Venice was an important trading 44 nation and it has been suggested that Near Eastern plant ash glass technology was directly transferred 45 to the city through its trading network (Jacoby, 1993; Whitehouse, 2014). Furthermore, in 1124 46 Venice laid siege to and conquered the city of Tyre, where it maintained an enclave until its conquest 47 by the Mamluks in 1291. Literary and documentary evidence shows that Tyre was well known as a 48 source of high-quality glass material (Carboni et al., 2003) and it was the location of a major 49 production site of raw glass (10th-11th century), excavated by Jennings et al. (2001) (Aldsworth et al., 50 2002). Implicit in the documents is that raw glass was transported from Tyre to Venice and 51 Whitehouse has suggested the possibility that Tyre played a role in the transmission of glassmaking 52 know-how to Venice (in Carboni et al., op. cit.: 149). On the other hand, since plant ash glass was 53 widely used in Italy during the medieval period (Cagno et al., 2008, 2010, 2012a; Gallo and Silvestri, 54 2012; Posedi et al., 2019), the technology might have come to Venice through some other Italian 55 centre.

56 Both documentary and archaeological evidence (Carboni and Whitehouse, 2001; Krueger, 57 2018; Mack, 2002; Mathews, 2014; Zecchin, 1990, 1989, 1987) have shown that significant exchange 58 of glass raw materials and entire objects between the Islamic world and Italy took place throughout 59 the medieval period. The issues around the origin of Venetian glassmaking should therefore be 60 amenable to investigation through the analysis of the glass materials. However, while decorative 61 Venetian glass of the Renaissance has been subjected to intensive study (Biron and Verità, 2012; 62 Janssens et al., 2013; McCray, 1999, 1998; Šmit et al., 2005, 2004; Thornton et al., 2014; Verità, 63 1985; Verità and Zecchin, 2009b, 2008) the history of Venetian glass production prior to the 15^{th} 64 century, and its relationship with other glassmaking industries such as those in the Islamic World, 65 have not been addressed in any detail.

66 The present paper is part of a larger project on the technology of medieval glass from Venice 67 which addresses key questions related to the raw materials used and their provenance. It concerns 68 the compositional investigation of glass retrieved from the Basilica of SS. Maria e Donato in Murano, 69 dated between the 12th and 15th century. The results are used to investigate the raw materials employed, 70 to assess compositional similarities with other medieval Venetian and Italian glass assemblages as well 71 as to identify analogies with glass from the Eastern Mediterranean.

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2. Archaeological context

The Basilica of SS. Maria e Donato is located in Murano, the island where all Venetian glassmaking was located from 1291 A.D, when a decree emitted by the State banned the presence of furnaces in Venice and relocated the production of glass to the island of Murano, mainly for safety 77 reasons but also to have better ventilation and to provide more space for the workshops (Zecchin 78 1987:6). The church was probably founded in the 7th century A.D., restored in the 9th century A.D. 79 then rebuilt in the first half of the 12th century (Gasparetto, 1977). A new external building, which 80 comprised two sacristies, was added to the basilica and was probably built in the 16^{th} and 17^{th} centuries 81 (ibid). Between the end of the 17th century and the first half of the 19th century, a series of haphazard 82 building works altered the structure of the Basilica to the point that its stability was severely 83 compromised. In 1858, the Austrian government, which was at the time ruling Venice, directed a 84 series of restoration works in order to stabilise and conserve the church. During these works, in 1866, 85 the small external building which served as a sacristy, adjacent to the south-east corner of the right 86 nave of the basilica, was demolished. In 1973-6, a significant number of archaeological glass fragments 87 were found in this area during consolidation works on the church foundations and floor (Gasparetto, 88 1977) The glass was found in a small brick-made cell, circa 30x30 cm, at the level of the church floor, 89 which is lower than the external trampling floor. Its date and function are unclear. This cell might 90 have been made during the demolition in 1866 for the workers to deposit the glass fragments found 91 in the sacristy. Another possibility is that it was a sort of *sacrarium* (which is usually located 92 underground) where broken and unused glasses were discarded together with the holy water 93 employed in purification rituals. It could also have been a collection of broken ecclesiastical glass 94 kept for recycling (Marii and Rehren, 2009). No evidence of a glass workshop was found.

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3. Materials and methods

97 *3.1 Glass finds*

98 About 80 glass fragments were retrieved in the basilica of which 61 which presented indicative 99 features have been analysed (Tab.1). The chrono-typological characterisation of the finds will not be 100 discussed in detail here as it can be found in Gasparetto (1977). According to Gasparetto, (1977, 101 1979) the finds can be dated between the 12th and the 15th centuries; all were for common use and 102 include, bottles, beakers, lamps, window glass and liturgical ampoules (Tabs.1 and 2, Figs.1 and 2). 103 The bottles show varying typological features such as in the shape of the upper part of the neck and 104 in the shape of the rims. All the bottles analysed here belong to the typical Venetian "inghistere": with 105 a long neck and pot-bellied, mostly used to contain water and wine (Gasparetto, 1977) (Figs.1,2 and 106 Tab 2). Beakers of the same type analysed here are known to have been produced in Murano and 107 are the flat-based beaker called in the Venetian documents "moioli" (Gasparetto, 1979, 1958:87; 108 Zecchin, 1990:133). Glass lamps of the type analysed were called "cesendelli", a term that appears in 109 Venetian archives for the first time in 1313 (Zecchin 1990:137).

110 The finds are made of colourless, bluish-green, yellow and grey glass. No opaque glasses have111 been found. All the glasses are iridescent due to surface weathering.



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 $\begin{array}{c}112\\113\end{array}$ Figure 1: Examples of the inghistere bottles analysed. The differences in shape of the bottle necks are clearly visible.

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Table 1: Identified forms along with the number of samples analysed per type and colour of the samples.

Туре	No. analysed	Colour
Inghistera or anghistera	30	Weak blue, weak grey
Flat-based beakers	3	Weak blue
Hanging lamps "cesendelli"	3	Weak blue
Ampoules	11	Weak blue, weak grey
Window glass	3	Weak grey
Unidentified Fragments	11	Weak blue, weak grey

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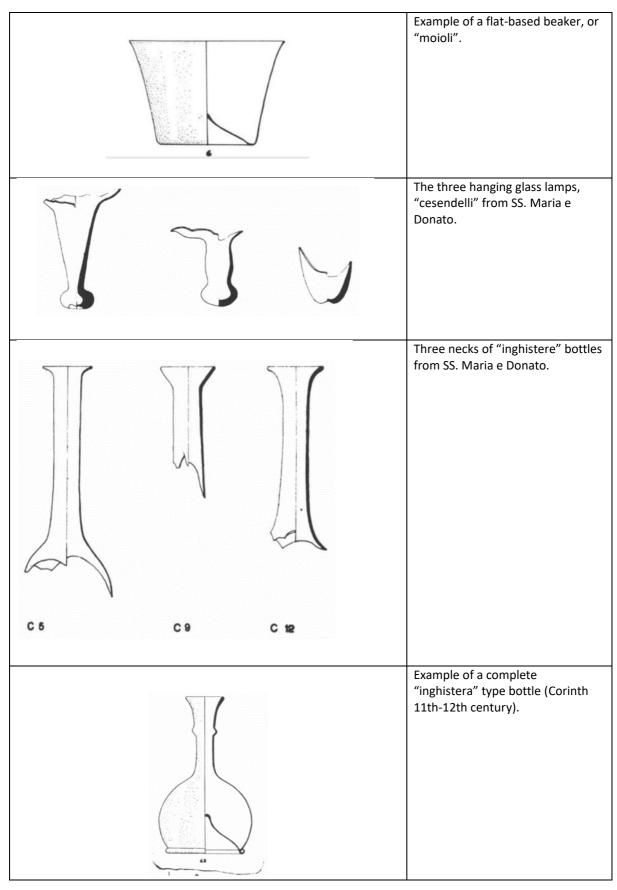




Figure 2:Representation of the typical medieval inghistera and liturgical ampoule in a 14th century fresco by Taddeo Gaddi in the Santa Croce Church, Florence. (Picture from: "Portale di Archeologia Medievale, Università di Siena, 126 Dipartimento di Scienze Storiche).

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128 Nonetheless, the finds cannot be securely attributed to Venetian production. Gasparetto 129 (1977:79) highlighted the presence of motifs and stylistic features which were widely used in the 130 Byzantine and Islamic world, such as the "inverted cone" shape of the mouths of some of the bottles 131 (e.g. C9 in Table 2), typical of some Syrian and Egyptian medieval bottles; the similarity of the hanging 132 lamps to those used in the Byzantine territories as well as later under Islamic administration. Given 133 the location of the assemblage on Murano and given that Venetian glass production had already 134 reached a substantial scale in the 13th century (Verità, 2013; Zecchin, 1987:6), some of these glasses 135 may represent an attempt of the Venetian glassmakers to imitate these characteristics (Gasparetto 136 1977). Just as it has been assumed that glass fragments retrieved from the Venetian lagoon were made 137 in local factories (Verità, 2013; Verità and Zecchin, 2009a), we assume that the vessels analysed here 138 were blown in Venice, although the raw glass may not have been there.

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140 3.2 Electron Probe Micro-analysis

141 61 samples were chosen for analysis, which included every form and typology identified in 142 the assemblage, as well as some unidentified fragments that were available. Small fragments of glass 143 of 2-3 mm³ were removed from the samples, embedded in epoxy resin, ground, polished using a 144 diamond paste up to 1 µm and then carbon coated. They were analysed using a JEOL EPMA JXA-145 8100 electron microprobe with three wavelength dispersive spectrometers, operated at 15 kV 146 accelerating potential, beam current 50 nA, working distance of 11mm, and a magnification of 800x 147 so that the areas analysed were of approximately $150 \times 110 \,\mu\text{m}$. Counting times were 20s for each peak

148 and 10s for each background for most elements, while for Al, Mg, Co, Zn, Ba, Fe, Ti, S, P, Cu, Sb, 149 Sn, Sr counting times were 60s on peak and 30s off for the background. The standards used for 150 calibration were a combination of pure elements, oxides and minerals of well-known composition. 151 Every sample was analysed 5 times in different areas and a mean composition calculated. Corning 152 Museum Glass Standards A and B (Brill, 1999) were measured several times at the beginning and at 153 the end of the analytical run (end of Tab. 3). Relative standard deviations were better than 0.2% and 154 15% for the major and minor elements respectively. Relative accuracy was better than 2% for SiO₂, 155 K₂O and Fe₂O₃, better than 5% for Na₂O, Al₂O₃, TiO₂, CaO, MnO, Sb₂O₃, SO₃, better than 10% for 156 MgO and usually not worse than 20% for the other minor elements (Tab.3). Detection limits varied 157 on the basis of the matrix of the samples, but they were about 0.03% for all elements for these 158 operational conditions. The analyses were performed at the Wolfson Archaeological Science 159 Laboratories, UCL Institute of Archaeology.

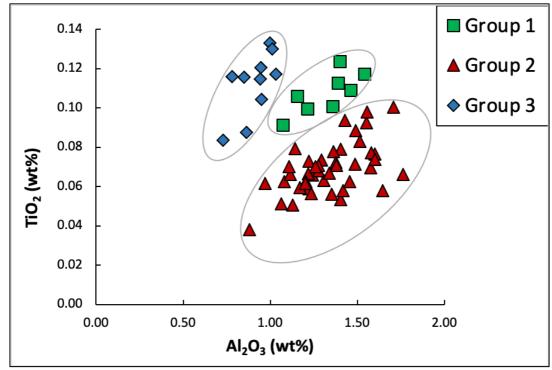
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4. Results

162 The electron microprobe results are presented in Tab. 3. All samples are soda-lime-silica 163 glass with relatively high levels of potash (K₂O) and magnesia (MgO) over 2%, consistent with the use 164 of soda ash as a flux (Lilyquist and Brill, 1993). Alumina ranges from 0.73 to 1.76%, and iron oxide from 0.28 to 0.72%. Manganese is present in variable quantities between 0.04 % and 1.56%. In most 165 166 of the glasses manganese was probably added intentionally as a glass decolouriser in order to 167 counteract the colouring effect of the iron (Savre, 1963) as it is high relative to the amount naturally 168 present in soda plant ashes (<0.06%; Barkoudah and Henderson, 2006) and in glassmaking sands 169 (around 0.02%; e.g. Schibille et al. 2017; Phelps et al. 2016).

The glasses analysed can be divided into three compositional groups, according to their differing amounts of alumina and titanium oxide (Fig. 3), which can be considered to represent the feldspar and heavy mineral contents of the glassmaking sand respectively (Freestone *et al.*, 2018; Schibille *et al.*, 2017). Mean group compositions are provided in Table 4. Differences between Groups 2 and 3 may be also observed in terms of iron oxide versus alumina (Fig.4); although Group 1 overlaps with the high iron glass of Group 2 in this figure, it is not identical and typically has a relatively high Fe₂O₃/Al₂O₃ ratio.

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185 Figure 3: Compositional groups based on the mineralogy of the sand showing the subdivision into three groups.
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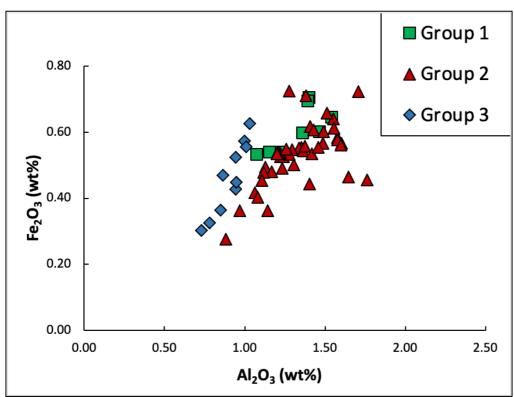




Figure 4: Biplot of iron oxide versus alumina for the groups identified. Differences mainly between group 3 and the other groups can be observed (colour in print).

190 In contrast to the concentrations of alumina, titanium and iron oxides, those of silica, soda, 191 potash and magnesia are very similar across all three identified groups. The presence in ten samples 192 of contamination by colourants and opacifiers such as lead, tin and copper oxides, in concentration between 100 ppm and 1000 ppm, are generally interpreted as an indication of recycling: these are
incorporated to the glass when small amounts of coloured glass are included (Ceglia *et al.*, 2019;
Freestone, 2015; Silvestri *et al.*, 2008).

196 <u>Group 1</u> encompasses a small group of eight samples and comprises beakers, bottle bases
197 and necks. It is characterised by relatively low contents of calcium oxide (mean 8.76%), moderate
198 contents of alumina (mean 1.33%) and relatively high contents of titanium oxide (mean 0.11%) (Table
199 4). Iron oxide, introduced as an impurity with the sand, is present in moderate quantities of on average

200 0.61% (Fig.4).

201 <u>*Group 2*</u> represents the majority of the glass fragments, encompassing 43 samples. This group 202 includes a range of forms such as bottle necks, beakers and bottle bases, window sheets, ampoules 203 and one lamp. The composition of this group resembles Group 1 in terms of both plant ash and sand 204 related elements, but it has significantly less titania (mean 0.07%), suggesting different sands were used 205 to make the glass (Table 4, Fig. 3).

206 <u>Group 3</u> is made of 10 samples and comprises one window fragment, one lamp, and several
207 beaker bases and bottle necks. It has the highest contents of lime with a mean content of 10.83%.
208 Group 3 differs significantly from all the other groups in terms of the sand-related elements (Table
209 4), having significantly lower alumina (mean 0.91%), slightly lower iron yet relatively high titania (mean

210 0.11%). It is therefore clearly separated in terms of TiO_2/Al_2O_3 and Fe_2O_3/Al_2O_3 ratios (Figs. 3, 4).

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Sample name	Glass type	Colour	Group	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	MgO	CaO	MnO	CuO	SnO ₂	ZnO	PbO	P ₂ O ₅	Cl	SO₃	BaO	Total
GB 1	Beaker base	Weak blue	1	69.3	1.4	0.71	0.12	10.9	3.04	3.39	7.84	0.41	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.4	0.72	0.23	0.03	98.51
sd				2.32	0.04	0.01	0.01	0.10	0.04	0.03	0.11	0.02	-	-	-	-	0.03	0.02	0.01	0.02	
PMPI 2	Beaker wall	Weak blue	1	71.32	1.39	0.69	0.11	11.04	3.05	3.37	7.84	0.37	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.36	0.74	0.23	0.03	100.57
sd				2.13	0.04	0.01	0.01	0.14	0.08	0.04	0.08	0.04	-	-	-	-	0.02	0.02	0.01	0.01	
F 8	Vessel Fragment	Weak blue	1	73.02	1.36	0.6	0.1	10.72	2.27	3.29	8.65	0.49	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.27	0.63	0.24	0.03	101.76
sd				0.34	0.04	0.02	0.01	0.07	0.04	0.08	0.07	0.02	-	-	-	-	0.02	0.02	0.01	0.03	
F 10	Vessel Fragment	Weak blue	1	74.18	1.07	0.53	0.09	11.77	2.1	3.35	8.95	0.26	b.d.l.	0.04	0.04	0.06	0.27	0.72	0.31	0.04	103.83
sd				0.46	0.01	0.01	0.02	0.16	0.02	0.02	0.12	0.03	-	0.02	0.02	0.02	0.01	0.02	0.02	0.02	
GB 2	Beaker base	Weak blue	1	72.65	1.46	0.6	0.11	10.71	2.33	3.39	8.95	0.48	b.d.l.	b.d.l.	0.03	b.d.l.	0.27	0.67	0.23	0.04	101.93
sd				0.49	0.04	0.01	0.01	0.08	0.05	0.03	0.08	0.02	-	-	0.00	-	0.02	0.01	0.02	0.02	
C 12	Bottle neck	Weak blue	1	68.78	1.22	0.54	0.1	12.69	2.12	3.6	8.96	0.28	b.d.l.	0.04	0.04	0.05	0.27	0.7	0.31	0.03	99.74
sd				1.89	0.03	0.02	0.01	0.11	0.02	0.02	0.06	0.03	-	0.01	0.01	0.03	0.01	0.01	0.01	0.01	
PI11	Bottle base	Weak blue	1	67.34	1.15	0.54	0.11	11.8	2.08	3.45	9.05	0.26	b.d.l.	0.04	0.05	0.06	0.27	0.72	0.29	0.04	97.28
sd				0.93	0.03	0.01	0.01	0.06	0.03	0.01	0.08	0.01	-	0.01	0.03	0.02	0.01	0.02	0.02	0.02	
C 20	Bottle neck	Weak blue	1	70.26	1.54	0.65	0.12	11.6	2.35	3.01	9.88	0.54	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.28	0.74	0.17	b.d.l.	101.25
sd				0.47	0.04	0.02	0.01	0.06	0.06	0.06	0.05	0.02	-	-	-	-	0.02	0.02	0.01	-	
B 16	Ampoule	Weak blue	2	69.98	1.22	0.53	0.06	11.81	2.3	3.53	7.4	0.48	b.d.l.	b.d.l	b.d.l.	b.d.l.	0.34	0.7	0.26	0.04	98.69
sd				0.87	0.02	0.02	0.01	0.04	0.03	0.03	0.13	0.01	-	-	-	-	0.02	0.02	0.02	0.01	
C 16 tr	Bottle neck	Weak grey	2	72.85	1.13	0.5	0.05	13.09	2.45	3.1	8.52	0.53	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.24	0.73	0.27	0.03	103.55
sd				1.28	0.02	0.02	0.01	0.18	0.05	0.04	0.14	0.03	-	-	-	-	0.02	0.01	0.02	0.01	
PI12	Bottle base	Weak grey	2	74.48	0.97	0.36	0.06	11.74	2.33	3.33	8.55	0.34	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.22	0.75	0.27	0.02	103.47
sd				2.69	0.01	0.01	0.01	0.07	0.04	0.03	0.13	0.02	-	-	-	-	0.03	0.01	0.02	0.02	
F 3	Vessel Fragment	Weak blue	2	69.43	1.24	0.53	0.07	11.64	2.24	3.52	8.65	0.37	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.26	0.71	0.27	0.03	99.03
sd				1.78	0.03	0.02	0.01	0.12	0.03	0.02	0.10	0.01	-	-	-	-	0.02	0.02	0.02	0.02	
C 2	Bottle neck	Weak grey	2	65.57	1.6	0.57	0.08	13.38	2.47	3.98	8.66	0.18	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.29	0.71	0.3	0.01	97.87
sd				1.73	0.04	0.01	0.01	0.12	0.02	0.03	0.10	0.01	-	-	-	-	0.01	0.02	0.01	0.01	

Sample name	Glass type	Colour	Group	SiO ₂	AI_2O_3	Fe_2O_3	TiO ₂	Na ₂ O	K ₂ O	MgO	CaO	MnO	CuO	SnO ₂	ZnO	PbO	P_2O_5	Cl	SO₃	BaO	Total
VP4	Window fragment	Weak grey	2	68.47	1.14	0.36	0.08	12.88	2.44	3.63	8.67	0.76	b.d.l.	b.d.l.	0.03	b.d.l.	0.26	0.68	0.26	0.03	99.75
sd				0.95	0.02	0.01	0.01	0.12	0.05	0.02	0.07	0.02	-	-	0.03	-	0.02	0.03	0.01	0.02	
B6	Ampoule	Weak blue	2	68.77	1.58	0.58	0.08	13.77	2.52	4	8.72	0.17	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.3	0.72	0.31	bdl	101.56
sd				0.93	0.02	0.02	0.01	0.03	0.01	0.03	0.04	0.01	-	-	-	-	0.01	0.01	0.00	-	
C3	Bottle neck	Weak blue	2	67.17	1.35	0.55	0.06	12.55	2.25	4.06	8.72	0.53	b.d.l.	b.d.l.	0.03	b.d.l.	0.28	0.76	0.28	0.02	98.68
sd				1.77	0.02	0.01	0.01	0.09	0.03	0.03	0.06	0.02	-	-	0.01	-	0.02	0.01	0.01	0.01	
B 14	Ampoule	Weak grey	2	64.36	1.4	0.44	0.05	12.43	2.63	3.93	8.75	0.42	b.d.l.	b.d.l.	0.03	b.d.l.	0.25	0.62	0.29	b.d.l.	95.63
sd				0.62	0.03	0.01	0.01	0.12	0.04	0.02	0.14	0.02	-	-	0.01	-	0.02	0.02	0.02	-	
C 8	Bottle neck	Weak blue	2	71.26	1.31	0.5	0.06	11.19	2.37	3.6	8.76	0.48	b.d.l.	b.d.l.	0.05	b.d.l.	0.27	0.61	0.3	0.03	100.84
sd				2.03	0.03	0.01	0.00	0.10	0.04	0.02	0.08	0.03	-	-	0.01	-	0.02	0.01	0.01	0.02	
B1	Ampoule	Weak blue	2	67.9	1.34	0.55	0.07	12.55	2.35	3.67	8.86	0.38	b.d.l.	b.d.l.	0.03	b.d.l.	0.28	0.68	0.26	0.04	98.95
sd				0.50	0.02	0.01	0.01	0.07	0.01	0.06	0.09	0.02	-	-	0.02	-	0.01	0.01	0.02	0.02	
Co504	Vessel Fragment	Weak blue	2	69.76	0.88	0.28	0.04	12.95	2.37	3.21	8.88	0.17	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.23	0.74	0.31	b.d.l.	99.87
sd				0.68	0.02	0.02	0.00	0.11	0.02	0.02	0.12	0.01	-	-	-	-	0.01	0.02	0.01	-	
C7	Bottle neck	Weak blue	2	74.01	1.29	0.55	0.07	11.68	2.32	3.07	8.94	0.47	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.34	0.76	b.d.l.	b.d.l.	103.79
sd				0.28	0.02	0.01	0.01	0.17	0.05	0.04	0.13	0.02	-	-	-	-	0.04	0.01	-	-	
B 13	Ampoule	Weak grey	2	71.68	1.06	0.42	0.05	12.28	2.11	3.71	8.94	0.5	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.25	0.72	0.32	0.03	102.15
sd				0.70	0.04	0.01	0.01	0.09	0.01	0.03	0.14	0.03	-	-	-	-	0.01	0.01	0.01	0.01	
F 5	Vessel Fragment	Weak blue	2	70.72	1.28	0.53	0.07	11.78	2.29	3.49	9	0.38	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.3	0.69	0.31	0.03	100.88
sd				1.41	0.04	0.01	0.01	0.04	0.03	0.05	0.12	0.01	-	-	-	-	0.02	0.02	0.01	0.01	
F1	Vessel Fragment	Weak blue	2	64.82	1.58	0.58	0.07	12.09	2.33	4.18	9	0.65	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.29	0.67	0.32	b.d.l.	96.57
sd				0.82	0.05	0.01	0.01	0.07	0.03	0.02	0.18	0.03	-	-	-	-	0.03	0.02	0.01	-	
B8	Ampoule	Weak blue	2	69.6	1.22	0.54	0.07	11.54	2.23	2.95	9.07	0.43	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.4	0.77	b.d.l.	0.04	99.06
sd				1.23	0.04	0.01	0.01	0.08	0.02	0.08	0.07	0.01	-	-	-	-	0.01	0.02	-	0.02	
C 13	Bottle neck	Weak grey	2	70.43	1.08	0.4	0.06	12.43	2.29	3.71	9.13	0.71	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.26	0.71	0.32	0.03	101.65
sd				0.51	0.01	0.01	0.01	0.12	0.02	0.02	0.07	0.03	-	-	-	-	0.01	0.02	0.01	0.02	
F7	Vessel Fragment	Weak blue	2	68.24	1.41	0.62	0.08	12.67	2.06	3.5	9.15	0.21	b.d.l.	b.d.l.	0.05	b.d.l.	0.3	0.69	0.29	b.d.l.	99.32
sd				0.92	0.05	0.01	0.01	0.07	0.03	0.02	0.04	0.01	-	-	0.03	-	0.01	0.03	0.02	-	

Sample name	Glass type	Colour	Group	SiO ₂	AI_2O_3	Fe_2O_3	TiO ₂	Na ₂ O	K ₂ O	MgO	CaO	MnO	CuO	SnO ₂	ZnO	PbO	P_2O_5	Cl	SO₃	BaO	Total
C 10	Bottle neck	Weak grey	2	71.75	1.22	0.54	0.07	10.48	2.25	3.65	9.15	0.67	0.03	b.d.l.	0.04	b.d.l.	0.25	0.7	0.31	b.d.l.	101.14
sd				1.23	0.02	0.01	0.01	0.09	0.03	0.04	0.12	0.01	0.01	-	0.01	-	0.02	0.02	0.01	-	
F 4	Vessel Fragment	Weak blue	2	70.81	1.21	0.54	0.06	10.08	2.22	3.54	9.16	0.64	0.03	b.d.l.	0.04	b.d.l.	0.25	0.73	0.3	b.d.l.	99.65
sd				0.90	0.02	0.01	0.01	0.11	0.04	0.03	0.08	0.02	0.03	-	0.01	-	0.02	0.01	0.01	-	
PI15	Bottle base	Weak grey	2	62.49	1.64	0.47	0.06	13.04	2.53	3.97	9.22	0.4	b.d.l.	b.d.l.	0.03	b.d.l.	0.26	0.74	0.34	0.03	95.24
sd				0.60	0.04	0.00	0.01	0.05	0.04	0.03	0.09	0.02	-	-	0.01	-	0.01	0.04	0.01	0.01	
B 10	Ampoule	Weak blue	2	69.68	1.43	0.61	0.09	11.44	2.75	2.96	9.69	0.55	b.d.l.	b.d.l.	0.03	b.d.l.	0.43	0.76	0.21	0.05	100.7
sd				0.60	0.04	0.01	0.01	0.14	0.02	0.08	0.07	0.02	-	-	0.03	-	0.01	0.02	0.01	0.01	
C5	Bottle neck	Weak blue	2	72.33	1.49	0.6	0.09	11.52	2.75	3.09	9.54	0.56	b.d.l.	b.d.l.	0.04	b.d.l.	0.33	0.75	0.18	0.05	103.39
sd				0.62	0.02	0.02	0.01	0.10	0.03	0.01	0.08	0.02	-	-	0.01	-	0.02	0.01	0.01	0.02	
S1	Lamp	Weak blue	2	67.25	1.55	0.64	0.09	13.62	2.04	3.17	11.59	0.22	b.d.l.	b.d.l.	0.04	b.d.l.	0.3	0.79	0.24	b.d.l.	101.58
sd				2.54	0.02	0.01	0.02	0.14	0.05	0.04	0.06	0.01	-	-	0.01	-	0.02	0.02	0.01	-	
C9	Bottle neck	Weak blue	2	65.22	1.56	0.61	0.1	11.07	2.48	3.61	10.13	0.49	0.03	b.d.l.	0.03	0.05	0.33	0.61	0.23	0.03	96.6
sd				0.49	0.05	0.01	0.02	0.07	0.02	0.01	0.13	0.01	0.02	-	0.02	0.04	0.01	0.02	0.01	0.02	
LA	Lamp	Weak blue	2	69.3	1.71	0.72	0.1	11.74	2.62	3.51	11.78	0.92	0.03	b.d.l.	0.04	b.d.l.	0.33	0.63	0.23	0.04	103.74
sd				0.59	0.02	0.01	0.01	0.11	0.03	0.04	0.04	0.03	0.01	-	0.01	-	0.01	0.01	0.02	0.02	
S2	Bottle base	Weak blue	2	69.45	1.36	0.54	0.08	12.53	2.23	3.05	10.79	0.4	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.28	0.77	0.21	0.04	101.75
sd				0.84	0.03	0.01	0.01	0.10	0.03	0.05	0.09	0.02	-	-	-	-	0.01	0.01	0.01	0.02	
C 17	Bottle neck	Weak grey	2	66.89	1.51	0.66	0.08	12.89	2.7	3.14	10	0.71	b.d.l.	b.d.l.	0.03	b.d.l.	0.28	0.79	0.24	b.d.l.	99.94
sd				0.26	0.02	0.01	0.01	0.07	0.07	0.02	0.04	0.01	-	-	0.02	-	0.02	0.03	0.02	-	
Co3	Vessel Fragment	Weak blue	2	67.56	1.17	0.48	0.06	11.84	2.36	3.87	9.69	0.04	b.d.l.	b.d.l.	0.04	b.d.l.	0.28	0.57	0.34	b.d.l.	98.34
sd				1.08	0.03	0.01	0.01	0.13	0.03	0.04	0.11	0.01	-	-	0.02	-	0.01	0.02	0.01	-	
C 19	Bottle neck	Weak grey	2	66.59	1.6	0.56	0.07	14.29	2.36	3.65	9.71	1.18	0.04	b.d.l.	b.d.l.	b.d.l.	0.27	0.72	0.32	b.d.l.	101.48
sd				0.23	0.03	0.01	0.01	0.25	0.02	0.10	0.04	0.02	0.01	-	-	-	0.02	0.02	0.03	-	
VP1	Window fragment	Weak grey	2	64.16	1.28	0.72	0.07	11.22	2.38	4.3	9.93	0.46	b.d.l.	b.d.l.	0.05	0.03	0.27	0.72	0.38	0.05	96.07
sd				1.48	0.03	0.01	0.01	0.08	0.04	0.04	0.06	0.02	-	-	0.02	0.02	0.02	0.01	0.02	0.01	
Β7	Ampoule	Weak grey	2	69.42	1.38	0.56	0.07	13.03	2.45	3.86	9.93	0.35	b.d.l.	b.d.l.	0.03	0.03	0.26	0.7	0.3	b.d.l.	102.38
sd				0.50	0.03	0.01	0.01	0.18	0.02	0.05	0.08	0.02	-	-	0.02	0.02	0.02	0.02	0.02	-	

Sample name	Glass type	Colour	Group	SiO ₂	AI_2O_3	Fe_2O_3	TiO ₂	Na ₂ O	K ₂ O	MgO	CaO	MnO	CuO	SnO ₂	ZnO	PbO	P_2O_5	Cl	SO₃	BaO	Total
C6	Bottle neck	Weak blue	2	71.56	1.42	0.54	0.06	12.41	2.27	3.13	10.31	0.4	b.d.l.	b.d.l.	0.04	b.d.l.	0.22	0.74	b.d.l.	b.d.l.	103.37
sd				0.36	0.01	0.01	0.04	0.11	0.03	0.02	0.03	0.02	-	-	0.02	-	0.01	0.02	-	-	
C1 tr	Bottle neck	Weak grey	2	68.74	1.2	0.53	0.06	13.06	2.23	3.65	10.44	0.83	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.21	0.79	0.26	b.d.l.	102.14
sd				0.17	0.01	0.02	0.01	0.13	0.04	0.03	0.14	0.01	-	-	-	-	0.01	0.03	0.02	-	
B 15	Ampoule	Weak grey	2	62.99	1.49	0.57	0.07	11.13	2.21	4.12	10.45	1.56	b.d.l.	b.d.l.	0.03	b.d.l.	0.27	0.68	0.26	0.04	95.89
sd				1.00	0.05	0.01	0.01	0.10	0.03	0.04	0.09	0.05	-	-	0.02	-	0.01	0.02	0.02	0.02	
C4	Bottle neck	Weak grey	2	69.34	1.46	0.56	0.06	12.84	2.16	3.46	10.55	0.36	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.23	0.9	0.21	b.d.l.	102.21
sd				0.40	0.02	0.01	0.01	0.09	0.03	0.03	0.04	0.01	-	-	-	-	0.03	0.01	0.02	-	
B 11	Ampoule	Weak blue	2	68.97	1.23	0.49	0.06	12.72	2.23	3.05	10.6	1.24	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.26	0.85	b.d.l.	0.04	101.99
sd				0.71	0.03	0.01	0.01	0.15	0.05	0.02	0.05	0.03	-	-	-	-	0.02	0.01	-	0.02	
C 21	Bottle neck	Weak grey	2	67.25	1.76	0.46	0.07	14.12	2.45	3.6	10.64	0.37	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.23	0.78	0.26	b.d.l.	102.07
sd				0.32	0.04	0.01	0.00	0.16	0.03	0.03	0.11	0.02	-	-	-	-	0.03	0.02	0.03	-	
PI 13	Bottle base	Weak blue	2	70.23	1.26	0.55	0.07	11.67	2.33	2.98	10.85	0.56	b.d.l.	b.d.l.	0.04	b.d.l.	0.3	0.68	0.26	0.04	101.84
sd				0.52	0.01	0.01	0.01	0.13	0.02	0.04	0.10	0.03	-	-	0.02	-	0.02	0.01	0.02	0.01	
PI 1	Bottle base	Weak grey	2	70.4	1.12	0.48	0.07	11.59	2.11	2.99	10.95	1.03	b.d.l.	0.03	0.03	0.07	0.26	0.72	0.28	0.06	102.23
sd				0.51	0.04	0.01	0.01	0.03	0.05	0.02	0.13	0.02	-	0.03	0.01	0.03	0.01	0.02	0.02	0.02	
C	Bottle neck	Weak blue	2	67.95	1.38	0.71	0.07	11.86	2.28	3.49	11.03	1.07	b.d.l.	b.d.l.	0.03	b.d.l.	0.23	0.69	0.25	b.d.l.	101.14
sd	a			0.21	0.03	0.00	0.01	0.03	0.05	0.01	0.19	0.03	-	-	0.01	-	0.02	0.02	0.01	-	
PI 3	Bottle base	Weak grey	2	69.19	1.11	0.45	0.07	12.06	2.17	3.03	11.25	0.68	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.3	0.75	0.24	b.d.l.	101.41
sd VP3	Window fragment	Week grou	3	0.57 64.84	0.02 0.73	0.01 0.3	0.01 0.08	0.15 12	0.05 2.35	<i>0.03</i> 3.81	<i>0.03</i> 10.08	0.01 0.53	- b.d.l.	- b.d.l.	- 0.04	- b.d.l.	0.02 0.31	0.02 0.78	0.01 0.45	- 0.03	96.39
sd	window fragment	Weak grey	3	04.84 1.91	0.73	0.3	0.08	0.21	2.35 0.07	0.05	0.17	0.53	- -	J.U.I.	0.04	- -	0.31	0.78	0.45	0.03	90.39
Su C 14	Bottle neck	Weak grey	3	70.31	0.78	0.33	0.12	12.22	2.7	3.48	9.59	0.41	- b.d.l.	- b.d.l.	b.d.l.	- b.d.l.	0.25	0.71	0.35	b.d.l.	101.3
sd	Dottle Heek	WeakBrey	5	1.27	0.01	0.01	0.01	0.07	0.04	0.04	0.08	0.04	-	-	-	-	0.02	0.01	0.01	-	101.5
B5	Ampoule	Weak grey	3	67.5	0.85	0.36	0.12	12.03	2.09	3.71	10.55	0.44	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.27	0.71	0.38	b.d.l.	99.06
sd	, inpoure	incom Brey	0	1.28	0.03	0.01	0.01	0.14	0.02	0.03	0.07	0.01	-	-	-	-	0.02	0.03	0.02	-	55100
PI 8	Bottle base	Weak blue	3	70.27	0.86	0.47	0.09	11.99	2.02	2.82	11.06	0.44	b.d.l.	b.d.l.	0.03	b.d.l.	0.28	0.75	0.27	0.06	101.46
sd			-	0.37	0.03	0.01	0.01	0.09	0.03	0.05	0.19	0.01	-	-	0.02	_	0.01	0.02	0.02	0.02	

Sample name	Glass type	Colour	Group	SiO ₂	AI_2O_3	Fe_2O_3	TiO ₂	Na ₂ O	K ₂ O	MgO	CaO	MnO	CuO	SnO_2	ZnO	PbO	P_2O_5	Cl	SO₃	BaO	Total
P17	Bottle base	Weak grey	3	70.16	0.94	0.43	0.11	11.64	2.23	4.03	10.45	0.79	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.24	0.78	0.34	0.05	102.27
sd				0.65	0.04	0.01	0.00	0.08	0.02	0.05	0.09	0.02	-	-	-	-	0.02	0.02	0.02	0.02	
\$3	Lamp	Weak blue	3	67.53	0.95	0.52	0.12	12.88	2.47	3.21	13.28	0.15	b.d.l.	b.d.l.	0.04	b.d.l.	0.3	0.82	0.24	0.04	102.57
sd				1.37	0.03	0.01	0.01	0.10	0.06	0.04	0.07	0.01	-	-	0.02	-	0.01	0.02	0.02	0.01	
C 11	Bottle neck	Weak grey	3	69.91	0.95	0.45	0.10	11.39	2.56	3.7	9.68	0.54	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.27	0.64	0.33	0.04	100.6
sd				0.61	0.03	0.02	0.02	0.05	0.04	0.03	0.06	0.02	-	-	-	-	0.02	0.01	0.01	0.02	
F9	Vessel Fragment	Weak blue	3	71.3	1	0.57	0.13	10.61	2.08	3.39	10.65	1.03	b.d.l.	b.d.l.	b.d.l.	0.03	0.26	0.66	0.34	0.08	102.18
sd				0.25	0.03	0.01	0.01	0.05	0.02	0.02	0.11	0.03	-	-	-	0.02	0.02	0.02	0.01	0.01	
F 6	Vessel Fragment	Weak blue	3	72.89	1.01	0.56	0.13	10.91	2.1	3.54	10.82	0.93	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.25	0.7	0.29	0.07	104.29
sd				0.51	0.02	0.01	0.01	0.10	0.03	0.04	0.08	0.03	-	-	-	-	0.01	0.02	0.02	0.02	
S4	Bottle base	Weak blue	3	68.28	1.03	0.63	0.12	12.12	2.3	2.94	12.18	0.4	b.d.l.	b.d.l.	0.04	b.d.l.	0.27	0.73	b.d.l.	b.d.l.	101.33
sd				0.51	0.02	0.01	0.01	0.10	0.04	0.05	0.12	0.02	-	-	0.01	-	0.01	0.00	-	-	
Corning A	Standard published	-	-	66.56	1	1.09	0.79	14.3	2.87	2.66	5.03	1	1.17	0.19	0.044	0.0725	0.0847	0.1	0.14	0.46	99.6
Corning A	Standard measured(n=5)	-	-	66.22	1.08	1.06	0.78	14.02	2.9	2.54	5.02	1.02	1.07	0.2	0.07	0.05	0.08	0.09	0.14	0.5	99.58
SD	-	-	-	0.21	0.05	0.01	0.01	0.42	0.02	0.05	0.02	0.03	0.03	0.03	0.03	0.02	0.01	0.01	0	0.03	0.014
Absolute error	-	-	-	-0.34	0.08	-0.03	-0.01	-0.28	0.03	-0.12	-0.01	0.02	0.9	0.01	0.026	-0.02	-0.01	-0.01	0	0.04	-0.02
Corning B	Standard published	-	-	61.55	4.36	0.34	0.09	17	1	1.03	8.56	0.25	2.66	0.0241	0.19	0.61	0.82	0.2	0.5	0.077	99.65
Corning B	Standard measured(n=5)	-	-	60.62	4.41	0.33	0.11	16.61	1.06	1.03	8.64	0.25	2.4	0.03	0.2	0.5	0.81	0.17	0.51	0.09	98.23
SD	-	-	-	0.1	0.02	0.02	0.02	0.67	0.01	0.02	0.1	0.01	0.03	0.01	0.01	0.02	0.08	0.01	0.03	0.02	1
Absolute error				-0.93	0.05	-0.01	0.02	-0.39	0.06	0	0.08	0	-0.26	0.01	0.01	-0.11	-0.01	-0.03	0.1	0.01	-1.42

	Group 1 (<i>n</i>	=8)	Group 2 (<i>n</i> =	43)	Group 3 (<i>n</i> =	=10)
	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.
SiO ₂	70.86	2.35	68.81	2.73	69.30	2.29
Na₂O	11.40	0.69	12.25	0.92	11.78	0.67
CaO	8.76	0.67	9.62	0.98	10.83	1.13
K ₂ O	2.42	0.40	2.35	0.17	2.29	0.23
MgO	3.35	0.17	3.51	0.38	3.46	0.38
Al ₂ O ₃	1.33	0.16	1.34	0.20	0.91	0.10
Fe ₂ O ₃	0.61	0.07	0.53	0.09	0.46	0.11
BaO	0.03	0.01	0.03	0.01	0.05	0.02
TiO ₂	0.11	0.01	0.07	0.01	0.11	0.02
MnO	0.39	0.11	0.56	0.31	0.57	0.27
PbO	0.05	0.01	0.03	0.02	0.03	0.01
Cl	0.71	0.04	0.72	0.06	0.73	0.06
SO₃	0.25	0.05	0.28	0.04	0.33	0.06
P ₂ O ₅	0.30	0.05	0.28	0.04	0.27	0.02
Total	99.57		99.11		101.14	

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5. Discussion

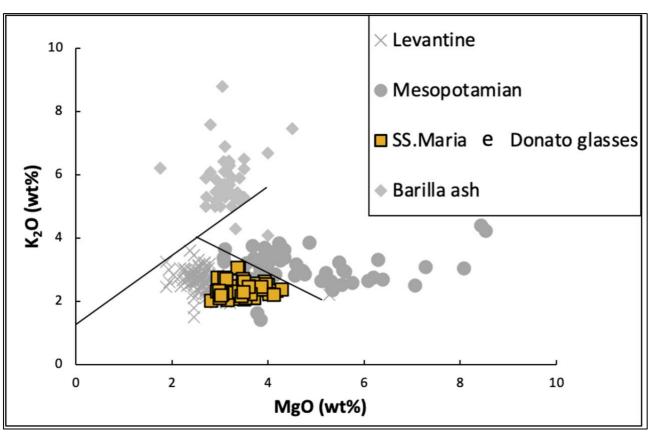
217 5.1 Raw materials and technology

Previous studies suggest that it is possible to distinguish the plant ashes used in glassmaking in different regions. The view put forward by Brill (1989) that soda plant ash glass from central Asia is particularly high in $K_{*}O$ (>4%) has been generally accepted (Abduraskov, 2009; Gan, 2009; Henderson *et al.*, 2018), while Freestone (2006) distinguished between those used for "Syrian" plant ash glass and those used in Mesopotamia, where the latter had higher MgO (typically above 4%). Similarly, *Barilla* originating from coastal regions in the western Mediterranean such as Spain, Sicily and Sardinia, is a type of soda plant ash with relatively high potash, resulting in glass with higher K_{*}O (Cagno *et al.*, 2010, 2008; Fernández Pérez, 1998; Tite *et al.*, 2006).

In this context, the remarkably consistent levels of the ash-related components across all glasses from SS. Maria and Donato are noteworthy. They are consistent with "Levantine" ash (used here as an umbrella term for the ash which appears to have been used in Syrian, Levantine and Egyptian glass) as shown in Fig. 5. Furthermore, the glass from all groups plots in a relatively limited area of the Levantine category, emphasising that these glasses are likely to have been exploiting a limited plant ash source with its own characteristics. Groups

230 1 and 2 from Raqqa, Syria (Henderson *et al.*, 2004) also lie in this region.





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Figure 5: K₂O vs MgO concentrations identifies differences between plant ash glasses from the "Levantine" Islamic tradition (Brill, 1999; Freestone, 2002; Henderson et al., 2016, 2004; Phelps et al., 2016), the Mesopotamian Sasanian tradition (Mirti et al., 2009, Henderson et al. 2016), and the "Barilla ash" tradition (Cagno et al., 2010, 2012a).

237 As noted, the glasses of SS. Maria and Donato appear to have been made using three different silica 238 sources (Figs. 3, 4). The main sources of silica suitable for glassmaking are quartz sand, quarried siliceous 239 minerals and rocks such as vein quartz, chert and quartzite, or pebbles composed of these materials. Legal texts 240 found in the Archives of Venice indicate that Venetian glassmakers made use of both sand and quartz pebbles 241 from at least as early as the late fourteenth century (Jacoby, 1993; Zecchin, 1987:17). Compositional criteria for 242 the use of pebbles or sand in glassmaking are not well defined, as sand can be very pure, while pebbles may be 243 impure. Late Bronze Age glass, generally accepted to have been made using pebbles, has Al₂O₃ typically below 244 one percent, Fe₂O₃ below 0.5% and TiO₂ below 0.1% (Shortland and Eremin, 2006). Alumina contents 245 significantly above one percent might be considered to indicate the use of a sand, rather than pebbles as a silica 246 source (Brill, 1995). However, Henderson et al. (2005) considered glass from Raqqa with mean Al₂O₈ of 1.17% 247 to have been made using quartz pebbles, which are common near the site.

Verità (2013) points out that sixteenth-seventeenth century Venetian *vitrum blanchum* was made using quartz pebbles and has around 1% Al₂O₃ with a fairly large dispersion, with around 0.35% Fe₂O₃ and 0.05% TiO₂. Groups 1 and 2 of the present study both contain higher concentrations of these components, with around 1.3%Al₂O₃ and 0.5-0.6% Fe₂O₃ (Table 4), so on balance are likely to have been made using sand. Group 3, however, has lower quantities and may have been made using quartz pebbles. Although Group 3 has high TiO₂ (c. 0.11%), the historic documents make clear that the glassmakers obtained quartz pebbles from different sources and their quality varied (Jacoby, 1993). Hence, we cannot be sure of the character of the silica source on the basis of our present data. However, irrespective of the precise origins of the silica, we are able to identify three potential sources on the basis of their TiO₂ and Al₂O₃ ratios (Fig. 3). All three silica sources were combined with the same Levantine ash, in about the same proportions, to make the glass (Fig. 5).

It is noted that the compositional groups have broadly similar iron contents and do not differ in the visual appearance of the glass fabric. The broadly similar compositions indicate that their working properties would also have been similar. Hence, they have not been selected for technical reasons and it seems that that the raw glasses were either produced in different workshops that were supplied with different raw materials, or were produced at different times, or both.

263

264 5.2 Technological Affinities

The analysis of the samples from SS. Maria e Donato have been first compared with data of similar medieval assemblages believed to be of Venetian manufacture, looking at both their sand related elements and plant ash ones (Fig.6, Tab. 5), in order to investigate their production technology and to advance hypothesis on their provenance.

Group 2, which represents the majority of the glass fragments, reveals strong similarities in terms of both plant ash and sand related elements with the *low alumina Venetian glass* group of the 11^{th} to 14^{th} centuries A.D identified by Verità and Zecchin (2009b) (Tab. 5) as well as with group A/1 of Gallo and Silvestri (2005) from Asolo, located just 70 km northwest of Venice and which they dated to between the 12^{th} and the 15^{th} centuries (Fig. 6 and Tab. 5). The same group also has a chemical composition similar to the one of the 11^{th} - 14^{th} century glass from S. Leonardo in Fossamala, an island northern the lagoon (Verità and Toninato, 1990) (Fig. 6 and Tab.5).

Glass from Ferrara (8th-12th century), a site in the Venetian hinterland located around 100 km from Venice, and
two samples of 10th-12th century glass from S. Arian, another small island in the lagoon (Verità and Toninato,
1990), also have a composition similar to Group 2 (Fig. 6) but given their early dating, they cannot be
unquestionably attributed to a Venetian production (Verità, 2013).

280 Group 2 also presents some similarities with the 15th-16th century Venetian glass categorised as "vitrum 281 blanchum" (Fig. 6 and Tab. 5) (Verità, 1985; Verità and Zecchin, 2009a, b) but our group contains slightly more 282 aluminum, iron and titanium oxides, suggesting that a somewhat less pure silica source, but still of a very good 283 quality, may have been used in earlier centuries. Indeed, documentary evidence reports that from at least the 284 late 13th-early 14th century Venetian glassmakers were producing glass of diverse qualities, to be used for different 285 products and probably made using distinct raw materials. A distinction between white ("vitrum blanchum", 286 colourless) and green glass (naturally coloured) is indicated in an article of the Capitolare dei cristalleri dated to 287 the 14th century (Zecchin, 1990:137). Moreover, a sentence dated 1284 reports that it was forbidden to falsify 288 rock crystal using the already mentioned "white glass", hence providing evidence that glass of a very high quality, 289 to be mistaken for rock crystal, was already being produced in Venice in the 13th century (Monticolo, 1914).

In the light of this, it is interesting that the SS Maria and Donato assemblage appears to have contained no examples of an iron-rich, green low-quality glass. This is likely to reflect the use of the best quality glass for ecclesiastical purposes, but the possibility that Venice first produced high quality glass, and began producing cheaper "common glass" later, as market demand increased, cannot be dismissed at this stage.

294 Group 1 has a mean composition which is in many respects comparable to Group 2 (Fig.3, Tab.4) and, 295 similarly, it might be a group of glasses produced in Venice. However, it should be noted that its higher levels of 296 titanium, as previously highlighted, separate this group from Group 2, and clearly separate Group 1 from the 297 other medieval Venetian glasses, while Group 2 plots with them in Fig. 6. Therefore, we regard Group 1 as 298 likely to have an origin distinct from that of Group 2. Furthermore, to the authors' knowledge, no data on 299 assemblages of medieval glass attributed to Venice match the compositional characteristics of Group 1. These 300 differences, although dependent upon a single component, TiO₂, suggest a different provenance for the glasses 301 of Group 1. We note that TiO_2 is a well-measured component and has proved a very useful indicator in 302 provenance investigations of glass, for example it has been shown to separate most glass made in Egypt from that 303 made on the Levantine coast (Foy et al., 2003; Nenna, 2014) and can separate closely related groups from Egypt 304 (Freestone, 2021).

305 Group 3 has on average lower levels of alumina and higher levels of titanium oxide than the other 306 samples analysed (Fig. 3, Tab. 4). Comparison with other medieval Venetian glasses (Fig. 6) indicates that these 307 higher levels of titanium, in combination with very low levels of alumina, are not commonly found in Venice 308 (Verità, 2013; Verità and Zecchin, 2009a, 2009b). Nevertheless, fourteenth century soda-lime-silica stained glass 309 windows from Santa Croce Basilica (Florence), were tentatively attributed to Venetian production by Verità et 310 al., (2019), and also show high levels of titanium (on average 0.13%) and low levels of alumina (below 1%) (Fig.6). 311 All the samples analysed differ considerably in terms of their sand-related elements to another group of 312 11th-14th century glasses from Ferrara and S. Leonardo in Fossamala, (Verità and Toninato, 1990), as well as 313 groups A/2 and A/3 from Asolo (Gallo and Silvestri, 2012), which correspond to the high alumina Venetian glass 314 group identified by Verità and Zecchin, (2009b) (also dated 11th - 14th centuries) (enclosed in dotted line in Fig.6). 315 and which appear equivalent to the naturally coloured "green glass" mentioned in the documentary evidence (in

316 Cecchetti, 1874:224).

The restricted variation of our samples in terms of plant ash components and their similarities to other medieval glasses attributed to Venetian production (Tab.5) can be explained by the mandatory use in Venice, from at least 1255, of Levantine plant ash, "alume catino" as a flux (Zecchin, 1990:175, 1987:5, 1997), which was imported, together with raw glass to be remelted, from Syria and Egypt, the ash from the latter considered of poorer quality (Zecchin 1990:173). Use of other types of ash, such as the wood ash used in northern Europe and possibly in other Italian centres such as in Florence (Verità *et al.*, 2019), Pavia (Messiga and Riccardi, 2006) and Orvieto (Kunicki-Goldfinger *et al.*, 2013), was strictly forbidden by the Venetian State (Ashtor and Cevidalli,

324 1983; Jacoby, 1993; Zecchin, 1990:176).

325 Table 5: Mean chemical composition of Group 2 compared to group A/1 from Asolo (12th-15th century) (Gallo and Silvestri 2012),

326 the group "low Alumina Venetian glass" identified by Verità and Zecchin 2009b (11th-14th century), Vitrum Blanchum from Fusina

327 328 (15th-16th century)(Verità, 1985) and the low-Al glass samples from the island northern the lagoon of S. Leonardo in Fossamala

(11th-14th century) (Verità and Toninato, 1990).

	Group 2 (n	=43)	Venetian glas Al"	s "low	Asolo glass	A/1	Vitrum Bland Fusina	chum,	S. Leonard Fossama	
	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.
SiO_2	68.81	2.73	67.26	1.58	67.36	1.48	67.3	1.07	69.03	0.84
Na ₂ O	12.25	0.92	12.75	1.4	12.49	1.03	13.14	1.18	12.23	0.46
CaO	9.62	0.98	8.97	1.53	10.1	0.98	10.14	1.17	9.75	1.94
K_2O	2.35	0.17	2.41	0.22	2.41	0.22	2.58	0.59	2.45	0.87
MgO	3.51	0.38	3.28	0.57	3.76	0.44	3.55	0.61	2.3	1.01
Fe ₂ O ₃	0.53	0.09	0.51	0.21	0.6	0.22	0.36	0.09	0.38	0.09
Al_2O_3	1.34	0.20	1.47	0.58	1.59	0.44	1.01	0.36	1.75	0.3
TiO_2	0.07	0.01	0.11	0.06	0.08	0.02	0.04	0.02	0.06	0.02
MnO	0.56	0.31	0.97	0.52	1.24	0.72	0.5	0.22	0.58	0.33
P_2O_5	0.28	0.04	0.34	0.09	0.27	0.04	0.2	0.22	0.37	0.02

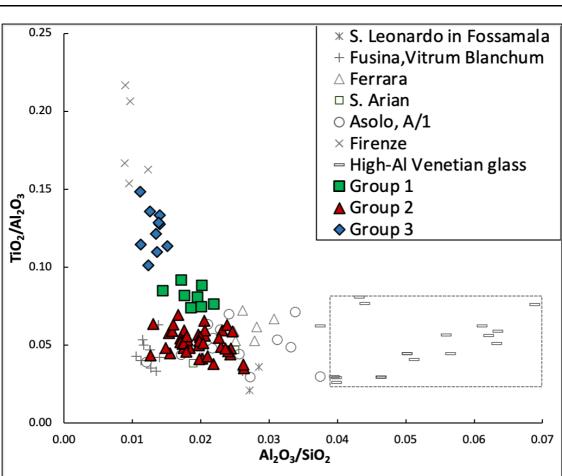


Figure 6: TiO₂/Al₂O₃ vs Al₂O₃/SiO₂ of SS. Maria e Donato groups and medieval Venetian glass from S.Leonardo in Fossamala (11th-14th century, Verità 1985), Fusina (15th-16th century, Verità 1985), Ferrara (8th-12th century, Verità and Toninato 1990), S. Arian (10th-12th century, Verità and Toninato 1990), Asolo A/1 (12th-15th century, Gallo and Silvestri 2012), Firenze (14th century, Verità et al. 334 335 2019). Similarities can be seen between Group 2 and medieval Venetian glass categorised as "low-Al Venetian glass", as opposed to the high-Al Venetian glass (enclosed in dotted line, data from: Verità and Toninato 1990, Gallo and. Silvestri 2012).

337 Comparison with other Italian medieval glass assemblages is shown in Fig.7. We recognise three main 338 technological categories: LEV-Si glass made with Levantine ash and a relatively pure source of silica lower in 339 Al₂O₃, (Cagno et al., 2012b, 2010, 2008) which has a composition broadly similar to Venetian glass (Verità and 340 Zecchin, 2009a), LEV-Al comprising Levantine ash plus local sands richer in feldspars, with Al₂O₃ contents well 341 above 3.5% (Cagno et al., 2012a, 2010, 2008;); and BAR-Al made with Barilla ash plus high Al₂O₃ local sands 342 (Basso et al., 2008; Cagno et al., 2010, 2008). Combination BAR-Si was used less frequently (Cagno et al., 2010) 343 presumably because the lower quality barilla ash was not used to make high quality glass with pure silica (Fig. 7). 344 Similar combinations of raw materials has been recognised by Cagno et al., (2010) for the production of medieval 345 glass from Tuscany.

While glass from regions other than Venice in the LEV-Si category presents compositions that are similar to our samples and to medieval Venetian glass (Fig.7), the latter having levels of Al₂O₃ which generally do not exceed 3.5% (Verità and Zecchin, 2009a), it tends to have on average higher levels of alumina and iron oxides, pointing to the use of different silica sources than our samples (Fig.8).

10 🛇 Bar-Al **BAR-Al BAR-Si** + Lev-Si O Lev-Al 8 — Bar-Si Group 1 6 K20 (wt%) Group 2 Group 3 4 LEV-Al LEV-Si 2 0 2 5 7 0 1 6 3 Al₂O₃ (wt%)

351

336

Figure 7: K₂O and Al₂O₃ biplot (wt%) for SS. Maria e Donato glasses, and the technologies recognized, depending upon the combination of ash type and sand quality, here called LEV-Si (data from Verità 1985, Verità and Toninato 1990, Verità and Zecchin 2009, Gallo and Silvestri 2012, Verità et al. 2019, Cagno et al. 2010, 2012b, Genga et al., 2008; Posedi et al., 2019; Vandini et al., 2018) LEV-Al (Cagno et al., 2010; Posedi et al., 2019) and BAR-Al (Basso et al., 2008; Bianchin et al., 2005; Cagno et al., 2012a, 2010), BAR-Si (Cagno et al. 2010). Venetian low-Al glasses dated between the 9h and the 14th century (Verità 1985, Verità and Zecchin 2009, Gallo and Silvestri 2012, Verità et al. 2019) are also compared (dotted ellipse) and are part of the broader LEV-Si category.

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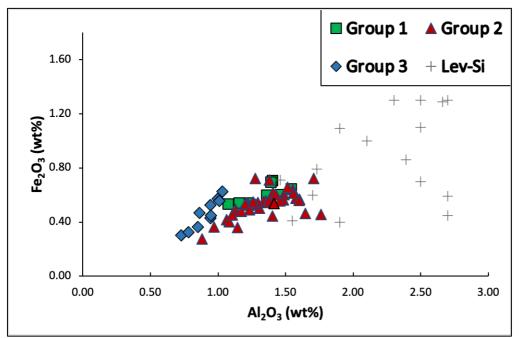


Figure 8: Fe₂O₃ vs Al₂O₃ contents of SS. Maria e Donato groups and the non-Venetian Italian glass of the LEV-Si category shown in Fig.7 (data from Cagno et al 2010, 2012b, Posedi et al. 2019, Vandini et al. 2018, Genga et al. 2008).

366 5.3 Comparison with glass from the Eastern Mediterranean

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367 We have observed that the SS Maria e Donato glass was made using Levantine ash, and that this is 368 consistent with historical records of Venetian glassmaking. However, it is documented that the Muranese 369 glassmakers imported raw glass, as well as raw materials, from the Middle East (Zecchin 1987:5; Verità 2013). 370 Therefore, we have compared our data with the compositions of medieval glass from Syria and the eastern 371 Mediterranean. As discussed above, plant ash used in Venice at this time was imported from the Middle East, 372 so that all three of our groups resemble middle eastern glasses in terms of their ash-related components 373 impurities, while their sand-related components can serve for further comparisons with the eastern examples, 374 shown in Fig. 9.

In particular, Group 2 resembles the composition of 11th century glass from Tell Fukhkhar in Al Raqqa (Henderson *et al.*, 2004) and shows some similarities with a group of 13th century glass from the Crusader castle at Montfort (Upper Galilee, Israel; Whitehouse *et al.*, 2017), whereas it differs from glass produced on the Levantine coast in Tyre, Lebanon (Freestone, 2002) and of "Tyre type" (Phelps, 2016) (Fig.9, Tab.6). It should be noted that the glass from Montfort has been divided in two groups by the present authors in order to highlight the different titania contents of the glasses, as well as different iron oxide and alumina contents (Fig. 9, Tab.6), which might denote different raw materials and hence different sources for the two groups of glass.

382 Group 1 resembles a group of six glasses from Khirbat-al Minya, Israel (Henderson *et al.*, 2016).

On the other hand, Group 3 shows similarities to a group of glasses from Banias (11th-13th centuries) (Israel,
Freestone *et al.*, 2000) and the "high-TiO₂" Montfort (Israel) group (Whitehouse *et al.*, 2017)(Fig.9, Tab.6).

385 Group 3 also shares lower alumina to iron oxide ratios with the Banias and Montfort glasses (Tab.6). High TiO₂

386 contents are especially characteristic of sand of an Egyptian origin, as supported by several studies (e.g in Kato

387 *et al.*, 2010; Nenna, 2014; Picon and Vichy, 2003; Schibille *et al.*, 2019), and there is a possibility that the glass

from Banias, the "high TiO₂" glass group from Montfort and our Group 3 may represent an Egyptian glass type.
Indeed, glass analysed by Kato et al. (2010) from the port of Raya on the Sinai Peninsula, (group PA-1b, 10th11th centuries), and believed to have been produced in Egypt, show high levels of titanium and a broadly
comparable TiO₂/Al₂O₃ ratio to Group 3 (Fig.9 and Tab.6).



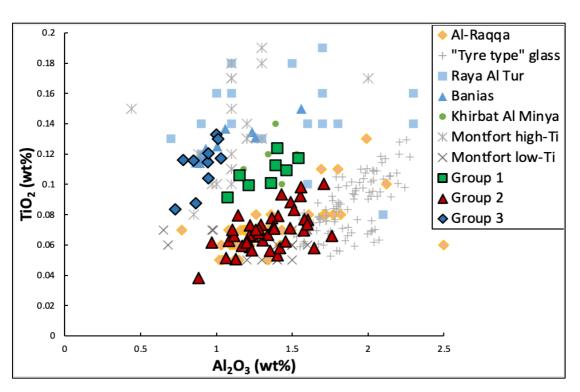


Figure 9: Similarities, according to the sand characteristics, between the groups identified and middle eastern glass assemblages
from Al-Raqqa (Henderson et al. 2004), Raya Al Tur (Kato et al. 2010), Banias (Freestone unpublished), Khirbat Al Minya
(Henderson et al. 2016), Montfort (Whitehouse et al. 2017) and "Tyre type glass" (Phelps 2016).

- -

	Group 1 (r	i=8)	Group 2 (<i>n</i>	=43)	Group 3 (<i>n</i>	=10)	Raya Al Tur,	Egypt	Al-Raqqa, Fukhkha		Banias	5	Montfort "lov	w TiO₂"	Montfort " TiO ₂ "	high	Tyre typ)e
	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.	Mean wt%	s.d.
SiO2	70.86	2.35	68.81	2.73	69.3	2.29	66.2	2.6	67.66	1.49	71.62	1.18	68.12	2.32	69.58	1.3	67.92	1.69
Na₂O	11.4	0.69	12.25	0.92	11.78	0.67	17.9	-	12.18	0.95	11.96	0.58	13.58	1.67	11.33	1.79	12.38	1.07
CaO	8.76	0.67	9.62	0.98	10.83	1.13	7.5	0.8	10.18	1	8.6	0.98	8.02	0.91	8.84	1.01	9.48	1.17
K ₂ O	2.42	0.4	2.35	0.17	2.29	0.23	2.2	0.4	2.48	0.33	1.51	0.34	2.64	0.35	2.55	0.36	2.35	0.35
MgO	3.35	0.17	3.51	0.38	3.46	0.38	2.1	0.3	3.38	0.28	2.4	0.57	3.26	0.3	3.3	0.42	3.02	0.51
Al ₂ O ₃	1.33	0.16	1.34	0.2	0.91	0.1	1.8	0.8	1.24	0.17	1.22	0.63	1.30	0.3	1.16	0.3	1.86	0.2
Fe ₂ O ₃	0.61	0.07	0.53	0.09	0.46	0.11	0.82	0.15	0.55	0.25	0.68	0.49	0.48	0.25	0.67	0.29	0.50	0.12
TiO ₂	0.11	0.01	0.07	0.01	0.11	0.02	0.17	0.06	0.06	0.01	0.13	0.12	0.07	0.01	0.15	0.03	0.08	0.02
MnO	0.39	0.11	0.56	0.31	0.57	0.27	1.02	0.28	1.09	0.51	0.83	0.28	0.67	0.34	0.64	0.22	1.00	0.38
CI	0.71	0.04	0.72	0.06	0.73	0.06	na	-	0.73	0.08	0.86	0.07	0.85	0.08	0.85	0.07	1.00	0.38
P ₂ O ₅	0.3	0.05	0.28	0.04	0.27	0.02	na	-	0.27	0.03	0.24	0.04	0.31	0.08	0.41	0.08	0.30	0.06

403 Table 6: Average chemical compositions of the SS. Maria e Donato groups, of glass from Raya al Tur (Kato et al. 2010), A-Raqqa (Henderson et al. 2004), Banias (Freestone unpublished),
 404 Montfort (divided in two groups by the present authors)(Whitehouse et al. 2017) and the "Tyre type" glass (Phelps 2016).

406 407

6. Conclusions

408 This paper presents a new dataset for medieval glass retrieved from an archaeological context on the 409 Island of Murano, where Venetian glassmaking was situated after 1291 A.D. (Zecchin 1987:6). The SS. Maria 410 e Donato glasses were made using ash from the Levant and form three groups on the basis of the minor oxides 411 contributed by their silica sources. They have relatively low K₂O and Al₂O₃ and are distinguished from much of 412 the medieval glass made in central Italy which melted barilla ash from the western Mediterranean with an 413 alumina-rich siliceous sand. Current evidence suggests that Levantine ashes were used elsewhere in medieval 414 Italian glassmaking centres but, on the basis of the minor elements, the sands used appear to have differed from 415 those of the SS Maria and Donato assemblage. This evidence is consistent with the understanding gleaned from 416 contemporary sources on the Italian glass industry, particularly on the regulations imposed by the Venetian 417 government on the exclusive use of Levantine ash. This imported soda ash was an indispensable raw material 418 for the Venetian glassmaking industry and was a characteristic trait of virtually all the Venetian glass over the 419 several centuries of its production.

The largest group identified, Group 2 closely resembles previous analyses of medieval glass believed to have been made by Venetian artisans between the 11^{th} and 15^{th} centuries and it also shows similarities with the later *vitrum blanchum* of the 15^{th} - 16^{th} century, strongly suggesting that this group represents a rarely accessible assemblage of medieval Venetian glass made in the island. Group 1 has a composition similar to Group 2 but its average higher levels of titanium dioxide do not match precisely any Venetian glass groups similar to Group 2, and they might be suggestive of a different provenance.

426 Group 3, on the other hand, differs from the other Venetian medieval assemblages due to its 427 considerably lower levels of Al_2O_3 and higher contents of TiO₂. Only a single northern Italian medieval 428 assemblage shows similar levels of these elements and is a small group of windows glass from Florence which 429 have been tentatively suggested to have been made in Venice (Verità *et al.*, 2019).

430 In spite of some similarities to Venetian products, particularly in the case of Group 2, the SS. Maria e 431 Donato groups also resemble glass from the Eastern Mediterranean. In particular, Group 2 resembles Syrian 432 glass (El Raqqa) and a lower TiO_2 group of glass from Montfort. While there is the possibility that Venetian 433 glass was exported to Crusader Montfort, its use in Raqqa seems improbable. However, records indicate that 434 raw glass, cullet and sand was exported from the Levant and worked in Venice and this assemblage might 435 represent imported glass or glass made with imported sand. Group 1 resembles a group of glasses from Khirbat-436 al Minya, Israel and may therefore be a Levantine type. Group 3 on the other hand resembles a second group 437 from Montfort (here named "high-TiO₂"), as well as glass from Banias, Israel and glass from the Rava port, on 438 the Sinai Peninsula, Egypt. High TiO_2 is particularly characteristic of Egyptian glass and the high TiO_2 of this 439 group of glasses might suggest an Egyptian origin.

440 These relationships leave a number of issues unclear. While it seems likely that the high-TiO₂ Group 3 441 reflects an imported raw material, Group 2 resembles other glass thought to be made in Venice, although it 442 cannot be distinguished from some Syrian glass on the basis of the present analyses, while the origin of the 443 intermediate Group 1 is also ambiguous. This is likely to be a reflection of the complex emergence of Venice 444 as one of the major centres of glassmaking in the Middle Ages. In their search for high quality raw materials, not 445 only ash but also raw glass and even sand was imported from the Levant and the Venetian State created a 446 monopoly in their importation, sale and use, in this way ensuring Venice's supremacy in glassmaking (Jacoby, 447 1993, 1991; Zecchin, 1987:5). Information on the type of raw materials used and their provenance can be found 448 in the written evidence. The Archives of State of Venice indicate that the Muranese glassmakers were importing 449 both glass cullet and sand: glass cullet was imported from the Levant and from Tripoli (Lebanon) in the 13th 450 century (Zecchin, 1990:173), while sand was imported from Crete (1293-1302) (Zecchin, 1997) and Sicily 451 (1340)(Zecchin 1990:176) and silica pebbles were also imported from the Ticino river and Verona (1394) 452 (Jacoby, 1993:73). However, local raw materials, such as local sand, called "sablone roseto" (red sand) or 453 "sabbion" in the Archives, was probably used as well in Venice (Zecchin, 1987:7; Moretti and Hreglich, 2013; 454 Verità, 2013, 1985; Zecchin, 1990:176) and further analysis are needed in order to be able to distinguish it from 455 the other sources.

As a consequence, the chemical composition of medieval Venetian glass is likely to reflect a complex situation of trade in raw materials and glass as well as a probable transfer of technology and/or artisans, which is reflected in the very similar recipes apparently used by both Italian and Levantine glassmakers. clarification of these issues will clearly require further work with trace elements and possibly isotopes. It is clear, however, that we are able to achieve some discrimination between glass groups using minor elements such as Ti, Fe and Al and that these allow a preliminary sorting of the data and identification of the key issues to be addressed.

462

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- 472

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