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# The glass from the *Barco de las Pipas*: typological and analytical study of a glass assemblage from a 17<sup>th</sup>-century Dutch shipwreck off the coast of Dominican Republic

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### RESEARCH ARTICLE

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The glass from the Barco de las Pipas: typological and analytical study of a glass assemblage from a 17<sup>th</sup>century Dutch shipwreck off the coast of Dominican Republic

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### **ABSTRACT**

This article presents the typological and chemical analysis of a small glass assemblage recovered from a, likely Dutch, early 17thcentury shipwreck known as Barco de las Pipas, found off the coast of the Province of Montecristi, Dominican Republic. All fifteen glass fragments recovered during underwater excavation were typologically characterised, sampled, and analysed using Electron Micro-Probe Analysis (EMPA) for major and minor elements and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for trace elements to determine their provenance. The results of this analysis are compared with existing datasets of 16th- and 17th-century European glass, and their potential raw ingredients and technology are assessed. In addition, arguments are presented to challenge several long-held assumptions concerning glassmaking on the European continent during the seventeenth century, including the poorer quality of some Western European plant ashes, compared to Levantine ones. Finally, the paper highlights the potential of the approach for future studies investigating the nature of transatlantic trade in the Early Modern Period.

### **KEYWORDS**

17th-century glass; chemical analysis and typology; Spanish Caribbean; Dutch glass; Barco de las Pipas

### Introduction

This article presents an assemblage of fifteen glass fragments excavated from the Barco de las Pilas shipwreck, found off the northern coast of the province of Montecristi, Dominican Republic (Figure 1), on the island known to Spanish colonists as Hispaniola. The most significant element in this cargo were approximately 20,000 Dutch clay pipes made of kaolinite (for the importance of clay pipes as an archaeological material see Hunt and Jackson 1997), which have to date been the main argument behind identifying the ship as Dutch. Other finds include various

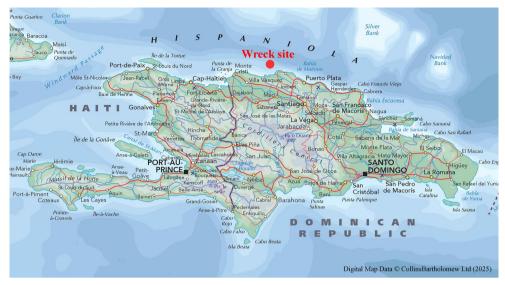


Figure 1. Location of the Barco de las Pipas shipwreck.

bronze thimbles, hooks, weights, and keys, as well as a number of silver coins, mostly Spanish *reales de a ocho* (Ruth Pliego pers. comm).

The research presents a typological and chemical characterisation of the glass to provenance the material, establish location of manufacture, and identify the technical processes and ingredients involved in its production. Recent literature has offered an increasingly clear picture of glassmaking activity in Europe during the Early Modern Period, and consequently we have a far greater understanding of the technological characteristics of the output from several major glass-production centres. Based on the safe assumption that the glass found in the Barco de las Pipas was produced in Europe and exported to colonial America, the results are examined in the context of European production during the late 16th and early 17th centuries. Although, from a technological perspective, the assemblage is only relatable to glass production in the Old World, this paper aims to contribute to a greater understanding of the nature of glass goods being exported across the Atlantic during this period. To our knowledge, barely a handful of samples, related to the early Spanish settlement in the Caribbean (Brill et al. 1987; Brill and Hoffman 1987; Deagan and Cruxent 2002), and a small assemblage of out-of-context and undated glass objects from Mexico City (Peralta, García, and Alvízar 2024) have been subject to chemical analysis to date, and this paper makes a small contribution to redressing this serious gap in our historical understanding of glass production and trade in the early colonial period.

Although documentary sources for 17th-century trade are relatively abundant, archaeological evidence can present a much more nuanced understanding of commercial dynamics (aside from the problematic issue of contraband, which, by its very nature, can be elusive to the archival record). Within this endeavour, the chemical characterisation of glass using modern analytical techniques is a crucial tool because, unlike some other archaeological materials such as ceramics, its macroscopic features only allow for a very tentative identification of provenance and the technological

processes involved in production. During the seventeenth century, this was compounded by the simultaneous operation in Europe of a large number of glass production centres, which interacted with one another in complex ways and strove to dominate a very active market with all the means available to them, including widespread imitation, as discussed below.

For the non-glass expert, a few introductory notes about the chemistry of historical glass and the potential of analytical techniques are in order. In essence, what these techniques do is to allow us to make inferences about raw materials and the technological processes involved in glass production, based on the composition and the basic molecular structure of glass (Rehren and Freestone 2015). In general, attention is paid to three constituent ingredients within the glass. The first, silica, is the main network former in glass, and its associated elements (often brought in as impurities in the source of silica) act as a reflection of the geological makeup of the silica source (e.g. sand, quartzite pebbles), helping to establish the provenance of the glass. Next are fluxes, typically metallic alkalis (e.g. soda, potash), which bring down the melting point of silica and come from mineral- or vegetal-based raw materials. Finally lime, which acts as a stabiliser, and which can also provide information about both silicaand flux-bearing raw materials. Similarly, the presence of some trace elements, such as antimony, cobalt, and copper are often used as markers of recycling.

# The glass assemblage

The assemblage consists of fifteen fragments of vessel glass, and although highly fragmented, most are distinctive and identifiable (Figure 2). Typologically, the glass can be divided into four types, which is significant as they correspond very closely to those identified chemically (see below).

### Type 1 knop-stemmed goblets (Low Countries c.1625–1650)

Ten samples belong to this type. The most complete, BP13 and BP14, are goblets with a sharply ribbed knop attached to a simple flaring base, and in the case of BP13 the remains of a shallow moulded bowl attached to the upper stem. The glass has a distinctive green tint typical of this form found across the Low Countries in the first half of the seventeenth century. Consequently, such vessels are usually assumed to have been produced at one of the workshops in the region (Bitter et al. 1997, 123; Henkes 1994, 213-215; Ruempol and van Dongen 1991, 190). Two further bases, BP5 and BP15 and a fragment of lower bowl BP12 almost certainly are from identical or very similar vessels, as are the pieces of ribbed rims (BP2-3, 6, 8 & 11). However, some caution is required here as their precise form cannot be reconstructed in the absence of the characteristic stem. Indeed, given the fragility of these portions of the goblet, some of these rim fragments might even belong to the same vessel, although it is impossible to tell for certain.

### Type 2 ice glass beaker (Low Countries c.1600–1650)

A single fragment, BP7, comes from a clear ijsglas (ice glass) beaker, which is easily identifiable from the crazed pattern on its outer surface. The effect was caused by

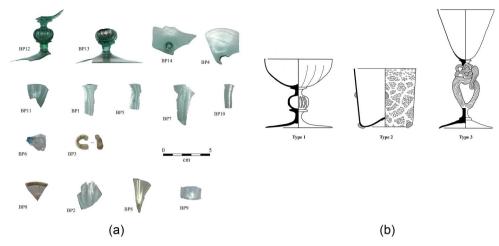


Figure 2. The glass (a) and the reference shapes mentioned in the text (b).

plunging the partially formed vessel into water while still hot, which caused small surface cracks that were further expanded as the glass continued to be inflated and worked. Although ice glass was probably a Venetian innovation in the late sixteenth century, it became popular in the first half of the seventeenth century in the Low Countries; ice glass beakers were found in the manufacturing waste of the both the Soop and De Twee Rozen glasshouses in Amsterdam (Gawronski et al. 2010, 83; Hulst 2024, 72). BP6 can be placed in this latter tradition due to the application of a small blue raspberry-coloured prunt foot, a typical Low Country embellishment (Bitter 1995,61; Henkes 1994, 167–169; Willmott 2002, 15–16).

### Type 3 serpentine goblet (façon de Venise c.1600-1650)

A single fragment of fine ribbed hollow tube, BP4, is from a clear serpentine stem. This distinctive type was formed by heating and manipulating the glass into a twisted and knotted design, requiring considerable skill on behalf of the glassmaker and resulting in a highly decorative, if impractical, goblet stem. This technique almost certainly originated in Venice at the end of the sixteenth century. However, it rapidly became the signature of *façon de Venise* glassmakers in Northern Europe during the early seventeenth century, including at centres such as London (Willmott 2002, 65), Antwerp (Tait 1991, 174–175; Veekmaan 2002, 88) and Amsterdam (Gawronski et al. 2010, 41, 92–93).

# Type 4 stemmed goblets of uncertain form (façon de Venise c. 1580-1650)

The remaining fragments are all from good-quality clear glass goblets but, in the absence of distinctive stems, are hard to attribute typologically with any certainty. BP1 is a large portion of a base with an under-folded edge, whilst the remainder are two fragments from lower bowls (BP3, 9-10) in a clearer tinted glass. These base and lower bowl fragments are of the type and quality that might be expected to

accompany a serpentine goblet or similar façon de Venise form. However, any such association is speculative typologically.

Although small, the assemblage represents a diverse range of related forms, all dating to the first half of the seventeenth century. Perhaps most significantly, they are all tablewares; more utilitarian containers that might be expected for everyday use onboard a ship appear to be absent. Whether this demonstrates that they formed part of a trade cargo cannot be said for certain, but it seems the most likely explanation. At least two of the types, the ribbed goblets and the ice glass beaker, were produced almost without question in the Low Countries. Whilst it is not possible to make such an assertion about the remaining fragments on purely typological grounds, it is entirely conceivable they were too, although other façon de Venise centres cannot be discounted.

For ease of reference, the basic typology, chronology, and compositional grouping of each sample is presented in Table 1.

# **Analysis and results**

All glass fragments recovered from the shipwreck were sampled, including two samples from BP7: BP7a for the colourless glass and BP7b for the raspberry-coloured prunt. They were analysed by electron microprobe analyser (EMPA) for major and minor elements and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for trace elements to determine their provenance. With some elements, EMPA yielded results that deviated over 10% relative from the published contents (Vicenzi et al. 2002), notably sodium, iron, antimony, lead, and titanium. In addition, the analysis of the Corning C standard yielded virtually no manganese, although the reported amount of MnO in Corning C glass is 0.82 wt.% MnO. As such, for these elements (except for antimony, which was one of the few elements in for which the LA-ICP-MS data was found to be less accurate than EMPA data) we shall be using the more accurate LA-ICP-MS data. When comparing oxides of these elements, the LA-ICP-MS data will be expressed as oxides, after conversion (element ppm multiplied by the oxide stoichiometric conversion factor/10,000). The EMPA results from BP7a (colourless glass) yield a total of 55.25 wt.%, probably due to instrumental error,

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Sample number	Typology	Typology-based chronology	Chemical group
BP1	Stemmed goblets	1580–1650	BPG2
BP2	Knop-Stemmed Goblet	1625-1650	BPG2
BP3	Knop-Stemmed Goblet	1625-1650	BPG1
BP4	Serpentine goblet	1600-1650	BPG1
BP5	Knop-Stemmed Goblet	1625-1650	BPG2
BP6	Knop-Stemmed Goblet	1625-1650	BPG2
BP7	Ice Glass Beaker	1600-1650	BPG1
BP8	Knop-Stemmed Goblet	1625-1650	BPG2
BP9	Stemmed goblets	1580-1650	OUTLIER
BP10	Stemmed goblets	1580-1650	BPG2
BP11	Knop-Stemmed Goblet	1625-1650	BPG2
BP12	Knop-Stemmed Goblet	1625-1650	BPG2
BP13	Knop-Stemmed Goblet	1625-1650	BPG2
BP14	Knop-Stemmed Goblet	1625-1650	BPG2
BP15	Knop-Stemmed Goblet	1625-1650	BPG2

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Label SiO<sub>2</sub> Na<sub>2</sub>O  $K_2O$ Fe<sub>2</sub>O<sub>3</sub> Al<sub>2</sub>O<sub>3</sub> MgO Sb<sub>2</sub>O<sub>5</sub> CaO PbO TiO<sub>2</sub> CuO Total BP1 69.50 16.16 2.90 0.70 1.32 1.94 0.12 0.67 4.79 0.09 0.13 0.15 98.50 BP2 69.67 16.07 2.93 0.68 1.28 1.97 0.14 0.66 4.89 0.07 0.10 0.14 98.64 BP3 70.71 16.17 2.73 0.24 0.79 2.01 0.11 0.56 5.16 0.01 0.07 0.02 98.58 BP4 70.49 16.02 2.71 0.27 0.84 2.02 0.07 0.55 5.21 0.00 98.30 0.02 0.08 BP5 1.93 97.92 69.39 15.78 2.92 0.66 1.31 0.14 0.63 4.82 0.13 0.09 0.11 BP6 69.40 15.98 2.94 0.68 1.91 0.13 4.82 0.09 0.18 98.25 1.34 0.61 0.12 BP7a 39.10 10.98 1.08 0.05 0.50 1.21 0.05 0.16 2.00 0.04 0.04 0.01 55.25 BP7b 66.56 15.68 2.20 0.36 0.69 1.82 0.25 0.21 4.07 0.27 0.08 0.70 92.93 BP8 69.69 16.05 2.96 0.74 1.40 1.92 0.15 0.63 4.78 0.17 0.10 0.14 98.79 BP9 69.93 16.98 0.70 0.19 2.82 0.21 0.03 0.00 8.21 0.01 0.09 0.01 99.17 BP10 69.46 15.87 2.95 0.74 1.33 1.93 0.18 0.59 4.79 0.12 0.11 0.15 98.29 BP11 69.58 16.06 2.99 0.71 1.33 1.95 0.19 4.83 0.09 0.14 98.59 0.62 0.06 BP12 69.58 16.05 2.91 0.70 1.29 1.90 0.15 0.59 4.89 0.08 0.09 0.15 98.44 **BP13** 69.53 16.04 2.88 0.69 1.30 1.92 0.16 0.63 4.84 0.11 0.09 0.16 98.39 **BP14** 69.40 15.83 2.88 0.70 1.37 1.93 0.19 0.64 4.88 0.17 0.11 0.14 98.32 **BP15** 69.60 15.94 2.92 0.76 1.38 1.95 0.17 0.63 4.82 0.13 0.10 0.12 98.55

Table 2. EMPA data for the glass samples from the Barco de las Pipas.

so this sample was dismissed. Tables 2 and 3 present the results of the EMPA and LA-ICP-MS analysis of the samples, and Table 4 shows the precision and accuracy parameters for each technique.

Although the analytical protocols are described at length in Appendix A, a little explanation of the way the results are presented is necessary. In this paper, owing to the typology, context, and chronology of the assemblage, as well as to the fact that Venetian glass was regarded at the time as the glass of reference for European glassmakers, we shall give preference in the comparison of the data to known assemblages from Venice and the Low Countries, although other assemblages will also be considered. We shall largely deal with average compositions, as this is the way the data for Venetian and Flemish glass is typically presented in publications. The composition of individual samples is generally difficult to access, which means that we have to operate with the compositional groups suggested by previous studies, even if we have found no way to test them and the criteria to distinguish them is not always altogether clear, e.g. the distinction between imitation vitrum blanchum and façon-de-Venise glass. An important exception for the assemblage at hand is presented by the data recently published by Kunicki-Goldfinger, Hulst, and Freestone (2024). For ease of reference, and to reduce the number of in-text references and figures, the average compositions of the oxides/elements discussed further below are compiled in Table 5.

All the glass samples analysed are soda-lime-silica glass, but one of them (BP9) stands out sharply from the rest and will be discussed separately. Concerning the remaining samples, the main network former, silica, ranges from 70.71 wt.% to 66.56 wt.% SiO<sub>2</sub>; the main fluxing agent is soda, ranging from 16.77 wt.% to 16.38 wt.% Na<sub>2</sub>O; and the main stabilising agent is lime, ranging from 5.21 wt.% to 4.07 wt.% CaO.

The soda, potash (ranging from 2.99 wt.% to 2.20 wt.% K<sub>2</sub>O), and magnesia (ranging from 2.02 wt.% to 1.82 wt.% MgO) contents of all glasses are compatible with the fluxing of the glass with soda-rich plant ashes (e.g. Salsola Soda), the use of which was widespread in European glassmaking during this period. It is well known that Venice imported plant ashes from the Levant and that another producing region, the

Table 3. LA-ICP-MS data for the	glass samples from the Barco de las Pl	pas.
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Label	Li	В	Na	Mg	Αl	Р	K	Ca	Sc	Ti	٧	Cr	Mn	Fe	Co	Ni	Cu	Zn
BP1	26.5	81	122,832	115,79	7551	798	258,71	385,66	1.59	620	13.2	10.7	4929	6061	12.5	15.135	1190	56.7
BP2	26.3	81	123,060	115,84	7498	779	255,97	385,58	1.62	599	12.9	10.5	4847	6091	12.3	14.945	1166	54.2
BP3	19.3	86	124,261	118,91	4474	752	23,412	412,12	1.17	421	7.77	8.5	4293	2356	4.51	8.926	180	47.4
BP4	20.3	86	124,056	119,37	4441	747	231,49	408,23	1.12	421	7.84	8.4	4189	2345	4.52	8.918	181	47.1
BP5	26.9	82	124,395	115,65	7309	780	256,65	384,59	1.60	596	12.5	10.3	4868	6145	12.4	14.894	1178	55.5
BP6	25.1	81	121,647	120,05	8845	789	255,49	384,34	1.82	660	14.3	11.2	4733	5688	11.7	14.614	1062	54.2
BP7	14.7	84	121,483	108,61	4693	685	211,61	362,61	1.17	458	8.36	7.7	1647	3123	93.1	69.511	7381	54.4
BP8	26.6	82	122,383	115,92	7593	791	255,08	384,14	1.64	606	13.0	10.5	4860	6081	12.3	14.848	1154	55.4
BP9	3.4	51	130712	1287	14929	150	5905	64181	1.16	439	30.6	20.9	62.0	1459	0.75	5.790	4.28	7.4
BP10	26.3	83	122,890	114,95	7369	786	255,66	381,58	1.59	598	12.8	10.4	4865	6074	12.4	14.954	1176	55.6
BP11	26.6	81	122,411	115,27	7404	796	255,78	382,54	1.53	598	12.8	10.4	4869	6084	12.3	14.807	1172	55.8
BP12	26.4	82	122,498	116,03	7618	794	255,76	382,40	1.58	610	13.1	10.6	4848	6008	12.2	14.922	1155	55.6
BP13	26.8	81	122,829	114,44	7265	803	258,78	384,48	1.58	600	12.9	10.5	4930	6118	12.5	14.893	1209	57.0
BP14	26.3	81	122,219	115,41	7484	803	257,61	384,60	1.60	610	13.2	10.5	4914	6118	12.5	15.102	1193	56.4
BP15	26.8	82	123,493	114,99	7330	798	260,16	387,34	1.58	609	12.9	10.5	4942	6151	12.6	15.036	1208	56.7

	Sr	Υ	Zr	Nb	Мо	Sn	Sb	Cs	Ва	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
BP1	333	4.84	78.4	2.07	1.212	394	408	0.68	421	4.85	8.83	1.13	4.42	0.978	0.148	0.990	0.148	0.903
BP2	326	4.74	77.5	2.01	1.150	389	392	0.66	410	4.67	8.66	1.09	4.17	0.948	0.152	0.955	0.142	0.883
BP3	364	4.16	73.3	1.44	0.805	7	102	0.31	412	3.22	5.71	0.766	3.24	0.849	0.117	0.934	0.144	0.839
BP4	360	4.13	72.5	1.44	0.793	7	103	0.31	402	3.18	5.68	0.791	3.15	0.801	0.118	0.869	0.136	0.866
BP5	326	4.70	77.6	1.97	1.192	394	392	0.63	411	4.60	8.37	1.04	4.26	0.919	0.156	0.944	0.145	0.826
BP6	329	4.95	77.5	2.18	1.123	330	376	0.74	420	5.16	9.64	1.18	4.73	1.00	0.166	1.04	0.153	0.925
BP7	320	2.98	74.4	1.45	1.066	160	1465	0.34	184	3.21	5.86	0.695	2.74	0.592	0.104	0.559	0.084	0.506
BP8	329	4.76	77.8	2.02	1.122	388	399	0.66	413	4.72	8.69	1.10	4.35	0.873	0.142	0.928	0.142	0.864
BP9	125	2.61	133	0.79	0.168	-1	2.5	0.14	246	1.92	2.82	0.416	1.64	0.329	0.103	0.318	0.052	0.356
BP10	326	4.73	77.5	2.01	1.206	400	399	0.64	409	4.62	8.49	1.07	4.19	0.973	0.145	1.00	0.142	0.872
BP11	325	4.70	77.7	1.99	1.231	397	399	0.64	412	4.64	8.54	1.08	4.21	0.935	0.150	0.917	0.137	0.844
BP12	327	4.76	77.3	2.03	1.159	383	397	0.66	413	4.71	8.72	1.10	4.29	0.970	0.151	0.959	0.148	0.898
BP13	331	4.75	78.3	2.00	1.234	403	408	0.63	418	4.67	8.53	1.09	4.25	0.975	0.148	0.942	0.142	0.889
BP14	331	4.79	78.5	2.03	1.224	402	408	0.63	418	4.80	8.69	1.09	4.23	0.950	0.150	0.981	0.144	0.896
BP15	333	4.80	78.8	2.03	1.222	403	408	0.68	423	4.74	8.72	1.10	4.37	0.908	0.143	0.960	0.145	0.930

	Но	Er	Tm	Yb	Lu	Hf	Ta	TI	Pb	Th	U
BP1	0.179	0.516	0.072	0.509	0.073	1.91	0.143	0.07	1178	1.31	1.20
BP2	0.169	0.484	0.068	0.478	0.073	1.89	0.142	0.05	1147	1.26	1.18
BP3	0.158	0.463	0.067	0.458	0.067	1.78	0.107	0.12	108	0.933	1.02
BP4	0.162	0.460	0.069	0.449	0.062	1.72	0.106	0.12	110	0.925	1.02
BP5	0.173	0.477	0.066	0.485	0.069	1.89	0.140	0.06	1170	1.27	1.19
BP6	0.174	0.504	0.073	0.522	0.077	1.85	0.150	0.06	960	1.41	1.20
BP7	0.101	0.310	0.044	0.305	0.051	1.72	0.102	0.03	2491	0.850	1.61
BP8	0.171	0.514	0.076	0.458	0.072	1.90	0.151	0.05	1130	1.28	1.19
BP9	0.087	0.285	0.047	0.375	0.068	3.25	0.059	0.03	22.0	0.330	0.313
BP10	0.172	0.495	0.071	0.491	0.070	1.89	0.135	0.05	1181	1.27	1.17
BP11	0.170	0.499	0.070	0.468	0.076	1.89	0.139	0.05	1170	1.27	1.15
BP12	0.173	0.494	0.070	0.488	0.072	1.87	0.145	0.06	1138	1.29	1.18
BP13	0.166	0.492	0.071	0.511	0.075	1.87	0.145	0.06	1204	1.29	1.20
BP14	0.173	0.498	0.075	0.499	0.074	1.88	0.140	0.06	1195	1.29	1.19
BP15	0.171	0.513	0.071	0.478	0.072	1.93	0.144	0.06	1202	1.30	1.19

Spanish southeast, exported their ashes (known as barrilla) to London, Amsterdam, Hamburg, and Lisbon (Girón 2018: 225-226).

Taken at face value, these variables, and also those corresponding to the lime contents (lime can be brought into the glass as shell in the sands often used as a silica source, as a component of plant ashes, and as added calcite) are strongly reminiscent

Table 4. Precision and accuracy of the analysis undertaken on the glass samples from the Barco de las Pipas.

Table 4. Lecision	מומ מרר	i recisioni and accuracy of the	c allalysis	מומכוימויי		. yıdısı saı	III Caldi	יוור שמיי	מביות	ripus.					
	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	$AI_2O_3$	MgO	Sb <sub>2</sub> O <sub>5</sub>	MnO	CaO	PbO	TiO <sub>2</sub>	CuO			
CORNING-A (=15)	99:99	14.43	2.83	98.0	0.92	2.67	1.78	1.01	4.87	0.05	0.83	1.26			
S.D.	0.23	0.19	0.09	0.04	0.03	0.03	0.07	0.04	0.11	0.04	0.03	0.03			
Vicenzi et al. (2002)	96.59	14.30	2.87	1.09	1.00	5.66	1.75	1.00	5.03	0.12	0.79	1.17			
Acc %	0.00	-0.91	1.39	21.10	8.00	-0.38	-1.71	-1.00	3.18	58.33	-5.06	-7.69			
CORNING-B (=15)	62.21	16.49	1.00	0.28	4.41	1.03	0.44	0.23	8.43	0.43	0.11	2.98			
S. D.	1.51	3.26	0.38	0.03	60:0	0.04	90.0	0.03	0.19	0.05	0.02	0.07			
Vicenzi et al. (2002)	61.55	17.00	1.00	0.34	4.36	1.03	0.46	0.25	8.56	0.61	60:0	2.66			
Acc %	-1.07	3.00	0.00	17.65	-1.15	0.00	4.35	8.00	1.52	29.51	-22.22	-12.03			
CORNING-C (=18)	34.68	1.23	2.86	0.27	0.82	2.56	60.0	0.00	5.04	34.53	1.03	1.18			
S.D.	0.19	80.0	0.11	90.0	0.04	90.0	90.0	0.01	0.16	0.45	0.03	0.04			
Vicenzi et al. (2002)	34.87	1.07	2.84	0.34	0.87	2.76	0.03	0.82	2.07	36.70	0.79	1.13			
Acc. %	0.55	-14.54	-0.61	19.81	5.32	7.09	-189.50	99.70	0.54	5.91	-30.13	-4.10			
CORNING-D (=18)	55.03	1.33	11.15	0.38	5.13	3.92	1.31	0.54	14.47	0.20	0.40	0.37			
S.D.	0.21	0.04	0.49	0.04	0.08	0.05	80.0	0.05	0.59	90.0	0.03	0.05			
Vicenzi et al. (2002)	55.24	1.20	11.13	0.52	5.30	3.94	0.97	0.55	14.80	0.48	0.38	0.38			
Acc. %	0.38	-11.08	-0.13	26.10	3.30	0.59	-35.55	2.27	2.24	57.57	-6.50	2.05			
	=	æ	Na	Mg	A	۵	¥	ල •	χ	j	Ⴆ	Mn	Fe	ဒ	Z
BCRD (=18)	9.6	5.7	23680	20446	71108	1313	14940	50573	33.3	12889	428	15.5	1503	97194	12.5
S.D	0.4	0.7	318.5	217.5	445.2	18.9	167.8	680.4	0.4	161.9	5.6	0.3	15.2	872.9	0.2
Cert.comp	6		23962	21467	70913	1615	14900	50429	33	14100	425	17	1550	96385	13
Acc. %	7	#N/D	-1	-2	0	<del>-19</del>	0	0	1	6-	1	6-	-3	1	7
	3	Zn	As	Rb	Sr	>	Zr	qN	Мо	Sn	Sb	S	Ba	La	Ce
BCRD (=18)	19.1	158	1.4	47.1	336	33.6	179	11.7	258	2.6	0.2	1.2	649	24.8	52.0
S.D	9.0	3.9	0.3	0.7	4.4	0.5	2.0	0.2	4.7	9.0	9.0	0.0	10.5	0.4	0.7
Cert.comp	21	125	#N/D	47	342	35	184	12.5	270	2.6	0.35	1.16	683	24.7	53.3
Acc. %	6-	27	#N/D	0	-5	4-	-3	9-	4-	_	-47	0	-2	0	-5
	Pr	PN	Sm	Eu	РS	Тb	Dy	Н	ģ	Tm	۸þ	n	Ŧ	Та	F
BCRD (=18)	6.5	27.7	6.5	1.9	6.7	1.0	6.3	1.2	3.6	0.5	3.3	0.5	4.8	0.7	0.2
S.D	0.1	0.5	0.2	0:0	0.2	0.0	0.2	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0
Cert.comp	6.7	28.9	6.59	1.97	6.71	1.02	6.44	1.27	3.7	0.51	3.39	0.503	4.84	0.78	0.3
Acc. %	-3	4-	-2	-2	0	-4	-3	2	-3	4-	-3	-3	-1	-10	-22
	Pb	돈	n												
BCRD (=18) 5.D	11.1	5.7	1.7												
	!													, , , , , ,	5

Cert.comp	2.1	1.7	2.0									
Acc. %	11	5.9	1.69									
	ij	В	Na	Mg	ΑI	Ь	¥	Ca	Sc	<b>;</b>	Ċ	
NIST612 (=18)	41.2	35.6	104196	65.5	11071	113	60.7	89738	41.4	40.6	40.7	
S.D	9.0	0.8	754.1	1.3	51.3	2.8	0.8	1131.4	9.0	1.3	0.5	
Cert.comp	40.2	34.3	103858	89	11167	47	62	85002	39.9	44.0	38.8	
Acc. %	2	4	0	4-	Τ	143	-3	5.57	4	8-	2	
	3	Zn	As	Rb	Ş	>	Zr	<b>Q</b>	Mo	S	Sb	ొ
NIST612 (=18)	40.4	35.9	33.2	31.7	81.9	41.4	40.8	40.3	38.3	37.1	35.2	
S.D	0.7	6.0	1.1	9.0	1.1	9.0	0.7	9.0	0.8	1.2	1.0	
Cert.comp	37.8	39.1	35.7	31.4	78.4	38.3	37.9	38.9	37.4	38.6	34.7	
Acc. %	7	<b>%</b>	-7	-	4	∞	∞	4	7	-4	_	
	Ą.	PN	Sm	品	В	ФŢ	Dy	운	Ъ	π	γp	
NIST612 (=18)	39.3	36.9	39.3	37.7	40.8	39.1	37.6	39.8	40.1	38.2	40.5	
S.D	0.8	0.7	8.0	0.7	0.7	9.0	0.7	0.7	0.7	0.7	0.8	
Cert.comp	37.9	35.5	37.7	35.6	37.3	37.6	35.5	38.3	38.0	36.8	39.2	
Acc. %	4	4	4	9	6	4	9	4	9	4	3	
	Pb	Th	n									
NIST612 (=18)	39.3	38.5	38.5									
S.D	6.0	0.7	9.0									
Cert.comp	2.2	1.8	1.7									
Acc. %	38.6	37.8	37.4									

Table 5. Selection of average compositions of early modern glass compositional groups based on the literature.

Group	Reference	SiO <sub>2</sub> wt.%	Na <sub>2</sub> O wt.%	CaO wt.%	K <sub>2</sub> O wt.%	MgO wt.%	Al <sub>2</sub> O <sub>3</sub> wt.%	Fe <sub>2</sub> O <sub>3</sub> wt.%	TiO <sub>2</sub> wt.%	Zr ppm	Ce ppm	Y ppm	Sr ppm
Venetian <i>cristallo</i>	Verità (2013)ª; Janssens et al. (2013) <sup>b</sup>	70.5	17.2	4.88	2.93	1.81	0.68	0.24	0.03	14	m	7	285
Venetian <i>vitrum</i> blanchum	Verità (2013) <sup>a</sup> ; Janssens et al. (2013) <sup>b</sup>	6.99	13.8	8.6	2.88	3.35	0.98	0.35	0.05	36	7	∞	850
Antwerp <i>cristallo</i>	Janssens et al. (2013)	70.0	15.2	4.81	4.55	1.7	1.6	0.32	ı	75	8	2	360
Antwerp vitrum blanchum	Janssens et al. (2013)	0.99	14.6	10.0	2.2	3.5	1.3	0.36	1	40	2	∞	870
Antwerp facon-de-Venise	Janssens et al. (2013)	63.9	14.6	9.6	2.6	5.9	2.9	0.4	1	40	6	7	630
Amsterdam	Kunicki-Goldfinger, Hulst,	96:59	12.85	9.00	4.41	3.54	1.34	0.51	0.15	ı	ı	1	1
Twee Rozen Keizersgracht	and Freestone (2024)												
Amsterdam Twee Rozen	Kunicki-Goldfinger, Hulst,	65.20	13.63	89.8	4.82	3.13	1.60	0.72	0.15	ı	ı	ı	ı
Rozengracht	and Freestone (2024)												
Old Broad Street	Janssens et al. (2013)	64.5	13.1	6.7	5.4	3.1	1.8	9.0	1	ı	ı	1	ı
Beja	Coutinho et al. (2016)	64.68	16.47	6.48	3.75	2.58	3.54	0.57	0.11	1	1	1	1
-6													

<sup>a</sup>For major and minor elements. <sup>b</sup>For trace elements.

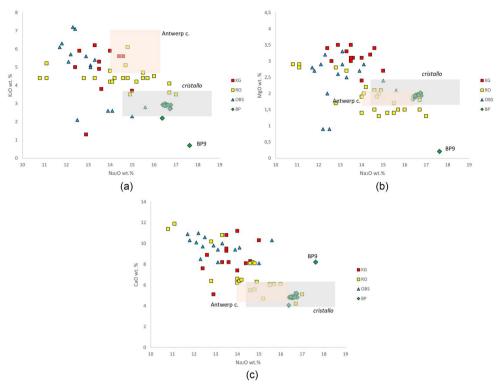


Figure 3. Contents of soda and potash (a), soda and magnesia (b), and soda and lime (c) of the Barco de las Pipas glass, the two phases of the De Twee Rozen glasshouse in Amsterdam, Keizersgracht (KG) and Rozengracht (RO) (data from Kunicki-Goldfinger, Hulst, and Freestone 2024), and the Old Broad Street workshop in London (data from Mortimer 1993). Data to outline the rough area where Venetian (grey), and Antwerp (salmon) cristallo would fall from Verità (2013), Janssens et al. (2013), Verità and Zecchin (2009), De Raedt et al. (2001), and De Raedt, Janssens, and Veeckman (1999). The greater affinity of BP glass with Venetian glass in terms of fluxdiscriminating oxides is apparent.

of the coeval cristallo glass made in Venice and less so of the imitation cristallo glass produced in Antwerp, especially because the potash content of the latter is significantly higher. The glass differs from other groups notably in terms of lime, soda, and often also potash, for instance, the glass from the Amsterdam workshop of De Twee Rozen; Antwerp-made façon-de-Venise and vitrum blanchum; and glass from the glass workshop in Old Broad Street, London (Figure 3).

As such, the flux-discriminant oxides found in the Barco de las Pipas samples suggest the use of plant ashes whose composition or processing methods were similar to those used in Murano. It is widely held that the high quality of Venetian glass was partially the result of the use of very pure sodic ashes with a low potash content imported from the Levant, and that, in top quality Venetian cristallo glass, this was compounded by the purification of the ashes prior to use (Verità 2013, 524, 528). Figure 4 illustrates the result of applying the methodology developed by Cagno, Janssens, and Mendera (2008) to the Barco de las Pipas samples, which suggests the

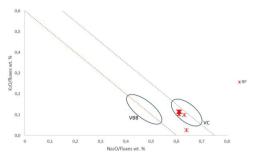


Figure 4. The result of normalising sodium and potash contents to the sum of all flux-discriminant oxides (Na<sub>2</sub>O, K<sub>2</sub>O, MqO, P<sub>2</sub>O<sub>5</sub> and CaO) suggests that the Barco de las Pipas glass was subject to similar purification processes as those applied to Venetian cristallo glass.

use of purified ashes similar to those used in Venetian cristallo glass. Only slightly less pure are the *cristallo* imitations produced in Antwerp (Janssens et al. 2013). Other production evidence, such as Antwerp vitrum blanchum and façon-de-Venise glass from De Twee Rozen workshop, most of the samples from Beja, Portugal, and the glass from the workshop at Old Broad Street, London (see also Mortimer 1993), present less pure ash compositions (i.e. a lower Na<sub>2</sub>O + K<sub>2</sub>O/total flux discriminant oxides ratios). As such, it is generally held that high-quality glass like Venetian cristallo used purified, high-soda ashes imported from the Levant (for a list of potentially Syrian glass-worthy species, see Barkoudah and Henderson 2006), whereas secondrate glasses used western Mediterranean barrillas, higher in potash than the Levantine ashes,

Regarding the sources of silica, recent research has shown that the presence of such impurities as alumina, iron, and titania can be of great use to characterise the geological makeup of silica sources and thus to help provenance glass or at least the sands/quartz pebbles used to make it (Rehren and Freestone 2015). It is known, for instance, that Venetian glassmakers began using comparatively pure silica sources in the form of quartz pebbles from the Ticino and Aldage rivers to make high-quality (i.e. clearer) glass in the Late Middle Ages (Smit et al. 2005; Verità and Zecchin 2009: 603-604).

In this regard, the Barco de las Pipas glass can be divided into two groups. One (BPG1), comprising samples BP3, BP4, and BP7, presents comparatively low levels of alumina (ranging from 0.69 wt.% to 0.84 wt.% Al<sub>2</sub>O<sub>3</sub>), iron (ranging from 0.34 wt.% to 0.45 wt.% Fe<sub>2</sub>O<sub>3</sub>), and titania (ranging from 0.07 wt.% to 0.08 wt.% TiO<sub>2</sub>). The second group (BPG2), comprising samples BP1, BP2, BP5, BP6, BP8, BP10, BP11, BP12, BP13, BP14, and BP15, presents significantly higher alumina (ranging from 1.28 wt.% to 1.40 wt.% Al<sub>2</sub>O<sub>3</sub>), although still within a low-alumina range, and iron (ranging from 0.81% to 0.88 wt.% Fe<sub>2</sub>O<sub>3</sub>), and slightly higher titania (ranging from 0.10 wt.% to 0.11 wt.% TiO<sub>2</sub>), suggesting the use of different silica sources in these two groups.

Compared with other coeval glasses, BPG1 is compatible with Venetian cristallo in terms of alumina and iron. However, it presents over twice as much titania, while it has less alumina, roughly the same iron, and elevated titania compared to Venetian vitrum blanchum. Compared to known glasses from the Netherlands, BPG1 presents

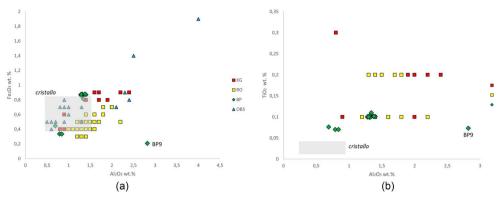
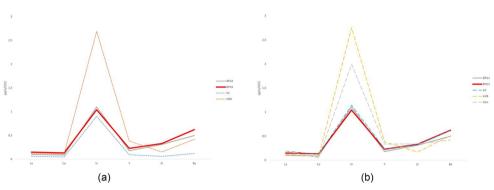


Figure 5. Contents of alumina and iron (a) and alumina and titania (b) of the Barco de las Pipas glass, the two phases of De Twee Rozen glasshouse in Amsterdam, Keizersgracht (KG) and Rozengracth (RO) and the Old Broad Street workshop in London.

lower alumina and iron than Antwerp glasses and most glasses from the De Twee Rozen glasshouse in Amsterdam. BPG2, for its part, presents alumina and titania compatible with Venetian vitrum blanchum glass and with Antwerp and some sodarich Amsterdam glasses. However, its iron contents appear to be too high for all these groups but the Amsterdam-made glasses (Figure 5).

The trace element signature of the Barco de las Pipas glass is of great interest, beginning with the fact that BPG1 and BPG2 present almost identical profiles. Such is the case for zirconium, which potentially reflects the silica-bearing raw material, and which features in BPG1 at 73 ppm Zr on average and at 79 ppm Zr in BGP2. Significantly, this is within the zirconium range typically found in northwestern European glasses and significantly higher than that found in Venetian high-quality glass, suggesting a silica source similar to that used in known Antwerp and Amsterdam glasses rather than that used in Venice. A similar picture is found with regard to other silica-related trace elements such as hafnium (an accessory element in most zirconium minerals) (1.7 ppm Hf on average in BPG1 and 1.9 ppm Hf on average in BPG1); cerium (6 ppm Ce on average in BPG1 and 8 ppm Ce in BPG2) and yttrium (4 ppm Y on average in BPG1 and 5 ppm Y in BPG2), which is also consistent with that found in northwestern European glass.

With regard to plant ash-borne trace elements, the picture is again similar. Strontium (348 ppm Sr on average in BPG1 and 329 ppm Sr in BPG2), which is typically associated with calcium; barium (333 ppm Ba on average in BPG1 and 415 ppm Ba in BPG2), which can also be affected by the manganese content, as barium is typically present in manganese minerals; and arsenic (78 ppm on average in BPG1 and 38 ppm in BPG2), the content of which can reflect ash purification procedures (Cagno et al. 2010, 3035), are all compatible with those found in northwestern, rather than Venetian glasses. The greater affinity of the Barco de las Pipas glass to northwestern glasses than to Venetian cristallo in terms of trace elements is illustrated in Figure 6.



**Figure 6.** Comparison of content in a selection of trace elements of the two glass groups in *Barco de las Pipas* with Venetian (a) and Antwerp (b) glass (data from Janssens et al. 2013). VC: Venetian *cristallo*; VBB: Venetian *vitrum blanchum*; AC: Antwerp *cristallo*; AVB: Antwerp *vitrum blanchum*; FDV: Antwero *façon-de-Venise*. For better visualisation, the absolute contents have been normalised to the concentrations of these elements in the upper continental crust (after Wedepohl 1995).

Throughout history, glassmakers have used a variety of additives to colour, decolour, and opacify glass. In the Early Modern Period, 'clear' (colourless or lightlytinted) glass was achieved either by the choice of very pure, or purification of, ingredients, in addition to the use of additives that offset the colouring properties of some impurities brought in with raw materials (notably iron, which 'naturally' imparts a green/yellowish colour to glass). Decolourants used historically include antimony (e.g. added to the batch as stibnite) and manganese (e.g. as pyrolusite), both of which were systematically used, for instance, during the Roman period (Foster and Jackson 2010). Since antimony is found in early modern clear glass only in minimal quantities, it is held that the standard decolouriser used during this period was manganese, and its use is documented in Venice as early as the thirteenth century (Verità 2013, 527). Venetian recipes indicate that rather than being included in fixed amounts to the primary batch, manganese was added gradually until the desired decolouration effect was achieved in response to the amount of iron present in the batch. This, in principle, should be reflected in the glass chemistry in a relatively strong positive correlation between iron and manganese oxides, as reported, for instance in the later Twee Rozen glass from Amsterdam (Hulst and Kunicki-Goldfinger 2017, 549-550), and it has been argued that a regular ratio between these two oxides suggests the use of more homogeneous raw materials and, therefore, more controlled production processes (Cagno et al. 2012: 5-6). In the case of the Barco de las Pipas samples, BPG1 presents a very strong negative correlation (Coef. Cor.: -0.99) and BPG2 a very strong positive one (Coef. Cor.: 0.84). In any case, the relevance of this is limited owing to the small number of samples involved. However, it is probably safe to say that the amount of manganese detected in all samples except for BP7 (0.21 wt.% MnO) was a deliberate addition, as any content of >0.50 wt.% MnO is unlikely to have entered the glass as an impurity with the raw materials (Jackson 2005). Concerning the raspberry-coloured prunt on BP7, it seems clear that the colouring was achieved by the addition of copper (0.70 wt.% CuO) since its content in cobalt (93 ppm Co) seems much too small to suggest deliberate addition.

In fact, the presence of colourants, decolourants, and opacifiers in glass in amounts too small to suggest deliberate addition but too high to indicate that they have entered the batch as impurities in the raw materials is typically taken as evidence for recycling. This is due to the assumption that when coloured glass is introduced as cullet in the batch, the colourants, decolourants and opacifiers that they contain will remain visible in the bulk composition of the batch in diluted amounts. However, it must be taken into account that this principle has been largely developed in the context of the study of Roman and late Roman glasses (Duckworth 2020; for glass recycling in Antiquity and the Middle Ages, see Freestone 2015; Paynter and Jackson 2016) which are, in general, characterised by a much neater compositional profile than later glasses fluxed with plant ash (the vast majority of Roman- and late Roman-period glasses were fluxed with natron, a mineral source of soda; see Shortland et al. 2006). As such, the natural thresholds used here - 50-100 ppm Cu; 50-75 ppm Pb; 25 ppm Sn; 10-20 ppm Sb (based on Rehren and Brüggler 2015) which are based on contents in glass assumed not to have undergone recycling, must be taken with caution, since these glasses were likely made with very different silica sources to those employed in early modern glass. Based on these thresholds, all samples in BPG2 appear to present some recycled glass within them (>1000 ppm Cu; >900 ppm Pb; >300 ppm Sn; >300 ppm Sb), whereas samples BP3 and BP4 (>180 ppm Cu; >100 ppm Pb; c. 100 ppm Sb) are also above the thresholds used, although in this instance the amount of colourant-bearing cullet mixed in the batch seems to be much smaller. The amounts of colourants/opacifiers other than copper found in BP7 (2491 ppm Pb; 160 ppm Sn; 1465 ppm Sb) can plausibly have entered the glass as impurities in the source of copper used as a colourant.

One very important factor for interpreting this assemblage is that the samples in BPG2 form an exceptionally tight cluster in nearly every variable (with the possible exception of BP6). It is often thought that glass is an entirely homogenous material in terms of composition, but this is not the case, especially in preindustrial conditions in which temperatures/melting times were often sub-optimal. In this way, we can expect even glass samples from a single batch to present some compositional variation. However, the range of compositions found in these, especially with small batches, will be relatively narrow and can in fact, as a general rule, be a result of instrumental error as much as of small inhomogeneity in the glass (Freestone, Price,

Table 6. Glass samples forming group BPG2. The close composition of these samples suggests that they were melted as part of a single glass batch.

	$Na_2O^a$	MgO	$Al_2O_3$	$P_2O_5^a$	$K_2O$	$Fe_2O_3$	CaO	$TiO_2^a$	$MnO^a$	$Fe_2O_3^a$
BP1	16.56	1.94	1.32	0.18	2.90	0.87	4.79	0.10	0.64	0.87
BP2	16.59	1.97	1.28	0.17	2.93	0.87	4.89	0.10	0.63	0.87
BP5	16.77	1.93	1.31	0.17	2.92	0.88	4.82	0.10	0.63	0.88
BP6	16.40	1.91	1.34	0.18	2.94	0.81	4.82	0.11	0.61	0.81
BP8	16.50	1.92	1.40	0.18	2.96	0.87	4.78	0.10	0.63	0.87
BP10	16.57	1.93	1.33	0.18	2.95	0.87	4.79	0.10	0.63	0.87
BP11	16.50	1.95	1.33	0.18	2.99	0.87	4.83	0.10	0.63	0.87
BP12	16.51	1.90	1.29	0.18	2.91	0.86	4.89	0.10	0.63	0.86
BP13	16.56	1.92	1.30	0.18	2.88	0.87	4.84	0.10	0.64	0.87
BP14	16.48	1.93	1.37	0.18	2.88	0.87	4.88	0.10	0.63	0.87
BP15	16.65	1.95	1.37	0.18	2.92	0.88	4.82	0.10	0.64	0.88

<sup>&</sup>lt;sup>a</sup>Based on LA-ICP-MS data converted to oxide

and Cartwright 2006). Table 6 illustrate that, for most major and minor elements, the contents of most samples are very close, which strongly suggests that these glass samples are the result of the same primary melting event, that is, they belong to a single batch. Furthermore, some of the differences in the composition of these samples can be plausibly explained. For instance, differences in the soda contents could be due to volatilization of sodium during the process, so vessels shaped last could present lower sodium levels than those that were made before. This is reinforced by some negative correlation between soda and alumina and titania, which, due to corrosion of the clay glass crucibles in use would increase in the batch over time (that is, the reverse effect observed in sodium) This conclusion is reinforced by the idea that all the items were part of a discrete, typologically consistent archaeological assemblage.

Finally, sample BP9 is entirely different to the rest of the assemblage. For one, its potash (0.70 wt.% K<sub>2</sub>O), magnesia (0.21 wt.% MgO), and phosphorus (150 ppm P) contents strongly suggest the use of a mineral flux, which, to the best of our knowledge, were not used in Europe at any point during the Early Modern Period. In addition, it has much higher alumina (2.82 wt.% Al<sub>2</sub>O<sub>3</sub>) and lime (8.21 wt.% CaO) and significantly lower iron (0.21 wt.% Fe<sub>2</sub>O<sub>3</sub>) than the rest of the assemblage. From a compositional perspective, this glass is comparable to some Roman glasses in some variables. Low strontium (125 ppm Sr) suggests the use of a relatively pure source of silica, such as quartz pebbles (Brems, Ganio, and Degryse 2014), but the high alumina contradicts this. It is known that in 18<sup>th</sup>-century Mexico City some glass types were made using an evaporitic salt, known as tequesquite, collected in Lake Texcoco in the Mexico Basin (Peralta 2013: 10), but since very little glass from colonial contexts in Spanish America has been analysed to date, and none of these glasses allegedly fluxed with mineral salts have been identified, an association of BP9 (which, in addition, fits the rest of the assemblage typologically) with this tequesquite-fluxed glass, must be put on hold and this sample will not be discussed further.<sup>2</sup>

### **Discussion**

Based on the arguments that dominate the literature on high-quality early modern glass, these results are contradictory. On the one hand, the flux-related variables fall within ranges that are typically associated with the use of Levantine ashes, and these variables are often used to argue for a 'genuine Venetian origin' of glass objects as opposed to façon-de-Venise or imitation Venetian glass from other centres, which are assumed to have used different ashes richer in potash, such as Spanish barrillas (e.g. Coutinho et al. 2016; Janssens et al. 2013). However, it must be pointed out that very little attention has been paid to the composition of plant ashes potentially used in glassmaking, and especially those sourced from the Iberian Peninsula. For instance, studies by Ashtor and Cevidalli (1983), Barkoudah and Henderson (2006), and Tite et al. (2006) have focused almost entirely on Levantine and eastern plant ashes. As such, the widespread assumption that Spanish barrillas were more potash-rich than Levantine ashes seem not to be supported by any evidence.

Furthermore, the claimed advantage obtained by Venetian glassmakers through their methods and glass recipes may have been somewhat overblown. For one, it has

been abundantly attested that the measures the Republic of Venice imposed to stop the emigration of glassmakers from the city were a failure (Verità 2013, 531). For instance, Venetian glassmakers are recorded at work in Portugal, the Low Countries, and London, sometimes as early as the sixteenth century (Coutinho et al. 2016: 437-438; De Raedt, Janssens, and Veeckman 1999, 493; Hulst and Kunicki-Goldfinger 2017, 547), and Antwerp was soon to be recognised for its imitation of Venetian glass (De Raedt et al. 2001, 1014; Janssens et al. 2013, 538). If this was not enough to ensure a widespread knowledge of Venetian glassmaking technology, the 'secrets' of the trade, as practised in Venice, were put down in writing profusely in a period in which the circulation of technical manuals and treatises was accelerating rapidly, although modern notions of the word 'secret' may have coloured our interpretation of these documents (e.g. Verità 2013, 528; for a review of the place and role of technical literature specifically on the dissemination of glassmaking see Govantes-Edwards, Duckworth, and Córdoba 2016, Govantes-Edwards, López, and Duckworth 2020; Govantes-Edwards and Pearson 2023). It has been argued that the publication of L'arte Vetraria by Antonio Neri in 1612 contributed to the spread of Venetian glassmaking technology, but the publication of comprehensive technical manuals, beginning in the sixteenth century, including Biringuccio's De la Pirotechnia in 1540 and Agricola's De re Metallica in 1556, were more likely the end of a stage in the dissemination of technical information, rather than its beginning.

As a last argument concerning this point, in some publications the circulation of plant ashes is sometimes oversimplified, presenting a more or less clearcut dichotomy between Venice/Levantine ashes vs. façon-de-Venise centres/other ashes. This dichotomy, however, neglects the fact that Spanish barrillas were also exported to Venice (Montojo 2013; Verità 2013, 521), and these seemed to have been well regarded, judging by a passage in a manuscript dated to approximately 1700, which reads:

Ashes that are used in Murano come from many countries. From Spain, and these are very good for making glass just as those that come from Tripoli in Syria, but those that come from Aleppo, from Acris, from Carthage are inferior, and are called thin ... they struggle to make glass, but they also come from Alexandria, but these are not good at making anything other than black glass (original quote in Ashtor and Cevidalli 1983, 217; translation by authors)

Furthermore, although it is very likely that the Venetians were the first to import Levantine ashes for glassmaking as early as the thirteenth century, and that the Venetian government went to some lengths to try to control the circulation of this product (Verità 2013, 524), Venice never held a monopoly over the source, and the ashes were also shipped elsewhere, for instance their import to The Netherlands and England is well attested (Ashtor and Cevidalli 1983, 507). The conclusion that must be drawn is that identifying glass samples based on ash-discriminant oxides alone is spurious, a point already raised by Marco Verità (2013, 531).

Consequently, the only reliable way to distinguish between various glass productions lies with the silica sources. It has been convincingly argued that plant ashes were the only major raw material used in glassmaking likely to have been brought from any significant distance (although some of the manganese used in Venice was imported from abroad; Verità 2013, 52), and analyses undertaken to date have confirmed the affinity of the sands from La Casina/La Cava and some of the glass made in nearby Tuscan glass workshops (Cagno et al. 2010, 3032-3023). Indeed, pebbles collected in the Ticino River, mentioned in the written sources as the silica source of high-end Venetian glass, present a level of impurities consistent with this glass (Verità 2013, 524). In any case, care should be taken not to rely entirely on major impurities (e.g. alumina, iron, titania), as the advantages of using highly pure silica sources were known beyond Venice, and Coutinho et al. (2022) have demonstrated experimentally the viability of producing low-impurity glass with Portuguese quartzite pebbles (see also Coutinho et al. 2016, 444-445).

This leaves consideration of the trace elements. As previously noted, the trace element profiles of BPG1 and BPG2 are fairly similar, including those that reflect the underlying geology of the source of silica, notably zirconium, hafnium, cerium, and yttrium, and this profile is much closer to that presented by Dutch rather than Venetian glasses. Together with their typology and depositional context, this leads us to conclude that the glass that sunk with the Barco de las Pipas was likely made in, what is today, The Netherlands or Belgium, during the first half of the seventeenth century. It was most likely made using a local silica source and Levantine or other purified ashes. The high iron content of BPG2 makes it tempting to argue for an Amsterdam production, and it is important to note that two vessels in the other group, the ice glass beaker (BP7) and the serpentine stem (BP4), are both of the highest quality of manufacture and represented among the working waste excavated at De Twee Rozen workshop in the city. However, two factors recommend caution.

First, the fact that the glasses in group BPG2 were potentially made in a single batch makes it more plausible for some 'accidental' rather than structural factor to slightly alter the glass composition. For example, in the case of iron, some undetected 'peeling off' of metal scale from the blowing iron into the melt could affect its overall chemical composition. Second, in the late 16<sup>th</sup> and early seventeenth century, a common approach to glass production seems to have formed in the northwestern European region, including Flanders and south-eastern England. Strong compositional similarities in glasses found in Antwerp, Amsterdam, and London have been pointed out (Janssens et al. 2013, 554), and the circulation of glassmakers between the Netherlands and England has been abundantly attested in the historical sources (Cagno et al. 2012, 1). As such, until more data is made available to make more reliable distinctions, the provenance of these glasses should be approached with caution.

Finally, the compositional and typological homogeneity of the assemblage strongly suggest that the cargo of the Barco de las Pipas included a small consignment of glass (probably no more than a crate or two), purchased as a set in a single transaction directly from a workshop or a specialised merchant. The high quality of the vessels all but rules out them being owned and used by a crew member, even the captain, for the asperities of transatlantic crossings would have made this sort of shape totally impractical for use aboard ship.

### Conclusions

The analytical study of glass in Spanish/Portuguese colonial America has barely begun, and we have not yet fully defined what questions should be asked of the data. What sort of glass was sent across the Atlantic to these colonies? Were some types of glass preferred over others? And if so, why? When did colonial societies begin making their own glass from raw ingredients, rather than remelting the glass cullet from imported glass? Did they focus on certain types of glass, relying on Europe for the rest? These are just a few possible questions, but many more will surely arise as the field expands.

Instead, the evidence presented in this paper makes a much more valuable contribution to our understanding of European glassmaking in the early seventeenth century, rather than its reception in colonial America. From a compositional perspective, the glass was made in the northwestern European tradition that included the Low Countries and England, primarily based on the evidence provided by the trace elements. At the same time, some degree of contradiction between flux- and silicarelated components in this glass, when compared to existing datasets and interpretations, has also helped emphasise a point already made by Marco Verità: that the provenancing of glass compositions based on flux-related variables is, to say the least, hazardous. First, because the dichotomy drawn between Venice and Levantine ashes versus those from elsewhere, such as Spanish barrillas, is contradicted by some evidence. Second, the supposed superior suitability of Levantine compared to other ashes is not supported by archaeological or analytical evidence.

While it is beyond doubt that Venice may have spearheaded glass technology in the West during the Late Middle Ages and up until the sixteenth century, the picture provided by the written, archaeological, and archaeometric evidence is one of enormous dynamism in the European glass sector by the seventeenth century, especially considering the failure of the Venetian Republic to keep the 'secret' of Venetian glass an actual secret.

Whilst our assemblage is too small and archaeologically narrow to make conclusive statements concerning the role played by the glass trade within early colonial societies, it can be said that the people who sent the Barco de las Pipas across the Atlantic believed there was a market for first-rate glass tableware. What is more, the purchase of what seems to be a single consignment of glass vessels of matching forms suggests that they also believed that there were customers in the colonies willing to buy tableware sets rather than just single vessels. Consequently, this paper, although restricted in scope, has significant ramifications for our understanding of wider exchange networks, and provides a methodological template for future studies in this still poorly understood area.

### **Notes**

- 1. The exact ppm count of Hf is not reported systematically in the publications used as references; it is only mentioned indirectly in-text for some groups.
- 2. The first author is currently working with research and development unit VICARTE (Universidade NOVA de Lisboa) to characterise tequesquite-fluxed glasses. Experimental work undertaken with Ines Coutinho and Andreia Ruivo in February 2025 has demonstrated the viability of using tequesquite as a flux for glass at temperatures that could be easily achieved by preindustrial glass furnaces.

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# Appendix A. Materials and Methods

The samples were taken by David Govantes-Edwards at the facilities of the Oficina Nacional de Patrimonio Subacuático, Santo Domingo, Dominican Republic, and consisted of fragments approximately 4 × 4 mm in size. The samples were then mounted in epoxy resin, ground, and polished with  $a < 1 \,\mu m$  diamond paste. Chemical analysis of the samples included Electron Micro-Probe Analysis (EMPA) for major and minor elements (>0.01 wt.%) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for trace elements (<0.01 wt.%).

EMPA analysis was undertaken by Victoria Sainsbury at the Research Laboratory for Archaeology and the History of Art, University of Oxford, using a JEOL-8600 wavelength dispersive electron microprobe with 15 kV accelerating voltage, 7 nA current and 10 µm diameter beam. Peak counting times were 20 s for calcium and potassium; 30 s for silicon, aluminium, and magnesium; 40 s for iron; 50 s for chlorine, manganese, and lead; 60 s for tin and antimony; and 80 s for phosphorus and copper. The microprobe was calibrated using mineral standards and quantified using the PAP absorption correction method. The accuracy of the electron microprobe analyses was verified using Corning reference glasses. Three samples were taken per reading, and the results shown are the average of these. Results are given in wt.%.

For the detection of trace elements (reported as parts per million), LA-ICP-MS analysis was conducted by Elliot Hamilton at the Centre for Environmental Geochemistry, British Geological Survey (Keyworth). The carbon coating was removed from the sample blocks using alcohol wipes and the samples outlined with permanent marker on the resin block to aid in their location. A NewWave FX 193 nm excimer laser with integral microscope and ablation cell was coupled to an Agilent 7500c series ICP-MS using a helium gas flow. Laser conditions were: 75 × 75 μm square spot, 20 Hz repetition rate, 25% power, 20s ablation time per spot with 3s washout between each. Quantification was performed using. NIST SRM610 and GSD1G, with NIST SRM612 and BCR2G, were used as quality control samples. Calibration was undertaken using Iolite software. Internal calibration of the ICP-MS data was realised using the silica (SiO<sub>2</sub>) results obtained by EMPA. Each sample was ablated three times, and the results presented are the average of these.