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In the quest for historical Lisbon through 17th century *Millefiori* glass

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A R T I C L E I N F O

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A B S T R A C T

Being Lisbon one of the world's most important trading port and a place where historical documents attest the presence of at least four glass furnaces working between the 16th and 17th centuries, the authors decided to investigate one of the most luxurious coeval glass decorative techniques (*millefiori*) found in Lisbon to try to understand the trade route and raw-materials provenance of these artefacts.

For this work, two Lisbon archaeological contexts were selected: Largo do Chafariz de Dentro (*LCD*) and Santana Convent (*LCS*) due to their significant amount of interesting *millefiori* fragments (eight fragments) and the presence of production waste (one in LCD and three in LCS). The analysis, comparison and discussion of glass production waste (PW) and archaeological glass artefacts will be carried out for the first time.

For this work, macroscopic and microscopic observations were combined with the chemical characterization of colourless and coloured glass to make the morphological characterization and to determine which raw materials were employed in its production. The chemical characterization was made by using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to obtain the major, minor and trace elements composition, including rare earth elements (REE).

The chemical composition of the selected samples revealed that all the *millefiori* glasses are of soda-lime-silica type (part of them made with Levantine ashes and the other part with *barilla*) while the glass type of PW is was not attributed.

Regarding the Lisbon *millefiori* glass fragments, there is a notable relation between the concentration of major components associated with the silica source, namely SiO_2, Al_2O_3 and TiO_2. Moreover, upon analysing the geochemical patterns exhibited by the production waste found in LCS context and comparing it with the pick-up glass fragments, a consistent trend emerges, implying that both were made by using either the identical silica source or, at the very least, a closely related silica source. For this reason, the possibility of a Portuguese local production may be proposed, especially when some decorative patterns are clearly from Portuguese inspiration (e.g. caravel and cross of Christ), while the authors admit that more data analysis is still required to prove this hypothesis.

1. Introduction

In the 15th century, Portugal began its overseas discoveries, conquering Ceuta (North Africa) in 1415 and discovering the sea route to India by Vasco da Gama and the sea route to Brazil by Pedro Álvares Cabral at the end of the 15th century. In the 16th century, Portugal was already considered the "first European Maritime Empire" with a significant political and economic influence (Arnold, 2017, 92).

The trade connections between Europe and the Levant via the Mediterranean and Venetian Republic changed at the beginning of the 16th century, to Antwerp and Lisbon through an Atlantic Sea route. This change not only brought a greater quantity and diversity of products,

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but also gave a greater profit margin to Portugal (Arnold, 2017, 96-97; Subacchi, 2002, p. 23).

Lisbon (Portuguese capital), located on the north bank of the Tagus River (Fig. 1), became one of the most important import–export trade markets for its colonial products (e.g. tobacco, silk, cotton and spices like pepper, cocoa, coffee and sugar) and for precious and exquisite products from China, Japan, Venice, the Low Countries, among others (Arnold, 2017, Varela Gomes et al., 2015, p. 94). Nevertheless, Lisbon was also a very important trade market which linked Central Europe and Western Africa with commodities like brass-copper, glassware, and linen textiles (Arnold, 2017, p.96).

Between the 15th and 17th centuries, Venice was Europe's reference centre for glass making due to its style, quality, and techniques. Venetian glassmakers were responsible for the invention and improvement of *cristallo* glass (the clearest and purest type of glass of the Renaissance) and were highly skilled in making and combining coloured glasses. *Millefiori* glass is, probably, the best example of that perfect colour combination, having been described by the Italian historian Marcantonio Coccio Sabellico, in his book "*De Venetian Urbis Situ (1500)*" dated to 1495, as: "(…) includes in a little ball all the sorts of flowers which clothe the meadows in spring. (…)" (Charleston, 1967; Whitehouse, 2012).

Venetian glass was so famous that several attempts were made, over Europe, to imitate it and *façon de Venise* is the current term attributed to these objects (Verità and Zecchin, 2009). Some works point out that Venetian glassmakers working abroad still were importing the traditional flux agent, making these *façon de Venise* glass composition quite similar to genuine Venetian glass (e.g. Baart, 2002; Bronk et al., 2000; de Raedt et al., 2002).

From the 15th century onwards, Venetian glassware has become desired among the wealthiest Portuguese society, as seen throughout Europe (Coutinho et al., 2016; Mendera, 2002, p. 263). On 15th July of 1563, a royal charter forbade the entry of Venetian glass into the country to protect Portuguese glass production as it was very developed and had a remarkable quality comparable to the Venetian glassware (Matos Sequeira, 1932, p. III, Medici et al., 2017).

The location of the Portuguese furnaces producing this good quality glass are so far unknown.

Historical documents state that, in 1551, at least 16 workshops with different targets (e.g. optics, plain glass and mirrors) were established in Lisbon and the names of several glassmakers are mentioned (Valente, 1950, p. 36; p. II, Medici et al., 2017, p. 413). The exact location of these glass furnaces is not known due to the big earthquake that happened in 1755, which caused fires and a tsunami that destroyed the Lisbon waterfront. Moreover, there are records of places in Lisbon whose names are linked to glass production: Rua do Vidro (literary Glass Street), Beco do Vidro (literary Glass Alley), Forno do Vidro (literary Glass Furnace) and Horta do Vidro (vegetable garden of glass) (Amado Mendes, 2002; Barosa, 2022; Matos Sequeira, 1932).

Although no archaeological evidence of glass furnaces has been discovered so far, nor glass objects linked with these production locations known, some scholars pointed out that they could be placed in what is nowadays known as Campo de Santa Clara, Santos, Alcantara and Rua dos Correeiros (Barosa, 2022; Pulido Valente et al., 2018).

The *pick-up* technique was rediscovered and developed by Venetian glassmakers during the 15th century and can be divided into two main decorative types: **1) *millefiori***, which has sliced glass canes that have drawings in its cross-section (*murrine*) fused in the body glass and **2) *splashed***, which have plane colored glass slices fused in the body glass (for the detailed description of this process see Pulido Valente et al., 2021).

Glass objects decorated with the *pick-up* technique are rare (Baart, 2002; Medici, 2012) and their production is so complex that the origin of this type of artefact has been mainly attributed to a genuine Venetian production (Pulido Valente et al., 2021). However, these types of artefacts were already found in production centres located outside Venice and some of them can be considered locally made due to their chemical composition (see Table.1).

In fact, although *millefiori* glassware is among the most exclusive and famous Venetian glass due to its elaborate production, there are only few compositional studies done on those objects (only the greyish highlighted references of Table. 1 are exclusively focused on it).

Combining this data survey with historical sources it becomes clear that *pick-up* glass objects (in both types: *splashing* and *millefiori*) were also produced outside Venice, for instance, in Catalunya and in Amsterdam (Doménech, 2004; Gawronski et al., 2010; Baart, 2002). Moreover, some archaeological contexts in Europe yielded production waste (PW) suggesting a local production: e.g. Buda Palace in Hungary (Holl-Gyürky, 1986), and Lisbon and Coimbra in Portugal (Medici, 2014).

A small *millefiori* glass with a gourd shape, found in Moura (Portugal), has been considered as being a probable local production. Gourd-shaped vessels were the focus of previous studies and are considered a Portuguese product (Coutinho et al., 2017; Medici, 2012).

Previous investigations show that Portugal is the country where the greatest number of pick-up decorated archaeological glass fragments have been found and studied so far (Pulido Valente et al., 2021). In addition, several archaeometrical studies performed on archaeological glass unearthed in Portugal addressing the study of Venetian and *façon-de-venise* glass artefacts have been developed in the last ten years (e.g.

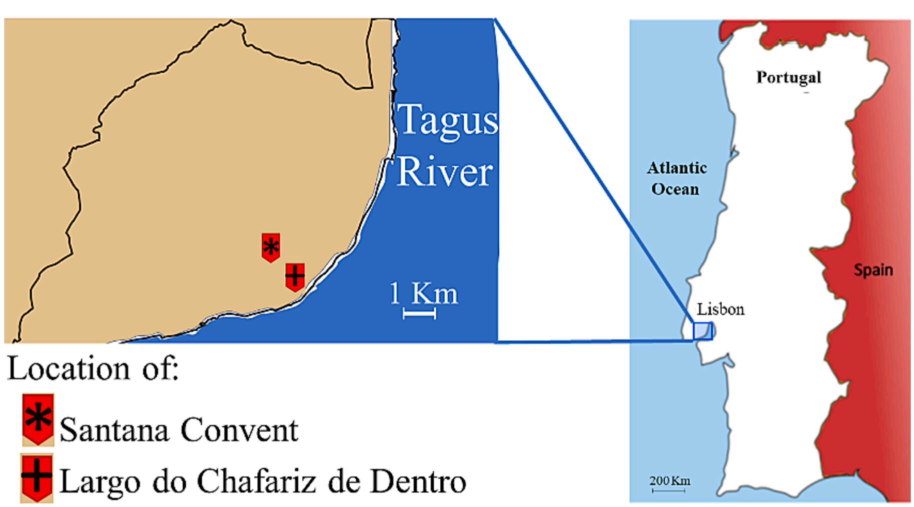


Fig. 1. Nowadays Lisbon and archaeological context's location.

Table 1
Organization of literature where archaeometrical investigation in *pick-up* glass fragments was performed. (See above-mentioned references for further information (Lima, 2010; Ulitzka, 1994).)

References	Country	*millefiori*	*splashed*	Century	Production Centre	Glass Type
Hulst 2013	Netherlands	√		17th	De Twee Rozen, Amsterdam	SL
Coutinho et al. 2021a	Spain		√	16th/17th	Calle Horno del Vidrio, Granada	SL
Dungworth et al. 2006	England		√	17th	Silkstone	HLLA
Gawronski et al. 2010	Netherlands	√	√	17th	De Twee Rozen, Amsterdam	SL
Lazar & Willmott 2006	Croatia	√	√	16th	Venice (?)	SL
Lima 2010 (*)	Portugal	√	√	17th	Some are Venetian	SL
Lima et al. 2012 (*)	Portugal	√	√	17th	Some are Venetian	SL
Mendera 2002	Italy	√		16th	Local (Gambassi)	MA/ SL
Pulido Valente et al. 2019a(1)	Portugal	√	√	16th/17th	(?)	SL
Teixeira 2014	Portugal		√	16th/17th	(?)	SL
Ulitzka 1994(1)	Spain or Nevers	√	√	17th	n.a.	n.a.
Verità 1985	Italy	√		16th	Venice	SL
Verità and Zecchin 2008	Italy		√	16th	Venice	SL

(*) Both are discussing the same fragments.
( ) The works that are exclusively focused on *pick-up* glass are highlighted in this table.
(1) Study of several assemblages.
HLLA – High-lime Low-alkali; MA – Mixed-alkali;; SL – Soda-lime.
n.a. – not applicable.

Coutinho et al., 2016; Lima et al., 2012; Medici et al., 2017; Varela et al., 2018).

Recently, potential raw materials – sand and quartz pebbles - collected from Coimbra and Águeda areas (Portuguese cities where local glass production was established) were melted in the laboratory at VICARTE to produce glass to then compare their chemical composition with historical samples. This project showed that three glass fragments from Santa Clara-a-Velha Monastery have a chemical composition compatible with silica sources collected in Coimbra (Coutinho et al., 2022).

In the present work, a selection of *millefiori* glass fragments and production remains excavated in two different sites in Lisbon was analysed and the results will be presented and discussed for the first time. This study attempts to determine if it is possible to identify the raw materials used in the production of the analysed glass and relate this information to try to answer to two major questions: (1) Are they genuine Venetian artefacts? (2) If they are *façon-de-Venise*, is it possible to attribute some of the fragments to their production centres?

2. Analysed glass fragments and its contexts

2.1. The fragments

Eight *millefiori* glass fragments (Fig. 2) were selected from two different archaeological contexts located in Lisbon: Largo do Chafariz de Dentro (*LCD*) and Santana Convent (*LCS*), which are about 2 km away from each other (Fig. 1).

Four glass production remains found in the same contexts (Fig. 2) were also analysed, for the first time, to compare their chemical composition with the selected glass artefacts. For the sample selection, the work carried out by Teresa Medici (2014) was fundamental to survey the archaeological glass data of the modern period found in Portugal. For the scope of this work, peculiar characteristics, and shapes (e.g., unique decorative patterns such as cross, caravel and flower; and the

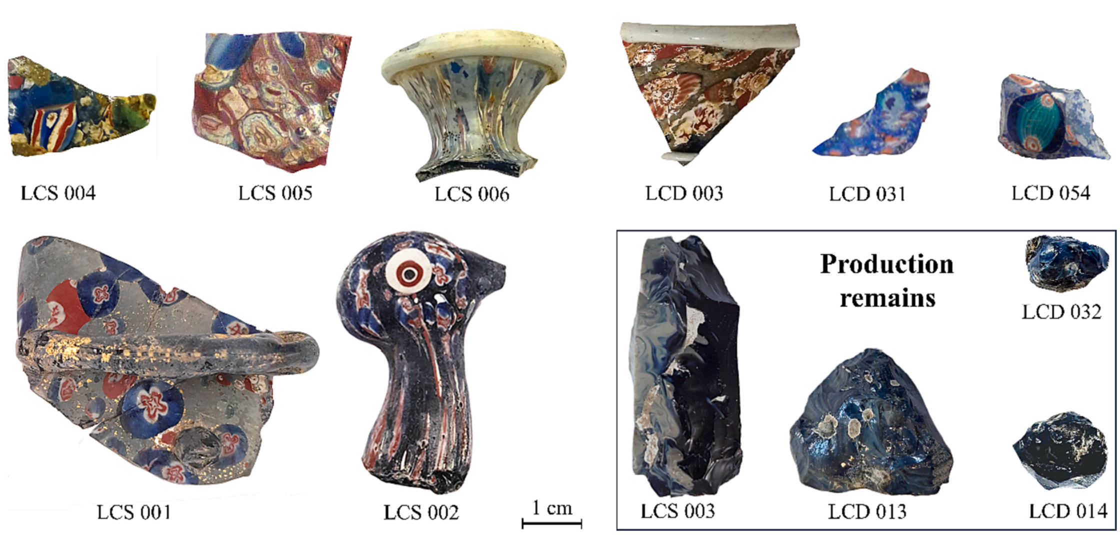


Fig. 2. The selected glass fragments decorated with picked-up technique (LCD – Largo do Chafariz de Dentro and LCS – Santana Convent).

bird head shape) were target factors (Fig. 3).

Caravel (Fig. 3, LCS 001) can represent the Portuguese expansion, being evangelization one of the main objectives. Portuguese Discoveries were supported by the military Order of Christ (derived from the Order of the Templars, which had been dissolved by Pope Clement V in 1312) (Vasconcelos and Mantero, 1999, 53-54). The **cross of Christ** (LCD 003), also known as the Portuguese Cross, is the symbol of this military Order and is so important to Portuguese identity that it was also used on contemporary Portuguese coins, in the sails of caravels and architectural ornaments (Vasconcelos and Mantero, 1999, 86). Forever associated with Portuguese discoveries, this cross is still used today by entities such as the Portuguese Air Force on their aircraft and in the flag of the Portuguese Autonomous Region of Madeira.

The **bird head** (LCS 002) is a really interesting fragment because, at the end of the 17th to the 18th centuries, glass objects representing dogs, birds, fishes and fantasy creatures were used by the European extremely wealthy society (e.g. in Venice, Germany, Belgium, or the Netherlands) to decorate dinner tables (Kitty Laméris et al., 2023, p. 190). This type of glass, which consisted of glassware simulacra is known as *trick glass* and was used at important receptions and parties where the festive tables were also decorated with artfully folded napkins and trick dishes (Laméris et al., 2023, p.190–191). These decorations created allegorical scenes and should represent all known kinds of fruits and animals (Laméris et al., 2023, p.191). Concentric circles representing the eyes of animal's glass objects are known in some contemporary trick glass decorated with *filigrana* technique dated to the end of the 16th - early 17th centuries with a production attributed to Antwerp (Laméris et al., 2023, p.192–194).

The **concentric circles** of those *filigrana* trick glass have always three layers of coloured glass: blue, white and red (arranged from the core to the edge) and they are in relief (Laméris et al., 2023, p.192–194). However, in the LCS 002 fragment, the concentric circle that represents the bird's eye is completely embedded in the body glass and has a last layer of white glass which remains unillustrated in the mentioned *filigrana* trick glass.

Rosette is the most spread pattern through *millefiori* glass (Pulido Valente et al., 2021).

Regarding the PW an observation of the fragments was performed both on the surface (Fig. 2) and in cross-section (Fig. 4).

The amorphous shape and the lighter shadows of LCDpw (Figs. 2 and 4) can indicate that the glass is not homogeneously melted and was discarded by dripping. They are translucent with a brownish colour.

LCS 003 was considered a PW because of the amorphous form of the fragment that presents a colour gradient (from whitish to bluish colour), but mainly, because this amount of glass is attached to a surface that looks like a light-coloured ceramic (Fig. 5).

Can the light-coloured ceramic be considered part of the crucible and the white part represents the diffusion area between the glass and the crucible?

2.2. The contexts

LCD is situated in one of the oldest Lisbon squares near Tagus River where, between 2007 and 2008, some excavations for the improvement of the wastewater treatment system took place. The finds were stratigraphically dated by the archaeologists to the 16th –17th centuries (Banha da Silva et al., 2012).

The assemblage presents a very rich variety of artefacts, evidencing that the contemporaneous Portuguese wealthy society had a huge desire for luxurious items reflecting its economic status. The artefacts found there include, for instance, Chinese ceramics and porcelains (Celadon and Ming dynasty – one has a Cross of Christ drawing, witnessing that some porcelains were made to order from Portugal), Italian maiolica, German stoneware, Spanish ceramics, Hispano-Moresque tiles and Venetian or *façon-de-Venise* glass (e.g. *millefiori* and *filigrana*).

The three analysed glass fragments are presented in Fig. 2 and described in Table. 2.

Santana Convent (*LCS*) is located on a hill named Santana and dates to the second half of the 16th century (1562) (Varela Gomes et al., 2015, p. 94-95). It was constructed from the existing ancient Santana hermitage which fulfilled the function of a church (Varela Gomes et al., 2015, p. 95). The convent was one of the most important religious buildings in Lisbon and was occupied by nuns of the Third Order of Saint Francis that should preach poverty, chastity, enclosure, and obedience. However, the luxurious items uncovered there (e.g. excellent quality porcelain, some of them presenting erotic cobalt blue pictures, jewellery, Venetian or *façon-de-Venise* glass and exotic beads) do not reflect this reality. This observation can be linked to the fact that becoming a nun in those times was more a matter of social status than of a personal devotion (Varela Gomes et al., 2015, p. 93-96). In 1884, with the suppression of the female religious orders, the building was abandoned and in 1897 part of the convent, including the church, was demolished to construct the *Real Instituto Bacteriológico* (Varela Gomes et al., 2015, p. 95).

Several deformed and broken canes (including a *filigrana* rods) and beads (one chevron bead) were found in this context along with some production waste of canes for the production of glass beads that can be considered indicators of glass working there or nearby (Gonçalves et al., 2020).

The assemblage uncovered from this context was found in two stages: the first took place in 2002–2003 and the second in 2009–2010. These findings were in cesspits inside the cloister and some questions are still without answer: were all those fragments personal objects of the nuns? Were they gifts from the loyal pilgrims or nun's lovers? Or this local was considered safe, by the Inquisition, to hide from the community some "heretic" objects? (Varela Gomes et al., 2015, p. 95, 97).

The five analysed glass fragments are presented in Fig. 2 and described in Table 2.

3. Experimental

3.1. Samples

The combination of morphological observation (technological production, typology, decorative motifs and chosen colours palette) with compositional analyses was performed.

In this way, morphological observation was first used to select the 12 glass fragments which were sampled to avoid erroneous results by analysing and quantifying corrosion layers or deposits of environmental

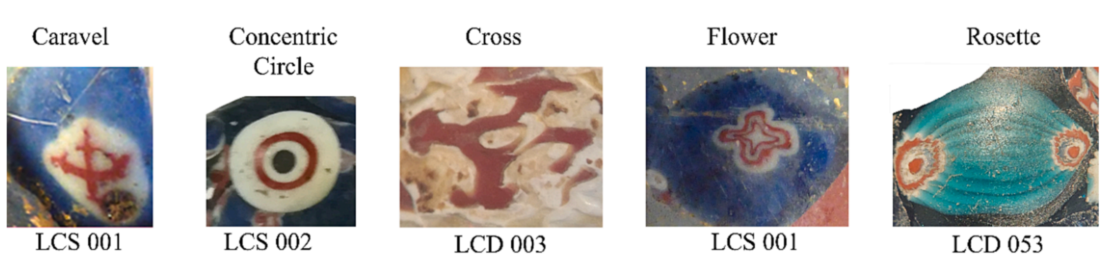


Fig. 3. Representation of patterns found in Lisbon assemblages.

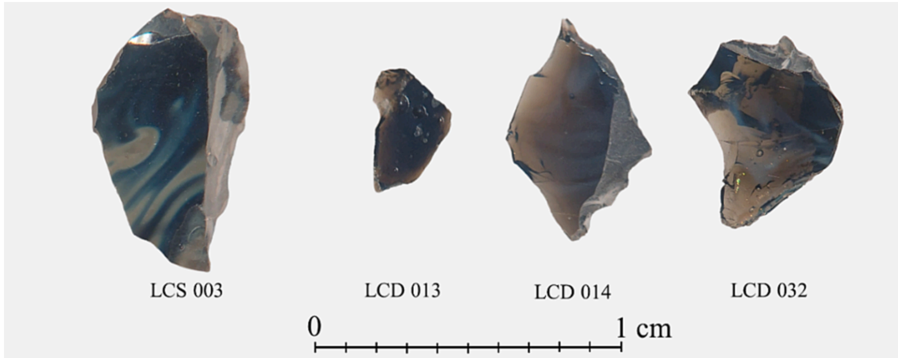


Fig. 4. Samples of the analysed PW in cross-section, where some blue and white veins can be observed in the LCS sample whilst lighter shadows can be seen in LCD samples.

Fig. 5. Illustration of the "whitish ceramic" of LCS 003.

particles instead of pristine glass. The description of the samples is in Table 2.

LCD 003, LCS 004 and LCS 006 show some corrosion layers, which makes it difficult to see their *murrine* patterns. In these three fragments, to take the photographs and to make visual observations of the murrina, we had to carefully wet those surfaces with purified water.

Small samples of a few mm^2 were taken from the selected fragments picking up the largest number of colours as possible. These fragments do not have possible connections with other fragments and were dry-cut with a diamond wire. The sampled fragment was then mounted in cross-section in an epoxy resin and polished with SiC sandpapers down to 4000 mesh.

3.2. LA-ICP-Ms

Laser ablation – Inductively coupled plasma – Mass spectrometry (LA-ICP-MS) was chosen to determine the concentration of each element/ oxide present in each glass layer because this technique has a very high sensitivity with very low detection limits (can go down to ng/g) and can give, not only the major and minor elements, but also the trace elements these including the rare earth elements (REE) allowing for deeper conclusions on what type of raw material was used to produce the glass. This information is of great importance for provenance studies. LA-ICP-MS analysis was carried out on the embedded glass cross-section. The ablation system used consists of a Resonetics M50E excimer laser working at 193 nm coupled with a Thermo Fisher Scientific ELEMENT XR mass spectrometer (IRAMAT-CEB, CNRS/Orléans Univ. France). The excimer laser was operated at 5 mJ with a repetition rate of 10 Hz. Single spot analyses were performed with a beam diameter of 100 µm for transparent glass and adjusted to the size of the filigree for the cane. A pre-ablation time of 15 s and an acquisition time of 25 s were set. Calibration and calculation were performed according to the analytical protocol describe by Gratuze (2016). These values are presented in Table 3.

4. Results and discussion

Clear glass will be presented and discussed along with the base glass of coloured layers. The base-glass (of clear and coloured glass) is calculated by subtracting the colorants (cobalt, copper, iron, and manganese), opacifiers (antimony, tin) and correlated elements (arsenic, bismuth, lead, nickel, etc.) and then normalizing to 100%. With this reduced composition (Table 4) the original clear glass used to produce the coloured glass is estimated and it can be used to compare with the coeval Venetian and *façon-de-Venise* glass composition published on the literature (Biron and Verità, 2012, p. 2710; Lima et al., 2012, p.1240; Thornton et al., 2014, p. 6; Verità and Biron, 2015, p. 180).

For white opaque glasses, the combined presence of PbO and SnO_2 ranges from 20 wt% to 49 wt% of the overall composition. This variation makes more fallible the task of determining the raw materials employed in these glasses, particularly considering that the average content of the

Table 2
Presentation of samples. Inventory number, probable type, part preserved, body color, presence of gold life, cane colors and canes patterns of the artifacts under study.

Archaeological context	Fragment	Type	Part Preserved	Body color	Gold leaf	Cane colours	Patterns
Largo do Chafariz de Dentro (LCD)	LCD 003	Undetermined	Part of wall with rim	Blue	No	Clear, Red and White	Rosette
	LCD 031	Undetermined	Part of wall	Blue	No	Red	Undefined
	LCD 054	Undetermined	Part of wall	Blue	No	Clear, Amber and White	Rosette
Santana Convent (LCS)	LCS 001	Undetermined	Part of wall	Clear	Yes	Blue, Turquoise, Red and White	Flower/ cross and Caravel
	LCS 002	Undetermined	Bird head	Clear	Yes	Blue, Red and White	Flower/ cross
	LCS 004	Undetermined	Part of wall	Blue	No	Blue, Red and White	Undefined
	LCS 005	Undetermined	Part of wall	Red	No	Blue, Turquoise, Red and White	Rosette
	LCS 006	Little flask	Neck	Blue	No	Blue, Turquoise, Red and White	Rosette

Table 3
Composition of the analysed PW and *millefiori* glass fragments unearth in Lisbon determined by LA-ICP-MS in weight percent of oxides up to iron oxide and in μg/g for all the remaining oxides, unless it was marked differently.

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SrO	SnO_2	ZrO_2	BaO	PbO	Bi
LCD 003	B	Body	15.8	2.8	5.0	58.5	0.43	0.91	5.49	7.18	0.21	0.54	1.18	3408	1058	322	125	7832	686	501	153	431	626	4993
LCD 031		Body	17.7	2.8	4.3	61.4	0.41	1.08	3.07	6.78	0.14	0.38	0.77	1594	562	934	70	2191	437	1558	80	190	1683	704
LCD 054		Cane	17.3	2.7	4.2	62.7	0.33	1.12	2.92	6.54	0.13	0.49	0.68	1224	367	3549	57	1827	430	469	77	203	463	484
LCD 054		Body	17.6	2.8	4.3	62.1	0.29	1.12	3.09	6.80	0.14	0.38	0.69	1000	360	610	56	1456	450	1172	75	190	1267	464
LCS 002		Cane	15.1	3.0	6.5	57.0	0.45	0.74	5.54	7.45	0.26	1.13	1.42	2030	527	460	145	3774	610	870	208	733	961	2592
LCS 004		Body	18.1	3.3	5.4	58.7	0.41	1.03	4.25	6.31	0.21	0.60	1.05	844	189	130	72	1516	537	954	107	390	1542	368
LCS 006		Body	18.2	3.4	5.3	58.5	0.41	1.02	4.20	6.36	0.21	0.60	1.04	840	181	139	73	1545	539	971	109	389	1558	389
LCD 003	C	Cane	17.1	3.4	5.0	57.7	0.35	0.95	4.95	8.99	0.19	0.42	0.70	52	32	43	49	75	846	680	158	301	814	64
LCS 001		Body	16.2	3.4	6.1	57.9	0.32	0.84	5.34	7.73	0.28	0.44	1.03	134	44	99	67	200	639	492	285	363	482	154
LCS 002		Body	16.2	3.4	6.1	57.8	0.40	0.88	5.29	7.81	0.29	0.45	1.04	139	45	97	66	217	635	531	292	363	517	163
LCS 005		Body	16.6	2.0	5.3	60.9	0.41	1.03	3.55	5.97	0.25	0.37	1.74	1053	297	12162	141	1354	595	736	155	357	819	546
LCD 031	R	Cane	15.9	3.1	4.3	59.9	0.38	0.98	3.01	6.80	0.15	0.31	1.77	74	73	22752	468	168	416	3141	76	156	4224	49
LCD 054		Cane	15.8	3.5	4.8	59.6	0.42	0.96	2.91	7.22	0.17	0.24	1.94	58	67	15293	115	123	506	3430	83	154	4089	52
LCS 001		Cane	14.8	3.1	6.5	54.6	0.48	0.63	5.47	7.69	0.26	0.80	3.56	129	68	16108	172	237	587	1574	219	556	1653	124
LCS 002		Cane	14.8	3.1	6.5	54.8	0.48	0.63	5.50	7.73	0.26	0.81	3.52	129	66	12074	169	237	584	1513	217	547	3328	120
LCS 004		Cane	17.6	3.0	5.0	58.0	0.48	1.10	4.52	4.98	0.22	0.12	2.93	14	25	15104	81	61	547	1504	95	211	1453	11
LCS 005		Body	16.1	1.9	5.0	58.3	0.37	1.13	3.27	5.71	0.23	0.10	4.08	24	35	26289	239	76	556	900	128	222	657	22
LCS 001	T	Cane	15.5	3.1	5.9	55.6	0.40	0.79	4.63	7.43	0.28	0.27	1.29	64	69	43039	92	188	636	1582	283	272	1399	88
LCS 006		Cane	17.0	3.0	5.1	57.0	0.42	1.13	4.22	5.07	0.24	0.14	1.32	<10	45	46479	127	85	426	2692	102	226	2309	14
LCD 003	W	Cane	6.8	1.3	2.2	33.2	0.20	0.81	2.88	3.37	0.09	0.08	0.30	13	58	88	57	283	268	21.1 wt%	80	102	27.4 wt%	21
LCD 054		Cane	10.4	1.4	2.6	40.6	0.18	0.99	1.72	3.38	0.09	0.09	0.33	40	51	3538	34	59	225	16.6 wt%	66	82	21.0 wt%	15
LCS 001		Cane	12.4	2.3	4.5	47.7	0.43	0.89	4.36	5.60	0.22	0.45	0.90	42	34	1738	92	279	415	6.7 wt%	215	291	13.0 wt%	45
LCS 002		Cane	12.5	2.3	4.4	46.3	0.41	0.83	4.15	5.36	0.21	0.44	0.90	46	43	2178	88	274	402	10.9 wt%	210	289	10.9 wt%	46
LCS 004		Cane	12.5	2.1	3.1	41.3	0.33	0.98	2.66	3.84	0.13	0.18	0.65	15	41	8239	69	278	324	13.9 wt%	60	160	17.5 wt%	14
LCS 005		Cane	11.0	1.9	3.2	40.0	0.29	0.96	3.14	4.95	0.13	0.25	0.58	32	42	483	72	148	454	11.5 wt%	106	183	21.9 wt%	40
LCD 014	A	PW	1.7	3.3	13.5	53.9	0.80	0.13	4.52	16.69	0.60	0.13	4.42	19	37	58	115	13	881	<10	219	470	21	<10
LCD 014	D	PW	4.5	3.4	13.6	53.2	0.80	0.13	4.33	17.44	0.61	0.13	4.42	20	38	59	121	13	896	<10	218	471	20	<10
LCD 032	A	PW	5.4	1.8	12.8	60.6	0.59	0.11	4.76	10.02	0.51	0.06	3.13	<10	21	17	62	<10	247	<10	264	426	10	<10
LCD 032	D	PW	4.5	2.1	11.8	62.4	0.73	0.11	5.25	8.93	0.53	0.08	3.35	<10	24	17	72	<10	245	<10	290	426	10	<10
LCS 003	B	PW	1.4	2.4	13.8	61.9	0.33	0.08	5.31	9.45	0.70	0.07	4.18	<10	25	16	85	16	1309	<10	325	411	12	<10
LCS 003	D	PW	1.5	2.3	13.6	62.5	0.40	0.08	6.39	8.58	0.69	0.08	3.53	<10	20	17	62	13	1136	<10	351	463	<10	<10
LCS 003	W	PW	1.3	3.4	11.6	61.4	0.89	0.08	5.51	11.08	0.60	0.14	3.60	<10	26	19	69	<10	1293	<10	359	510	<10	<10

( ) Different colours present in the same layer (red body glass) of LCS 005_glass fragments are highlighted in this table.
A = Amber; B = Blue; C = Clear; D = Dark Blue; R = Red; T = Turquoise; W = White.
PW = Production waste.

Table 4
Composition of the main components of clear glass and reduced compositions in wt% of the base glasses produced by subtracting the colorants, opacifiers and correlated elements and then normalizing it to 100%. The chemical composition of red and clear glass presented in body glass of LCS 005 are highlighted.

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2
LCD 003	Blue	Body	16.4	2.87	5.2	60.8	0.37	0.94	5.71	7.46	0.22
LCD 031		Body	18.1	2.85	4.4	63.0	0.30	1.11	3.14	6.93	0.14
LCD 054		Cane	17.7	2.74	4.2	64.1	0.30	1.15	2.99	6.69	0.13
LCD 054		Body	17.9	2.81	4.4	63.2	0.29	1.15	3.15	6.93	0.14
LCS 002		Cane	15.7	3.14	6.8	59.3	0.47	0.77	5.77	7.75	0.26
LCS 004		Body	18.5	3.42	5.5	60.1	0.41	1.05	4.36	6.46	0.21
LCS 006		Body	18.7	3.46	5.5	59.9	0.42	1.05	4.30	6.51	0.22
LCD 003	Clear	Cane	17.3	3.41	5.1	58.6	0.32	0.97	5.03	9.13	0.19
LCS 001		Body	16.5	3.47	6.2	59.0	0.40	0.86	5.44	7.87	0.29
LCS 002		Body	16.5	3.50	6.2	58.9	0.41	0.89	5.40	7.96	0.29
LCS 005		Body	17.6	2.10	5.5	63.1	0.37	1.07	3.62	6.35	0.27
LCD 031	Red	Cane	17.3	3.40	4.7	63.3	0.43	1.03	3.14	7.15	0.16
LCD 054		Cane	16.6	3.69	5.0	62.5	0.44	1.00	3.05	7.57	0.17
LCS 001		Cane	15.8	3.28	7.0	58.4	0.51	0.66	5.86	8.23	0.28
LCS 002		Cane	15.8	3.29	6.9	58.4	0.52	0.67	5.86	8.25	0.28
LCS 004		Cane	18.5	3.18	5.3	61.1	0.51	1.17	4.75	5.25	0.23
LCS 005		Body	18.2	1.99	5.4	62.8	0.40	1.22	3.52	6.16	0.25
LCS 001	Turquoise	Cane	16.5	3.34	6.3	59.4	0.43	0.84	4.95	7.94	0.29
LCS 006		Cane	18.2	3.23	5.5	61.2	0.45	1.22	4.53	5.44	0.25
LCD 003	White	Cane	13.4	2.47	4.3	65.4	0.39	1.60	5.66	6.63	0.17
LCD 054		Cane	17.0	2.23	4.3	66.2	0.29	1.62	2.80	5.51	0.15
LCS 001		Cane	15.8	2.98	5.8	60.8	0.55	1.13	5.55	7.13	0.27
LCS 002		Cane	16.3	2.97	5.7	60.6	0.54	1.09	5.43	7.02	0.27
LCS 004		Cane	18.6	3.19	4.6	61.7	0.49	1.47	3.98	5.75	0.19
LCS 005		Cane	16.8	2.87	4.9	61.0	0.45	1.46	4.79	7.56	0.20
LCD 014	Amber	Production waste	1.8	3.47	14.2	56.7	0.84	0.14	4.75	17.54	0.63
LCD 014	Dark Blue		1.7	3.57	14.3	56.0	0.84	0.14	4.55	18.33	0.64
LCD 032	Amber		5.6	1.88	13.3	62.7	0.61	0.11	4.93	10.37	0.52
LCD 032	Dark Blue		4.7	2.21	12.3	64.7	0.76	0.11	5.45	9.27	0.55
LCS 003	Clear Blue		1.5	2.48	14.5	64.9	0.35	0.08	5.57	9.90	0.73
LCS 003	Dark Blue		1.6	2.47	14.2	65.0	0.42	0.08	6.64	8.92	0.73
LCS 003	White		1.3	3.57	12.1	64.0	0.93	0.08	5.74	11.55	0.63

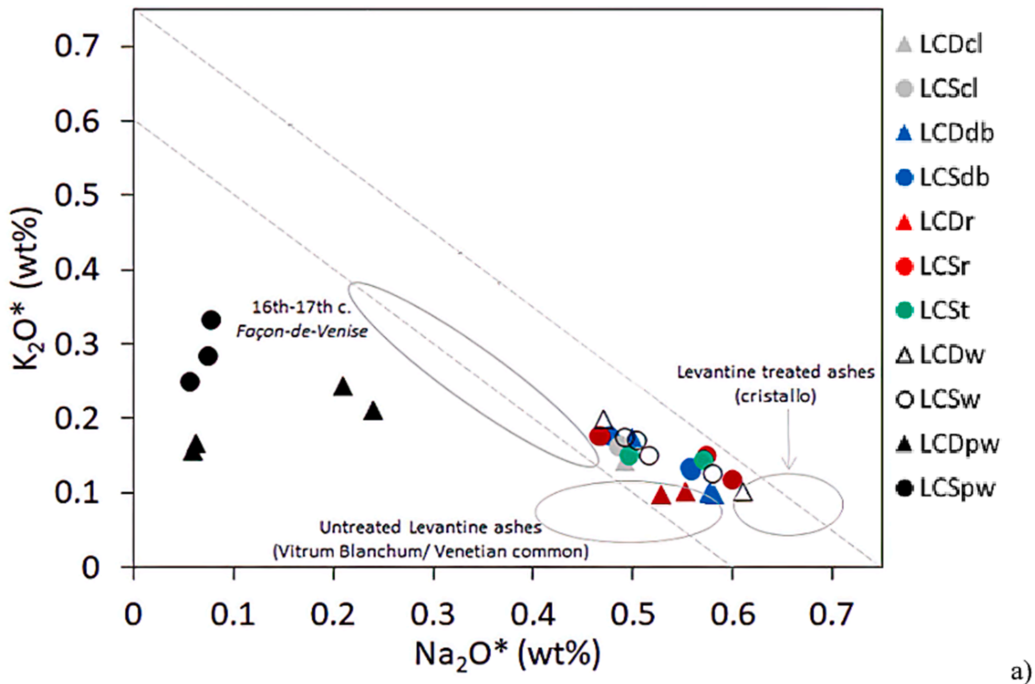
( ) Different colours present in the same layer (red body glass) of LCS_05_glass fragments are highlighted in this table.

components constituting the reduced composition of white glasses amounts to 66.6 wt%, in stark contrast to the corresponding average of 95.9 wt% for the remaining glasses (both coloured and colourless).

The next sub-sections apply only to vessel glass, and the separate last sub-section (3.5. Production waste/ Slag) deals with the comparison with the glass vessels under studied and the PW.

4.1. Alkali source

All clear and base glass have contents of Na_2O between 13.4 and



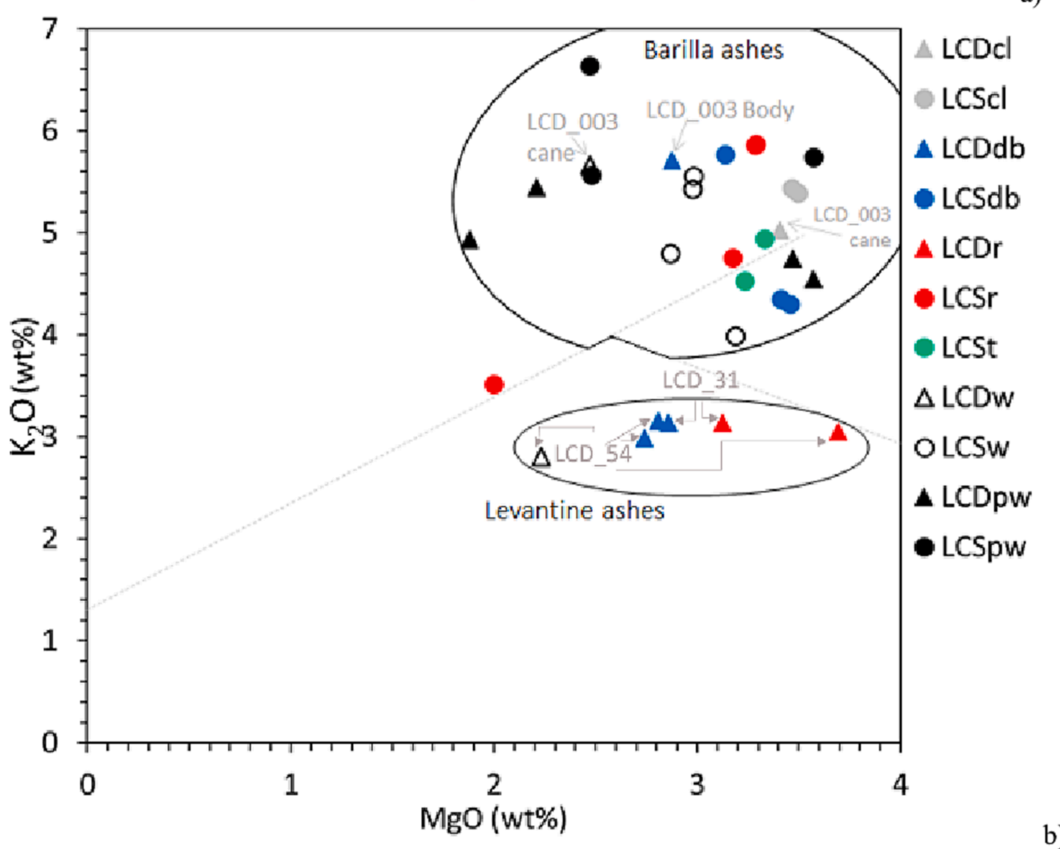


Fig. 6. (a) Normalized Na_2O^* ($Na_2O/(MgO + P_2O_5 + K_2O + CaO)$) and K_2O^* ($K_2O/ (Na_2O + MgO + P_2O_5 + CaO)$) are plotted with the correlation lines $Na_2O^*+K_2O^*=0.6$ and 0.7 indicating the use of, respectively, unpurified, and purified ashes (Coutinho et al. 2021). (b) K_2O and MgO content to identifies what kind of plant ashes was used in the glass making. “Levantine” or “Barilla” (Occari et al., 2021). *cl = Clear; db = Dark Blue; r = Red; t = Turquoise; w = White; pw = Production waste.

18.7 wt%, of K_2O bwtewwn 2.8–5.9 wt% and of CaO between 5.25 and 8.99 wt%, making them of soda-lime-silica type, which means that were made by using halophytic plant (coastal plant) ashes as fluxing agent (Lima et al., 2012). According to the values that have been proposed by the literature, soda-lime silica glass is characterized by having sodium content higher 10 wt%, potassium lower than 10 wt% and Na_2O/CaO higher than 0.5. This type of glass was profusely used in the production of high-quality objects during the medieval and post-medieval periods (e.g. Dungworth, 2003, p.4, De Raedt et al., 2002).

According to the values proposed by Cagno and co-authors 2012a,c, the colourless layers of LCS 001, LCS 002 and LCD 003 samples have an amount of Fe_2O_3 (0.7–1.04 wt%) and MnO (0.42–0.45 wt%) consistent with the natural raw materials. This information suggests that it is not probable a deliberate addition of manganese to neutralize the colour given by the presence of iron oxide.

To distinguish and predict different kinds of glass based on the type of ash used in glassmaking as raw material, a normalization of fluxing oxides has been profusely used (e.g. Cagno et al., 2012a, b, c, Janssens et al., 1998, Šmit et al., 2009). The proposed values associated to Na_2O^* and K_2O^* are calculated by dividing the respective oxides by the oxides associated to the fluxing agent (Na_2O, MgO, P_2O_5, K_2O and CaO) and the two correlated lines of $Na_2O^* + K_2O^* = 0.6$ and $Na_2O^* + K_2O^* = 0.75$ represent, respectively, the use of unpurified and purified ashes (Coutinho et al., 2021). With this normalization the influence of the ratio of fluxing agent and silica sources is eliminated (Wouters and Fontaine, 2009).

Fig. 6.a shows that, all LCS and LCD glass fragments, are located between the two correlated lines of Na2O* + K2O*. This observation can indicate that 1) a semi-purification process of the ashes was made, 2) different recipe or 3) a sodic plant ashes mixture was added to the glass batch to lower the melting temperature. For instance, *barilla* (a plant from the Western Mediterranean and named *Maçacote* (Portuguese term) or *Salsola Kali* (in Latin)) was the sodic plant ash profusely used as a flux agent in the Iberian Peninsula, Sicily, and Sardinia (having a higher K_2O content) while Venetian glass makers only used Levantine plant ashes up to the end of the 17th century (Cagno et al., 2012b; Verità and Toninato, 1990; Valente, 1950).

Looking at K_2O and MgO content (Fig. 6.b), one can note that a great part of Lisbon fragments seems to be made by adding *barilla* to the glass batch while, combining data from both graphs in Fig. 6, there is a strong indication that all analysed coloured layers of LCD 031 and LCD 054 can be considered as *Vitrum Blanchum* glass type made from unpurified Levantine plant ashes.

Levantine ashes (imported from Syria or Egypt) were profusely used by the Venetian glassmakers of the 16th century in their three types of clear glasses: common (ordinary glass, slightly coloured), *Vitrum Blanchum* (colourless glass of intermediate quality) and *Cristallo* glass (the best kind of colourless glass) (Verità, 1985; Verità 2018). Contemporaneous recipe books attest to the use of this type of fluxing by Venetian glassmakers: e.g. Trattatelli (recipe 24 of the first book and 9 of the second), Darduin's (recipe 35) and Anonimo (recipes 17, 18, 26, 38, 39, 43 and 45) (Verità, 2018). For *cristallo* glass, the ashes must undergo a purification process to decrease the amount of impurities such as iron oxide, which were responsible for tinting the glass (Verità, 1985). The purification procedure entailed grinding the ashes, sieving, dissolving them in boiling water, decanting, filtering, and subsequently drying to induce crystallization, yielding the crystalline salt termed "*sal de Cristallo*" (Verità, 2013, p. 528). In this process some oxides responsible for the glass matrix stabilisation (e.g. calcium and magnesium) were also removed due to their insolubility in water which made the glass more susceptible to weathering (Verità and Zecchin, 2009).

The LCD 054 white layer (*murrine*) seems to have a content of alkali source compatible with purified Levantine ashes. Note that this *murrina* has estimated between 20 and 30-star tips and seven layers of different coloured glass. Although Moretti (2005) pointed out that the Venetian *murrine* usually has seven glass layers and the earliest beads usually have "a light green transparent layer of glass and, in very rare specimens, the core and the fifth layer are red" (as observed in LCD 054 fragment), the number of star tips of Venetian beads are frequently 12 although circa of 40 star tips have already been mentioned on the literature (supplementary material Pulido Valente et al., 2021). In fact, the number of star tips found in this fragment is not compatible with what has been described in the literature in any Venetian or *façon-de-Venise* glass. The different number of star tips implies the use of different moulds. For this we propose two hypotheses: 1) a new number of star tips for Venetian or *façon-de-Venise* bead production is here presented and yet to be explored or, 2) this number of star tips may be characteristic of Portuguese production. However, looking for the alkali sources the use of Levantine ashes is compatible with genuine Venetian production.

Fragment LCD 003 is an interesting object because only the blue colour from the *murrine* has a base glass composition that is consistent with Venetian tradition (use of Levantine ashes); in the blue body glass and in the other analyzed *murrine* canes the flux agent seems to be compatible with *barilla* (Fig. 6.b). This observation was already pointed by Augusta Lima and co-authors (2012) in some *millefiori* glass fragments unearthed in Santa Clara-a-Velha Monastery (Coimbra) and they suggest that it can indicate that different recipes were used to produce those objects. It can be possible that some coloured glass canes could be imported to produce the *murrine* canes, or recycling of coloured glass was used to produce the different coloured glass layers as it seems to be happening with LCS 005 red body glass that falls right between Levantine and barilla ashes (Fig. 6.b).

4.2. Silica source

Historical documents attest that Venetian glassmakers were using quartz pebbles from the Ticino and Adige rivers as silica sources (Verità, 2013; Verità and Toninato, 1990). On the other hand, in *façon-de-Venise* glass centres, glassmakers were usually using local silica sources for glassmaking (e.g. Cagno et al., 2010; De Raedt, Janssens and Veekman 2002; Šmit et al., 2005). Therefore, the content of SiO_2, TiO_2, and Al_2O_3 can be of paramount importance in tracking the origin of raw materials because they are the main components of silica sources.

Silica sources can present different types and quantities of accessory minerals, depending on its nature (e.g. quartz sand or quartz pebbles) and their geological setting (Occari et al., 2021). These differences will lead to different geochemical patterns, which may be useful to predict its origin. Higher concentrations of trace elements indicate that a less pure quartz sands were used in batch glass (Brems and Degryse, 2014, Verità and Zecchin, 2009).

For this part the reduced composition (of the base glass) was used to compare them with the reported in the literature as the base glass has been considered most closer to the original glass before the addition of glass pigments (Biron and Verità, 2012, p. 2710; Lima et al., 2012, p.1240; Thornton et al., 2014, p. 6; Verità and Biron, 2015, p. 180, Verità et al., p. 243).

In Fig. 7 the chemical composition of the glass and the mineralogy of the glass making sands are related, being that: SiO_2 represents the quartz content, Al_2O_3 the amount of feldspars and TiO_2 the heavy minerals present in silica sources (Coutinho et al., 2021, Schibille et al., 2017).

Fig. 7 shows that the silica sources used in most of the archaeological glass found in Lisbon (Casa dos Bicos – sodic glass fragments – LCD and LCS) have a higher amount of feldspars when compared with the analysed glass fragments from Low Countries (Kunicki-Goldfinger and Hulst, 2017), Spain (Coutinho et al., 2021) and Venice (Verità, 1985, Verità and Zecchin, 2008).

Comparing the *millefiori* glass found in Lisbon with the glass artefacts found in London (Mortimer, 1995), Diósjenő glasshouses (Kunicki-Goldfinger et al., 2013) and Savona (Cagno et al., 2012a), it is possible to see that while they have samples of each different group located in Lisbon region of Fig. 7, they also appear spread through the graph.

Concerning Diósjenő glasshouse, its production is made by mixing

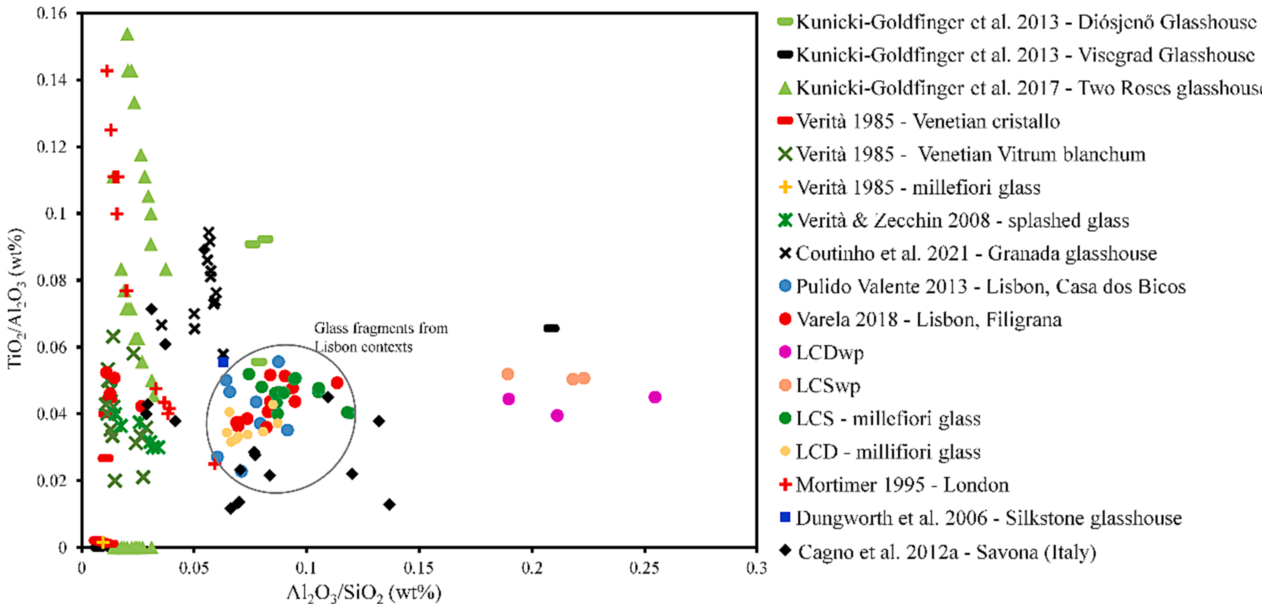


Fig. 7. Binary plot of TiO_2/Al_2O_3 and Al_2O_3/SiO_2 of LCD and LCS glass fragments and some contemporary glass fragment reported on the literature. The clusters are grouped based on the mineralogy of the glass making sands. *pw = production waste. (See above-mentioned references for further information Pulido Valente, 2013)

wood ashes as alkali sources (Kunicki-Goldfinger et al., 2013) while in London context, three different types of glass: Sodic, Potassic and high-lime, low-alkali (HLLA) (Mortimer, 1995) were identified.

On the other hand, all the samples from Savona and *façon-de-Venise* glass fragments found in Lisbon contexts are of soda-lime silica type.

Note that the four filigrana glass samples that are outside the circle (Fig. 7 – identified by red circles), were previously attributed to a Venetian production (Varela, 2018).

Fig. 8 enhances our comprehension of the relationship between alumina and titanium oxides. This graphical representation reveals a noteworthy correlation (r = 0.75) between alumina and titanium oxides in both the previously investigated Lisbon glass assemblage and the *millefiori* glassware. Notably, when focusing exclusively on the *millefiori* fragments, the Pearson correlation coefficient notably rises to 0.87.

Conversely, the examination of the Savona (Italy) samples displays a dispersed distribution on the graph. In a prior study, Cagno and co-authors (2012a, p. 2195) reported the absence of trace elements linked to alumina oxide and suggested the potential deliberate incorporation of a relatively pure source of aluminium as an additional raw material.

Previous work regarding Portuguese *millefiori* glass classified the glass composition according to their alumina content (Lima et al., 2012, p. 1246) as: 1) low alumina (LA) - $Al_2O_3 < 2$ wt% and $SiO_2 > 70$ wt% for *cristallo* samples; 2) medium alumina (MA) - $Al_2O_3 = 2–3$ wt%; 3) high alumina (HA) - $Al_2O_3 = 3–6$ wt%; 4) very high alumina (VHA) - $Al_2O_3 >$ 6 wt%. According with that work, HA and VHA is not common for Venetian and *façon-de-Venise* glass artefacts.

According with more recent information that the authors add access, glass fragments of the 16th-17th centuries with Al_2O_3 content around 4 wt% were also found in Granada (Coutinho et al., 2021), Tuscany (Gambassi and S. Giovanni Valdarno) (Cagno et al., 2010), in the island of Sumatra and Kenya (in these two last sites the natron glass was not

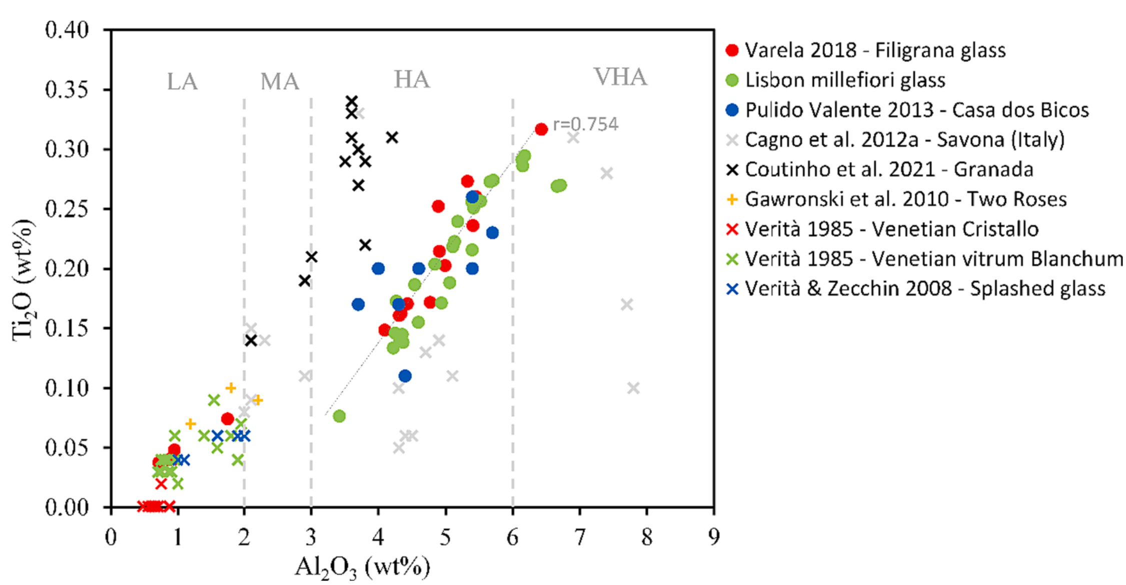


Fig.8. Binary chart of titanium and alumina content. *LA = Low Alumina, MA = Medium Alumina, HA = High Alumina; VHA = Very High Alumina; pw = production waste. (See above-mentioned references for further information Pulido Valente, 2013)

considered) (Dussubieux, 2009; Dussubieux, Gratuze and Blet-Lemarquand, 2010).

Unfortunately, the provenance of Asiatic and African glass assemblages was not yet attributed (Dussubieux, Gratuze and Blet-Lemarquand, 2010).

Lisbon glass artefacts belong apart from the internationally studied glass production centres; this result comes to reinforce the idea that a different silica source was used in the production of *millefiori* glass artefacts found in Lisbon.

Zr and Hf have been widely used to distinguish sand quarries (e.g. Coutinho et al., 2016; De Raedt et al., 2001) and has been accepted that Venetian glass show the lowest content of Zr (<30 μg g–1) while *façon-de-Venise* glass production centres has a higher amount of those elements (De Raedt et al., 2001, Lazar and Willmott, 2006, Šmit et al., 2005). This consideration is linked with the fact that Venetian glassmakers improved the clear glass using the best raw material to produce it, so a lower content of minor, trace and REE suggests the use of a purer quartz sands (Brems and Degryse, 2014). Looking to trace elements such as zirconium, no sample can be considered as having Venetian origin (Fig. 9).

The lowest content of Zr and Hf belong to the white glass layers of LCD 054 and LCS 004 samples. It seems that while LCD 054 sample was made with Levantine ashes (according to K_2O and MgO content), the LCS 004 sample was made with *barilla*. This observation indicates that, although similar amount of Zr content was detected in these samples, two different recipes were employed in the production of these white glasses – one in Venetian way and other with the fluxing agent most used in Portugal – *barilla* (Valente, 1950).

On the other hand, a remarkable amount of Zr (around of 200 μg/g or higher) in LCS 001 (clear body and turquoise layer), in LCS 002 (clear body) and in the production waste of LDC and LCS can suggest that the sand purity was not important in the raw material choice (Cagno et al., 2012c). However, the presence of gold leaf in LCS 001 and LCD 002, together with the fact that LCD 002 belongs to the bird head fragment, which reflects a high skilled work, not only in its shape, but also in the presence of unique and accurate *murrine* selection patterns for its decoration, are not consistent with a lack of care in raw material selection. Nevertheless, in fact, the "clear" body glass of those fragments presents a slightly darker grey tone.

4.3. Geochemical patterns

In geochemistry, an indication of the different origin of minerals can be traced based on relative abundance of trace and rare-earth elements (REE) by the normalisation of those elements present in glass composition to the upper Earth crust (Cagno et al., 2012b, Coutinho et al., 2021, Kunicki-Goldfinger et al., 2008, Šmit et al., 2005). For this normalisation the used values were taken to Wedepohl et al. (2011) work.

The geochemistry gives us distinction patterns based on different mineralogical composition of the sands used in glass production, which are not easily fractionated during the sedimentation process of the sands and will lead to different trace elementary patterns that may be attributed to a certain region (Brems and Degryse, 2014, Kunicki-Goldfinger et al., 2008).

Fig. 10 presents the geochemical patterns of clear (which has been profusely studied) and blue (as it is the colour most present in our assemblage) glass layers of the analysed *millefiori* fragments where all the presented elements were normalized to the upper Earth crust. In these charts the alumina and titanium were added because they were important in the characterisation of our assemblage. Rb and Sr were also used to our charts (Fig. 10) because, according with Brems and Degryse, 2014 (p. 118), Rb comes exclusively from the sands and Sr can also be linked with sand (in these samples the Pearson correlation coefficient of Sr and Ti/Al is 0.6 or higher).

In Fig. 10 one can note that, although different recipes were used to produce the final glass (whether in Levantine ashes or barilla), the same or identical silica source was used in the analysed artifacts.

The high range of Zr value [44–266 μg g–1] found in the analysed fragments reinforces the theory developed by Šmit and co-authors (2005) suggesting that "Zr is not distributed uniformly within SiO_2 but is present in the form of large zircon crystals", meaning that the attribution of glass fragments to a certain production centre based only on

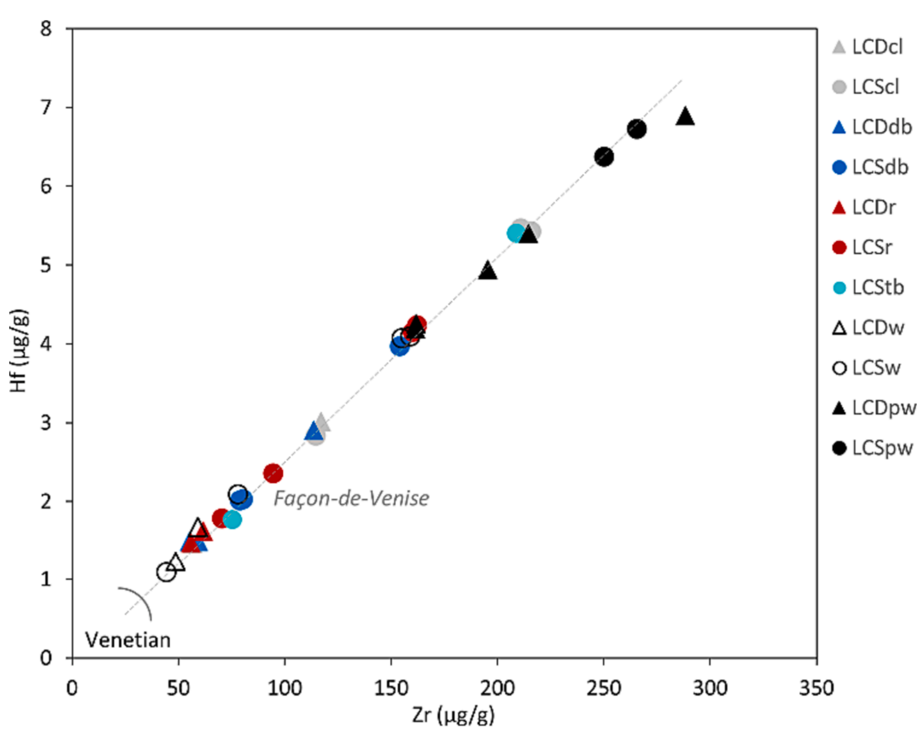


Fig. 9. Binary chart of zirconium vs. hafnium (Cagno et al. 2012c, De Raedt et al. 2002). *cl = Clear; db = Dark Blue; r = Red; t = Turquoise; w = White; pw = Production waste.

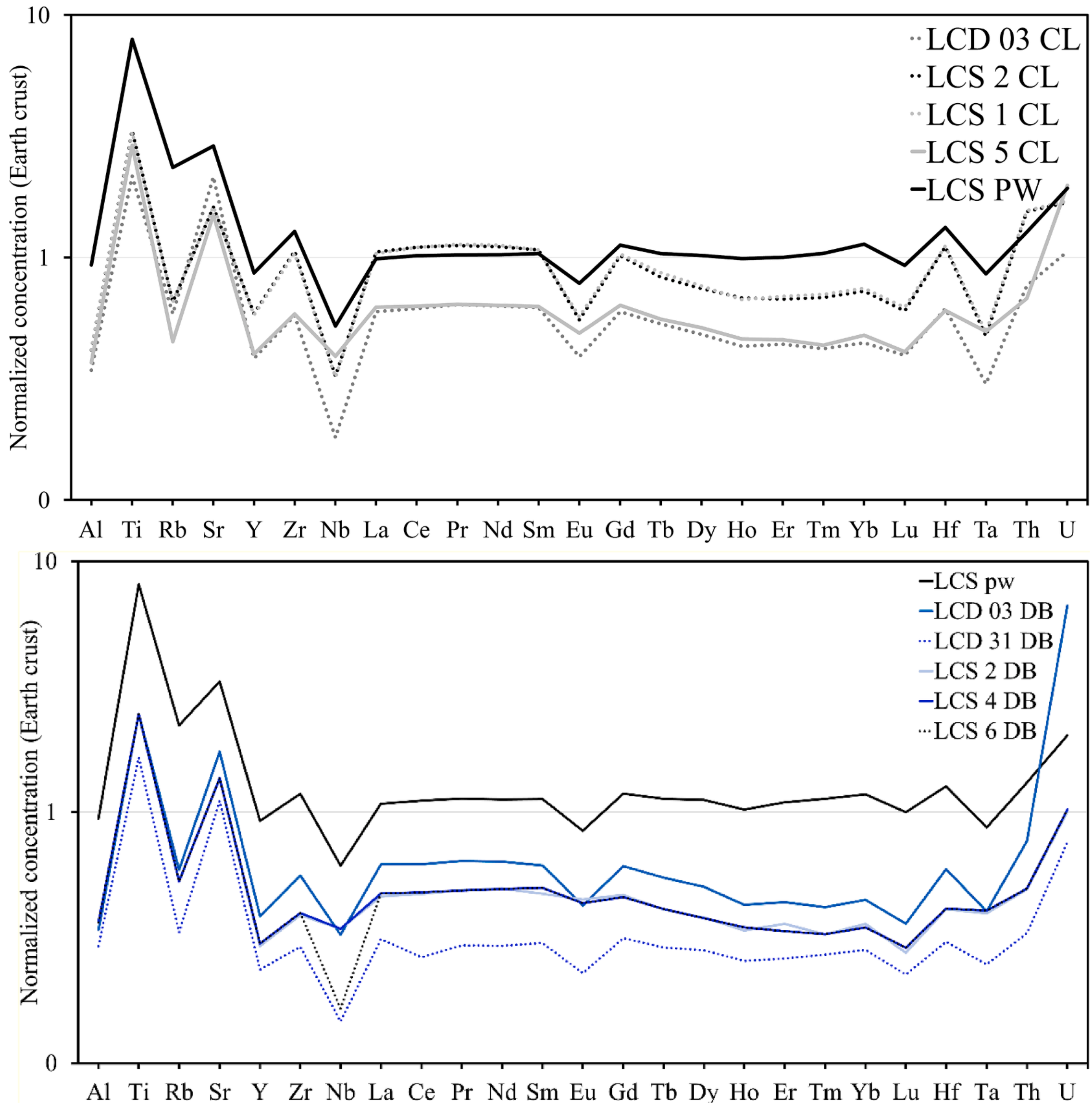


Fig. 10. Selected elements associated with silica sources of the samples normalized to the upper Earth crust and presented in logarithmic scale. *CL = Clear; DB = Dark Blue; pw = production waste.

zirconium content can be precipitated.

Resuming all the information previously discussed, to the authors' knowledge, no Venetian or any known *façon-de-Venise* glass centres have the same geochemical pattern found in these *millefiori* glass fragments and glass production waste found in Lisbon. Moreover, Maria Varela (2018) obtained the same patterns in some 17th century *filigrana* glass found at Largo do Chafariz de Dentro in Lisbon (Varela, 2018).

4.4. Glass colorants

A brief description and discussion of the existent colours will be presented.

Morphological observation shows that besides clear glass, blue, red, turquoise, and white layers were noted. LA-ICP-MS provided information about the pigments that were added to clear glass for colouring it: cobalt for blue, iron and copper for red, copper for turquoise and a combination of lead and tin oxides (originating cassiterite clusters) for white.

These colorants were very popular in contemporary glassmaking and several glass recipe books attest their applications: e.g. *Darduin*, *Dell'arte del vetro per musaico*, *Ricette vetrarie del Rinascimento* (also known as *Anonimo*), Trattatelli (Moretti and Hreglich, 2007; Verità and Zecchin, 2008, Verità et al., 2018).

These glass pigments were also detected in contemporaneous *millefiori* and *splashed* glass fragments found in Portugal (Lima et al., 2012) and outside. Those pigments were also detected, for exemple, in a *chevron* bead found in Germany (Gradmann et al., 2013), in filigrana glass fragments found in England (Mortimer, 1995) and in a Catalonian ewer (Wouters and Fontaine 2009), in Venetian enamels (Thornton et al., 2014, Verità and Biron 2015), and were used in glazed ceramics and tiles (Coentro et al., 2014).

In clear glass, iron is regarded as an unwanted impurity due to its tendency to impart undesired natural hues that may range from bluish to yellowish, encompassing various shades of green. These colorations result from the relative proportions of ferric ions (Fe^{3+}), which impart a yellowish hue, and ferrous ions (Fe^{2+}), which give a bluish tint to the glass matrix (Lima et al., 2012).

To avoid those "natural hues" glassmakers could add manganese oxide to the glass batch to oxidise the ferrous ion (Fe^{2+}) into ferric ion (Fe^{3+}) and thus convert MnO_2 into MnO resulting in a clear glass almost colourless (Lima et al., 2012; Volf, 2011, p. 343).

Fig. 11 illustrates that a majority of the red and white glass layers in *millefiori* glass were likely produced without the inclusion of MnO for decolorization purposes. Conversely, in the case of the red layers in LCS 001 and LCS 002, as well as the blue layer in LCS 002 samples, it appears plausible that manganese oxide was deliberately introduced into the glass batch. The discussion about the presence of these oxides will be deeply deliberated in the blue and red sections.

The content of MnO considered naturally present and introduced through raw-materials is a non-consensual subject:

1) Some authors accept that MnO ranging from 0.3 and 0.8 wt% were used as a decolourant (Lima et al., 2012, p. 1244; Moretti and Hreglich, 2013, p. 32; Jackson, 2005, p. 765).
2) Other authors defend that the amount of MnO lower than 1 wt% is consistent with the natural content of this oxide present in the glass sand used as raw-material (Cagno et al., 2012a, c).

In fact, all the authors seem to be in accordance with the fact that Venetian and *façon-de-Venise* glassmakers usually added MnO as decolourant while this oxide have been also used to coloured the glass.

MnO has a hight colouring effect (10–20 times less than the CoO), producing a dark colour in glass as little as 3–4 wt% (Volf, 2011, p. 341). Deep purple glasses dated to the 17th century were analysed and the amount of MnO was of 1.1 wt% (e.g. Coutinho, 2016p. 281). This is related with the redox conditions within the furnace and the glass batch itself.

4.4.1. Blue

Blue colour in *millefiori* glassware is the consequence of the presence of CoO in the glass matrix. Apart from LCD_003 fragment, all the other blue glasses have contents of CoO of 0.2 wt% or less (Table. 5), this result is consistent with the results reported on the literature for beads (Dussubieux and Karklins, 2016) and blown glass (Lima et al., 2012, Verità and Zecchin, 2008, Verità et al., 2018). Nevertheless, LCD 003 has CoO levels that can be considered high (0.34 wt%) for blown glass (Verità and Biron, 2015).

The content of MnO in LCS 002 assemblage (1.13 wt%) can suggest that this oxide was intentionally added to enhance the colour. It is interesting to note that similar amount of MnO was detected in a black glass on a Venetian polychrome goblet of the 16th century (Veritá and Zechhin, 2008).

Table 5
Chemical composition of the oxides and bismuth that have been associated to cobalt ore in wt%.

Samples	CoO	Ni O	ZnO	As_2O_3	Bi
LCD 003b	0.34	0.11	0.013	0.78	0.50
LCD 031b	0.16	0.06	0.007	0.22	0.07
LCD 054b	0.10	0.04	0.006	0.15	0.05
LCS 002m	0.20	0.05	0.015	0.38	0.26
LCS 004b	0.08	0.02	0.007	0.15	0.04
LCS 006b	0.08	0.02	0.007	0.15	0.04

b – body glass
m – *murrine* (decoration)

Some oxides can suffer variations according to its geological origin and treatment (Thornton et al., 2014, p. 5; Verità and Zecchin, 2008, p. 111). The coexistence of arsenic and bismuth has been considered as a time indicator (latter than 1520–1530) and presence of nickel and zinc (Table. 4), has been attributed to the use of cobalt ore imported from Schneeberg in Erzgebirge (Germany) (Thornton et al., 2014, p. 5; Gratuze at al. 1996, p. 80, Zucchiatti et al., 2006).

In blue layers, the amount of As_2O_3, NiO and Bi are increased when compared with the other colored layers, suggesting that its production is later than 1520/30 and the cobalt ore was imported from Schneeberg (Thornton et al., 2014, p. 5; Gratuze at al. 1996, p. 80, Zucchiatti et al., 2006).

4.4.2. Red

In Roman times, copper oxide was already profusely used to produce red glass (Bandiera et al., 2020, Moretti and Gratuze, 2000). In reducing conditions, metallic micro particles of copper (Cu^0) or crystals of cuprite (Cu_2O) precipitate on the glass matrix and red colour is formed (Bandiera et al., 2020, Lima et al., 2012). Historical recipes suggest that glassmakers added, besides the colorant, iron, antimony, lead and tin oxides to the glass batch as they can act as reducing agents (Lima et al., 2012; Moretti and Gratuze, 2000; Verità and Zecchin, 2008).

In Table. 6, samples LCS 001 and LCS 002 are the only red glass

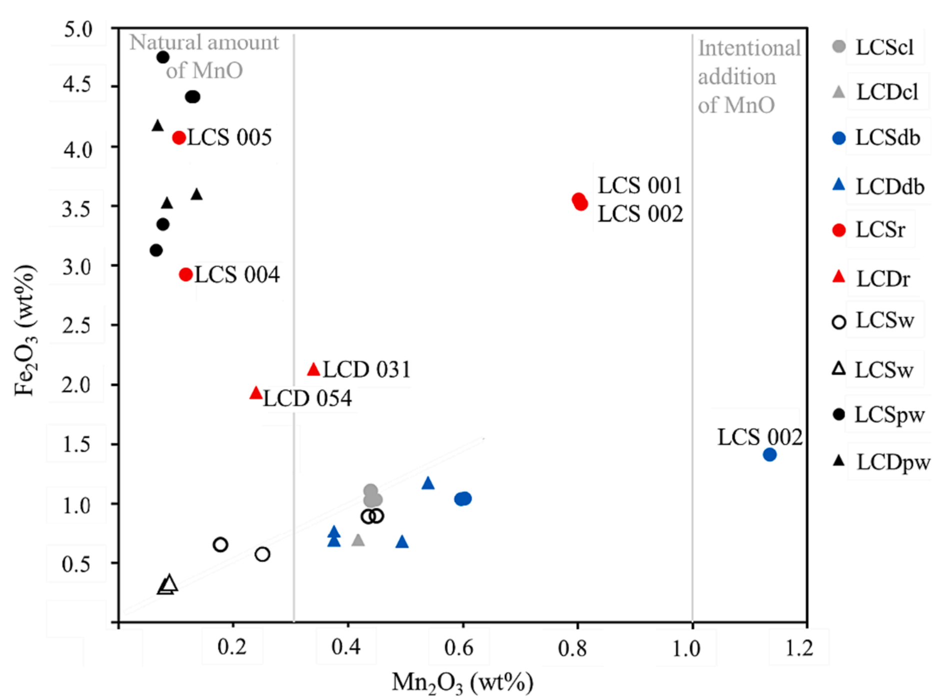


Fig. 11. Binary chart of MnO vs. Fe_2O_3. *cl = Clear; db = Dark Blue; r = Red; w = White; pw = Production waste.

colours that have a high MnO content (around 0.80 wt%). This result suggests that MnO may deliberately added to change the final colour or suggests that remelting cullet was used as noted in recipes 7 and 8 of Darduin treatise (Cagno et al., 2012b; Verità and Zecchin, 2008).

Moreover, the increased values of Fe_2O_3 showed in Fig. 11 [1.94 and 2.13 wt% for LCD and higher to 1.90 wt% (2.93–4.08 wt%) for LCS] can be linked with the fact that iron oxide in combination with tin oxides have been pointed as a good reducing agent for the production of nanoparticles of metallic copper dispersed in the glass matrix (Bandiera et al., 2020; Lima et al., 2012; Verità and Zecchin, 2008).

LCS 005 and two glass fragments from Santa Clara-a-Velha Convent (Coimbra, Portugal) are the only known *millefiori* glass fragments that have red body glass over Europe (Lima et al., 2012; Pulido Valente et al., 2021). In cross-section, LCS 005 body glass presents some layers of clear glass (Fig. 12) with 1.31 wt% of CuO and 2.36 wt% of Fe_2O_3. Those colourless layers can be unintentionally caused by the presence of cuprous ion (Cu^{+}) that is formed when the reduced conditions were not perfectly/ homogeneously acquired (Bandiera et al., 2020).

Other possible explanation for the observation of these clear glass layers in the red body glass of this artefact is the usage of the flashed glass technique.

Flashed glass consists of fusing different coloured and colourless glass in parallel layers to control the translucence and colour of the final glass (Gudenrath, 2012; Palomar et al., 2022). It was profusely used in Medieval stained-glass windows (e.g. Kunicki-Goldfinger et al., 2014; Royal Monastery of Saint Mary in Burgos (Alonso et al., 2009) or St Gatien Cathedral in Tours (Farges et al., 2006)) especially in ruby-red coloured glass (Palomar et al., 2022).

Flashed technique was used also in Roman cameo glass or Bohemian glass of the 19th century (Gudenrath, 2012) but, to the authors knowledge, this observation in glassware of coeval period was never referred.

In the body glass of LCS 005 fragment, it is interesting to note that, when comparing the content of MnO on both layer (red has 0.11 wt% and clear has 0.44 wt%), the result seems to indicate that, although the silica source used in both glasses looks like quite similar, clear glass appears to be less pure than red from strontium forward (Fig. 13). If this observation is correct, this glass was made in flashed technique, which was profusely used in stained glass of this period but, to the authors knowledge, was never mentioned in coeval glassware.

The addition of manganese oxide to clear glass is the evidence that glassmakers did not want that the natural hues of the clear glass would influence the red final colour and indicate that, once again, these glass objects were produced by very skilled glassmakers who know exactly what they were making. This observation is not consistent with a negligent selection of raw materials, being more probable that they were working with a local source.

The increased value of Fe_2O_3 and CuO in colourless glass (when compared with the other colourless glass) may be due to a contamination through the diffusion of these elements present in red layers (Dussubieux and Karklins, 2016).

The analysed red glass layers used to decorate pick-up artefacts

Table 6
Chemical composition of the oxides that have been associated to red recipe in wt %.

Samples	Mn O	Fe_2 O_3	Cu O	Sn O_2	Sb_2 O_3	Pb O
LCD 031m	0.28	1.41	1.97	0.24	0.01	0.30
LCD 054m	0.24	2.13	1.53	0.34	0.01	0.41
LCS 001m	0.80	3.56	1.61	0.16	0.01	0.17
LCS 002m	0.81	3.52	1.21	0.15	0.01	0.33
LCS 004m	0.12	2.93	1.51	0.15	0.01	0.15
LCS 005b	0.10	4.08	2.63	0.09	0.01	0.07
LCS 005bc	0.37	1.76	1.21	0.07	<0.01	0.08

b – body glass
c – clear glass
m – *murrine* (decoration)

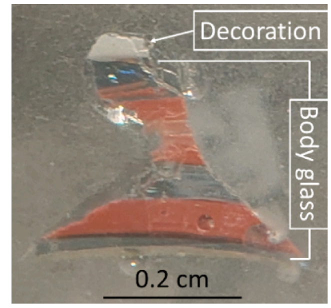


Fig. 12. LCS 005 *millefiori* glass fragment in cross-section showing the colorless layers in between the red glass layers.

found in Portugal (also in Lima et al., 2012; Teixeira, 2014) show higher level of copper oxide (usually near 1 wt% or higher) when compare with Venetian or *façon-de-Venise millefiori* or *splashed* red objects of coeval period (<0.5 wt%) (Lazar and Willmott, 2006; Verità and Zecchin, 2008). In an investigation focused on the red glass technology development, Cesare Moretti and Bernard Gratuze (2000) pointed out that CuO had same high contents (1.04–2.5 wt%) detected in some Venetian red glass fragments (bead or tesserae). On the other hand, some red glass beads unearth in *Asd/Kg10*, today known as being part of *De twee Rozen* glasshouse, (a Dutch beadmaking house in Amsterdam which worked from 1621 to 1657) show CuO contents around 1 wt% (0.85–1.68) (Hulst, 2013; Sempowski et al., 2003). The increased values of this chromophor may be attributed to the fact that the colours must be intensified when used in thin layers, otherwise the final colour will be change when applied over another coloured layer (Verità and Zecchin, 2008, p. 111).

4.4.3. *Turquoise blue*

Turquoise made with copper oxide is the oldest known colouring agent being widely used by the Egyptian glassmakers (Navaro, 2003). This colorant has been considered easily obtainable by adding copper oxide to the glass batch and melting it in oxidation conditions (Moretti and Gratuze, 2000). The colour is the result of the presence of cupric ion (Cu^{2+}) in glass matrix (Bandiera et al., 2020; Lima et al., 2012).

Only one turquoise glass, belonging to a murrina of LCS 001 fragment, was analysed. This fragment has a CuO content of 4.30 wt% and some parallels were observed in Santa Clara-a-Velha Monastery, Coimbra (V_108 = 4.03 wt% of CuO) (Lima et al., 2012).

4.4.4. *White*

The oldest opaque white glass dates to the 15th century BCE and is produced by the precipitation of calcium antimonate in the glass matrix (Moretti and Hreglich, 2007). Although this opacifier does not belong to Venetian tradition, its presence in Venetian glassware was already detected (Veritá and Zecchin, 2008).

Venetian glass makers replaced the older calcium antimonate by the tin and lead oxides which opacified the glass by the precipitation of cassiterite crystals (Moretti and Hreglich, 2007; Verità et al., 2018). This new white glass, called *lattimo*, is dated to the middle of 15th century and was made by adding lead and tin calx to the batch glass (Lima et al 2012; Verità and Zecchin 2008). Other opacifier profusely used in the 15th century onwards is the bone ash and is characterized by having a high content of P_2O_5 (Thornton et al., 2014, p. 5), in a filigree glass of 17th century, the level of this oxide was higher than 4 wt% (Sedláčková and Rohanová, 2015).

The two oxides that are increased, when compared with the other glass layers, are SnO_2 and PbO (Table. 7). This result indicates that the most popular Venetian recipe was applied in the production of these white glasses. *Trattatelli* and *Darduin* treaties report some recipes for this white glass making (Verità and Zecchin, 2008).

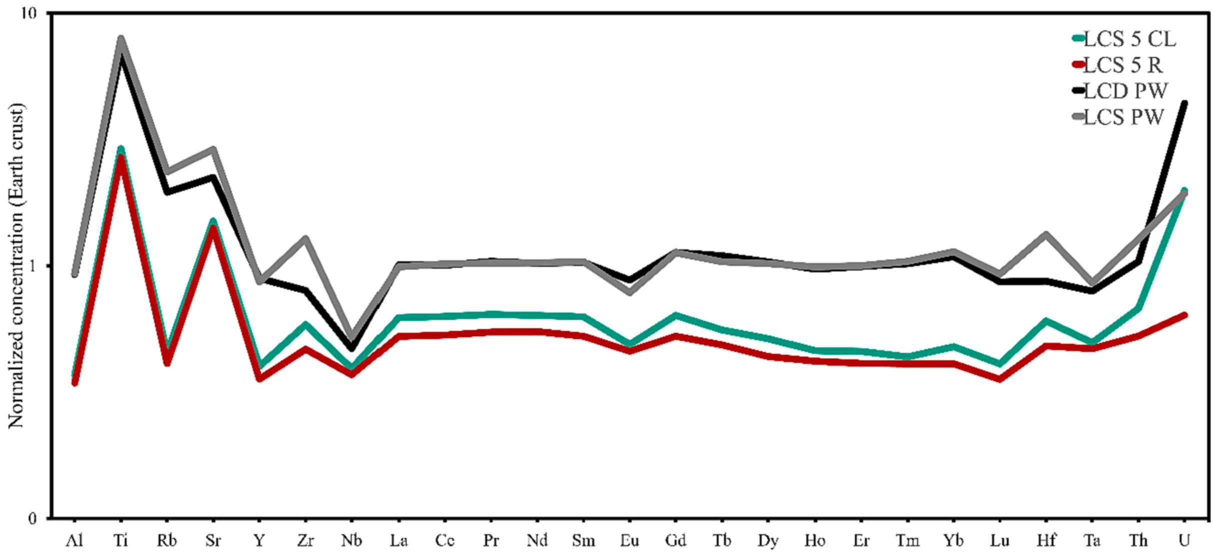


Fig. 13. Selected elements associated with silica sources of the samples normalized to the Earth crust presented in logarithmic scale. *cl = Clear; r = Red; pw = Production waste.

Table 7
Chemical composition of the oxides that have been associated to white recipe in wt%.

Samples	P_2O_5	CaO	SnO_2	Sb_2O_3	PbO
LCD 054	0.18	3.38	16.65	0.01	21.04
LCS 001	0.43	5.60	06.69	0.02	13.04
LCS 002	0.41	5.36	10.87	0.02	10.89
LCS 004	0.33	3.84	13.85	0.01	17.46
LCS 005	0.29	4.95	11.45	0.02	21.92

4.5. Production waste/Slag

The chemical composition of PW has an amount of Na_2O between 1.5 and 5.6 wt%, K_2O of 4.5–6.6 wt%, CaO of 8.92–18.33 wt% and SiO_2 of 53.2–62.5 wt% (Table. 3).

This composition does not feet with any type of glass due to the low content of alkali sources ($Na_2O + K_2O < 10$ wt%) and lime is to low to be considered HLLA (Cagno, 2012c; Dungworth et al., 2006). Examining the major components, the production remnants consistently appear isolated, both in the figures related to alkali sources (Fig. 6.a and.b) and those associated with silica sources (Fig. 7).

Dungworth (2008) and Velde (2009) demonstrate that, the glass composition can be affected by the crucible's composition during the fusion and glass working time.

Usually, in the interface of glass and crucible, the Na_2O content tend to decrease (Dungworth 2008), it can be explained by the re-working and re-melting process since, above 1000 °C, there are a sever loss of sodium by its volatilization (Rodrigues et al., 2018; Velde, 2009). On the other hand, K_2O, MgO, Al_2O_3 and TiO_2 can be introduced in the glass matrix through the diffusion of those oxides from the crucible, especially if the crucible is rich in potassic feldspars (Reheren et al., 2019; Velde, 2009; Veronesi et al., 2019).

Comparable amount of K_2O, Na_2O, CaO and Al_2O_3 were detected in metallurgic slags found in Jamestown (Veronesi et al., 2019) but, in that case, some clusters of metallic inclusions were observed within the glassy material.

All the discovered PW, found in the Lisbon, exhibits no discernible inclusions under microscopic examination. The archaeologists overseeing the LCS excavation do not report any evidence of metallurgical activities. However, they have encountered distorted glass canes, which may be regarded as indicative of glass working processes (Gonçalves et al., 2020).

On the contrary, despite the pronounced dark hue of the PW glass fragments, discernible streaks of lighter tones (Fig. 4) are evident, accompanied by highly irregular shapes. This observation lends further support to the hypothesis that these fragments may be categorized as remnants of PW.

Millefiori glass fragments found in Lisbon seem to be made by using alkali and silica source purer than the one used in the analysed PW (Figs. 6 and 7), with lower content of feldspars. Other important observation of the waste glass fragments is that the glass composition is very heterogeneous even in the same fragment, see LCS pw in Fig. 6, where the different results represent the different analysed coloured area of the same sample as it was not perfectly fused together.

On the other hand, regarding Zr and Hf contents, some PW appears near the analysed *millefiori* fragments.

For LCD 003 (PW), no significant amount of CoO was detected (below 20 μg/g) when compared with the blue layers of *millefiori* glass fragments but, remarkable amount of Fe_2O_3 was detected (respectively 3.53–4.18 wt% and 0.07–0.14 wt%) and in LCS (respectively 3.13–4.75 wt% and 0.06–0.13 wt%) (Table. 3).

No other colorant seems to be intentionally added to PW, when compared their content with the coloured *millefiori* fragments, and the glass compositions of PW are quite similar. So, the observed range of colours may be linked with glass devitrification or different fired conditions (different furnaces or different part of the furnace).

Fe_2O_3 can be found in the glass matrix in two coordination numbers (ferrous ion [Fe^{II}] and ferric ion [Fe^{III}]) and Fe^{II} is responsible for blue colour while Fe^{III} is responsible for yellow colour, it means that in a reduced atmosphere the prevalent ion will be Fe^{II} (blue) while in oxidation atmosphere will be the Fe^{III} (yellow) (Navarro, 2003; Volf, 2011).

Only two PW/ slag (LCD 014 and LCS 003) have geochemical pattern comparable with the analysed *millefiori* glass fragments, the other PW do not have the same pattern (Fig. 14).

Moreover, the geochemical patterns associated with PW appears in higher position when compared with the analysed glass artefacts (Fig. 13), this observation reinforce the idea that PW are less pure (less refined or selected) than the *millefiori* fragments (Lazar and Willmott, 2006).

Although this glassy material can be considered most likely PW, we assume that we cannot reject the possibility to have glassy material disconnected from glass production.

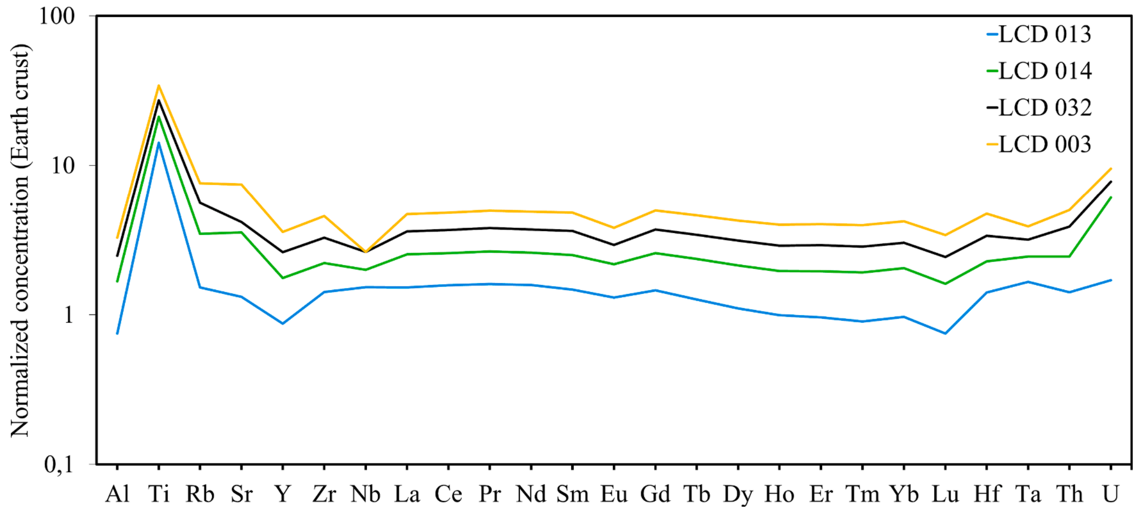


Fig. 14. Selected elements associated with silica sources of the samples normalized to the Upper Earth crust presented in logarithmic scale. *cl = Clear; r = Red; pw = Production waste.

5. Final remarks and future work

In this work eight glass fragments decorated with pick-up technique decoration were selected for compositional studies (in total 25 glass layers were analysed) plus four glass PW found in the same archaeological contexts where the fragments were found.

The range of colours used in these artefacts are consistent with the ones used for Venetian and *façon-de-Venise* glass production of the same chronology: blue, red, turquoise and white.

Compositional analyses show that all *millefiori* glass fragments can be considered as soda-lime-silica type while the original composition of PW could not be determined and, according to major components (e.g. Na_2O, K_2O, CaO, Si_2O, TiO_2, Al_2O_3, MgO) their compositions were disconnected when compared to the glass artefacts.

All the analysed LCS glass samples were made with barilla as fluxing agent while most of the LCD glass samples were produced with Levantine ashes. This information suggests that two different recipes were used and can mean that they were produced in two different furnaces or, it can reflect an improvement of recipe.

An interesting result is related with the major components associated to silica sources (SiO_2, Al_2O_3 and TiO_2) as they are grouped together while different content of these oxides was observed from the already known Venetian or *façon-de-Venise* production centres.

While similar and unusual hight amount of Al_2O_3 content [2–8 wt%] have been reported in Savona by Cagno and co-authors (2012a) they seem to be disconnected with the ones found in Lisbon. Moreover, the values of Al_2O_3 versus TiO_2 of Lisbon glass samples appear isolated from the already known Venetian or *façon-de-Venise* production centres.

By looking at the coloured glass layers, was possible to notice that blue layers were caused by the presence of CoO in the glass matrix with its association with As and Bi indicating a time stamp posterior to 1520–1530. The blue glass samples unearthed in LCS show a higher content of MnO (0.6–1.13 wt%) when compared with the blue samples from LCD (0.38–0.54 wt%). In the case of turquoise and red glass layers, the coloration is caused by the presence of CuO and the red body glass of LCS_005 sample is an interesting case study due to probably being made in flashed technique (to the authors knowledge this observation was never mentioned in the literature for this chronology). For white glass layers, all the selected samples were produced with the new Venetian *lattimo* glass by the addition of lead and tin oxide to the glass matrix which caused the precipitation of cassiterite crystals.

PW is also an interesting case study because the blue/amber colors seem to be caused by the presence of iron oxide in the glass matrix in different ionic stages: ferric ion (Fe^{3+}) produce yellow while ferrous ion (Fe^{2+}) produce blue color.

According to geochemical patterns, the studied *millefiori* glass fragments and the PW follow the same tendency which means that the silica source used in both glasses are related.

Looking at the provenance study, none of the fragments can be considered of genuine Venetian production nor can be attributed to any known *façon-de-Venise* production centres. This result opens the possibility of Lisbon glass production centres being here disclosed although further studies are still required to confirm this attribution.

This statement is supported by historical documents that attest the presence of glass furnaces in Lisbon at coeval, by the original *rosette* patterns found in LCD (cross) and LCS (caravel and flower), and by the geochemical patterns that group all *millefiori* glass fragments and PW together.

CRediT authorship contribution statement

F. Pulido Valente: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Project administration, Supervision, Funding acquisition. **I. Coutinho:** Methodology, Validation, Investigation, Resources, Data curation, Project administration, Supervision. **T. Medici:** Methodology, Validation, Formal analysis, Resources, Project administration, Supervision. **B. Gratuze:** Software, Validation, Formal analysis, Funding acquisition. **L. C. Alves:** Software, Validation, Formal analysis, Project administration. **R. Varela Gomes:** . **M. Varela Gomes:** Methodology, Validation. **M. Vilarigues:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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