NOVA SCHOOL OF SCIENCE & TECHNOLOGY

DEPARTAMENT OF
CONSERVATION AND RESTORATION

DECODING THE PAST THROUGH *PICK-UP* DECORATED GLASS:

Glass fragments unearthed in Portugal dated to 16th-17th centuries.

Maria Francisca Vasconcelos Raposo Pulido Valente Monteiro Cabral

Master in Conservation and Restoration

DOCTORATE IN CONSERVATION AND RESTORATION
OF CULTURAL HERITAGE

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Dedicated to God.

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ABSTRACT

This project provides an overview and a crosscutting investigation about one of the most important and intricate glass decorative techniques of the Renaissance (end of 16th – 17th centuries): the *pick-up* decoration, including *millefiori* and *splash* technique.

Millefiori (literally means "thousand flowers") is characterised by the usage of embedded *murine* (thin sliced glass canes with colourful concentric patterns in cross-section) fused into the surface of its body glass. While, *splash* technique is characterized by glass objects that have sparkling coloured pints, produced by the fusion of sliced coloured glasses, that are fused in it surface.

Different subjects of investigation are linked in this work: I) history and nomenclature, II) production technique, III) a survey of literature on archaeological findings, and IV) composition characterisation of some fragments unearthed from four different Portuguese archaeological sites: Santa Clara-a-Velha Monastery (SCV) in Coimbra, Largo do Chafariz de Dentro (LCD) and Santana Convent in Lisbon (LCS) and São João de Tarouca Monastery (SJT) in Lamego.

The present study involves the meticulous selection of 31 glass samples according with its patterns, colour choice and forms representativity. A total of 105 distinct glass layers were chemically analysed, from a comprehensive assemblage of over 200 *pick-up* fragments. The research conducted by Teresa Medici (2014) played a crucial role in the survey of archaeological glass fragments/ objects from the late medieval and Modern periods found in Portugal. To ensure the appropriateness of the selected samples for this project, specific criteria were adopted, including: shapes, range of colours, the presence of gold leaf, the occurrence of corroded layers, and certain distinctive attributes (e.g., unique decorative patterns like crosses, caravels, flowers, and bird head shapes).

In addition to the aforementioned glass fragments, we also performed analyses on four glass waste products, retrieved from LCD (3 fragments) and LCS (1 fragment) sites, to compare their chemical composition with that of the selected *pick-up* glass fragments.

For the material characterization, was adopted a comprehensive approach encompassing macroscopic and microscopic observations, as well as compositional characterization was employed to discern the raw materials used in the production of both colourless and coloured glass artifacts.

The morphological investigation entailed the application of stereoscopy and optical microscopy. Compositional analysis was carried out utilizing two distinct techniques: 1) particle induced X-ray emission (μ-PIXE) mapping, which facilitated visualization of the distribution of different oxides across various layers, and 2) laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), enabling the determination of the major, minor, trace, and rare earth elements (REE) in the composition.

Additionally, μ-Raman spectroscopy was employed to investigate the opacifiers, while UV-Visible reflectance spectroscopy was utilized to assess the presence of chromophores within the glass samples.

The analysed coloured glass exhibits a prevailing trend commonly observed in coeval European artifacts: cobalt imparts the characteristic blue hue, while copper contributes to the *aventurina*, red, and turquoise colours (at different oxidizing states). Iron is responsible for the amber and greenish tinges, whereas manganese accounts for the black colour when accompanied by a minimal CoO content. In the case of white-coloured glass, the opacifier employed in all examined layers is cassiterite, as extensively utilized by the Venetian glassmakers.

Based on the findings of this study, it can be confirmed that all the examined *pick-up* glass fragments fall under the category of soda-lime-silica type.

However, despite extensive analysis, a definitive attribution to Venetian production was not attainable in any sample. This observation is of particular significance, as *pick-up* glass artifacts dating from the 15th to 17th centuries are commonly associated with a Venetian origin.

Furthermore, one of the geochemical patterns identified in the results for one of the production remains found in Lisbon (LCS 0003) aligns with approximately 60% of the samples. Combining this finding with the identification of several glass fragments, as pointed out by Teresa Medici (2014), that exhibit distinct morphological characteristics (as gourd-shaped vessels and original flower pattern of SCV 360 fragment) are that likely of Portuguese origin. Notably, most of these fragments were likely produced using barilla ashes as the alkali source, with the principal components associated with the major components of silica sources, here attributed, to a probable Lisbon provenance by taking the graph which combine TiO_2/Al_2O_3 and Al_2O_3/SiO_2 information.

By integrating these empirical findings with corroborative historical documentation, it becomes plausible to propose that the revealed 6th geochemical pattern can be probably attributed to Portuguese origin. However, it is essential to acknowledge that further comprehensive investigations are warranted to definitively establish this attribution.

Keywords: *millefiori* glass, Renaissance, Archaeology, Portugal, Venetian, and *Façon-de-Venise* glass

RESUMO

Este projeto oferece uma abordagem geral e abrangente à cerca de uma das técnicas decorativas de vidro mais importantes e elaboradas do Renascimento (fim do século XVI - século XVII): a decoração *pick-up*, a qual inclui o vidro *millefiori* e *splash*.

O vidro *millefiori* (significa, literalmente, mil flores) é caracterizado pela utilização de *murrinas* (finas secções de cana que apresentam padrões concêntricos coloridos em corte transversal) fundidas na superfície do objeto de vidro. Já o vidro splash é caracterizado por apresentar pontos coloridos dispersos pela superfície do objeto. Este efeito é produzido pela fusão de lascas de vidro colorido que cor sólida.

São feitas diferentes abordagens ao tema relacionando: I) história e nomenclatura, II) técnica de produção, III) revisão da literatura sobre artefactos de vidro encontrados em contexto arqueológico e IV) caracterização da composição de alguns fragmentos descobertos em quatro sítios arqueológicos portugueses diferentes: Mosteiro de Santa Clara-a-Velha (SCV) em Coimbra, Largo do Chafariz de Dentro (LCD) e Convento de Santana em Lisboa (LCS) e Mosteiro de São João de Tarouca (SJT) em Lamego.

O presente estudo envolveu a meticulosa seleção de 31 amostras de vidro decoradas com a técnica *pick-up*, o que originou um total de 105 camadas de vidro distintas. Para esta seleção, o trabalho conduzido por Teresa Medici (2014) desempenhou um papel crucial no levantamento de objetos de vidro arqueológico do período tardo-medieval e Moderno encontrados em Portugal. A seleção das amostras para serem analisadas teve em conta critérios específicos que incluíram: a formas dos objetos, variedade de cores, presença de folha de ouro, existência de camadas de corrosão e outras características singulares (p.e., padrões decorativos únicos como cruzes, caravelas, flores e cabeças de pássaros).

Além dos fragmentos de vidro mencionados anteriormente, também foram analisados quatro restos de produção (ou escórias) de vidro, recuperados dos sítios LCD (3 fragmentos) e LCS (1 fragmentos), a fim de comparar sua composição química com a dos fragmentos de vidro.
No estudo da caracterização do material, foi adotada uma abordagem abrangente que incluiu observações macroscópicas e microscópicas dos fragmentos, bem como a caracterização da composição química para tentar discernir quais foram as matérias-primas utilizados na produção destes artefactos de vidro.
A investigação morfológica foi realizada através de estereoscopia e microscopia ótica enquanto, a caracterização da composição química dos fragmentos foi realizada por duas técnicas analíticas distintas: 1) μ-PIXE, que possibilitou a visualização da distribuição dos diferentes óxidos nas diferentes camadas que compõem cada fragmento, e 2) LA-ICP-MS, permitindo a determinação da composição dos elementos maioritários, minoritários, traço e elementos associados às terras raras (REE).
Para além das técnicas analíticas anteriormente citadas, a espectroscopia μ-Raman foi utilizada na investigação dos opacificantes, enquanto a espectroscopia de reflectância UV-Vis foi utilizada para avaliar a presença de cromóforos nas amostras de vidro.
O vidro colorido analisado exibe uma tendência predominante comummente observada em artefactos europeus contemporâneos: o óxido cobalto confere a tonalidade azul, enquanto o óxido de cobre contribui para as cores *aventurina*, vermelho e turquesa (em diferentes estados de oxidação do cobre). O óxido de ferro é responsável pelos tons âmbar e esverdeados, enquanto o óxido de manganês determina a cor preta, quando acompanhado de uma quantidade mínima de CoO. No caso do vidro branco, o opacificante utilizado em todas as camadas examinadas é a Cassiterita, extensivamente empregada pelos vidreiros venezianos. Além disso, em determinadas amostras brancas (SCV_240 e SCV_250), a coexistências de cristais de cassiterite e malayaita foi comprovada.
Com base nos resultados obtidos por este estudo, foi possível verificar que todos os fragmentos de vidro com decoração *pick-up* analisados neste projeto podem ser classificados como sendo do tipo sodo-cálcico silicatados. No entanto, a atribuição definitiva a produção Veneziana não pôde ser conferida a nenhum dos fragmentos ou camadas de vidro. Esta observação é particularmente relevante uma vez que, artefactos de vidro decorados com a técnica *pick-up* datados do século XV ao século XVII são frequentemente atribuídos à produção Veneziana.

Além disso, o 6º dos padrão geoquímico mostrou ter uma notável compatibilidade entre o resto de produção LCS 003 e, aproximadamente, 60% dos fragmentos selecionados para análise que são decorados através da técnica *pick-up* (provenientes dos contextos de Lisboa e SCV). Ao combinar esta descoberta com a identificação de vários fragmentos de vidro, como apontado por Teresa Medici (2014), que exibem características morfológicas singulares (como os recipientes em forma de cabaça e o padrão original de flor do fragmento SCV 360), torna-se provável que estes objetos possam ter uma produção portuguesa. Notavelmente, a maioria desses fragmentos foram, provavelmente, produzidos utilizando cinzas de barilla como fonte alcalina e têm os componentes maioritários, associados às fontes de sílica, situadas na região de Lisboa.

Reunindo todas estas descobertas com documentação histórica corroborativa, torna-se plausível propor que o 6º padrão geoquímico aqui revelado possa ter origem em Lisboa. No entanto, é essencial reconhecer que investigações mais abrangentes são necessárias para estabelecer definitivamente essa atribuição.

Palavas chave: vidro *millefiori*, Renascimento, arqueologia, Portugal, vidro veneziano e *Façon-de-Venise*.

Works resulting from this project:

- The author was invited to write a book chapter with Michel Hulst, Jerzy Kunicki-Goldfinger, Adelphine Bonneau, Márcia Vilarigues, Inês Coutinho and Teresa Medici about Dutch glass beads production in Soop Glasshouse.
- The author won the Quebec governmental *Bourses d'excellence pour étudiants étrangers (PBEEE)* 2023, with the best application from a total of three awards. She will work in Sherbrooke University from November 2023 to March 2024 with Professor Adelphine Bonneau.
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Glossary

Splash	This terminology is used for the glass objects that were decorated by picking-up sliced coloured glass without any regular pattern.
Millefiori	For the glass objects that were decorated by picking up *murrine*.
Mosaic	For the glass objects which are made by fusing side by side sliced canes in order to form a plaque that was then slumped over a mould.
Murrine	For sliced glass canes that have a decorative pattern which can be seen in cross-section
Pick-up tecnique	for the glassware that was decorated by picking-up (by rolling a molten glass bubble over them) *murrine* or sliced glass without decorative motifs
Rosette	for the pattern that is similar to the image present in Fig.1.6.

ACRONYMS

μ-PIXE	Micro – Particle Induced X-ray Emission
HREEs	Heavy Rare Earth Elements
LA-ICP-MS	Laser Ablation Inductively Couple Plasma Mass Spectroscopy
LCD	Largo do Chafariz de Dentro, Lisbon
LCS	Santana Convent, Lisbon
LREEs	Light Rare Earth Elements
REE	Rare Earth Elements
SCV	Santa Clara-a-Velha Monastery, Coimbra
SJT	São João de Tarouca, Lamego
UV	Ultra Violet
Vis	Visible

1

INTRODUCTION

1.1 Research Objectives and Motivation[1]

Historical research and documentation are of paramount importance to preserve and value cultural heritage; therefore, a survey that combines formal and morphological observation with chemical characterization was started to expand our knowledge about the history of *pick-up* glass objects. Shape and decoration are the first elements that can give the researcher a clue about the origin or provenance of a certain object. In this way, a deeper knowledge about technological development and decorative motifs can help scholars determining the origin and, possibly, the chronology of glass objects decorated with this technique. This work will help archaeologists, collectors and art history researchers that could not perform expensive and time-consuming analyses to propose an origin for these kind of glass fragments/ objects.

As a conservator, the research of this specific period represents a huge challenge being of particular interest for the reconstruction, valorisation and dissemination of the legacy left for future generations, the main goal of this project.

This work is the first systematic study of early modern glass decorated with canes. It aims: (i) to advance the knowledge on the development of this technique and its trading by exploring the distribution and spreading of its decorative patterns and discussing the chemical compositions of the employed glass; (ii) to compare compositional data of glass objects decorated with *pick-up* techniques, reported in the literature, with historical sources, in order to better understand the evolution of the production technique and of the glass composition not

[1] This chapter was partially published in: Pulido Valente, F., Coutinho, I., Medici, T. and Vilarigues, M. 2021. Glass colored by glass: Review of the *pick-up* decoration in early modern Europe. J. Archaeol. Sci. Rep. 36, 1-16: https://doi.org/10.1016/j.jasrep.2021.102832.

only in Venice but also in the other glass centres; (iii) to standardize the nomenclature applied to this subject; and (iv) to study the provenance of *millefiori* glass fragments unearthed in Portugal.

1.1.1. **The 15th century as a key to the 16th and 17th centuries**

In the beginning of the 15th century the old economy based on agriculture was slowly replaced by an economy based on manufacturing and new product trading which favoured the development of European cities, production methods and the emergence of a new wealthy social class of merchants and traders (Janson & Janson 2010, p. 572).

This fact is linked with the great exploration and expansion of European countries into "unknown" territories, where "new" resources, people and cultures were explored, causing economic, religious, cultural, social, and political changes between 15th and 17th centuries. Along with commercial and economic reasons, the colonization and evangelization were the objectives of Portuguese Discoveries 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 & Mantero 1999, 53-54).

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 (Fig. 1.1) in 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).

Portugal achieved a remarkable level of academic education, thanks to substantial investments made by the monarchy in the establishment of Portuguese universities. These initiatives were undertaken in response to the clergy's request and carried out with the authority of the Pope (Vasconcelos & Mantero 1999, p. 37). The first university was created around 1290 in Lisbon and was transferred to Coimbra in 1308, by El-Rei Dom Dinis (Vasconcelos & Mantero 1999, p. 232). In the 17th century, the Portuguese university surpassed the universities of Salamanca, Bologna, Paris, and Oxford (Vasconcelos & Mantero 1999, p. 37).

In those universities the improvement of intellectual, scientific, technical and spiritual knowledge was of paramount importance (Vasconcelos & Mantero 1999, p. 37).

The investment in the Universities lead to a scientific progress in astronomy, geography, shipbuilding (originating the Portuguese caravel) which was at the basis of long-distance naval voyages (Vasconcelos & Mantero 1999, p. 37).

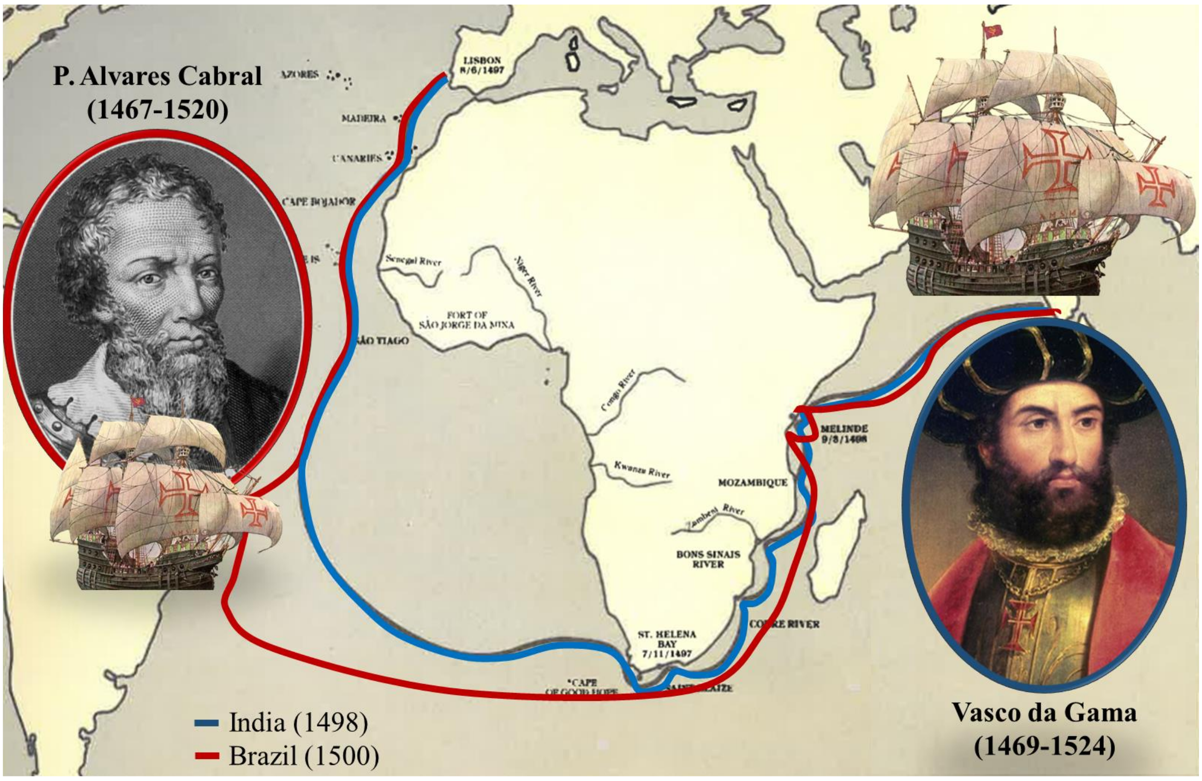


Fig. 1.1: Map representing the discovery of the sea route to India by Vasco da Gama in 1498 and the sea route to Brazil by Pedro Álvares Cabral in 1500.

In the arts, various innovations such as advancements in the introduction of oil painting (yielding more realistic artworks), the advent of printing (allowing faster and more cost-effective reproduction of multiple copies), and improvements in glass making served as pivotal springboards for the ensuing centuries (Janson & Janson 2010, p. 484, 512).

In the 15th century, venetian and *façon-de-Venise* glassware enhanced the value of collector's items, increasing their demand by connoisseurs of art who used them as indicators of wealth social prestige and cultural distinction (Doménech 2004, Spenlé 2014). Those artefacts were displayed among the most precious objects (e.g., silver and gold) and its demand by clergy, aristocracy and upper bourgeoisie was proportionally great (Spenlé 2014, p. 43).

From the mid-15th century onwards, the Venetian glassmakers produced three types of transparent clear soda-lime-silica glass: (i) the *cristallo* glass (the finest); (ii) the *vitrum blanchum* glass, slightly greyish and turbid (due to the adding of manganese to decolourize the glass because the silica sources used to produce this type of glass were usually less pure than the ones used for *cristallo*); and (iii) the *common* glass (richer in impurities) that was considered the vulgar type due to its slight greenish to yellowish or blueish hue (Lazar & Willmott 2006, Verità 2013). These types of clear glasses used different recipes and raw materials, which are reflected on the chemical composition (Table 1.1).

Table 1.1: Upper and lower limits of the main oxides of the three types of glass compositions (*cristallo*, *vitrum blanchum* and *common*) attributed to Venetian production between 15th and 18th centuries (adapted from Verità 2013).

Glass type		SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	SO_3	P_2O_5	Cl	TiO_2	Fe_2O_3	MnO	PbO	SnO_2
Cristallo	min.	68.5	0.48	14.7	2.50	4.10	1.10	0.18	0.09	0.75	0.03	0.17	0.15		
	max.	73.0	0.90	19.2	3.70	6.30	2.35	0.42	0.25	1.20	0.04	0.29	0.68		
Vitrum blanchum	min.	63.8	0.64	11.0	1.45	8.05	1.15	0.08	0.15	0.70	<0.03	0.22	0.21		
	max.	71.1	1.95	17.3	7.50	12.30	5.00	0.40	0.86	1.25	0.07	0.57	0.95		
Common	min.	62.5	0.88	10.5	1.95	9.10	2.50	0.06	0.25	0.45	<0.03	0.48	0.10		
	max.	69.5	2.62	15.8	5.55	12.50	4.50	0.40	0.55	1.00	0.28	1.08	2.75	0.40	0.40

The Venetians used to select hight quality raw materials to produce its best soda-lime-silica glass, which were relatively free of impurities: (i) pebbles from Ticino or Adige (less pure) rivers as silica source and (ii) coastal Levantine plant ashes (Salsola Kali, rich in soda and lime) as a flux and stabilizer agents (Verità 1985, Verità 2013, Verità and Zecchin 2009). These ashes, usually mentioned as *alume* or *alume catino* on recipes, were usually purified to remove impurities such as iron (responsible to tint the glass matrix in natural hues: depending on the redox conditions the colour can change from green to yellow), chromium or titanium (Lima et al. 2012, Verità 1985). If, on the one hand, this purification of raw materials left a discolourised, clarified and homogeneous glass resembling natural rock crystal (*cristallo* glass), on the other hand it also took away some fundamental oxides needed for glass stability such as calcium and magnesium oxides, making the glass more susceptible to deterioration process (Verità 1985, Verità 2013, Verità and Zecchin 2008).

Along with clear glass, Venetian glassmakers were able to make any colour combining them skilfully to make colourful objects such as beads, calcedonio, *millefiori* and *filigrana* glass (Polak 1976, p. 270).

To produce *façon-de-Venise* glass, glassmakers also frequently employed a soda-lime-silica glass, using halophytic plants (coastal plants that grow in salty soils) as a flux, which generated glass with contents of sodium oxide higher than 10 wt%, potassium oxide lower than 10 wt% and Na_2O/CaO lower than 0.5% (Coutinho et al. 2016, De Raedt et al. 2002, Rodrigues 2018). In some cases, *façon-de-Venise* glass was produced employing local raw materials (plant ashes and silica sources) and different recipes, generating different types of glass matrixes (fig. 1.2) (e.g. De Raedt 2002, Rodrigues 2018).

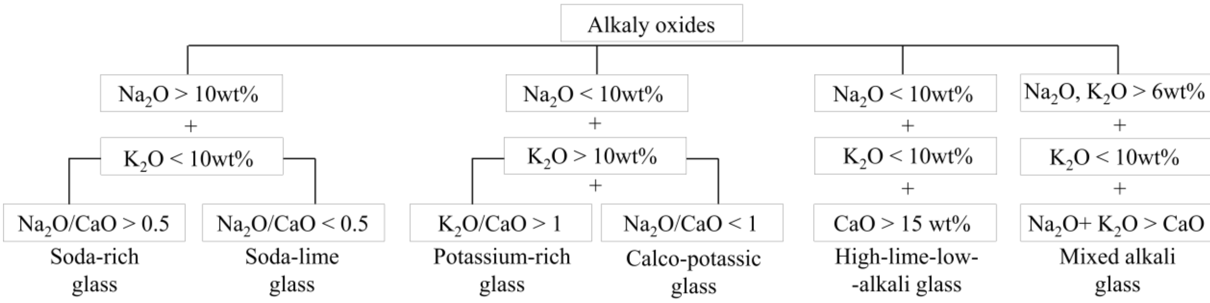


Fig. 1.2: Classification of different glass types according to its flux agent, adapted from Rodrigues 2018.

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 & Zecchin 2009). Some works point out that Venetian glassmakers working abroad still were importing the traditional flux agent. Thereby, making these *façon de Venise* glass composition quite similar to genuine Venetian glass is kite usual in the contemporary glassware (e.g. Baart 2002, Bronk et al. 2000, de Raedt, Janssens, & Veekman, 2002).

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

Unfortunately, the location of the Portuguese furnaces producing this good quality glassware are so far unknown.

1.1.2. **The 16th and 17th centuries**

The trade connections between Europe and the East, via the Mediterranean, through the and Venetian Republic changed at the beginning of the 16th century, to Lisbon and Antwerp through an Atlantic Sea route. This change allowed not only brought a greater quantity and diversity of products, but also gave a greater profit margin to Portugal (Arnold 2017, 96-97; Subacchi 2002, p. 23).

Lisbon (the Portuguese capital city), located on the north bank of the Tagus River (Fig. 1.3), became one of the most important import- export trade markets for its colonial products (e.g. tobacco, silk and cotton and spices like pepper, cocoa, coffee and sugar) and for precious and exquisite products from China, Japan, Venice, Dutch, 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 the Central Europe and West of Africa with commodities like brass, copper glassware and linen textiles (Arnold 2017, p.96).

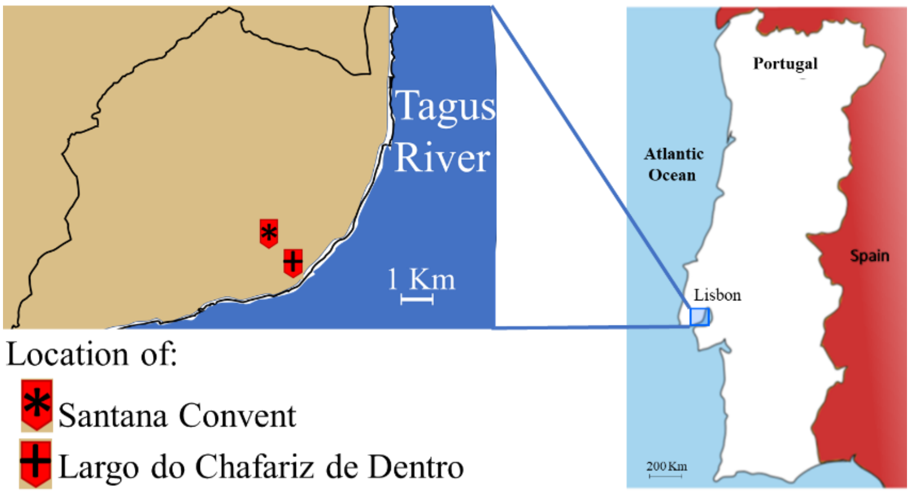


Fig. 1.3: Nowadays Lisbon and archaeological context's location.

Despite the attempt to monopolize glassmaking, the Venetian Government was unable to prevent the foundation of new glasshouses outside Venice; so, the production of those artefacts in the Venetian way (*à la façon de Venise*) began to start and, in the first half of the 16th century, glass made with Venetian techniques was already spread in Europe by skilled glassblowers (travelling from Murano and Altare), with such quality that, sometimes, it is almost impossible to distinguish between the genuine Venetian glass and *façon-de-Venise* objects by outward appearance (De Raedt et al. 1999, De Raedt et al. 2002, Medici 2014, Page 2004, Verità 2014, Verità and Zecchin 2009).

At that time, an artist (e.g., painters, sculptors, and glassmakers) was also a researcher and scientist improving the knowledge about how to understand, control, and imitate Nature (Spenlé 2014). Alongside painters, sculptors and architects and the glassmakers and glassmaking also had a significant influence taking inspiration from Classic culture (Dupré 2014, Spenlé 2014).

Glassmakers were truly alchemists as they gathered artisanal knowledge and production experience in the transmutation of natural substances (e.g., metal) to create a more noble artificial matter (glass) (Dupré 2014, Spenlé 2014). In other words, being a glassmaker implied knowledge of chemistry (raw-materials properties) and a great familiarity with difficult and laborious process of glassmaking at the kiln which contributed to the princely prestige and various privileges given to them (Dupré 2014, Spenlé 2014).

The first systematic Renaissance glassmaking treatise called as L'arte vetraria, written by the reputable priest and alchemist Antonio Neri (1576-1614) was published in 1612 which was quickly copied, translated and spread throughout Europe (Dupré 2014, Spenlé 2014).

1.2 *Millefiori* and *Splash* glass - historical overview

The use of coloured canes, whether in sections or in length, to decorate glass objects is one of the most ancient, intricate and interesting techniques in glass history (Barovier Mentasti 2012, Page 2014). Being previous to blown glass, it has its origins in the Hellenistic time in the third century B.C. with the *mosaic* technique (Hollister 1983, Barovier Mentasti 2012).

In fact, *millefiori* glassware uses sliced coloured glass canes to decorate its surface. This Renaissance decorative technique was so complex, delicate, exquisite, and luxurious, that rapidly spread throughout Europe (Page 2014; Revi 1958; Tait 2012). Moreover, these decorative techniques require technological and empirical knowledge and a skilled glassmaker aware of practical risk of glass objects becoming able to spontaneous cracking if different glasses used in the same piece have thermal incompatibilities [Verità, Zecchin and Tesser 2018].Chemical analysis demonstrated to be helpful in determining the probable origin of glass produced in Venetian style by discussing their composition (e.g. Cagno et al. 2010, Coutinho et al. 2016, De Raedt et al 2001 and Lima et al. 2012). However, when glassmaking centres outside Venice also imported the traditional Levantine soda ashes, as recorded, for instance, in London and the Low Countries (De Raedt 2002) that distinction between genuine Venetian and *façon-de-Venise* starts to be challenging. In this case, as the silica source was probably the only raw material of local provenience, the distinction between Venetian and *façon-de-Venise* glass can be made through minor and trace elements associated to SiO_2 (De Raedt 2002, Verità 2013). For example, abnormally high levels of alumina (5-7.84 wt%) detected in some *millefiori* and *façon-de-Venise* glass found in Portugal may suggest a local glass production, using a silica source rich in feldspar (Lima et al. 2012, Coutinho et al. 2016).

In other cases, the silica sources are also so similar to the ones used in Venice and differences can be found only in trace elements such as zirconium and hafnium (Cagno et al. 2012, De Raedt 2002). According to the literature, Venetian glass has the lowest Zr (between 20 and 40 μg/g) and Hf (below 1 μg/g) values (Cagno et al. 2012, De Raedt 2002).

Moreover, the use of geochemical patterns will help to identify differences in mineralogical composition of sands employed in glass production by using the relative abundance of trace and rare-earth elements (REE). These elements, which are not easily fractionated during the sedimentation process of the sands, are linked with the geographic location where they were collected (Brems & Degryse 2014, Kunicki-Goldfinger et al. 2008).

1.2.1. *Millefiori* and *splash* glass

The oldest known glass objects ornamented with sliced glass canes is dated to 1500 and 1000 BC and were found in today Iran and Iraq. They were obtained by *mosaic* technique, fusing the slices in a mould (Moretti, 2012; Barovier Mentasti 2012; Page 2014). The production of *mosaic* glass ended in the 13th century BC, emerging again in Egypt during the second half of the 5th century B.C. (Nenna and Gratuze 2009). It flourished during the 4th century BC, with Pharaoh Nectanebo II (c. 360-343 BC) and during the Hellenistic period (Tait 2012; Whitehouse 2012). In Roman times, magnificent artefacts made with this technique were also fond. These include glass vessels displaying a diversity of colour combinations and *murrine* patterns: animals, images of Gods, flowers, acanthus leaves, or theatrical masks (Moretti 2012; Tait 2012; Whitehouse 2012).

After the discovery of glassblowing in the first half of the 1st century BC, Romans developed the technique to decorate the surface of a glass object by picking up glass slices with a gather of hot glass (Moretti 2012; Tait 2012; Whitehouse 2012; Stern and Fünfschilling 2020).

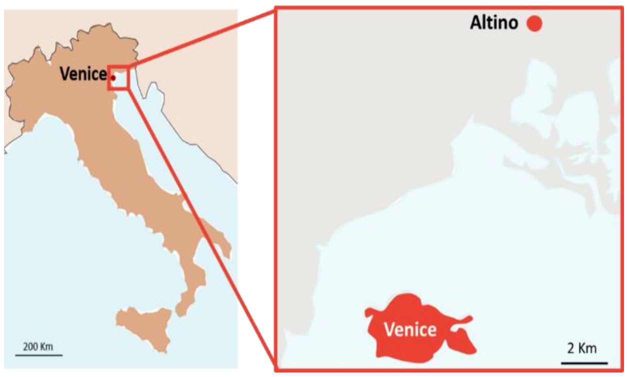
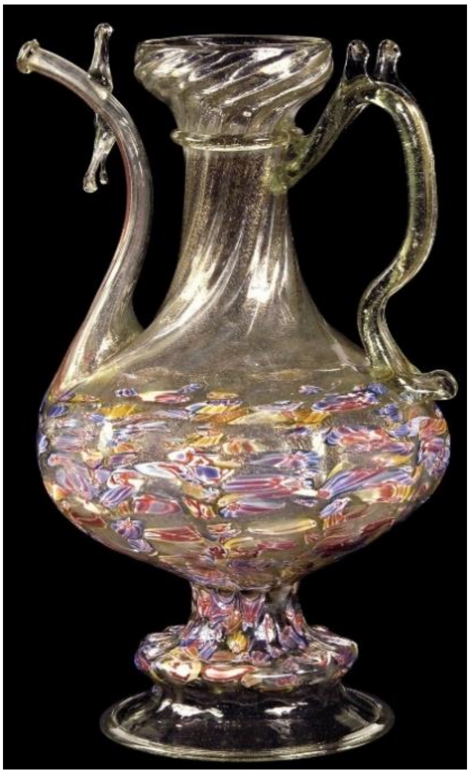


Fig. 1.4: Map of Italy with Venice and Altino are marked

This new technique was adopted for a short time by Islamic glassworkers in the Egyptian region, around 6th-8th century, but it is in the Renaissance that it reaches its apogee in the hands of the Muranese glass masters. They developed and improved complex pick-up glass decoration, possibly inspired by the observation of Roman *mosaic* glass recovered from Altino (Fig. 1.4), a site early known for its ancient glass treasures (Barovier Mentasti 2012; Eisen 1919; Helmut 1995; Moretti 2012).

The patterns resulting from the use of the pick-up technique can be divided in two big groups: *millefiori* and splashing (Fig. 1.5.a and 1.5.b). *Millefiori* is an Italian word that literally means "thousand flowers" and describes the final effect of an object that is produced with colourful sliced canes that have concentric patterns. The difference between *millefiori* and *splashing* decoration is that, instead of multi-coloured glass cane slices with concentric patterns, several coloured glass chips without any pattern are used to decorate the object which results in a speckled appearance (Gudenrath 2012; Moretti 2012).


a)

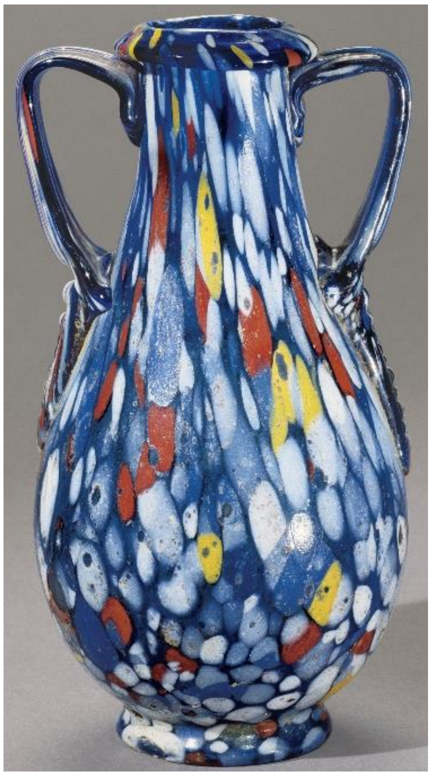

b)

Fig. 1.5: a) Ewer with *millefiori* decoration, 249 mm high, probably made in Spain, Catalonia, 16th century - © Corning Museum of Glass (2003.3.70). b) Jar with two handles with *splashed* decoration, 117 mm high, probably made in Italy, middle of 1st century - © Corning Museum of Glass (59.1.88).

Millefiori glass with its intricate and elaborated design seems to have been one of the first complex techniques that the Venetian glassblowers improved (Helmut 1995) and, maybe for that reason, it has been considered a perfect, emblematic and magnificent type of Venetian glass (Baumgartner 2015; Richter 1919). To produce *millefiori* objects, it is necessary a skilled glassmaker with experience, a solid knowledge about the properties of different glasses, and a great patience (Moretti 1985).

Historical sources and archaeological finds attest that *pick-up* glass (in both types: *splashing* and *millefiori*) was made outside Venice, for instance, in Catalunya and in Amsterdam (Domenech 2004; Gawronski et al. 2010; Baart 2002). Some glass remains that suggest a local glass production were found in Orléans in France (Page 2004), Buda Palace in Hungary (Holl-Gyürky 1986), Coimbra (Medici 2014) and Lisbon (Pulido Valente et al. 2023) in Portugal.

1.2.2. **Nomenclature**

The texts resulting from the survey of the literature were analysed and the terminology was interpreted to ensure comparability. A wide range of terms was recorded: (French*) chevron, millefiori, pastille;* (English) *blobbing, dotted glass, flecked glass, millefiori, miniature, pick-up, splashed* and *star pattern;* (Italian) *millefiori, murrine, rosette, picchiettato;* (Portuguese) *millefiori, sarapintado*.

Although different terminologies were attributed to *pick-up* objects (Apendix A.1), the most common ones are *millefiori, murrine* and *rosette*:

1.2.2.1. ***Millefiori* and *splash* glass**

It is generally assumed that the first time a renaissance *millefiori* glass was described was in 1495, in the book wrote by Marcantonio Coccio Sabellico and entitled "De Situ Venetae Urbis" (Charleston 1967; Barovier Mentasti 2012; Tait 2012; Whitehouse 2012; Baumgartner 2015). In his description Sabellico praised the Muranese glassmaking that "(...) includes in a little ball all the sorts of flowers which clothe the meadows in spring. (…)". He chooses a ball to exemplify a *millefiori* glass object and indeed such artefacts were not rare in the 16th and 17th

centuries (see for example Theuerkauff-Liederwald 1994). In addition to this description, Sabellico also refers that "Yet these things have been under the eyes of all nations as articles of export (…)" which reinforces the high relevance of this type of objects in this period as traded products (Charleston 1967).

However, the word *millefiori* does not appear in the Venetian documents of the 15th century (Zecchin 1968). It was first recorded by the antiquarian Heinrich F. von Minutoli in his "*Nachträge zu meinen Werke betitelt Tempel des Jupiter Ammon in der Libyschen wüste und nach oder-Aegypten in den Jahren 1820 und 1821*" (Supplements to my works titled Temple of Jupiter Ammon in the Libyan Desert and to Egypt in 1820 and 1821) published in 1827 (Hollister 1983). In that work, von Minutoli wrote that: "(...) *neuere Arbeit die man in Italien mit dem Namen Millefiori und auf der Insel Sicilien mit von Fiori di St Jennaro auch Vascafiori belegen pflegt und von welcher man Kugeln Platten zu Dosen Messerhefte u dgl m vorfindet sind viel unvollkommner als die alten Glasmosaiken.*" […more modern work which they call in Italy "*millefiori*" and on the Island of Sicily "*fiori di San Jennaro*", also "*Vasca Fiori*", and which one finds in spheres, knobs of walking sticks, plates for boxes, knife handles, and so on, are much less perfect than the genuine old glass *mosaics* (free translation by the authors from the original German text)] (Hollister 1983; Minutoli 1827). In this description von Minutoli was attributing the *millefiori* name to the modern technique rather than the oldest one, making clear that *millefiori* is different from "*mosaic* glass".

In the present work we chose to use the word *millefiori* to describe glass objects that were decorated by sliced glass canes that have drawings in their surfaces, and the word *splashing* for glass objects that were decorated by slices of coloured glass. Although *blobbing* has been used by us in previous publications, the term was replaced by *splashing* in order to avoid confusion with the technique of "…decorating hot glass by dropping onto the surface blobs of molten glass…" (CMG, 2019).

1.2.2.2. *Sliced canes: murrine, rosette, chevron*

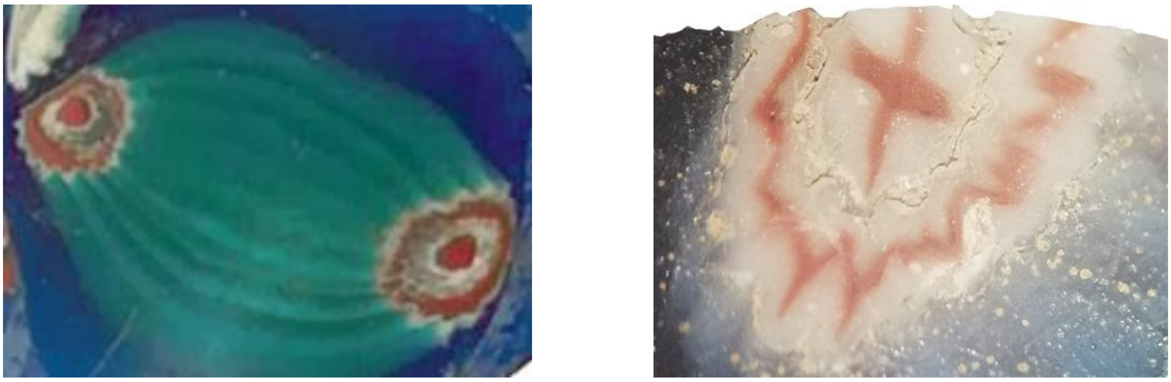
Different terms applied to *millefiori* sliced glass cane has been mentioned in the literature: *murrine*, *rosette*, chevron canes, *millefiori* canes, slices of coloured canes, *sezioni di canna rosetta*.

It is generally accepted that the first time that the word <u>murrina</u> (*myrrhina* in Latin) was mentioned was by Pliny the Elder in his "Naturalis Historia" (Loewental et al. 1949; Trowbridge 1922). Pliny (37, 8) wrote: "*The East sends* ***murrina****; they are found there in many places, not particularly noted, chiefly in Parthia; but the best ones are found in Carmania. Their moisture is believed to be solidified by subterranean heat. In size they never exceed a small tray; in thickness they are seldom as large as the cups mentioned above. Their brightness is not great, and it is more nearly a lustre than a brilliancy. But highly esteemed is the variety of colours with the spots one after the other turning into purple and white and a mixture of the two, with the purple, by a change of color, becoming flamecolored, or the milky white becoming red. Some praise particularly their edge and certain reflection of the colors, such as those seen in the rainbow. Again, others are pleased by opaque spots - translucency, or pallor, is a defect - and also crystals and warts, not projecting, but for the most part depressed, as in the human body (…)*" (Trowbridge 1922).

The interpretation of this text has generated some controversy. While some authors believed that Pliny was referring to glass objects (e.g. Richter 1919), it is generally assumed that he was referring to stone vessels (e.g. Barovier Mentasti 2012; Loewental et al. 1949; Moretti 1985).

In this work, *murrine* will be used to designate the cane slices used to make *millefiori* objects, as used by Moretti (1985) and Bruhn (1995), for example.

Murrine can have a variety of patterns. The most frequently found is the *rosetta* (Italian term) that corresponds to the chevron motif (fig. 1.6 a).



(a) (b)

Fig. 1.6: *Millefiori* glass fragments found in Portugal. (a) Example of a *rosette* motif (LCD_0054) and (b) *murrina* with a cross drawing in the core (SCV_0400).

The term *rosette* (in Italian, little roses) appears in the Venetian documents of the 15th century; the oldest use, known so far, belongs to a note dated to the 1482 related with "*pater-nostri a rosete*" (rosary beads with *rosette*) (Zecchin 1968; Zecchin 1990b; Moretti 2005; Barovier Mentasti 2012).

In the inventory of the glasshouse of Giovanni and Maria Barovier (sons of the famous glassblower Angelo Barovier) compiled on the 4th May of 1496 (Zecchin 1968), the *rosette* were used as a decorative pattern in, at least, 20 glass objects: 2 *sechietti de rosette*, 4 *manegi de cortelli de rosette*, 4 *manegi de pugnali de rosette*, 4 *oldani de rosette*, 5 *scudellini de azuro, con lo fondi de rosette* and 1 *zara de rosette* (Moretti 1985; Zecchin 1968). This information reinforces the idea that, by the end of 15th century, glass objects decorated with *rosette* were already made in Murano, at least in this glasshouse.

Rosette beads are one of the most luxurious and known Venetian beads due to its complex production process. Some authors defend that the *rosette* canes made to decorate glassware and to make beads were produced in the same glasshouses, with the same technique and the same raw materials (Barovier 2005; Gradmann et al. 2013).

In this work, we decided to use *rosette* to describe the patterns that are typologically similar to the Fig. 1.6.a. According to Paul Hollister (1983), in the 16th century *millefiori* glass objects show only the *rosette* / chevron patterns. Variations of rosette pattern, *e.g.* a *rosette* motif with a cross drawing in the core (Fig. 1.6.b), are nevertheless recorded by specimens found in Slovenia (Kos 1994) and in Portugal.

1.2.3. **Technological development**

To better understand the complexity of this glasswork the information about the making of these objects is here systematized. The description of the production process is reconstructed based on the consulted literature, confirmed by the direct observation (Bill Gudenrath making glass canes at the Corning Museum of Glass, 2006) and discussed with the glassmaker and Professor at *VICARTE* Robert Wiley.

1.2.3.1. **Making canes**

The most critical step (Barovier Mentasti 2012) and the fundamental element (Moretti 2012) of the production of *millefiori* glass object is the production of the glass canes. These canes have the particularity that the drawings can only be seen in cross-section.

Canes can be made by different methods. The most documented and used production method of *rosette* canes during the 16th and 17th centuries is the one where concentric coloured glass layers are successively pressed into dip-moulds with ribbed decoration (Hollister 1981).

The description of the *murrine* canes making is illustrated in Fig. 1.7 and the references of each step are in Apendix A.2.

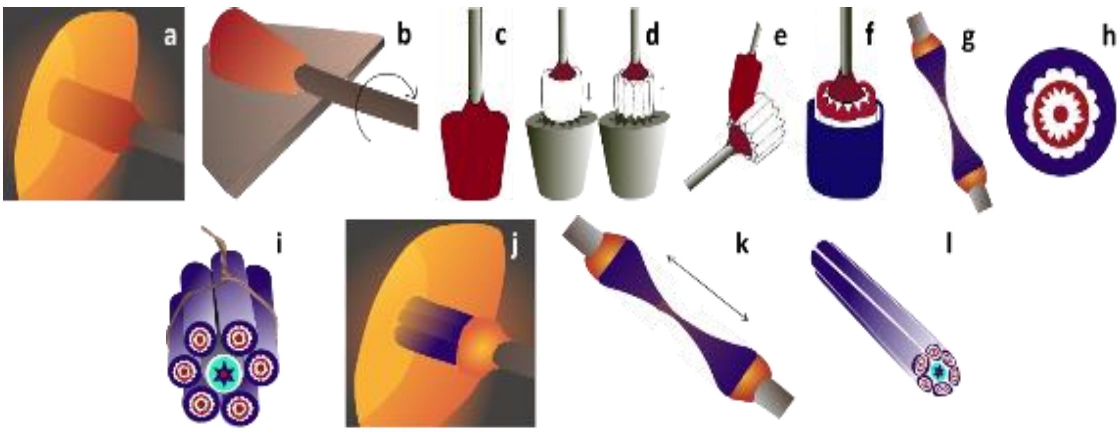


Fig. 1.7: Scheme of *murrine* glass canes making: a) picking-up a gather of molten glass; b) marvering to give a conical form to the glass gather; c) conical form of the glass gather; d) pressing the glass gather against the mould; e) filling-in each rib individually; f) different glass layers with different colours; g) stretching the glass gather; h) *murrine* drawing viewed in cross-section; i) grouping canes; j) fusing the canes; k) attaching the second pontil at the free end of the glass gather and stretching the glass gather; l) example of a glass cane made with the bundled technique (scheme adapted from Pulido Valente et al. 2017)

To start the production of the *rosetta* cane the glassmaker picks-up a gather of molten glass at the end of a pre-heated *pontil* rod (step 1; Fig. 1.7.a.) and shapes and cools the glass by rolling it back and forth over a *marver* - also called as *bronzino*, it is a flat metal table (Fig. 1.7.b.); the gather takes a slightly conic shape (step 2; Fig. 1.7.c.). The glass core that is formed is referred to as a *parison*. The initial *parison* may be circular or scalloped. To obtain the scalloped form, the glassmaker presses the still malleable glass into a ribbed dip mould (step 3). The first gather is then cooled until stable, then coated with a molten contrasting coloured glass (step 4), rolled on a marver to distribute the overlaid glass uniformly (step 5) and then strongly pressed within a dip mould of comparatively larger size than the previous one (step 6; Fig. 1.7.d.). Instead of coating all the moulded layer of glass with a plain colour, the glassworker may fill each rib individually with different colours (step 7; Fig. 1.7.e.). This method was probably used, for example, in one *murrina* of a *millefiori* ball belonging to the Historisches Museum Basel, Switzerland (Inv. 1917.824), which is dated to the 16th century and attributed to Venetian production. Alternating the successive coatings with the pressing it into the dip moulds the typical concentric layers of *murrine* are formed (step 8; Fig. 1.7.f.). The colours distribution is made alternating the opaque white with the other colours such as the blue, red and turquoise. Most of them have a clear or slightly green core.

When it has at least five layers of coloured glass (step 9) the *parison* is marvered for the last time but not moulded. Simultaneously, the assistant forms a disk of glass on a previously heated pontil. This disk (sometimes referred to as a post) is then attached to the free end of the *parison* (step 10). The glassmaker and the assistant walk in opposite directions, controlling their speed and turns, based on the size, temperature, and viscosity of the particular glass in hand. This stretching then thins and elongates the *parison* into a cane of glass (according to the required diameter, it can be ~70-75 meters in length). The result is a controlled stretching of the molded interior pattern, keeping the same proportions through the entire length of the cane (step 11; Fig.1. 7.g.). The long cane is then cut in smaller sections (step 12; Fig. 1.7.h.) each having a nearly identical design.

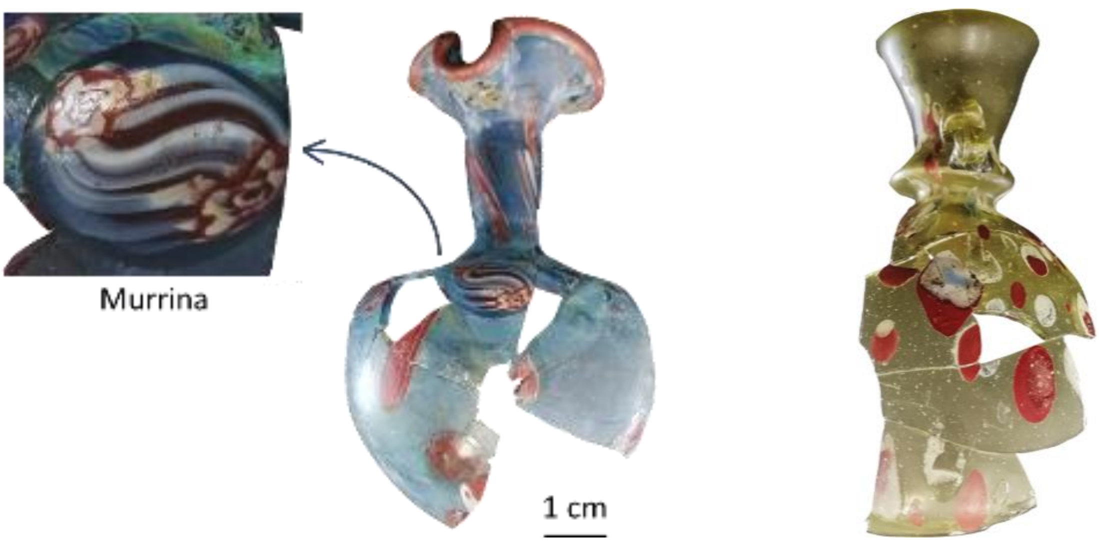
Rosette pattern usually has seven layers of glass and a twelve-pointed star drawing (Moretti 2005). Some can have the drawing of a cross in the core (fig. 1.6.b.) (Hollister 1983).

For more intricate designs, the glassmaker could use the bundled method, which consists in some canes arranged around a central cane and tightly bundled (step 13; Fig. 1.7.i.). They were then fused together (step 14; Fig. 1.7.j.), stretched (step 15; Fig. 1.7.k.) and cut into small pieces (step 16; Fig. 1.7.l.). A variation on this method was used, at least, in Amsterdam, by *De twee Rozen* (The Two Roses) glasshouse, between 1650 and 1680, for making glass rods with figurative drawings in its cross-section (e.g. the frag. RO21-5-234 showing a skull: Gawronski et al. 2010).

In Apendix A.2.of the supplementary material one can see the authors who mentioned each step of the production of *murrine* cane. The more mentioned steps are 7, 9, 10 and 11, which seem to be the most characteristic and which summarize in a very synthetic way how *murrine* are produced, recording that this type of cane has multiple layers (7), it is stretched in order to form the thin cane (9-10) and then sectioned to give rise to the *murrine* (11).

1.2.3.2. **Making objects**

As previously mentioned, *Pick-up* technique has two variations: (i) *Millefiori*, made by using *murrine* sliced glass canes (Fig. 1.8.a) and (ii) *splashing*, made by using coloured glass slices without any decoration pattern (Fig. 1.8.b).



(a) (b)

Fig. 1.8: (a) Little flask decorated with *millefiori* technique. Santa Clara-a-Velha Monastery, Coimbra, Portugal (SCV_0019 = V068) and (b) Little flask decorated with *splashing* technique. Santa Clara-a-Velha Monastery, Coimbra, Portugal (SCV_0018 = V067).

The description of *pick-up* glass decoration technique is illustrated in Fig. 1.9 and the references of each step are reported in Apendix A.3.

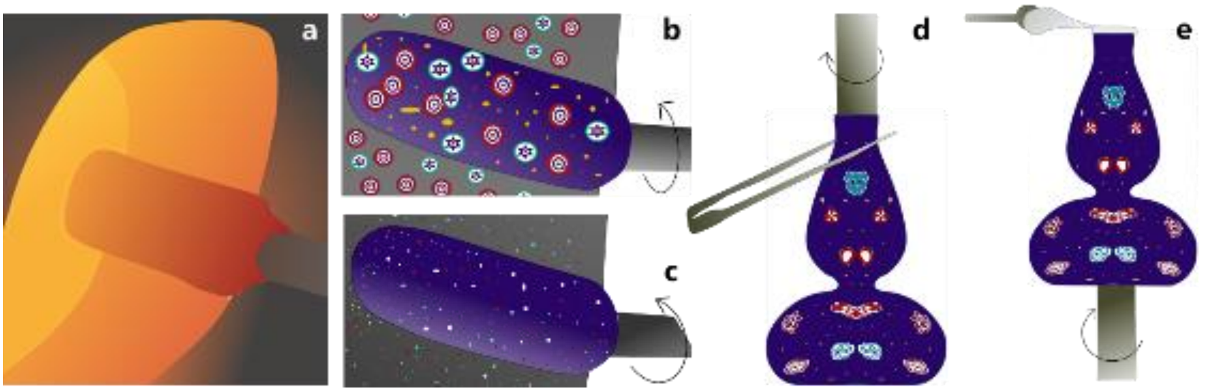


Fig. 1.9: Scheme of *pick-up* technique: a) collecting the gather of molten glass; b) picking-up the pre-heated *murrine* by rolling the glass gather over them; c) picking-up the coloured glass slices by rolling the glass bubble over them; d and e) blowing and working the bubble to shape the final object (scheme adapted from Pulido Valente et al. 2017).

First, the glassmaker collects a gather of monochromatic molten glass at the end of a pre-heated blowpipe (Fig. 1.9.a); usually, the gather of molten glass is slightly inflated by blowing (step 1). In some examples the master rolls the gather over a gold leaf (step 2). The slices of *murrine* cane or the coloured slices of glass were arranged without any pattern over a metallic or ceramic plate to be pre-heated, for example in the glory-hole or near the furnace door (step 3). At the end the *parison* was rolled over the pre-heated *murrine* (Fig. 1.9.b) or over the coloured slices of glass (in case of *splashing*; Fig. 1.9.c) to pick them up (step 4). Usually, this bubble is pressed into a dip-mould (step 5) and the glassmaker works on the object (blowing, marvering, reheating, etc.; Fig. 1.9.d and e) to shape it to the final object, having the coloured glass slices fused in its surface (step 6).

The more cited step is the one in which the glass bubble is rolled over the coloured glass slices or over the *murrine* to fuse them in its surface (step 4). This step seems to be the most characteristic and which summarize in a very synthetic way how this glass objects were made.

1.2.4. **State of the art**

An exhaustive search for published archaeological assemblages with glass artefacts decorated by pick-up technique dated to between the end of 15th and the 17th centuries was carried out.

For this work, 80 references dated from 1849 to 2019 were consulted. Most of them have been published during the last 40 years, reflecting a general trend of increasing interest in glass studies (Fig. 1.10).

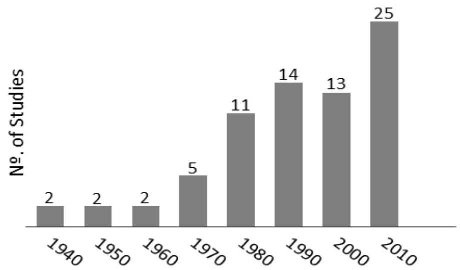


Fig. 1.10: Number of studies related with *pick-up* glass decoration technique by decades (the bibliographic survey ended in 2019).

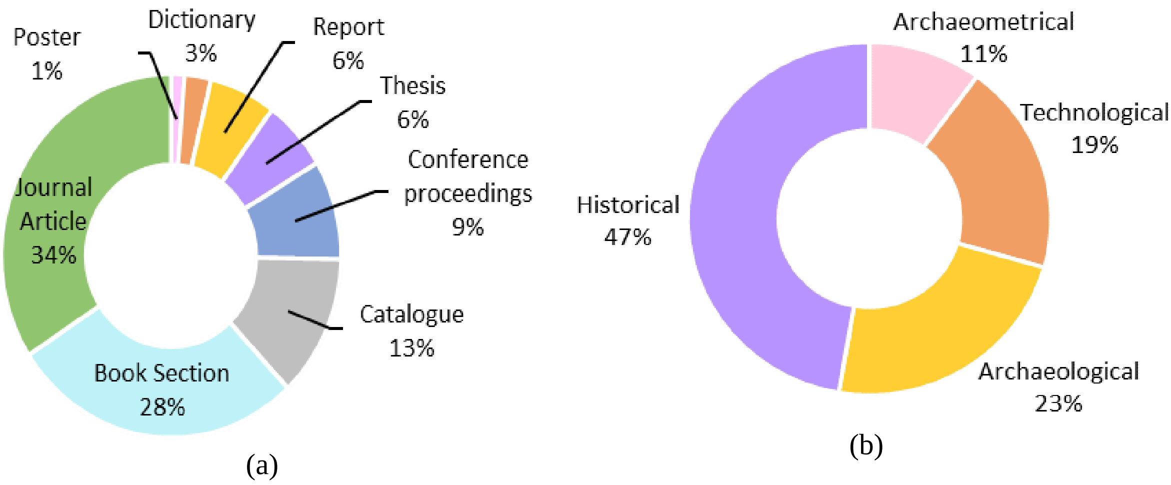


Fig. 1.11: Number of studies related with *pick-up* glass decoration technique by decades (the bibliographic survey ended in 2019) (a) with the division of the consulted literature in the different types of sources with their own representative percentage (b) and the percentage of the published works according to their approach (c)

The survey resulted in a diversity of literature (books, journal articles, thesis, conference proceedings, reports, catalogues, posters, and dictionaries) in different fields, such as archaeology, archaeometry, history and technology (Apendix A.4 and Fig. 1.11). As one can see, journal articles plus the book sections represent more than 60 % of the considered literature, followed by catalogues and conference proceedings. The less common types of literature are dictionaries and posters.

According to Fig. 1.11 almost 50 % of the consulted works tackles historical dimensions of this subject. The archaeological approach is represented in 23% of the works, followed by technological and archaeometrical approaches. About 39 % gave us a multiple approach, addressing the theme in a more interdisciplinary way (Apendix A.4).

Only about 21 % of the consulted references are fully dedicated to pick-up technique (Apendix A.4). This fact can indicate that, although this technique has a great importance, being widely described on historical, archaeological and technological literature as "a perfected type of glass" (Wood 2000), "one of the most magnificent Venetian glass" (Baumgartner 2015; Whitehouse 2012) and viewed as a work of art and, simultaneously, as a way to control, imitate and even surpass Nature through alchemy and master skills (Moretti 1985; Spenlé 2014) - more targeted cross-disciplinary works are missed.

The history of this technique and its use is extraordinarily rich and developed throughout the centuries. As shown, it has been widely mentioned on the literature and these works have resulted in valuable information on technical aspects, objects collecting, trading and contexts of use. However, little information is provided on the material characteristics of the glass, limiting our knowledge on production practices and circuits.

Only 4 out of 15 archaeometric studies which include pick-up decorated fragments are exclusively devoted to this type of glass. They are: Lima 2010 and Lima et al. 2012 (both on the same *millefiori* and *splashing* samples); Pulido Valente et al. 2019a (poster on *millefiori* glass fragments), and Verità & Zecchin 2008 (study of an archaeological glass object with *splashing* decoration). Results demonstrated the need for extensive and systematic archaeometric research, fundamental for the discovery of new insights into the history of our material culture.

In the 80 consulted works, at least 424 archaeological glass fragments decorated with pick-up technique in 30 archaeological contexts spread through 12 European countries were reported (Austria, Belgium, Croatia, England, France, Hungary, Italy, Netherlands, Portugal, Slovenia, Spain and Switzerland) and one in Western Asia (Syria) (Fig. 1.12 and Tab 1.2). In some cases, the exact number of fragments is not stated, leaving the possibility of having more glass fragments decorated with this technique than the ones described in Tab. 1.2. The number of glass objects found in Portugal was established in previous works (Medici 2014). For the remaining assemblages, if not mentioned otherwise, it was considered that each fragment refers to an object.

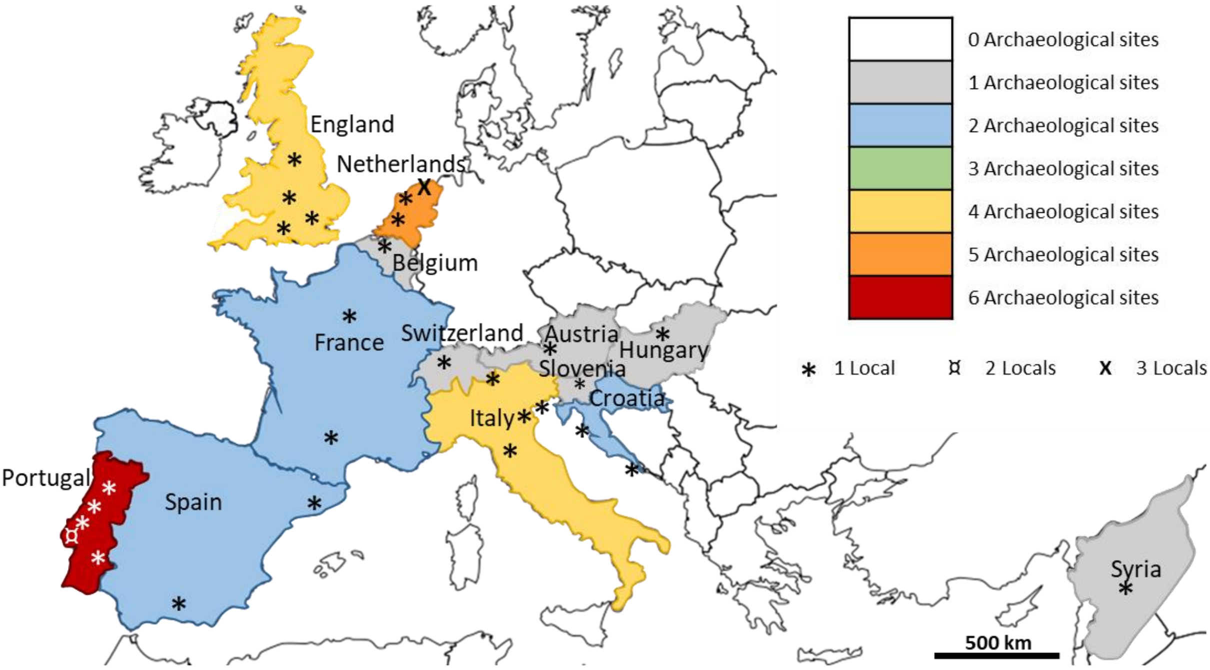


Fig. 1.12: Number of archaeological contexts, dated from the 15th to the 17th centuries, with glass fragments decorated with pick-up technique over Europe and Western Asia.

According to the consulted literature, the country with more studied archaeological contexts where glass decorated with *pick-up* technique was found is Portugal (six sites), followed by the Netherlands (four sites including two known production centres) and England and Italy (three sites each).

In addition to the archaeological glass fragments, 50 glass objects decorated with pick-up technique belonging to museums were also reported in the literature.

Tab. 1.2: Information about the archaeological context and the distribution of the glass fragments decorated with pick-up technique.

Countries	Cities	Contexts	Type	Date	Nº. frag.	Form	Dec. col.	Body col.	References
Autria	Tyrol	Medieval cemetery of the parish church of Innsbruck.	M	Before 1509	1	*Millefiori* bead	Ab, B, Bc, P, R, T	C	Personal information given by Mrs. Beatrix Nutz
Belgium	Antwerp	-	M	17th	1*	-	-	-	Henkes, 1994
Croatia	Gnalić	Gnalić wreck	S	16th-17th	2	Bottle and bowl	B, R, W	B	Lazar & Willmott 2006
			S	16th-17th	1	Bowl	B, R, W	R	
	Koločep	Koločep	S	17th	7	5 bowls, 1 vase and 1 jug	A, B, R	T	Medici 2010
			S	17th	3	2 bowls and tazza	A, B, R, T	W	
England	Coventry	Whitefriars	M	15th-16th	1*	Goblet	B, R, T, W	C	Willmott 2009
	London	Post Office Court	M	15th	2	Bowl	-	B	Charleston 1984; Tyson 1996; Willmott 2009
	Southampton	National Provincial Bank	M		1	Goblet	-	B	Charleston1984; Willmott 2009
	Yorshire	Silkstone (glass house)	S	17th	5	2 Beakers	W	Ab, B, C, Gn	Dungworth et al. 2006
France	Aveyron	*La Verrière* glasshouse	S	14th	6	-	B	G	Gratuze & Janssens 2004
	Orléans	-	M	16th	1*	Lid of a goblet	-	B	Barrera 1987; Page 2004
Hungary	Budapest	Buda Palace	M	15th	4*	Jars and chalices	-	-	Gerevich1952; Holl-Gyürky1986
Italy	Bormio	Piazza Cavour	M	15th-17th	2	Vessel	B, R, T, W	C	Uboldi 2015
	Ferrara	Sant' Antonio Monastery in Polesine	S	16th	1	Goblet	A, B, Bc, R, W	W	Verità & Zecchin 2008
	Gambassi	Piazza Del Castell	M	16th	6	-	-	-	Medici 2012; Mendera 2002
	Venice	Venetian Lagoon	M	15th	10	-	B, R, T, W	B/C	Moretti 2005; Verità 1985; Zecchin 1990a (1983)
Netherlands	Amsterdam	-	S	17th	1	Beaker	-	C	Henkes, 1994
		Soop glasshouse	Both	17th-18th	1M + 4	Unknown	B, R, W	-	Baart 2002
		"De Twee Rozen" (The Two Roses)	Both	17th	1M + 3	Unknown	B, R, W, Y	B, C, Gn, W	Baart 2002, Gawronski et al. 2010
	Delft	-	M	17th	2*	Beakers	B, R, W	C	Henkes, 1994
	Leiden	-	M	17th	1*	-	-	-	Henkes, 1994

Tab. 1.2: Information about the archaeological context and the distribution of the glass fragments decorated with pick-up technique (Continued).

Countries	Cities	Contexts	Type of effect	Date	Nº. frag.	Form	Dec. col.	Body col.	literature
Portugal	Batalha	Santa Maria da Vitória Monastery	S	17th	1	Unknown	R,W	B	Teixeira 2014
	Coimbra	Santa Clara-a-Velha Monastery	Both	17th	220M + 81	Bottle/ Bowl/ Cup/ flask/ jug/ Vessel/ unknown	A, B, Gn, P, R, T, W	B, G, Gn, R, T, W	Ferreira 2004; Lima 2010; Lima et al. 2012; Medici 2014; Pulido Valente et al. 2017
	Lamego	São João de Tarouca Monastery	M	17th	2	Little flask, unknown	B, R, T, W	B	Medici 2014; Pulido Valente et al. 2017
	Lisbon	Largo do Chafariz de Dentro	M	16th-17th	1	Little bowl (M), unknown	B, R, T, W	B	Medici 2014; Pulido Valente et al. 2017
		Santana Convent	Both	16th-17th	9M +1	bird head, bottle, flask	B, R, T, W	B, C, G, R	Pulido Valente et al. 2017
	Moura	Santa Clara Convent	Both	17th	4M +1	Flask, gourd bottle shape	B, R, W	B	Medici 2012; Medici 2014; Pulido Valente et al. 2017
Slovenia	Ljubljana	Mengeš	M	16th	1*	Chalice	-	C	Kos 1994; Page 2004
Spain	Barcelona	Born	S	16th	2	1 Tazza	R, W	C	Beltrán de Heredia & Miró i Alaix 2006
						1 Cup	B	W	Beltrán de Heredia & Miró i Alaix 2006
	Granada	Alhambra	Both	17th	3M + 4	Little bottle	B, R, T, W	5 B, 2 C	Cambil & Marinetto 2016; Medici 2012
Syria	-	-	M	-	1	Sprinkler	-	-	Bruhn 1995
Switzerland	Bern	Waisenhausplatz	M	16th	3	Bowl (?)	B, R, T, W	C	Baumgartner 2015, p. 336

* When the author of the publication does not mention the number of fragments, was assumed that at least one or two, in the case that speaks in plural, exemplary were found.

Ab: Ambar; A: *aventurina*; B: blue; Bc: black; C: clear; G: grayish; Gn: Green; P: purple; R: red; T: turquoise; W= white; Y= yellow

M: *millefiori*

S: *Splash*

Nº. frag.: Number of considered fragments.

Dec. col.: Range of colours used in decoration.

Body col.: Body glass colour.

The majority of the published glass objects and fragments are dated between the end of 15th and the beginning of 17th centuries. They are mostly considered of Venetian production. Exceptions are the archaeological fragments found in Antwerp and Liège (Henkes, 1994) and the fragments found in glasshouses such as *De Twee Rozen* (Gawronski et al. 2010) and *Soop* (Baart 2002) in Netherlands, that are considered as locally produced. The 14th century fragments found at La Verrière glasshouse (Aveyron, France) are of uncertain attribution to the group (Gratuze and Janssens 2004).

Characteristic features allow the attribution to Spain (probably Catalonia) of specific pick-up decorated objects, as for example the lion-shaped ewer belonging to the Museu de Les Arts Decoratives (today Museu del Disseny, Barcelona, Spain) and the ewer belonging to The Corning Museum of Glass (Corning, United States of America) (Tab. 1.3) (Doménech 2004).

Archeometric studies performed on archaeological Venetian and *façon de Venise* glass found in Portugal proved the presence of some genuine Venetian glass fragments in *Santa Clara-a-Velha Monastery* (Coimbra) and in *Largo do Chafariz de Dentro* (Lisbon). However, most *façon de Venise* glass fragments belong to unknown production centres, opening the possibility of having been produced in Portugal (Coutinho et al. 2016, Lima et al. 2012, Varela et al. 2018). Both local production of *façon de Venise* glass and import of Venetian objects in Portugal in the 16th century are reported in historical documents (Medici et al. 2017). Because neither archaeological data concerning the furnaces, nor glass objects directly associated with Portuguese manufactures are currently available so far, no link between national production and objects found in Portugal can be confirmed (Amado Mendes 2002; Pulido Valente et al. 2018).

Many authors have mentioned that glass objects decorated with pick-up technique are extremely rare (Baart 2002; Cambil & Marinetto 2016; Charleston 1984; Medici 2012; Page 2004; Tait 1979; Tait 2012; Uboldi 2015; Willmott 2009 and others) and the result of this survey proves that these artefacts (unbroken of fragmented) were really rare comparing with other Venetian and *façon de Venise* glass.

Table 1.3: Some information about *millefiori* glass in Museums.

Countries	City	Museums	Nº. Obj.	Forms	Colours	*Murrine* pattern	References
Czech Republic	Prague	Lanna Collection	1	Glass vessel with *millefiori* decoration only in the knop	-	-	Hollister 1981
England	London	Courtauld Institute of Art	2	1 handle bowl and 1 chalice	C (body glass), B, R, W	The murine have different mould drawings in the same murine; 7 different layers	Charleston 1967; Hollister 1981; Uboldi 2015
		British Museum	5	Ball; Bottle; Goblet; 2 miniature Ewer;	3 C and 2 B (body glass) and B, R, T, W, Y	Some *murrina* have a crossed design in the core; different number of star tips (4/ 5/ 12) different mould drawings in the same *murrine*. They are probably made between the end of 15th and early of 16th Centuries and attributed to Venice.	Bruhn 1995; Hollister 1981; Medici 2012; Tait 1979; Tait 2012; Tonini 2011; Uboldi 2015; Whitehouse 2012; Wood 2000.
		Victoria & Albert Museum	1	Bottle	C (body glass), B, G, R, T, W	The murine have rosette pattern with 12 star points and 7 layers. Probably made in the 16th Century and attributed to Venice.	V&A website [15th December of 2018]
			1	Bowl	C (body glass), B, G, R, T, W and Y	The murine have more than one drawing mould, rosette pattern with 12 star points and other with at least 40 star point. The *murrina* has at least 7 different layers; Some has a cross in the core.	Hills 1999; Hollister 1980
			3	Knife handles	B, G, R, T, W and Y	Probably made between 1680-1720 with rosette pattern.	V&A website [15th December of 2018]
	Oxford	Ashmolean Museum	1	Tazza	-	-	Hollister 1981
France	Paris	Louvre	2	1 ewer; 1 Solid ball;	-	The *murrine* are tactil on the surface and have gold leaf	Hollister 1982; Theuerkauff-Liederwald 1994;
Germany	Berlin	Kunstgewerbe-museum	2*	1 handled bowl and 1 goblet	-	Different mould drawings in the same *murrine*	Hollister 1981; Netzer 2000;
	Coburg	Veste-Coburg Palace	7	ball	-	-	Bruhn 1995; Hollister 1981; Theuerkauff-Liederwald 1994; Tonini 2011
	Düsseldorf	Kunstmuseums	4	1 Ribbed goblet; 2 Ribbed miniature ewers 1 vessel	B and C (body glass) B (body glass)	-	Charleston 1967; Helmut 1995; Hollister 1981; Uboldi 2015

Table 1.3: Some information about *millefiori* glass in Museums (Continued).

Countries	City	Museums	Nº. Obj	Forms	Colours	*murrine* pattern	References
Italy	Ferrara	Museo Nazionale Archeologico	1	Goblet	A, B, Bc, R and W	Decorated with monochromatic coloured glass slices	Verità & Zecchin 2008
	Milano	Museo Settala	4	Spheres	B, C, R, T, W and Y	*Rosette* pattern with 5 layers and at least 12 star tips and flower design	Tonini 2011
	Murano	Fondazione Mesei Civici Veneziani – Museo del Vetro	**4***	1 Bottle 1 Tazza (Catalunia?) 2 Glass fragments	-	-	Medici 2012; Moretti 2012; Uboldi 2015
Japan	Hakone	Hakone Glass Forest Ukai Museum	1	Ewer in form of lion	C (b) B and R with gold leaf	-	Medici 2014; Page 2004
Netherlands	Amsterdam	Rijksmuseum	2	Bottle Small ball	-	-	Charleston 1967; Baumgartner 2015; Ritsema Van Eck & Zijlstra-Zweens 1996;
Portugal	Moura	Municipal Museum of Moura	3	2 small bottles; 1 small flask;	B (b), B, R and W.	*Rosette* pattern	Medici 2012
Slovenia	Ljubljana	National Museum	1	-	C (b)	Cross-shaped core rounded by a circle, then have an eight pointed star-shaped and the last mould have a more than 40 pointed star-shaped.	Kos 1994
Spain	Barcelona	Museu de Les Arts Decoratives	1	Ewer in the Shape of a Lion	C (b), B, R, T, W, with gold leaf	-	Page 2004
Switzerland	Basel	Historisches Museum	2	1 Ball; 1 Bead	B, P, R, T, W and Y	Different number of star tips (8/ 10/ 12) different mould drawings in the same *murrine*.	Baumgartner 2015;
United States of America	Corning	The Corning Museum of Glass	1	Ewer	C (b), B, R, W and Y with gold leaf	Rosette patter with 8 star tips and 5 layers	Page 2004; Whitehouse 2012
	New Haven	Yale University Art Gallery	1	Bottle (sprinkler)	B (body glass)	-	Hollister 1981
	New York	The Metropolitan Museum	1	Glass fragment	C (b), B, R, T, W and Y	Different murine patterns in the same fragment, different number of star tips and different mould drawings in the same *murrine*.	THE MET 2018
	Washington D. C.	Smithsonian American Art	4	4 covered columns	-	-	Bruhn 1995

*These glass objects are presumed lost since World War II (Hollister 1981, p. 225; Netzer 2000, p. 162).

A: *aventurina*; (b): Body glass; B: blue; Bc: black; C: clear; G: green; P: purple; R: red; T: turquoise; W= white; Y= yellow

This observation opens the following questions:

- Why *millefiori* glass objects preserved in Museums do not follow the same tendency (form and colours choice) of those which were found in archaeological contexts?
- In the 16th century Venetian glassmakers had already long experience of producing coloured and colourless glass, being the latter known as being the most sought and improved (see e.g. Verità 1985; Charleston 1984). Was the colourless *millefiori* glass considered more luxurious than the *millefiori* with coloured body glass?
- Can this observation be related with the fact that only the considered master pieces were preserved by the collectors and, consequently, are preserved in the museums?
- Can it be linked with different production centres (the Venetian glassware or the best *façon de Venise* are in the museums)?

1.2.4.1. ***Façon-de-Venise*** **production**

The chemical compositions of the analysed glass fragments found in eight different archaeological contexts (one English, two Dutch and five Portuguese) plus the analysed *millefiori* glass object from Veste Coburg art collection are not compatible with Venetian production (Theuerkauff-Liederwald, A.-E. 1994).

Regarding pick-up fragments found in glasshouses spread across different countries it was assumed that the objects were locally made: the glass recovered from Silkstone glasshouse were studied by SEM (scanning electron microscope) with an attached X-ray spectrometer (Dungworth et al. 2006). The glass fragments recovered from this English glasshouse are of high-lime low alkali (HLLA) or lead glass types and its chemical compositions are representative of the technological improvement of the new English lead crystal glass.

In Netherlands *millefiori*, *splashed*, beads and *filigrana* rods were recovered in two glasshouses: De Twee Rozen (Gawronski et al. 2010) and Soop (Baart 2002). These evidences prove that skilled glassworkers in glass cane production were working there.

In the De Twee Rozen glasshouse original drawn canes (made with a variation of bundled method) were also found. The chemical glass composition of the three analysed (studied by EPMA) show that are all of soda-lime silicate composition. Two of them have chemical composition similar to Venetian *vitrum blanchum* with the exception of titanium and alumina oxides that are a bit higher and CaO which have an amount compatible with the Venetian *cristallo*. For the less pure sample, its chemical composition is comparable to Venetian Common type with the exception of calcium oxide (its content remains compatible with Venetian *cristallo* glass) and titanium oxide which content remains in the upper Venetian glass composition. These observations indicate that, although quite pure raw materials were used, a different silica source was employed in the glass batch (Gawronski et al. 2010).

In Portugal, besides the already mentioned Santa Clara-a-Velha Monastery (Lima et al. 2012 and Pulido Valente et al. 2019a), other archaeological contexts where pick-up fragments were reported have been studied: Largo do Chafariz de Dentro, Lisbon (Pulido Valente et al. 2019a), Santa Maria da Victória Monastery, Batalha (Teixeira 2014), Santana Convent, Lisbon (Pulido Valente et al. 2019a) and São João de Tarouca Monastery, Lamego (Pulido Valente et al. 2019a).

For the glass fragment of Santa Maria da Victória Monastery (Teixeira 2014), the reported glass composition was obtained by μ-EDXRF (X-ray fluorescence energy dispersive spectroscopy) performed in the scraped glass surface. The result of Na_2O+MgO for the blue body glass is 17.6 wt%, while for the red decoration is 19.4 wt%, in addition the content of Al_2O_3 and TiO_2 are also very different between the two colours (respectively, Al_2O_3 0.3 and 5.5 wt%; TiO_2 0.26 and 0.16 wt%). These values suggest, as observed by Lima and co-authors (2012) on some analysed glass fragments, that the glass used in the decoration have different glass composition of the body glass, indicating that they belong to different glass batches. It can indicate different production origins.

The purple splashed glass jar (decorated with white flakes) from Veste Coburg art collection (Theuerkauff-Liederwald, A.-E. 1994) is dated to the 2nd half of 17th century and attributed to Spain or Nevers (France). The reported glass composition for this object is compatible with potassium-rich glass type (Na_2O = 2.2 wt%; K_2O = 19.88 wt%; CaO = 10.58 wt%), so Venetian production is easily discarded. These values are more comparable to Central France production, where forest plant ashes were used as flux agent, than Spanish production where typically barilla (halophytic plant, that gives a soda-lime silica glass type) was used as flux agent (Gratuze and Janssens 2004, Rodrigues 2018).

The analyses made on *rosette* beads that were found in two German glasshouses, Neulautern and Walkersbach, show that a different glass was used to produce this type of ornaments. In Neulautern the glass is of soda-lime silica type, compatible with the Venetian *Vitrum blanchum*; in Walkersbach they used a mixed alkali glass type. As mentioned early, *rosetta* was also one of the most exclusive and wanted glass bead pattern having a huge importance, from the late 15th century onwards, in European expansions (Dubin 2009, Gramann et al. 2013). For this reason, the work of Gradmann and co-authors (2013) was included in this review: although no pick-up decorated glass objects were found, some *rosette* beads which were unearth in two German glasshouses (two in Neulautern and four in Walkersbach) were also chemically analysed by EPMA.

All the glass composition from the *rosette* bead of two glasshouses had the presence of SnO_2 (0.1-1.0 wt%) and PbO (0.1-0.9 wt%) – can these values be linked with the use of recycled glass or with element migration between the different coloured glass layers? The glass composition of the analysed glass layers of *rosette* beads from Neulautern are of soda-lime silica type and its main composition is comparable to Venetian *vitrum blanchum*. On the other hand, the *rosette* beads from Walkersbach present a mixed alkali glass type.

To summarize, most of the colourless/ base glass found in literature have chemical composition different from Venetian glass, being that only 6 out of 65 (less than 10%) of the studied pick-up fragments can be attributed to Venetian production (2 fragments) or have a chemical glass composition comparable to the glass that were produced in Venice (4 fragments). Note that when the chemical glass composition of the pick-up fragments was not discussed or mentioned by the authors, but they were found in a glasshouse (Soop, De Twee Rozen and Silkstone) it was considered that the results of given data are representative of the chemical glass composition produced there.

1.2.4.1. **Coloured glass**

AVENTURINE glass was identified by Lima and co-authors (2012) and Verità and Zecchin (2008) only in glass fragments decorated with splashed technique in a soda-lime silicate matrix. Its production was kept secret by the Venetian glassmakers until, at least, the 18^{th} century (Verità and Zecchin 2008). On both works this colour was made by mixing ordinary soda-rich glass with copper, iron, lead and tin.

BLACK glass was only referred by Verità and Zecchin (2008) and has high levels of iron (2.1wt% Fe_2O_3). The authors suggest that this colour was made by recycling cullet of different colour because of the lower concentration of CoO (0.04 Wt%) and the presence of trace elements such as lead, tin, copper and antimony which are unrelated with Fe_2O_3. This colour was identified in a genuine Venetian splashed glass object.

BLUE glass was observed by Gradmann and co-authors (2013), Lima and co-authors (2012), Teixeira (2014) and Verità and Zecchin (2008) and in all the works the chromophore responsible for the coloration is CoO. The lowest detected CoO value belongs to a splashed body glass fragment found in Santa Maria da Victoria Monastery (0.06 Wt%), being in accordance with the observation made by Verità and Zecchin (2008): *"(…) Cobalt ions have a high coloring efficiency, and their concentration in blown blue glass rarely exceeds 0.10 Wt%.* (…)".

In blue body glass of two fragments from Santa Clara-a-Velha Monastery (V68 and V108), the cobalt concentration is below the EPMA detection limit and only with UV-visible absorption spectroscopy its presence was confirmed through the characteristic triple band at 540, 590 and 640 nm (Lima et al. 2012). Higher concentrations of CoO (>0.10 wt%) are the most common levels for glass objects decorated with pick-up technique both in body glass and on decoration. Verità and Zecchin (2008) noted that these higher values can be linked with the thickness of glass layer and the nearby colours, to keep the colour visible even in a thin layer. This observation makes sense on different glass layers of the canes or in sliced glass bits.

Apart from German the *rosette* beads, the origin of the cobalt ore of the remaining blue glass colours are attributed to Schneeberg mines, in Erzgebirge (Germany), due to the presence of arsenic, bismuth, iron and nickel in small amounts.

RED colour was noted on Gradmann and co-authors (2013), Lima and co-authors (2012), Teixiera (2014) and Verità and Zecchin (2008) works. This glass colour is the consequence of the presence of copper and iron oxides. Lead and tin oxides were also detected; these oxides could be intentionally added to the glass batch or can indicate that recycled glass was used to produce the colour (these two recipes were described, for instance, on the contemporary Darduin treatise) (Verità and Zecchin 2008).

TURQUOISE glass is produced by the presence of Cu^{2+} ions in glass matrix which can be formed in melting oxidizing conditions. The presence of this ion was proved by UV-visible absorption spectroscopy where the characteristic broad band with a maximum wavelength at 780 nm was reported (Lima et al. 2012).

Venetian **WHITE** glass (called *lattimo*) was typically made by adding lead and tin oxides (usually calcined). These two oxides are responsible for the cassiterite (SnO_2) crystals formation which is responsible for colouring and opacifying the base glass. These crystals were identified by Raman microscopy in eight, out of ten, white glass layers found in Santa Clara-a-Velha Monastery (Lima et al. 2012) due to the presence of the characteristic peaks at 633 and 775 cm^{-1} and, frequently, a smaller peak at 474 cm^{-1}. Tin and lead oxides were also detected in German *rosette* beads [3.9 wt% > SnO_2 > 9.7 wt% and 9.4 wt% > PbO > 18.1 wt%] (Gradmann et al. 2013) and in splashed fragment from Santa Maria da Victória (Teixiera 2014) which can indicate that these oxides were intentionally added to the batch glass. Beyond cassiterite, the calcium antimonate (a less common Venetian opacifier) in its $Ca_2Sb_2O_7$ form was also identified by Raman microscopy in two white glass from Santa Clara-a-Velha Monastery (Lima et al. 2012) due to the presence of the characteristic peaks at 480 and 633 cm^{-1}. In Verità and Zecchin (2008) work, the presence of calcium antimonate crystal were analysed by SEM in backscattered mode. This document noted that the chemical composition of the white body glass is different from the white glass used on the decorative motive (which have higher content of aluminium and iron and lower amount of calcium oxide). This observation shows that these two white glasses were prepared based on two different batches. Although less common, calcium antimonate was also used by the venetian glassmakers and some recipes are reported in Trattatelli and Darduin treatises (Verità and Zecchin 2008).

2

PRESENTATION AND CONTEXTUALIZATION OF THE ASSEMBLAGES

Millefiori glass is known for its rarity; only a few examples are present in museums, private collections, and finds from European archaeological excavations (Medici 2014, 143; Pulido Valente et al. 2019; Pulido Valente et al. 2021). However, recent discoveries from four Portuguese archaeological sites - Largo do Chafariz de Dentro (LCD) and Santana Convent (LCS) in Lisbon, Santa Clara-a-Velha Monastery (SCV) in Coimbra, and São João de Tarouca Monastery (SJT) in Lamego (Fig. 2.1) - have yielded 311 glass fragments, which correspond to at least 34 objects with a wide variety of patterns. These fragments are dated to the late 16th and mid-17th centuries.

Fig. 2.1 also shows where the documented 16^{th} and 17^{th} century glass furnaces were located (Custódio 2002).

Out of the 313 glass fragments decorated with the pick-up technique unearthed in Portugal, 31 were selected (based on its representativity, original forms, decoration and colours choice) for analysis (Apendix A.5):

-3 glass fragments from LCD.

-5 glass fragments from LCS.

-21 glass fragments from SCV.

-2 glass fragments from SJT.

In addition to these glass fragments, 4 pieces of production waste or slag (unearthed in LCD (3) and LCS (1)) were also analysed for comparison.

The selection of the archaeological contexts and fragments was made under the supervision of Teresa Medici, who studied the Late Medieval and Modern archaeological glass found in Portugal for her PhD dissertation (Medici 2014).

In this section, as Teresa Medici has already studied all the pick-up glass fragments, which have been carefully described and presented in detail, along with their corresponding archaeological drawings, only the selected glass fragments studied in this project are presented. However, it is important to note that more *splashed* and *millefiori* glassware decorated with this technique has been unearthed in the SCV context (Medici 2014).

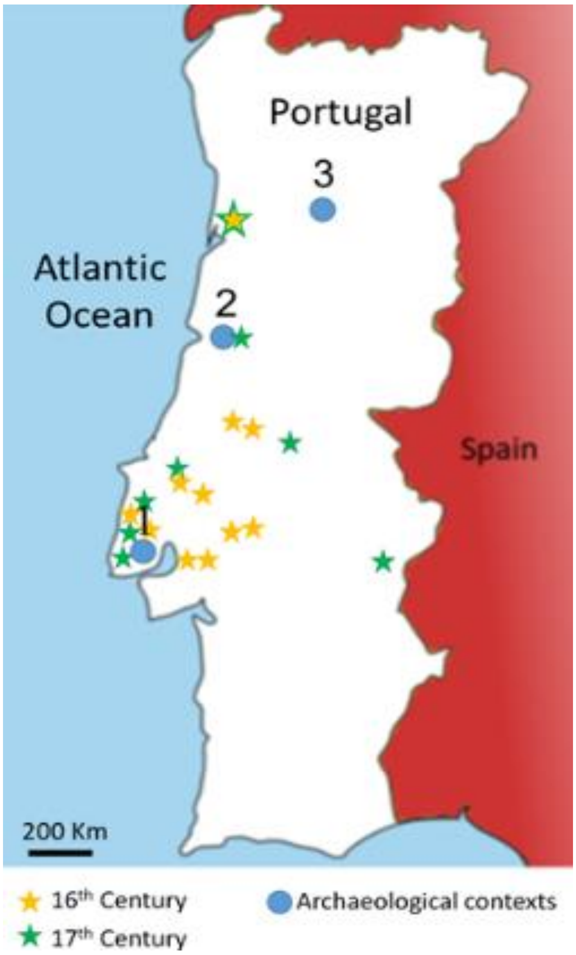


Fig. 2.1: Map of Portugal showing locations of 16th (yellow) and 17th (green) century glass furnaces and the archaeological sites at Lisbon (Largo do Chafariz de Dentro and Santana Convent) [1], Coimbra (Santa Clara-a-Velha Monastery) [2] and Lamego (São João de Tarouca Monastery [3].

For this study, particular attention was given to unusual characteristics and shapes, such as unique decorative patterns such as crosses, caravels, and flowers, as well as distinctive shapes like the bird's head. These aspects were considered important for the aims of this research.

2.1 Archaeological sites

2.1.1. Largo do Chafariz de Dentro (LCD)

The *LCD* context is the only non-religious archaeological site. It is situated in one of the oldest squares in Lisbon, near the River Tejo (Fig. 2.2); excavations were conducted here in 2007 and 2008 as part of a wastewater treatment system improvement project. Archaeologists stratigraphically dated the artifacts to the 16th-17th centuries (Banha da Silva et al. 2011). Although the exact contextualisation of the materials is not known, they are clear evidence of the repertoire of glassware consumed by society at this time, possibly in the environment close to where they are documented.

During the Renaissance, Lisbon was important as a major market for the export trade of colonial products from Brazil, Africa, and Asia. These products included items such as tobacco, silk, cotton, and various foodstuffs such as cocoa, coffee, and sugar. In addition, Lisbon also imported precious products from regions such as China, Japan, Venice and the Low Countries (Arnold 2013, Varela Gomes et al. 2015, *p. 94).*

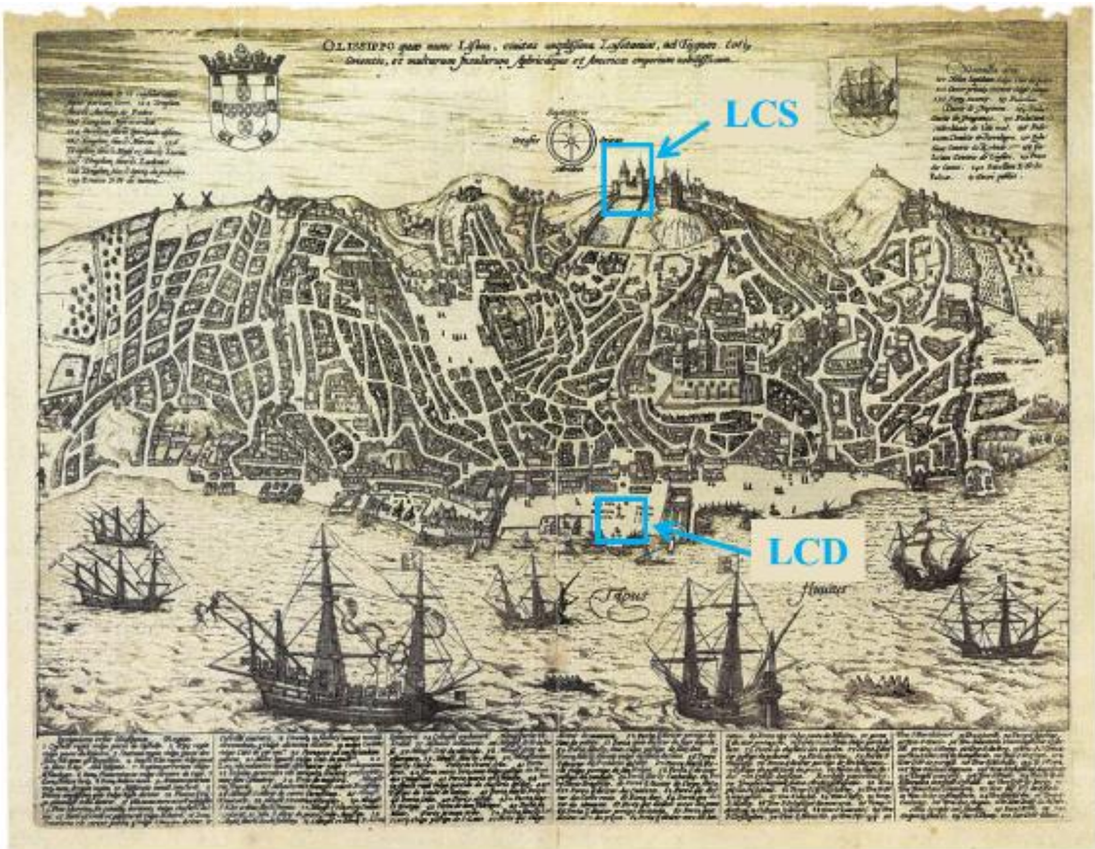


Fig. 2.2: Map of Lisbon in the 16th and 17th centuries showing the approximate locations of LCD and LCS (image adapted from © Vasconcelos & Mantero 1999, p. 95).

The assemblage from the modern stratigraphic layer reveals a wide range of artifacts, bearing witness to the taste for luxury items among the prosperous Portuguese society of that time. Among the outstanding finds from this context are Chinese pottery and porcelains, including celadon and Ming dynasty pieces. Notably, one of the porcelains bears a depiction of the Cross of Christ, indicating that certain porcelains were specifically commissioned for the Portuguese market. Additionally, the collection encompasses Italian maiolica, German stoneware, Spanish ceramics, Hispano-Moresque tiles, and Venetian or Venetian-style glass, such as *millefiori* and *filigrana*.

For compositional analyses, all the pick-up glass fragments and production waste (or slags) were systematically sampled, as illustrated in Fig. 2.3.

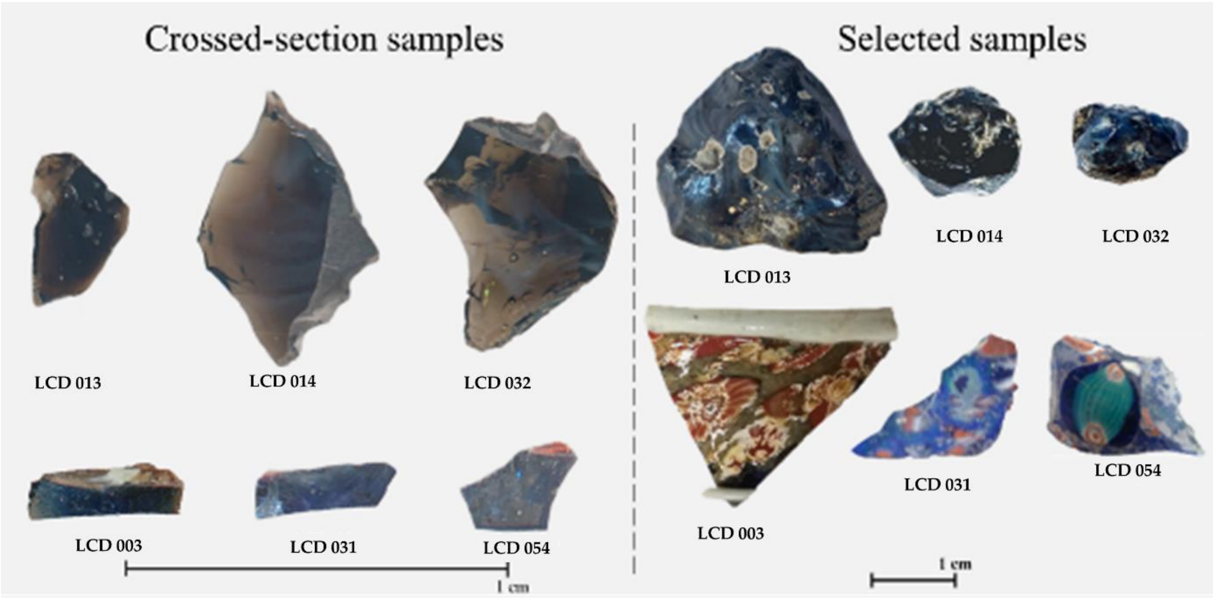


Fig. 2.3: Images of the glass fragments analyzed, in cross-section (left) and under the surface (right).

LCD_03 is a *millefiori* fragment adorned with intricate *rosette* and cross patterns, employing a combination of clear, red, and white colours, fused to a translucent blue base glass (see also Fig. 2.4). This fragment is part of a larger assemblage consisting of 13 fragments, collectively associated with an unidentified object characterized by a rim diameter of 5 cm. In addition to its *millefiori* decoration, this fragment exhibits the presence of applied white threads and a corroded golden layer, which makes it difficult to observe the intricate decorative patterns.

LCD_31 represents a *splashed* fragment featuring a blue body glass adorned with red dots. This fragment originates from an unknown part of an undetermined object and exhibits a localized whitish corroded layer (Fig. 2.3).

LCD_54 is a *millefiori* fragment decorated with a *rosette* pattern above a blue base glass (see also Fig. 2.4). This fragment belongs to an unidentified part of an undetermined object. The *rosette* pattern is composed of 17 star tips and incorporates five distinct layers of glass, namely red, white, red, white, and turquoise, progressing from the core to the outer edge.

LCD_13, LCD_14 and **LCD_32** are classified as glass production remnants or slags due to their amorphous shapes and the presence of lighter shadows. These characteristics suggest that the glass was not uniformly melted and was likely discarded through dripping, although the specific reasons for this remain unknown. They are translucent with a brownish colour.

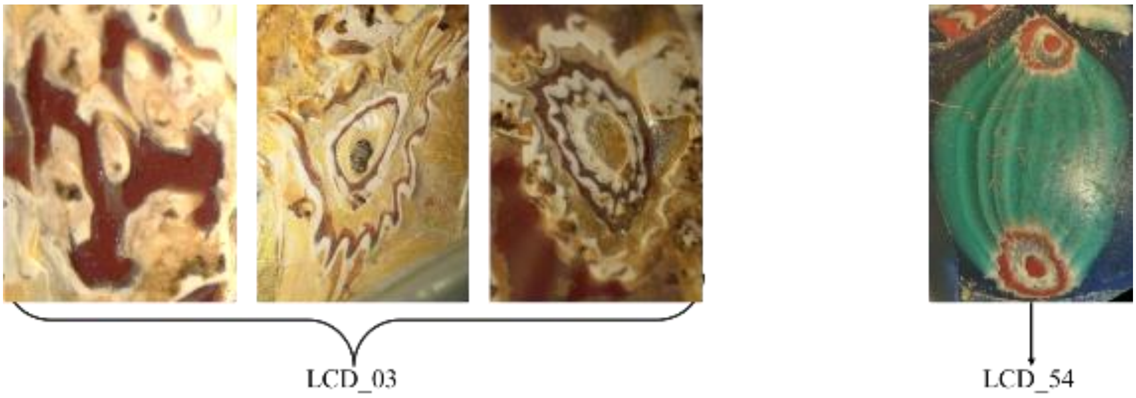


Fig. 2.4: *Murrina* patterns presented in LCD_03 (Cross of Christ and two different *rosette* patterns) and LCD_54 (*rosette* pattern) fragments.

2.1.2. **Santana Convent (LCS)**

LCS is located on Santana Hill in Lisbon (Fig. 2.2), which was established during the latter half of the 16th century. The construction of the convent involved the repurposing of the pre-existing old Santana hermitage, which formed the foundation for the church of the complex (Varela Gomes et al., 2015, p. 94-95). This monument was important as one of Lisbon's prominent religious institutions, housing nuns belonging to the Third Order of San Francisco, who adhered to vows of poverty, chastity, enclosure, and obedience. However, the excavation of the site revealed a surprising collection of luxury items, including high-quality porcelain (of which one piece displays erotic drawings in blue and white), jewellery, European glassware, and exotic beads. These finds seem in conflict with the expected lifestyle of the nuns and suggest that being a nun during that period may have been associated more with social status than personal devotion (Varela Gomes et al., 2015, p. 93-96).

Following the suppression of female religious orders in 1884, the LCS building was left abandoned. In 1897, a significant portion of the convent, including the church, was demolished to accommodate the construction of the *Real Instituto Bacteriológico* (Varela Gomes et al., 2015, p. 95).

The assemblage discovered in this context was unearthed in two stages: the first in 2002-2003 and the second in 2009-2010. These finds were discovered in cesspits located within the cloister area, raising intriguing questions about their origins and purpose. It remains uncertain whether all these fragments were personal objects belongings of the nuns, gifts from loyal pilgrims or lovers, or if perhaps the location was deemed a safe hiding place by the Inquisition to conceal "heretical" objects from the community (Varela Gomes et al. 2015, p. 95, 97). The glass samples chosen for analysis are shown in Fig. 2.5, which gives cross-section and surface views of the glass fragments.

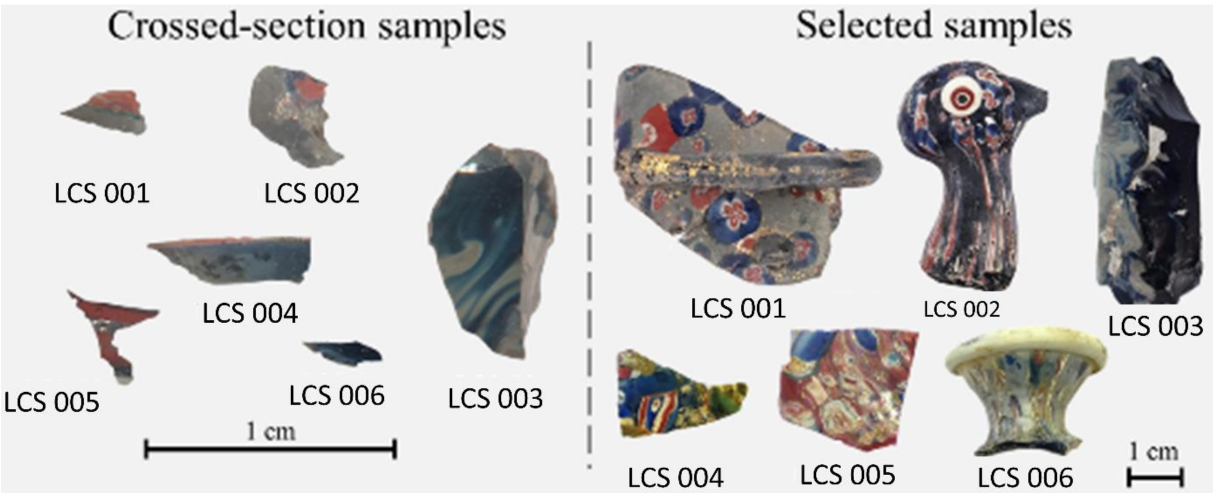


Fig. 2.5: Images of the analysed glass fragments, in cross-section (left) and under the surface (right).

LCS_01 is a *millefiori* fragment featuring intricate flower/cross and caravel patterns in blue, red, turquoise, and white colours. *Murrine* are embedded in a greyish body glass, as shown in Fig. 2.5. This fragment belongs to an unknown part of an undetermined object. In addition to the *millefiori* decoration, it exhibits applied greyish glass threads and gold leaf placed between the body glass and *murrina*. Remarkably, the fragment is exceptionally well preserved, devoid of any corroded layers to the naked eye.

LCS_02 is a well-preserved fragment of solid greyish glass, in the shape of a bird's head adorned with unique *millefiori* decoration. This shape in *millefiori* glass has not been previously documented. The body glass has intricate *murrina* designs, including concentric circles representing the eyes, as well as floral, cross, and caravel patterns in vibrant blue, red, and white colours (Fig. 2.6).

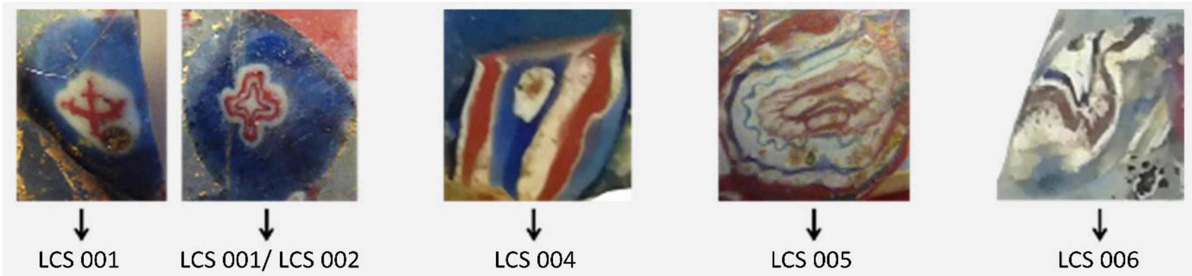


Fig. 2.6: Murrina patterns presented in LCS_01 (caravel and cross/ flower), LCS_02 (cross/ flower), LCS_04 (*rosette* patterns), LCS_05 (*rosette* patterns) and LCS_06 (*rosette* patterns).

LCS_03 presents an amorphous form with a distinctive color gradient, transitioning from a whitish hue to a bluish tint. However, what sets this fragment apart is its attachment to a surface that resembles light-coloured ceramic (Fig 2.7).

LCS_04 is a *millefiori* glass fragment decorated with *rosette* patterns, featuring shades of blue, red, and white. The *rosette* designs are displayed above a blue body glass (Fig. 2.6). The *rosette* pattern showcases a remarkable complexity with a total of seven layers of glass, arranged in the following sequence from the core to the edge: red, white, blue, white, red, white, and blue. This fragment belongs to an unknown part of an undetermined object; observation of it is hindered by a corroded whitish iridescent layer, making it difficult to discern the decorative patterns.

Fig. 2.7: Illustration of the "whitish ceramic" for LCS_03.

LCS_05 is a red body *millefiori* glass fragment decorated with *rosette* patterns showcasing a combination of blue, red, turquoise, and white colors (Fig. 2.6). This fragment belongs to a section of the wall of an undetermined object and displays no signs of corrosion to the naked eye.

LCS_06 is a blue *millefiori* glass fragment decorated with *rosette* murrina in blue, red, turquoise, and white colours (Fig. 2.6). Additionally, this fragment presents an applied white thread encircling the rim, adding an extra decorative element. This fragment belongs to the neck section of a small flask or jar; the presence of a corroded whitish iridescent layer hampers clear observation of the decorative patterns.

2.1.3. **Santa Clara-a-Velha Monastery (SCV)**

SCV is located in Coimbra on the south bank of the River Mondego and was founded during the 13th century (Fig. 2.8). The convent was occupied by the Poor Clares Order, which followed the same vows as the LSC nuns (poverty, chastity, enclosure, and obedience), until 1677 when a new location had to be chosen due to frequent flooding (Trindade & Gambini, 2009, p. 19-20).

Fig. 2.8: Left: Representation of Coimbra in 16th and 17th centuries with the SCV Monastery (© Vasconcelos & Mantero 1999, p. 37). Right: image of Santa Clara-a-Velha Monastery (June of 2018).

Following the death of King Dinis (1261-1325), his wife, Queen Isabel of Aragon (1271-1336), known as Holy Queen Isabel due to numerous miracles attributed to her, became associated with the miracle of turning bread into roses to conceal her charitable acts from her husband. This same miracle was also attributed to her great-aunt, Elizabeth of Hungary, who was related to several saints such as Edwig, Cunegundes, Margaret of Hungary, and Agnes of Prague.

According to legend, the first King of Portugal, D. Afonso Henriques, received his weapons (which served as inspiration for the Portuguese flag) from God, leading to the victorious Battle of Ourique in 1138. After this battle, D. Afonso Henriques was proclaimed king by his subordinates, and a close relationship was established between the Christian Portuguese kingdom and the Pope until the suppression of religious orders in 1834 (Vasconcelos & Mantero, 1999, p. 14). Although Portugal is a secular republic today, Christianity remains the predominant religion.

After becoming widowed, Holy Queen Isabel adopted the vestments of the Poor Clares and moved to the nearby Santa Ana Monastery, which she later donated to the order and became incorporated into the SCV (Trindade & Gambini, 2009, p. 24-25). Her wish to be buried in the SCV was fulfilled in July 1336, turning the site into an important place of pilgrimage; it became the most popular convent, remaining linked to noble families and the upper bourgeoisie (Trindade & Gambini 2009, p. 25-26).

This monastery was classified as a National Monument in 1910.

Archaeological excavations at the monastery took place from 1995 to 2022 and the assemblage uncovered is exceptionally abundant. In addition to utilitarian objects like metal shears, needles, spindles, and common glazed pottery, a wide variety of high-quality luxury artifacts were discovered, including coins, Chinese porcelain, ceramic objects with coats of arms, semiprecious stone decorations, and a significant collection of uncoloured and coloured glass. The glass collection features a large number of millefiori and splashed glass objects (Coutinho et al., 2016; Trindade & Gambini, 2009, p. 31-59). Most of the artifacts recovered from this site date to the first half of the 17th century, coinciding with the period of the Holy Queen's canonization on May 25, 1625 by Pope Urban VIII.

The archaeological context of SCV has yielded thousands of glass fragments in various colours, and extensive research has been conducted in recent years (e.g. Coutinho, 2016; Lima, 2012; Ferreira, 2004; Medici, 2014). These studies have focused on the diverse types of glass decorations found (e.g. enamelled, engraved, moulded, gilded, and pick-up techniques) and in chemical characterisation.

All the pick-up glass fragments selected for compositional analyses are shown in Fig. 2.9 and are described below.

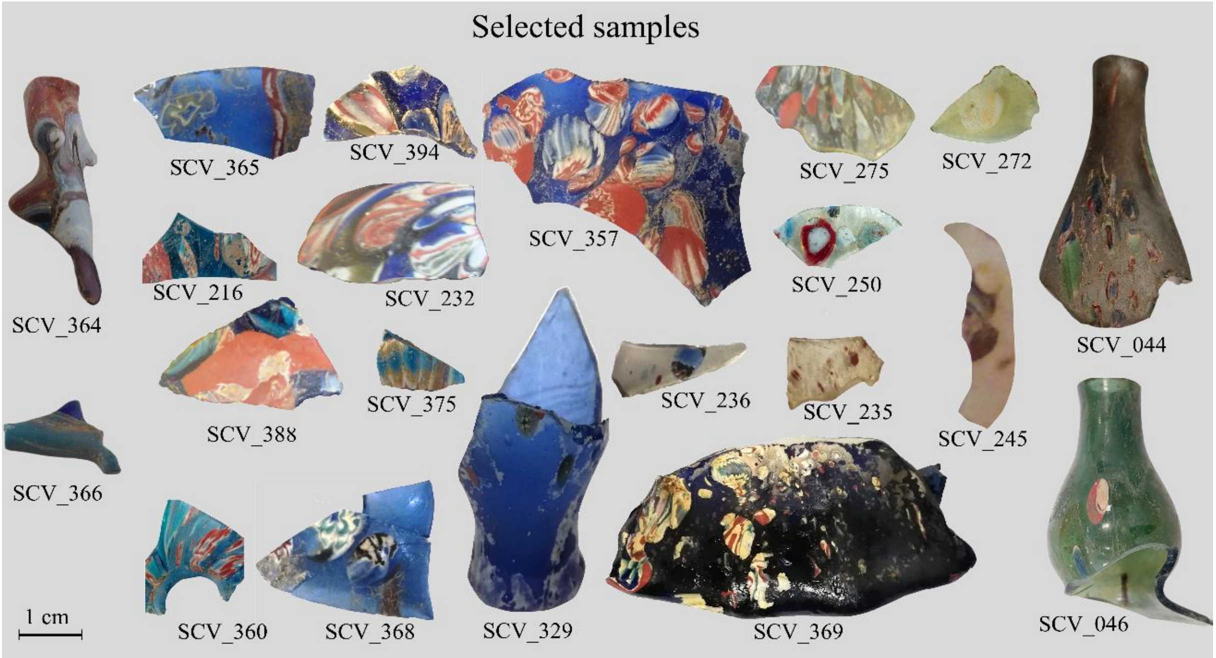


Fig. 2.9: Images of the *pick-up* fragments selected for conduction of compositional analyses on their cross-sections.

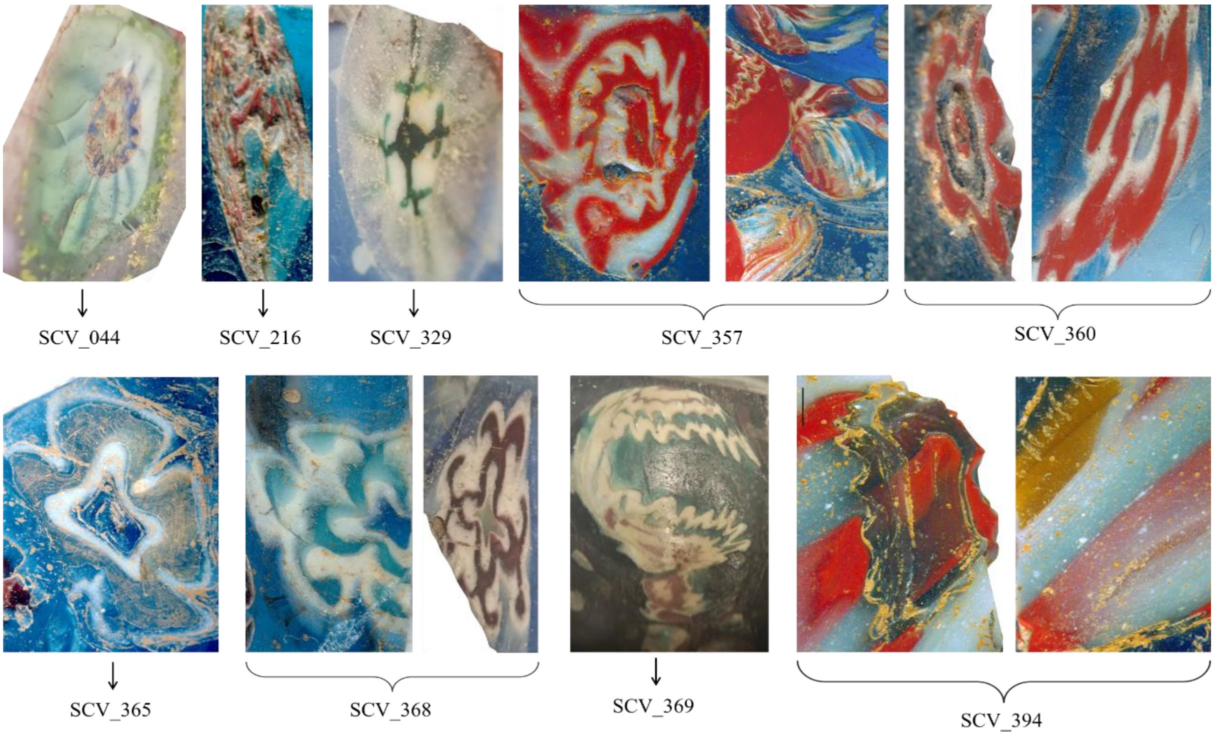


Fig. 2.10: *Murrina* patterns presented in SCV_044 (*rosette*), SCV_216 (*rosette)*, SCV_329 (hybrid/ cross pattern), SCV_357 (*rosette*), SCV_360 (flower and hybrid patterns), SCV_365 (flower pattern), SCV_368 (flower patterns), SCV_369 (*rosette*) and SCV_369 (*rosette*).

SCV_044 is a greyish *millefiori* glass fragment decorated with *rosettes* in blue, greenish, red, and white colours (Fig. 2.9). The fragment exhibits three different *rosette* patterns, although only one of them can be deciphered clearly. This particular pattern features 12 star tips and consists of at least seven layers of coloured glass, including red, white, turquoise, white, blue, white, and turquoise (from the core to the edge) (Fig. 2.10). Apart from *millefiori* decoration, the fragment also displays the presence of gold leaf between the body glass and *murrina*. It belongs to the neck and rim of a little flask, and upon examination, no signs of corrosion are visible to the naked eye.

SCV_046 is a green *splashed* glass fragment adorned with red and white dots. It belongs to the neck and rim of a gourd-shaped bottle and shows no signs of corrosion to the naked eye.

SCV_216 is a turquoise *millefiori* glass fragment decorated with a *rosette* pattern (Fig. 2.10). The *rosette* pattern exhibits a complex arrangement of colours, with at least 9 layers of coloured glass: turquoise, white, red, white, turquoise, white, red, white, and turquoise, arranged from the core to the edge. This fragment belongs to an unknown part of an undetermined object and displays a whitish corroded layer visible to the naked eye.

SCV_232 is a blue *millefiori* glass fragment decorated with undefined pattern with a range of colours that include blue, green, red and white (Fig. 2.9). This fragment belongs to an unknown part of undetermined object and does not show any signs of corrosion to the naked eye.

SCV_235 is a clear transparent *splashed* glass fragment decorated with red dots (Fig. 2.9). This fragment belongs to an unknown part of an undetermined object and does not show any signs of corrosion to the naked eye.

SCV_236 is a clear transparent *millefiori* glass fragment decorated with chevrons and red and turquoise dots (Fig. 2.9). The *rosette* pattern presents an undefined star tip and a range of colours that varies from blue, red and turquoise to white. This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_245 is a clear transparent *splashed* glass fragment decorated with red dots (Fig. 2.9). This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_250 is a clear transparent *millefiori* glass fragment decorated with an undetermined pattern (Fig. 2.9). This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_272 is a yellowish transparent *splashed* glass fragment decorated with whitish dots (Fig. 2.9). This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_275 is a clear transparent *splashed* glass fragment decorated with red and whitish dots (Fig. 2.9). This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_329 is a blue *millefiori* glass fragment decorated with a *murrina* that presents a hybrid/ cross pattern (Figs. 2.9 and 2.10) in white and green colours and some sparkled red dots. This fragment belongs to a neck and rim of a small bottle; a whitish corroded layer is visible to the naked eye.

SCV_357 is a blue *millefiori* glass fragment decorated with a *rosette* pattern in blue, red and white colours (Fig. 2.9 and 2.10). The *rosette* pattern presents 12 star tips and around 6-9 layers of coloured glass: blue, red, white, blue, red, white, red, white, and red (from the core to the edge). This fragment belongs to an unknown part of undetermined object; some whitish shadowy layers of corroded glass may be seen with the naked eye.

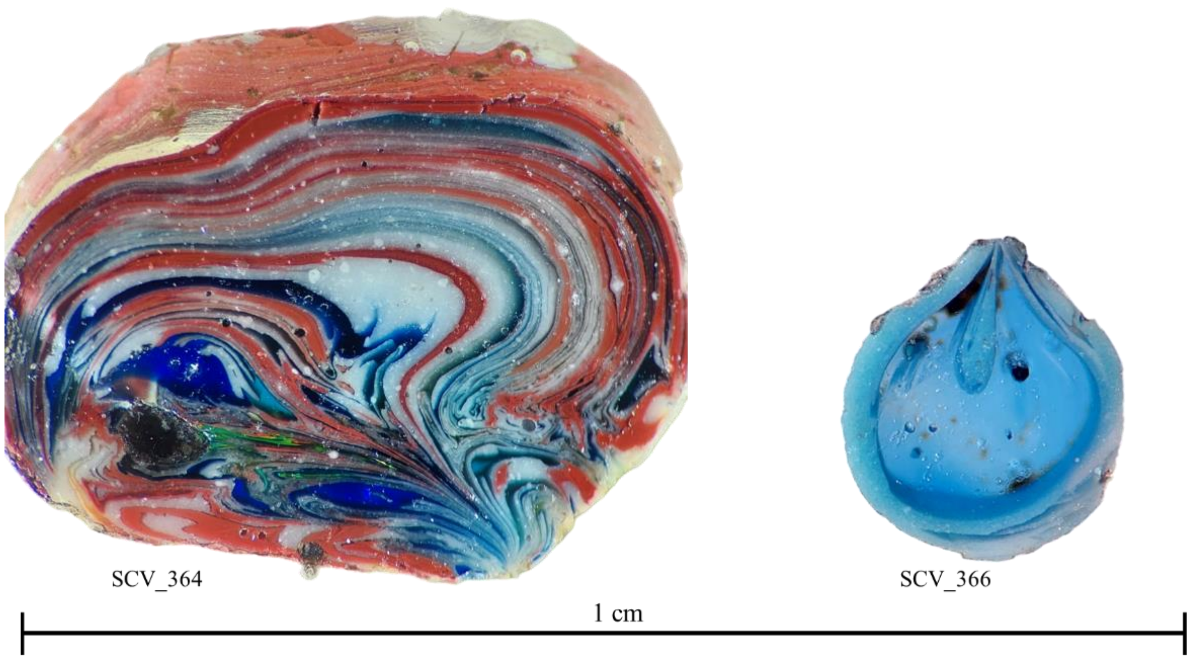


Fig. 2.11: Cross-section images of the *millefiori* glass canes (SCV_364 and SCV_366).

SCV_360 is a turquoise *millefiori* glass fragment decorated with flowers (with four petals) and hybrid patterns in blue, red and white colours (Fig. 2.10). The *murrina* have around 8 layers of coloured glass (blue, red, white, blue, white, red, white and blue - from the core to the edge); the hybrid *murrina* seem to be made with the lampworking technique. This fragment belongs to a base/ foot of an undetermined object and does not seem corroded to the naked eye.

SCV_364 is a *millefiori* cane fragment (?). The cross-section shows some colourful concentric patterns (blue, green, red, turquoise and white) (Fig. 2.11). This fragment does not appear corroded to the naked eye. This fragment can be interpreted as indicative of the presence of glass working in SCV or, at least, its proximity.

SCV_365 is a blue *millefiori* glass fragment decorated with flowers (with four petals). The flowers are made with concentric pattern sequences of blue, white, blue and white colours (from the core to the edge) as shown in Fig. 2.9. This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_366 is a *millefiori* cane fragment (?). The cross-section shows some colourful concentric patterns in white, turquoise, and white colours (from the core to the edge), as shown in Fig. 2.11. This fragment does not seem corroded to the naked eye. This fragment can be interpreted as indicative of the presence of glass working in SCV or, at least, its proximity.

SCV_368 is a blue *millefiori* glass fragment decorated with hybrid/ flowers (four petals) in two colour sequences (Fig. 2.10): 1) blue, white, turquoise, white, turquoise, white and blue; 2) blue, white, purple, white, purple and blue (both from the core to the edge). This fragment belongs to an unknown part of undetermined object and does not appear corroded to the naked eye.

SCV_369 is a blue *millefiori* glass fragment decorated with several *rosette* patterns (Fig. 2.10). This fragment belongs to a base or foot of a bowl and shows a hard golden iridescent layer of corrosion which makes it difficult to observe the decorative motives without carefully wetting the surface.

SCV_375 is a blue *millefiori* glass fragment decorated with a *rosette* pattern of four layers of glass (red, white, red and white - from the core to the edge). This fragment belongs to an unknown part of undetermined object and shows a yellowish layer of corrosion visible to the naked eye.

SCV_388 is a blue *millefiori* glass fragment decorated with undefined and *rosette* patterns (made with at least 4 layers of coloured glass: white, red, white and turquoise - from the core to the edge). This fragment belongs to an unknown part of undetermined object and has a whitish layer of glass corrosion visible to the naked eye.

SCV_394 is a blue *millefiori* glass fragment decorated with undefined patterns which present a range of colours: blue, olive green, red and white. This fragment belongs to an unknown part of undetermined object and shows no corroded layers to the naked eye.

2.1.4. **São João de Tarouca Monastery (SJT)**

SJT is located in the valley of the River Varosa (an affluent of the River Douro), next to two streams: Corgo da Cerca or Aveleira and Corgo do Pinheiro or Fraga or Fragua (Fig. 2.12). This Cistercian monastery, of which the first documentary reference dates to 1144, was classified as a National Monument in 1956 (Barroso Catalão 2018, p.13).

Fig. 2.12: Image of what remains of the SJT Monastery (© Direcção Regional de Cultura do Norte).

This monastery is linked to the French Clairvaux Monastery and was responsible for the foundation of other Portuguese monasteries: Santa Maria de Fiães, São Pedro das Águias and Santa Maria de Aguiar, being surpassed only by Santa Maria de Alcobaça Abbey (Sampaio & Sebastian 2002, p. 36).

The Cistercian monks were austere and took vows of poverty and simplicity. The assemblage uncovered from here between April 1998 and November 2007 is very heterogeneous – including, for instance, common ware pottery, a group of decorated faience with inscriptions attributed to St. Bernard (indicating a special production), Hispano-Moresque tiles, coins, pins, buttons, rings, some iron remains (suggesting metallurgical activity) and several glass artefacts (lamps, bottles and luxury glass fragments of *façon-de-Venise* type such as *millefiori* and *filigrana*) (Barroso Catalão 2018, p.4, Coutinho et al. 2016, Sampaio et al. 1999, p. 224-225).

In this period, small objects like glass beads could be made by lampworking (Beltrán de Heredia & Miró i Alaix 2006; Da Conceição Rodrigues 2003, p. 209; Hollister 1983) and historical documents relate that in some Cistercian monasteries, monks founded small glassworks where they were able to produce paternosters and "pilgrimage hardware" (Bellanger 2006).

In this context only two *millefiori* glass fragments were found, which were studied (Fig. 2.13).

SJT_01 is a blue *millefiori* glass fragment decorated with a *rosette* pattern. This fragment belongs to a part of the wall of a bowl with rim. Apart from *millefiori* decoration, this fragment also presents applied white threads over the rim and over the body glass. This fragment is very well preserved and does not show corroded layers to the naked eye.

SJT_09 is a blue *millefiori* glass fragment decorated with the Cross of Christ and *rosette* patterns. This fragment comprises part of the neck, the wall and base (diameter: 36 mm) of a small flask. Although its surface shows some evidence of scratching, it is very well preserved.

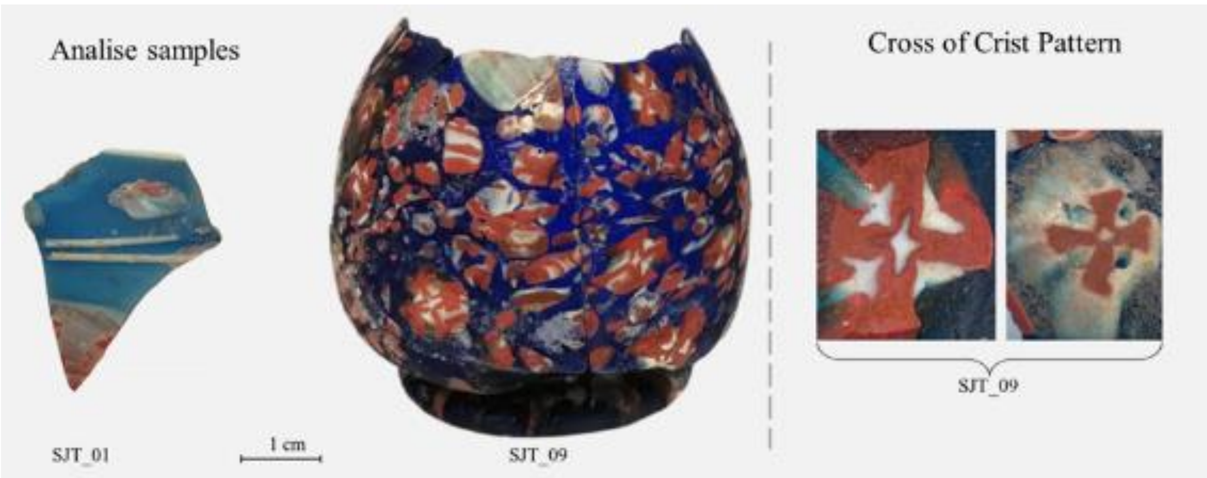


Fig. 2.13: Presentation of the fragments analysed and the Cross of Christ pattern on the SJT_09 fragment.

3

METHODOLOGY AND ANALYTICAL METHODS

The examination of cultural heritage items presents distinctive constraints and difficulties. The remarkable inherent significance of these artifacts as exceptional evidence of our collective history requires a meticulous approach towards their handling, sampling, and preservation. Consequently, the selection of analytical methods in cultural heritage research should ideally be non-invasive and non-destructive or, at most, minimally destructive.

The selection of the glass artifacts understudied was carefully made under the supervision of Teresa Medici, who conducted a comprehensive study on Portuguese glass from the 14^{th} to 17^{th} centuries, relying on archaeological findings (Medici, 2016).

In that study, the *pick-up* glass fragments were examined within their archaeological contexts, allowing us to determine which fragments were more representative based on colour choices, decoration patterns, the presence of gold leaf, and unique decorations not found outside Portugal. As Augusta Lima's samples (2010) had already been carefully studied, they were only included in this project to discuss the results (those fragments were not chosen to be sampled in this project).

The research methodology was developed through an interdisciplinary approach, integrating archaeometry, the evolution of glassmaking technology, history, and conservation science. By employing non-destructive techniques for chemical glass characterization, it becomes possible to ascertain the types of raw materials employed in the glassmaking process.

This knowledge can subsequently assist in proposing an origin or provenance of the glass artifacts.

As samples have already been inventoried, this work remains considering their institutional number.

Sampling is a delicate procedure that should be minimized or, ideally, avoided altogether. However, when minimal sampling is required, it should be conducted in a manner that does not aesthetically alter the object. This approach helps prevent excessive manipulation and transportation, which could potentially heighten the risks of damage. Bearing it in mind, the chosen glass fragments were also sampled to avoid erroneous results by analysing and quantifying corrosion layers or deposits of environmental particles instead of pristine glass. Small samples of a few mm^2 (2-5) were taken from the selected fragments picking up the largest number of coloured layers 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.

Optical microscopy and stereoscopy will assist in the morphological study, while for the glass characterization a combination of techniques was used, such as particle induced X-ray emission (μ-PIXE) mapping to visualize how the oxides are distributed through different glass layers of the glass fragments, laser ablation inductively coupled plasma mass spectrometry and (LA-ICP-MS) to obtain the major, minor, trace and rare earth elements of glass composition. For the colour investigation μ-Raman spectroscopy allow the study the white opaque glass layer, and UV-Visible absorbance and reflectance spectroscopy helped to assess the chromophores present in the glass.

3.1 μ-PIXE

The ion-beam analytical technique offers a notable advantage as the damage resulting from ion beam bombardment on glass artifacts is considered "almost negligible" (Coutinho 2016, p. 68). Furthermore, the combination of this technology with Particle Induced X-Ray

Emission (μ-PIXE) has been extensively employed in the analysis of historical glassware due to its exceptional analytical capabilities.

Particle Induced X-Ray Emission with micrometre lateral resolution (μ-PIXE) was performed using an Oxford Microbeams OM150 type scanning microprobe capable both of focusing down to 3 x 4 μm^2 the used 1 MeV proton beam and scanning a sample surface area as large as 3730 x3730 μm^2. The sample fragments were irradiated in a vacuum and a 30 mm2 Bruker SDD X-ray detector with 145 eV energy resolution (at the energy of the Mn Kα line, 5.9 keV) was used for X-ray collection. Equipped with an 8 μm thick Be window, it allows detecting X-ray energies as low as the ones of Na while preventing most of the protons from entering and damaging the detector crystal. From the initially obtained 2D elemental distribution maps (with typical dimensions of 750 x 750 μm^2), the body glass and the several layers of different colours belonging to decoration were properly identified and a representative region of interest selected to visualize the distribution of different oxides throughout layers.

3.2 LA-ICP-MS

When comparing Laser Ablation Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) with the previous technique of μ-PIXE, several observations can be made has a very high detection limit (can go to ng/g).

LA-ICP-MS has been widely performed in the study of cultural heritage on different materials, including on glass (Cagno 2012; Coutinho 2016, p. 69; Gratuze 1999; Gratuze 2013). Although the laser ablation leaves a crater (which can range between 20 and 200 μm) and can therefore be considered a destructive technique in a micrometres scale, whenever an analysis is performed, on the other hand it can give us, not only the major and minor elements, but also the trace and rare earth elements (REE) allowing for deeper conclusions on provenance studies (Coutinho 2016, p. 69-70; Gratuze 2013, p. 313).

To better discuss Rare Earth Elements (REE) within the glass matrix, it was necessary to normalize these elements using the REE values found in the Continental Earth's Crust. The normalization values used were obtained from Wedepohl's work (1995).

LA-ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry) consists of a Resonetics M50E excimer laser working at 193 nm coupled with the Thermo Fisher Scientific ELEMENT XR mass spectrometer. This equipment is located at the National Centre of Scientific Research (CNRS) in Orleans, France with Bernard Gratuze and the analyses were performed under the crossed-section sample that was embedded in epoxy resin. The excimer laser was operated at 5mJ with a repetition of 10 Hz. The beam diameter was precisely adjusted, ranging from 20 to 100 μm, to match the size of decorations present on the fragments. A pre-ablation time of 15 s is set in order to eliminate the transient part of the signal which is then acquired for 25 s. Calibration for glass was carried out using NIST610 and Corning B, C and D glass reference material (Gratuze, 2013). The detection limits range from 0.1 to 0.01 % for major elements, and from 20 to 500 ng/g for others.

The average values obtained during the analysis are presented in (Apendix A.6 – Lisbon contexts and Apendix A.7 – SCV and SJT contexts).

3.3 UV-Vis Absorbance and Reflectance Spectroscopy

The morphological observation allows us to realise that the glass fragments understudied present a wide range of colours: blue, colourless, red, turquoise and white.

This study was made by using UV-Visible absorbance spectroscopy (in the transparent colours that belong to the body glass) and reflectance spectroscopy (in the opaque colours) to identify the presence of the glass chromophores responsible for the colours and hues (Tab. 3.1).

Table 3.1: Most common ions responsible for glass colouration (Coutinho 2016, p.72; Fernández 2003, p.457)

Colour	Colour agent	Oxidation State	Absorption bands (nm)
Blue	Cobalt	Co^{2+}	540, 590, 640, 1400, 1600, 1800
	Iron	Fe^{2+}	440, 1100, 2100
Yellow	Iron	Fe^{3+}	380, 420, 440
Turquoise	Copper	Cu^{2+}	790
Red	Copper	Cu^{+}/Cu	560
Purple	Manganese	Mn^{3+}	499

The UV-Vis spectrums were measured with an Avantes AvaSpec-2048 fiber optical spectrometer with a 300 lines/mm grating. This analytical technique has an optical signal path between 200 and 800 nm with a resolution FWHM of 2.4 nm.

3.4 μ-Raman Spectroscopy

Raman analysis is a type of vibrational spectroscopy that examines the interaction between photons (or neutrons), identifying compounds on a molecular level. The low energy levels of materials, known as vibrational levels, are determined by the chemical composition (atomic nature) and structure (such as the level of crystallization) of the material. They correspond to the collective vibrations of atoms, molecules, or groups of atoms (Colomban, 2013, p.277, Coutinho 2016, 73).

During μ-Raman analysis, a concentrated monochromatic light source, typically a laser, is directed onto the sample, and the resulting scattered light is collected and measured. A portion of this scattered light possesses a different energy compared to the incident laser light. This energy shift occurs due to the interaction between the light and the molecules present in the sample. The magnitude of this energy shift is directly related to the specific vibration modes exhibited by the molecules, such as bending or stretching modes (Colomban, 2013).

Analyses were performed on polished cross-sections of *pick-up* glass fragments with a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 633 nm and a solid-state laser of 500 mW power operating at 532 nm. The laser beam was focused either with 50x or 100x Olympus objective lenses. The laser power was filtered to 10% incident power using a neutral density filter for all analyses. Analyses were performed both on the surface of the glazes and on polished cross-sections. Spectra were recorded as an extended scan. A mixed Gaussian-Lorentzian curve-fit provided by the LabSpec software (v 5.15.25) was used to determine the exact peak wavenumbers. The attribution of the Raman spectra was made using the RRUFF database project on minerals (RRUFF, 2014). The equipment was operated by the Susana Coentro.

This analytical technic provides numerous significant benefits in cultural heritage studies: (1) requires minimal or no sample preparation, allowing for the analysis of extremely small samples, including the detection of crystals as small as a few micrometres, (2) over X-ray diffraction is its capability to identify amorphous compounds and intermediate phases. However, it is essential to note that the laser used in μ-Raman analysis, when operated at high power, can induce thermal changes in iron oxides. To mitigate this issue, the use of filters is crucial in reducing the laser's power (Colomban, 2013).

This equipment was crucial for the identification of the opacifying crystals observed in white layer of the understudied glass fragments.

4

ARCHAEOMETRICAL RESEARCH

4.1 Morphological Characterisation[2]

4.1.1 Forms (*millefiori* and *splash* glass)

Glass objects decorated with *pick-up* technique are characterized by having simplicity of form and, frequently, reduced size. An exception to this general trend is the glassware attributed to Spanish origin, characterized by more complex shapes (Page 2004). They are usually mould-blown and sometimes could also have gold leaf under the *murrine* or the monochromatic glass slices (Barovier Mentasti 2005; Bruhn 1995; Gudenrath 2012; Hollister 1981; Medici 2012; Uboldi 2015; Whitehouse 2012). P. Hollister (1981) pointed out that specimens dating to the end of 15th and beginning of 16th century have rough pontil marks.

According with the knowledge of Paul Hollister (1981), who is one of the foremost scholars of 17th to 19th century glass study, cited different objects decorated with *millefiori* technique: bowl, goblet (chalice), cup, biconical glass, tazza, jar, flask, bottle, sprinkler, handled jug (ewer), ball. The forms that emerged from our survey are summarized in Fig. 4.1, comparing archaeological finds with objects in museum collections.

[2] This chapter was partially published in: Pulido Valente, F., Coutinho, I., Medici, T. and Vilarigues, M. 2021 Glass coloured by glass: Review of the *pick-up* decoration in early modern Europe. J. Archaeol. Sci. Rep. 36, 1-16 https://doi.org/10.1016/j.jasrep.2021.102832.

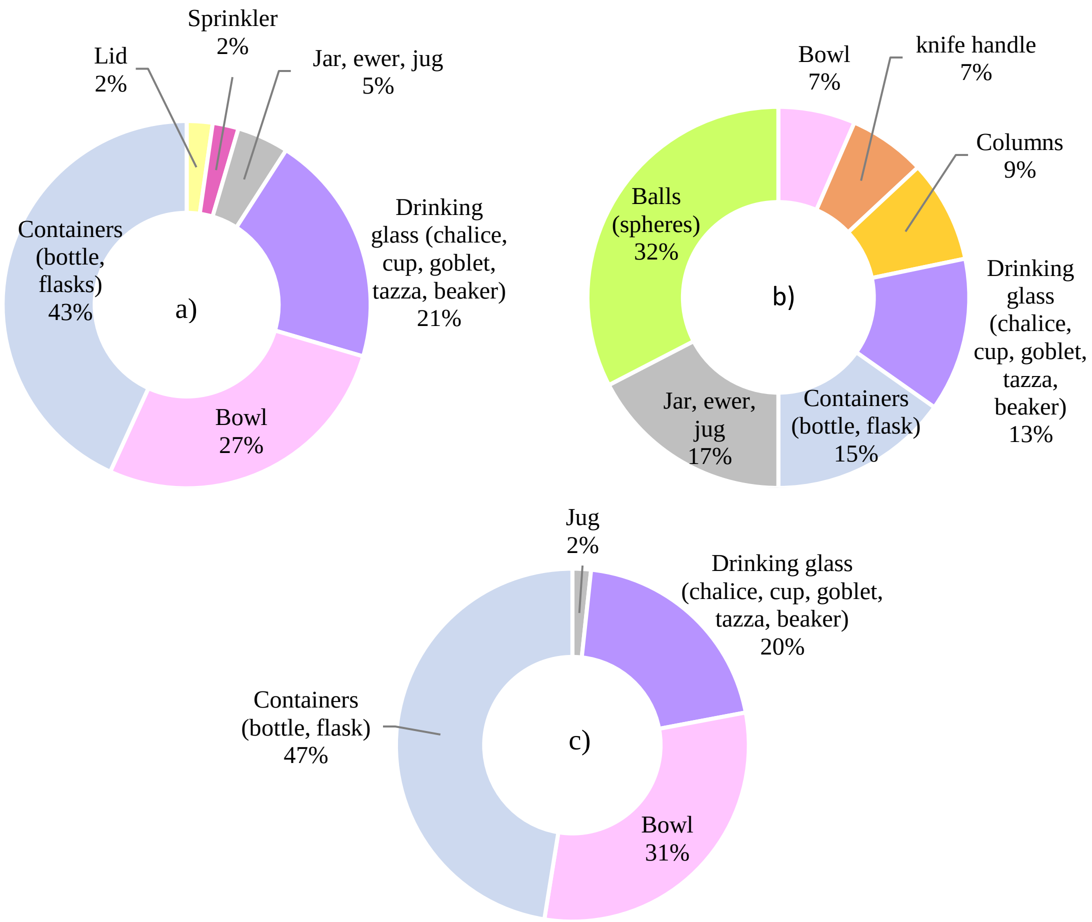


Fig. 4.1: a) Archaeological glass objects with *millefiori* decoration b) *Millefiori* glass objects in museological context. c) Archaeological *splashed* glass fragments with *Pick-up* decoration.

It is interesting to note that rare objects as *millefiori* balls and knife handles are only preserved in museum collections. At the same time, containers, and bowls (71%) have a greater representation in archaeological contexts when compared with museum collections (22 %), perhaps because they have a more utilitarian character and so they are more susceptible to damage and to be thrown away.

The small-size fragmented artefacts found in Portugal are in accordance with the theory most common in the literature (e.g.: Tait 1979; Tyson, 1996; Uboldi 2015) that defends that most of the *millefiori* glassware have a miniature size because they had a decorative or a curiosity character to present in *kunstkammer* or "cabinet of curiosities" rather than utilitarian purposes. For the assemblages outside Portugal the information about the size of the objects is usually missing thus the discussion about this subject is difficult. However, the forms of most of the artefacts found in archaeological contexts considered in this study allows the possibility of also having a utilitarian function (Fig. 4.1.a.).

Comparing *splashed* glass fragments with *millefiori* found in archaeological contexts, a reduced variety of forms were reported: jugs, drinking glasses, bowls and containers (Fig. 4.1..c., 4.1..a. and Tab. 1.2).

4.1.2 M*illefiori* glass fragments

4.1.2.1 Colours of Body Glass

Excluding the Portuguese glass fragments unearthed in LCS and SCV, all the archaeological *millefiori* glass fragments have blue or clear body glass.

The most popular is blue: almost 75% (206 out of 276) of the glass fragments with *millefiori* decoration have blue body glass, followed by 9% of fragments with colourless body glass (Tab1.2).

It is very interesting to note that turquoise, greenish, opaque red and greyish body glass were only observed in some *millefiori* fragments found in two Portuguese archaeological contexts: LCS in Lisbon and SCV in Coimbra.

This fact leaves some questions to be answered such as:

- Were the different hues of colourless glass deliberated (greyish/ greenish)?
- Could this observation mean that they were locally produced?
- Was it a matter of taste and fashion?

In museum contexts the clear glass is the most frequent on the body glass, followed by blue. The use of purple colour was noted only once in The Kunstmuseum, Düsseldorf (Helmut, 1995). The range of colours used in museological assemblages is reduced and different from which was found in archaeological assemblages.

This observation opens the following questions:

- Why *millefiori* glass objects preserved in Museums do not follow the same tendency of those which were found in archaeological contexts regarding form, size and colour?

- In the 16th century Venetian glassmakers already had a long experience of producing coloured and colourless glass, being the latter known as being the most sought and improved (see e.g. Verità 1985; Charleston 1984). Was the colourless *millefiori* glass considered more luxurious than the *millefiori* with coloured body glass?
- Can this observation be related with the fact that only the considered master pieces were preserved by the collectors and, consequently, are preserved in the museums?
- Can it be linked with different production centres (the Venetian glassware or the best *façon de Venise* are in the museums)?

Looking at the Portuguese assemblage the body glass colour can be broken down as follows: 22 are blue (two from LCD, two from LCS, two from SJT and 16 from SCV); six are greyish (one from SCV and five from LCS); five are dark green (from SCV); two are opaque red (one from LCS and one from SCV); two are turquoise (from SCV), and two are yellowish (from SCV). This result shows that most of the *millefiori* glass found in Portugal have a blue body glass (almost 60 percent), and this is the only colour that is present in all the considered contexts (Fig. 4.2).

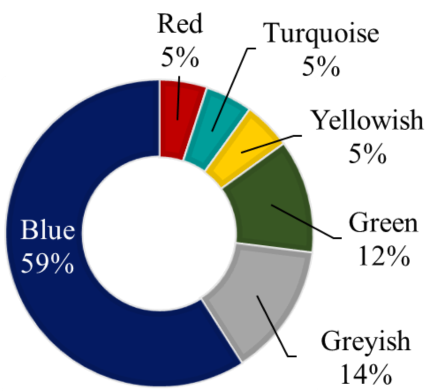


Fig. 4.2: Range of colours found in Portuguese *millefiori* body glass.

4.1.2.2 Colours of *murrine*

In the literature that describes *millefiori* glassware (such as the inventory of the Barovier glasshouse), when the range of colours used in cane-making is mentioned one can find blue, *berretino*[3], red[4], turquoise and white. Although an infinite combination of colours can be found in the *murrine*, the most common ones have: a translucent blue or turquoise blue in the core, in the fifth, and in the last layers (counted from the core to the surface); an opaque red colour in the third layer; and very thin layers of opaque white colour in between them (Bruhn, 1995;

[3] According to the treatise of Antonio Neri, translated and annotated by Paul Engle (1959), *berrettino* is an Italian term used to designate a grey or ashen colour

[4] called as brick-red or as rosso coppo in Murano: Moretti 2005.

Gudenrath 2012; Moretti 2005; Tait 2012). Gianni Moretti (2005) noted that the early beads also had a light green transparent layer of glass and, in very rare specimens, the core and the fifth layer are red.

More rarely, other colours can be seen in *murrine*: amber, emerald green, purple (ranging from lilac to amethyst) and violet (Bruhn, 1995; Hollister 1981).

Regarding archaeological assemblages (Tab. 1.2) the colours that were used more often are blue, red and white, followed by the turquoise blue. Green and purple in some *millefiori* glass fragments from Santa Clara-a-Velha Monastery in Coimbra.

In Portugal, *murrine* colours shows that red (171 fragments) and white (158 fragments) are the most popular, being present in almost all the 185 fragments (considering each fragment and not the number of times the same color appears within the same fragment). These colours are followed by cobalt blue (109 fragments) and turquoise (63 fragments). Less common are, respectively, the greenish (two fragments), purple (four fragments), and green (six fragments), all belonging only to SCV context (Fig. 4.3).

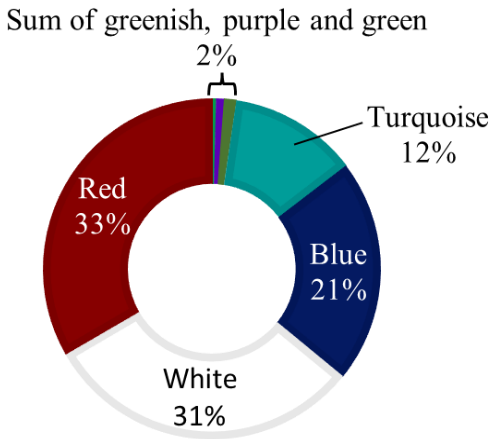


Fig. 4.3: Range of colours found in Portuguese *murrine* of *millefiori* glass.

Concerning *millefiori* glassware preserved in museums, the more common range of colours observed in the *murrine* are blue, red, turquoise and white; however, the yellow has been also very cited: in a total of 22 museum's collections, at least 7 (~ 30%) have glass objects showing yellow colour in the *murrine* (Tab. 1.3). This result show that yellow colour is less frequent in archaeological contexts (Tab. 1.2), than in museological contexts.

Yellow glass was only found in *De Twee Rozen* context in Amsterdam proving that the Dutch glassmakers used this colour in *murrine* canes of the 17th century, at least in this glasshouse (Gawronski et al. 2010); other glass pieces belonging to museums that also have this colour are attributed to Catalan (The Corning Museum of Glass) or Venetian production (Historisches Museum, Pinacoteca Ambrosiana, The British Museum, The Metropolitan Museum and Victoria & Albert Museum) and are dated to the end of 16th – 17th centuries or, in case of the knife handles, to the end of 17th- beginning of 18th centuries.

Concerning the green colour presented in the *murrine* of *millefiori* glassware only one example of a bowl belonging to Victoria & Albert Museum (Tab. 1.3) and glass fragments belonging to Santa Clara-a-Velha Monastery (Tab. 1.2) were found. According to Gianni Moretti (2005), the early *chevron* beads had a light green transparent layer of glass, this could indicate that maybe the cited bowl and glass fragments are oldest then the others.

On the other hand, the purple was only found in Santa Clara-a-Velha Monastery archaeological context (Portugal): can this characteristic be used as an indicator of provenance?

4.1.2.3 Patterns of *murrine*

Regarding *murrine* patterns, its identification was, sometimes, very difficult due to the corrosion layers that were observed in some glass fragments. Furthermore, the sliced canes often appear rolled and, consequently, in different angles due to the *millefiori* technique production process (Fig. 1.9); at the same time this characteristic gives the object a very interesting decorative effect.

It is generally assumed that the typical decoration pattern of Renaissance *millefiori* is the same used for making *rosette*/ *chevron* beads, without the hole (Baumgartner 2015; Barovier Mentasti 2005; Barovier Mentasti 2012; Charleston 1984; Hills 1999; Hollister 1983; Medici 2012; Tait 2012; Willmott 2009) and, occasionally, with a cross in the core (Hollister 1981; Kos 1994; Tait 1979; Theuerkauff-Liederwald 1994).

According to the consulted literature, Venetian chevron beads had usually twelve-pointed star drawing and, frequently, seven glass layers (Hills 1999; Moretti 2005). However other types of *rosette* are recorded in *millefiori* glass fragments also reported in the literature.

Besides *rosette* pattern, the *rosette with cross in the core* were found in Venetian territory (Italy), in Mengeš (Slovenia) and in Coimbra, Portugal (*SCV*) (Fig. 4.4) and it represents only 2 % of the total decorative motifs (with 5 glass fragments). *Flower motive* was only found in *SCV* context (Coimbra, Portugal) and encompasses six different groups of flowers (Fig. 4.4). The other three types of patterns (caravels, cross and concentric circles) do not have known equivalents in the rest of Europe and they represent significant symbols of Portuguese culture during the period understudied (Fig. 4.4). For the caravel pattern, the hypotheses of being a cross distortion was considered but, least 3 examples were counted in 2 different Portuguese archaeological contexts, reinforcing the possibility of it being considered a caravel.

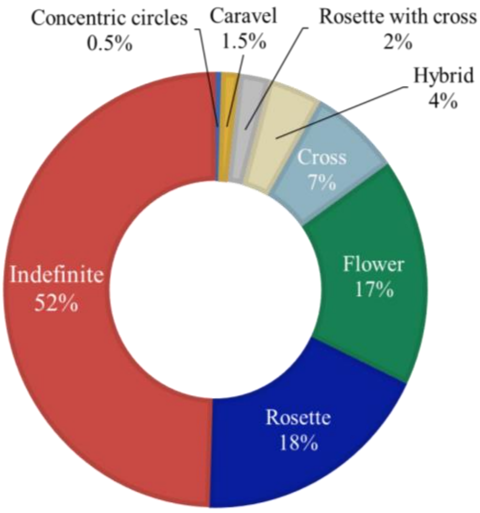


Fig. 4.4: Range of decorative motives presented in the studied Portuguese millefiori glass.

Looking at the Portuguese *murrine* patterns found in the studied *millefiori* glass, a variety can be distinguished in (Fig. 4.4):

- 108 fragments, the original pattern is impossible to determine due to corrosion layers or deformation from slice orientation.
- *Rosette* (40 fragments)[5].
- Flower (37 fragments).
- Cross (15 fragments).
- Hybrid (9 fragments).
- *Rosette* with a cross in the centre (5 fragments).
- Caravel (3 fragments).
- Concentric circles (1 fragment).

[5] This is the pattern most frequently found in *millefiori* glass objects (Hollister 1983, 202).

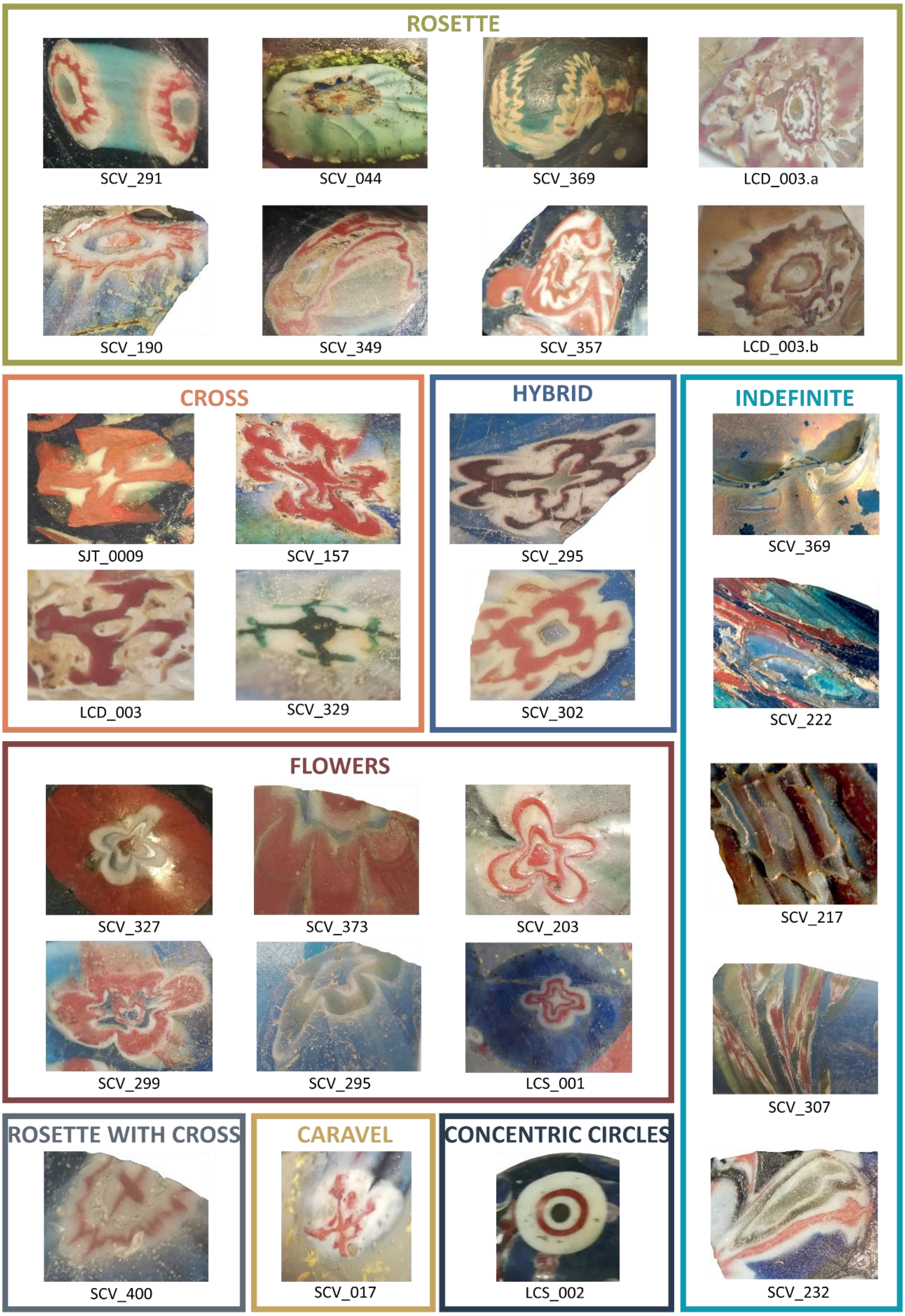


Fig. 4.5: Image representing, at least, one of each different category of patterns presented in Portuguese assemblages. The best representation of each pattern are here presented.

In Fig. 4.5 are presented the image of the different categories of patterns presented in Portuguese assemblages.

According with the literature that we had access, the patterns which were only found in Portuguese assemblages are: flower, cross, hybrid, caravel and concentric circle.

In the Netherlands, and without known parallels outside, some skulls and geometric drawings made by grouping canes (Fig. 1.7.i) was also noted in De Twee Rozen glass house (Gawronski et al 2010).

In addition to *murrine* patterns, some *millefiori* glass objects could also present *filigrana* canes (Baumgartner 2010; Tonini 2011).

4.1.3 *Splash* glass fragments

4.1.3.1 Colours of Body Glass

Regarding the archaeological glass fragments that have *splashing* decoration, green (92 glass fragments), clear (40 glass fragments), turquoise (17 glass fragments), opaque white (17 glass fragments), blue (6 glass fragments), amber (3 glass fragment), light blue (3 glass fragments), greyish (1 glass fragment) and red (1 glass fragment) colours in glass body glass were found (Fig. 4.6).

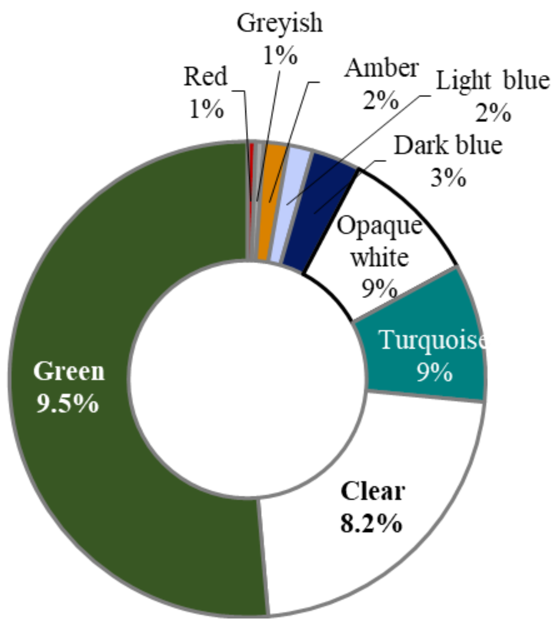


Fig. 4.6: Summary of the colours that were found in the body glass of archaeological fragments with *splashing* decoration.

It is interesting to note that the blue body is not prevalent among glass fragments with *splashing* decoration. On the other hand, green (like the green glass used in bottles) was only found at the Portuguese site of Santa Clara-a-Velha Monastery and in Silkstone (England), as well as turquoise transparent blue was only found in this Portuguese context (10 glass fragments) while opaque turquoise was only found in Koločep, Croatia (7 glass fragments) (Table

1.2). Amber, greyish, light blue and red colours seem to be very rare: amber was only found in Silkstone (Dungworth et al. 2006); light blue and red were only found in Koločep (Medici 2010); while greyish was observed in *La Verrière* (Gratuze & Janssens 2004). Clear glass with *splashing* decoration were only found in Santa Clara-a-Velha Monastery, in Born (Barcelona, Spain), in Silkstone and in two contexts located in Amsterdam with a representation of, respectively, 10, 7, 1, 1 and 2 glass fragments (a total of 21).

The most frequent colour for the bodies, concerning this technique, is the opaque white. Opaque white vessels with *splashed* decoration are well known from museum collections. Their origin is linked to the fact that Venetian glassmakers were trying to imitate the Chinese porcelain (see for ex. Henkes 1994 and Tonini, 2007). Excluding Portugal, where more than 100 fragments, corresponding to an estimated 17 glass objects, were reported, the survey of the literature resulted in a few fragments found in Croatian (2 glass fragments), Italian (1 glass fragment), Holland (1 glass fragment), and Spanish (2 glass fragments) contexts, being probably under-represented (respectively: Medici 2010, Verità & Zecchin 2008, Gawronski et al. 2010, Beltrán de Heredia & Miró i Alaix 2006).

4.1.3.2 *Splash* decoration

According to the consulted literature, and regarding the archaeological fragments, it seems to be clear that, for this technique, the glassmakers had a preference for the red colour representing about 37.7% of the total of glass fragment considered in this work. Red is followed by the white colour (19.5%) and then by the blue (18.2%). Less common seems to be the turquoise and *aventurina* (11.9%) and very rare is the black colour (0.6%).

Aventurina has been considered one of the most luxurious glasses because is characterized by having a sparkling gold aspect given by the presence of tiny metallic copper in the glass matrix (Lima 2010, Lima et al. 2012; Verità & Zecchin 2008). According to Venetian documents, *aventurine* glass (also known as *pasta stellaria*) was created by Muranese glassmakers in the first half of the 17th century (Verità & Zecchin 2008). Beside of this information Marco Verità and Sandro Zecchin (2008) studied one archaeological glass goblet with *splashing* decoration, which has *aventurine* chips, that was found in a closed context well dated to the second half of 16th century.

Interesting to note is that *aventurina* glass was only found in the decoration of *splashed* glass which has white body glass and in a *splashed* glass with turquoise body glass fragments found in a shipwreck located in Koločep, Croatia (Medici 2010).

4.2 Chemical Characterisation

4.2.1 **Lisbon Contexts**[6]

4.2.1.1 Clear glass and base glass

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 (Tab. 4.1) 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 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.

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[6] <u>This chapter was published in</u>: Pulido Valente, F., Coutinho, I., Medici, T., Gratuze, B., Alves, L. C., Varela Gomes, R., Varela Gomes, M. and Vilarigues, M. 2023. In the quest for historical Lisbon through 17th century *millefiori* glass. J. Archaeol. Sci. Rep. http://dx.doi.org/10.2139/ssrn.4484595

Tab. 4.1: 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_05 are highlighted.

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2
LCD_03	Blue	Body	16.4	2.87	5.2	60.8	0.37	0.94	5.71	7.46	0.22
LCD_31		Body	18.1	2.85	4.4	63.0	0.30	1.11	3.14	6.93	0.14
LCD_54		Cane	17.7	2.74	4.2	64.1	0.30	1.15	2.99	6.69	0.13
LCD_54		Body	17.9	2.81	4.4	63.2	0.29	1.15	3.15	6.93	0.14
LCS_02		Cane	15.7	3.14	6.8	59.3	0.47	0.77	5.77	7.75	0.26
LCS_04		Body	18.5	3.42	5.5	60.1	0.41	1.05	4.36	6.46	0.21
LCS_06		Body	18.7	3.46	5.5	59.9	0.42	1.05	4.30	6.51	0.22
LCD_03	Clear	Cane	17.3	3.41	5.1	58.5	0.32	0.96	5.02	9.12	0.19
LCS_01		Body	16.5	3.46	6.2	59.0	0.41	0.86	5.44	7.87	0.29
LCS_02		Body	16.5	3.49	6.2	58.9	0.42	0.90	5.39	7.95	0.30
LCS_05		Body	17.3	2.10	5.5	63.5	0.36	1.07	3.68	6.25	0.26
LCD_31	Red	Cane	17.1	3.13	4.7	63.3	0.43	1.03	3.14	7.15	0.16
LCD_54		Cane	16.6	3.69	5.0	62.5	0.44	1.00	3.05	7.57	0.17
LCS_01		Cane	15.8	3.28	7.0	58.4	0.51	0.66	5.86	8.23	0.28
LCS_02		Cane	15.8	3.29	6.9	58.4	0.52	0.67	5.86	8.25	0.28
LCS_04		Cane	18.5	3.18	5.3	61.1	0.51	1.17	4.75	5.25	0.23
LCS_05		Body	18.2	1.99	5.4	62.8	0.40	1.22	3.52	6.16	0.25
LCS_01	Turquoise	Cane	16.5	3.34	6.3	59.4	0.43	0.84	4.95	7.94	0.29
LCS_06		Cane	18.2	3.23	5.5	61.2	0.45	1.22	4.53	5.44	0.25
LCD_03	White	Cane	13.4	2.47	4.3	65.4	0.39	1.60	5.66	6.63	0.17
LCD_54		Cane	17.0	2.23	4.3	66.2	0.29	1.62	2.80	5.51	0.15
LCS_01		Cane	15.8	2.98	5.8	60.8	0.55	1.13	5.55	7.13	0.27
LCS_02		Cane	16.3	2.97	5.7	60.6	0.54	1.09	5.43	7.02	0.27
LCS_04		Cane	18.6	3.19	4.6	61.7	0.49	1.47	3.98	5.75	0.19
LCS_05		Cane	16.8	2.87	4.9	61.0	0.45	1.46	4.79	7.56	0.20
LCD_14	Amber	Production waste	1.8	3.47	14.2	56.7	0.84	0.14	4.75	17.54	0.63
LCD_14	Dark Blue		1.7	3.57	14.3	56.0	0.84	0.14	4.55	18.33	0.64
LCD_32	Amber		5.6	1.88	13.3	62.7	0.61	0.11	4.93	10.37	0.52
LCD_32	Dark Blue		4.7	2.21	12.3	64.7	0.76	0.11	5.45	9.27	0.55
LCS_03	Clear Blue		1.5	2.48	14.5	64.9	0.35	0.08	5.57	9.90	0.73
LCS_03	Dark Blue		1.6	2.47	14.2	65.0	0.42	0.08	6.64	8.92	0.73
LCS_03	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 005_glass fragments are highlighted in this table.

4.2.1.2 Alkali sources

All clear and base glass have contents of Na_2O between 13.4-18.7 wt%, of K_2O between 2.8-5.9 wt% and of CaO between 5.25-8.99 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) where 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. 4.7 shows that, all LCS and LCD glass fragments, are located between the two correlated lines of Na_2O^* + K_2O^*. 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 17^{th} century (Cagno et al. 2012b, Verità & Toninato 1990, Valente 1950).

Looking at K_2O and MgO content (fig. 4.7b), 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.

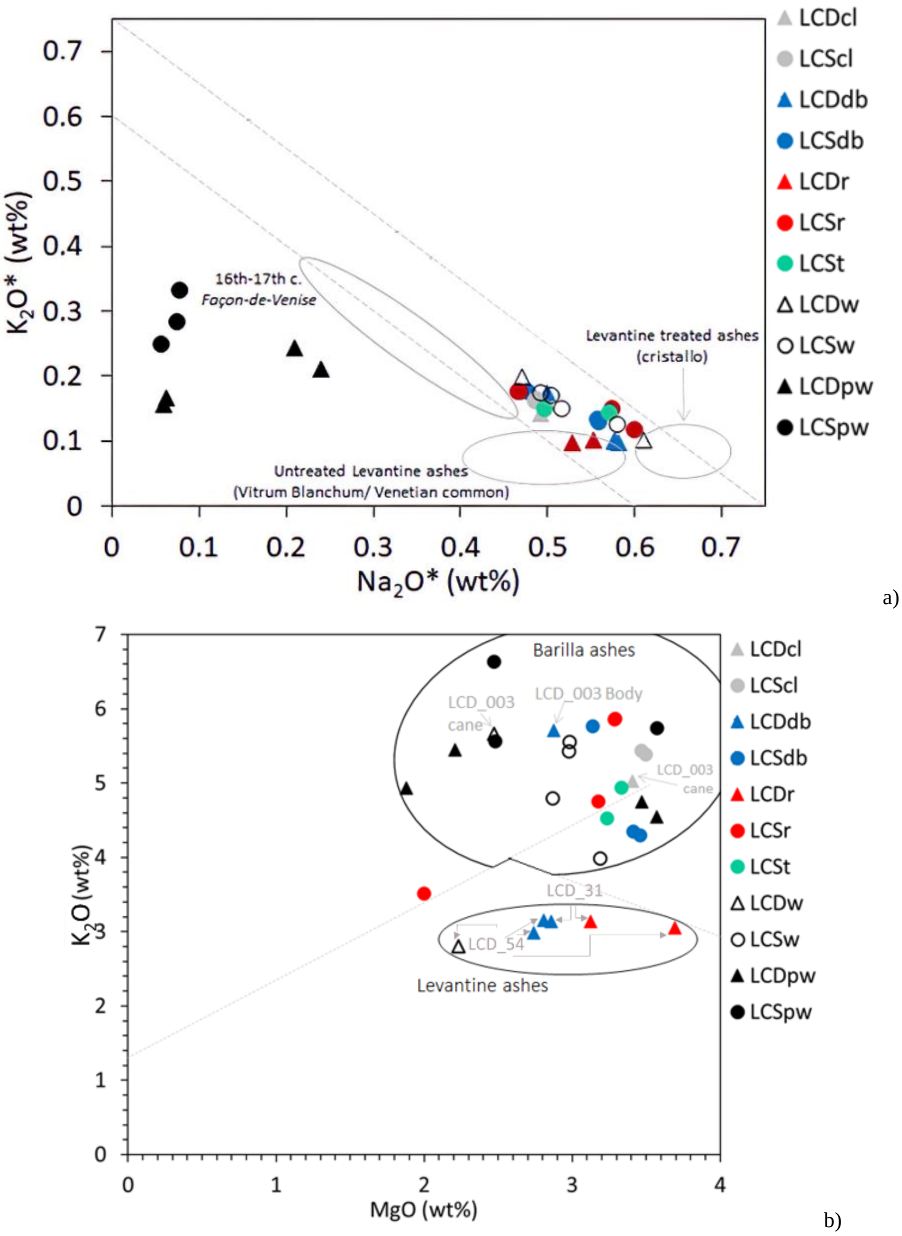


Fig. 4.7. (a) Normalized Na_2O^* ($Na_2O/(MgO+P_2O_5+K_2O+CaO)$) and K_2O^* ($K_2O/$ (Na_2O+ $MgO+P_2O_5+CaO$)) are plotted with the correlation lines $Na_2O^*+K_2O^*=0.6$ and 0.7 indicating the use of, respectively, unpurified, and purified ashes (Coutinho et al. 2021). (b) K_2O and MgO content to identifies what kind of plant ashes was used in the glass making: "Levantine" or "Barilla" (Occari, Freestone and Fenwich 2021). *cl= Clear; db= Dark Blue; r= Red; t= Turquoise; w= White; pw= Production waste

Looking to K_2O and MgO content (Fig. 4.7b), one can note that great part of Lisbon fragments seems to be made by adding *barilla* to the glass batch while, combining data from both graphs in fig. 4.6, there is a strong indication that all analysed coloured layers of LCD_31 and LCD_54 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 & 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 regarding 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 has 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 are compatible with genuine Venetian production.

Fragment LCD 003 is an interesting sample 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 analysed *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 is 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. 4.7b).

4.2.1.3 Silica sources

Historical documents attest that Venetian glassmakers were using quartz pebbles from the Ticino and Adige rivers as silica sources (Verità 2013, Verità & 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 material 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 pebbles of quartz) and its geological setting (Occari, Freestone and Fenwick 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 & Degryse 2014, Verità & Zecchin 2009).

For this part the reduced composition (of the base glass) was used to compare them with what is reported in the literature as the base glass has been considered most closer with 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. 4.8 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. 4.8 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 et al. 2017), Spain (Coutinho et al. 2021) and Venice (Verità 1985, Verità and Zecchin 2008).

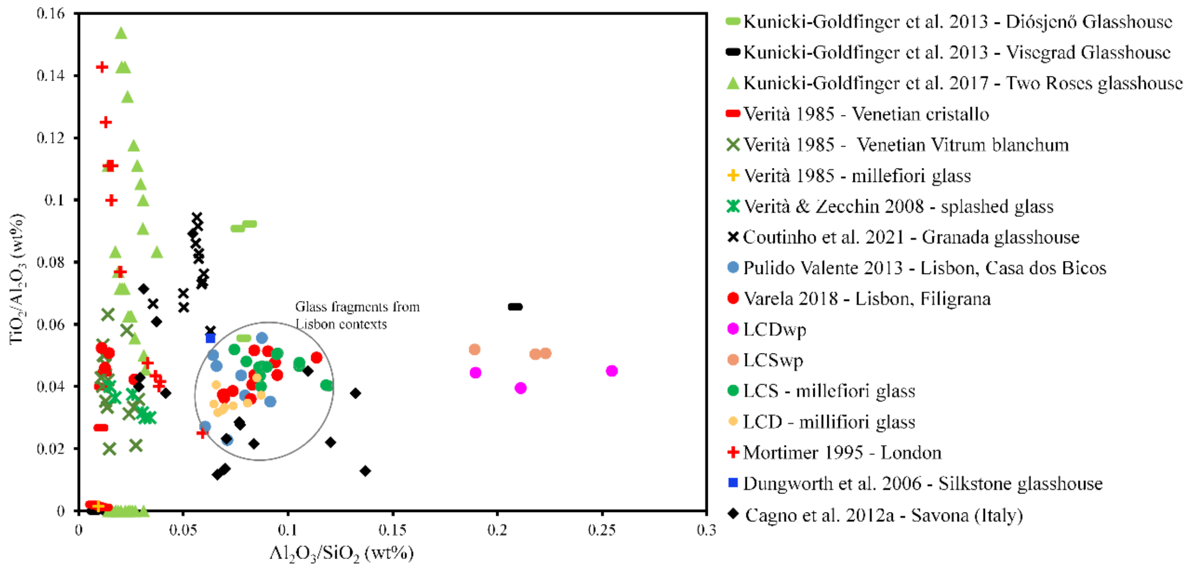


Fig. 4.8. Binary plot of TiO2/Al2O3 and Al2O3/SiO2 of LCD and LCS glass fragments and some contemporary glass fragment reported on the literature. The clusters are grouped based on the mineralogy of the glass making sands. *pw= production waste.

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. 4.8, they also appear spread through the graph.

Concerning Diósjenő glasshouse, its production is made by mixing 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. 4.8 – identified by red circles), were previously attributed to a Venetian production (Varela 2018).

Fig. 4.9 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.

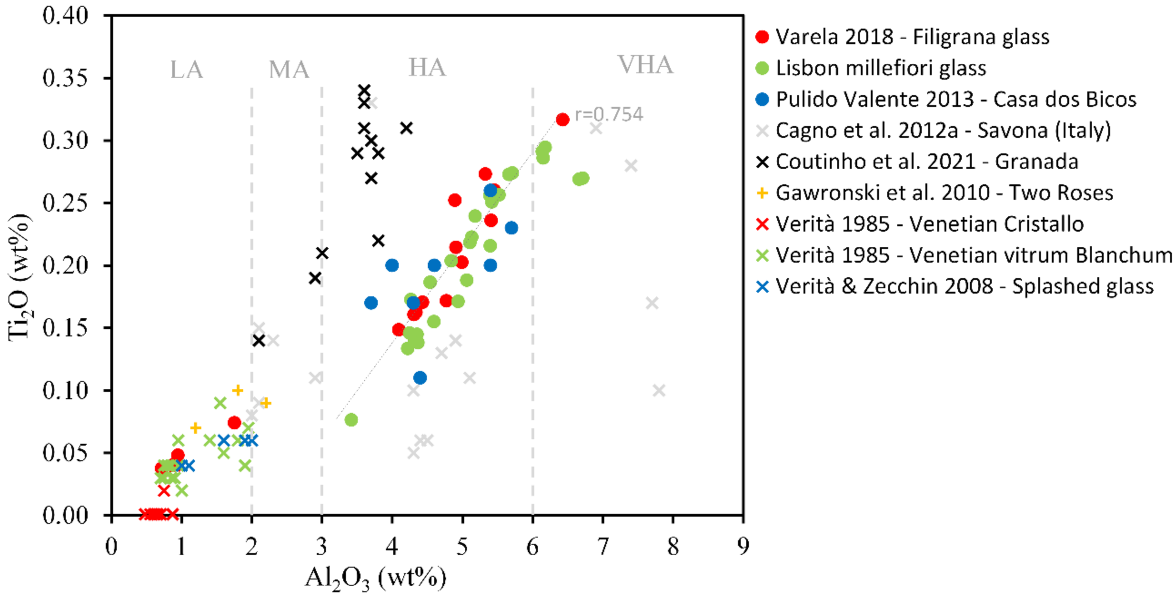


Fig.4.9: Binary chart of titanium and alumina content. *LA= Low Alumina, MA= Medium Alumina, HA= High Alumina; VHA= Very High Alumina; pw= production waste.

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 4wt% 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 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 and 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 & Willmott 2006, Šmit et al. 2005). This consideration is linked with the fact that Venetian glassmakers improved the clear glass recipe by using the best raw materials to produce it, so a lower content of minor, trace and REE suggests the use of a purer quartz source (Brems & Degryse 2014). Looking to trace elements such as Zr, no sample can be considered as having Venetian origin (Fig. 4.10).

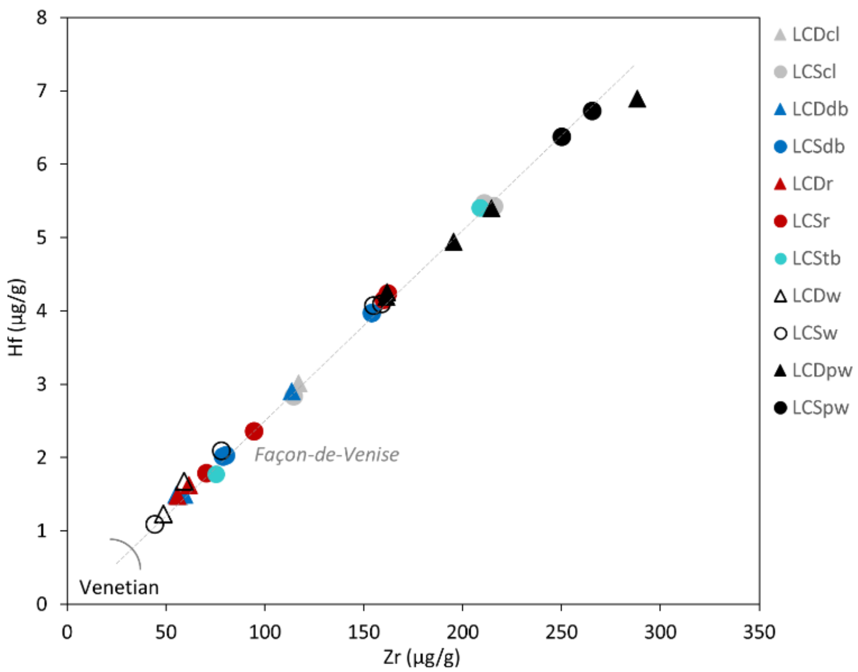


Fig. 4.10: Binary chart of zirconium vs. hafnium (Cagno et al. 2012c, De Raedt et al. 2002). *cl= Clear; db= Dark Blue; r= Red; t= Turquoise; w= White; pw= Production waste.

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 higher 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.

4.2.1.4 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, Simon, and Krons (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 & Degryse 2014, Kunicki-Goldfinger et al. 2008).

Fig. 4.11 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. 4.11) 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).

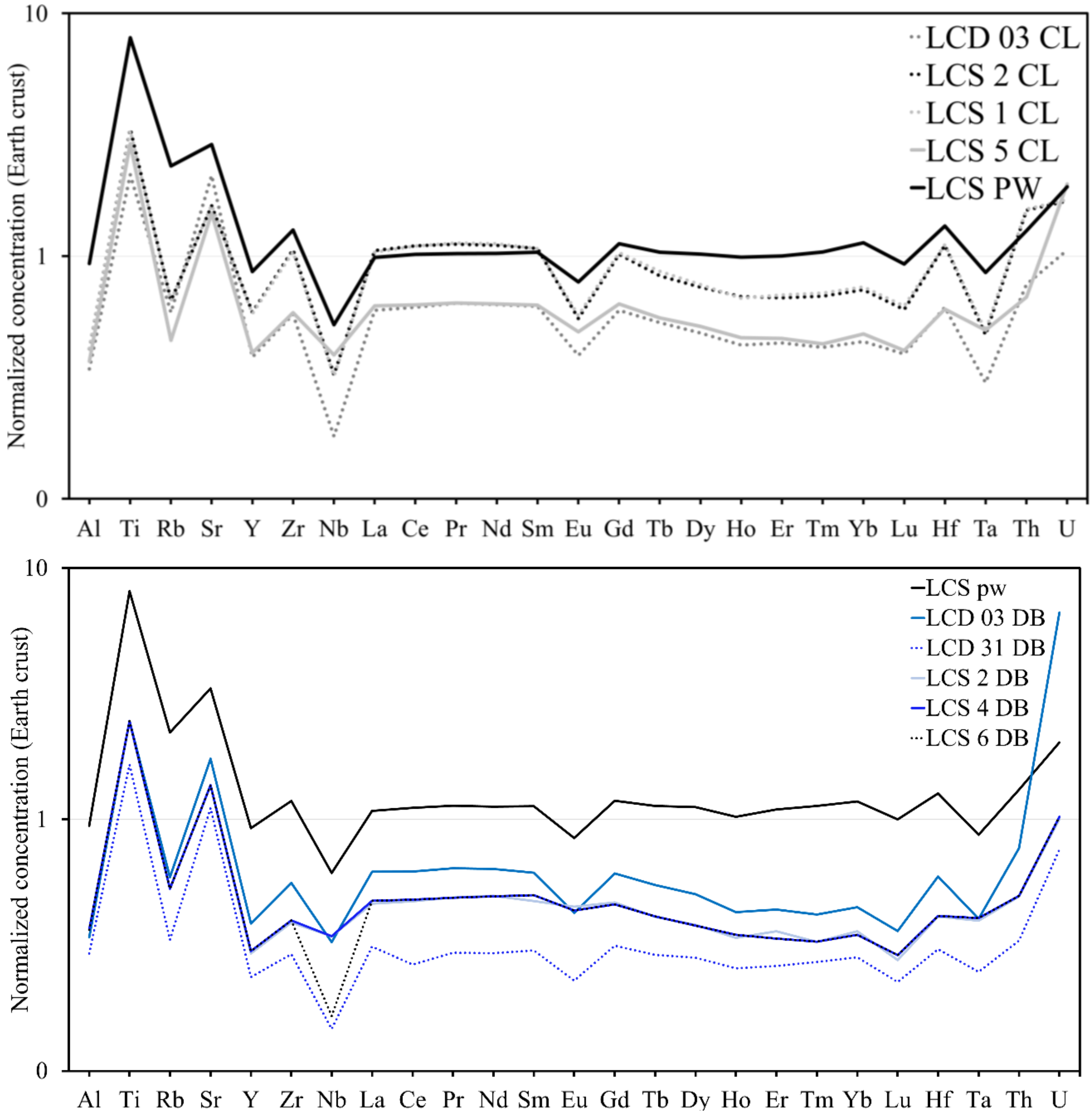


Fig. 4.11: Selected elements associated with silica sources of the samples normalized to the upper Earth crust and presented in logarithmic scale. *CL= Clear; DB= Dark Blue; pw = production waste.

In fig. 4.11 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 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).

4.2.1.5 Coloured glass

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

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 & Hreglich 2007, Verità & Zecchin 2008, Verità, Zecchin and Tesser 2018).

These glass pigments were also detected in contemporaneous *millefiori* and *splashed* glass fragments found in Portugal (Lima et al. 2012) and outside, for ex. 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 & 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. 4.12 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.

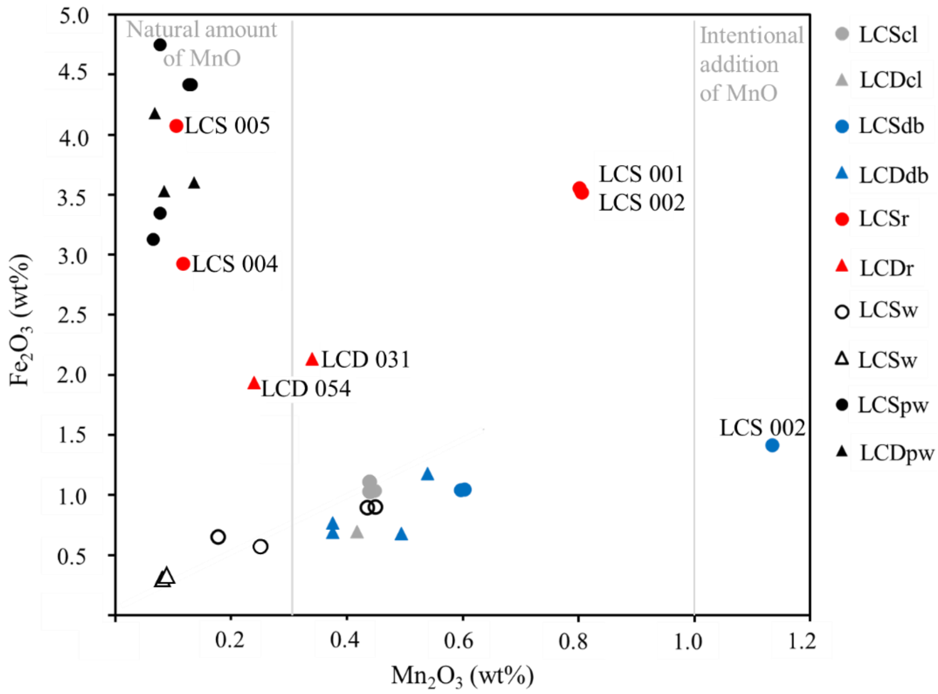


Fig. 4.12: Binary chart of MnO vs. Fe2O3. *cl= Clear; db= Dark Blue; r= Red; w= White; pw= Production waste

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 & 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 colour the glass.

MnO has a hight colouring effect (although 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 2016 p. 281). This is related with the redox conditions within the furnace and the glass batch itself.

4.2.1.6 4.2.1.5.1 Blue

Blue colour in *millefiori* glassware is the consequence of the presence of CoO in the glass matrix. Apart from LCD_03 fragment, all the other blue glasses have contents of CoO of 0.2 wt% or less (Tab. 5): this result being consistent with the results reported on the literature for beads (Dussubieux & Karklins 2016) and blown glass (Lima et al. 2012, Verità & Zecchin 2008, Verità, Zecchin and Tesser 2018). Nevertheless, LCD_03 has CoO levels that can be considered high (0.34 wt%) for blown glass (Verità & Biron 2015).

The content of MnO in LCS_02 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 & Zechhin, 2008).

Some oxides can suffer variations according to its geological origin and treatment (Thornton et al. 2014, p. 5; Verità & 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 (Tab. 4.2), 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).

Tab. 4.2. 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_03b	0.34	0.11	0.013	0.78	0.50
LCD_31b	0.16	0.06	0.007	0.22	0.07
LCD_54b	0.10	0.04	0.006	0.15	0.05
LCS_02m	0.20	0.05	0.015	0.38	0.26
LCS_04b	0.08	0.02	0.007	0.15	0.04
LCS_06b	0.08	0.02	0.007	0.15	0.04

b – body glass

m – *murrine* (decoration)

In blue layers, the amount of As_2O_3, NiO and Bi are increased when compared with the other coloured 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).

4.2.1.5.2 Red

In Roman times, copper oxide was already profusely used to produce red glass (Bandiera et al. 2020, Moretti & 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 & Gratuze 2000; Verità & Zecchin 2008).

Tab. 4.3. Chemical composition of the oxides that have been associated to red recipe in wt%.

Samples	Mn O	Fe_2O_3	Cu O	SnO_2	Sb_2O_3	Pb O
LCD_31m	0.28	1.41	1.97	0.24	0.01	0.30
LCD_54m	0.24	2.13	1.53	0.34	0.01	0.41
LCS_01m	0.80	3.56	1.61	0.16	0.01	0.17
LCS_02m	0.81	3.52	1.21	0.15	0.01	0.33
LCS_04m	0.12	2.93	1.51	0.15	0.01	0.15
LCS_05b	0.10	4.08	2.63	0.09	0.01	0.07
LCS_05bcl	0.37	1.76	1.21	0.07	<0.01	0.08

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

In Tab. 4.3, samples LCS_01 and LCS_02 are the only red glass colours that have a high MnO content (around 0.80 wt%). This result suggests that MnO was 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 & Zecchin 2008).

Moreover, the increased values of Fe_2O_3 showed in Fig. 4.12 [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 antimony and 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 & Zecchin 2008).

LCS_05 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_05 body glass presents some layers of clear glass (Fig. 4.13) 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).

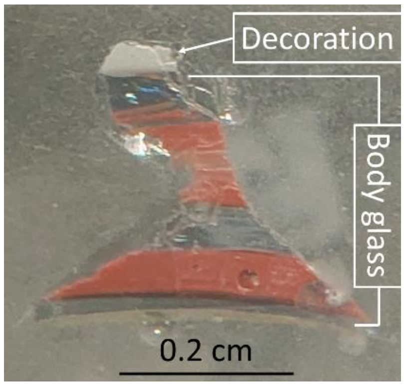


Fig. 4.13: LCS_005 *millefiori* glass fragment in cross-section showing the colorless layers in between the red glass layers.

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 should be noted 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.4.14). 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.

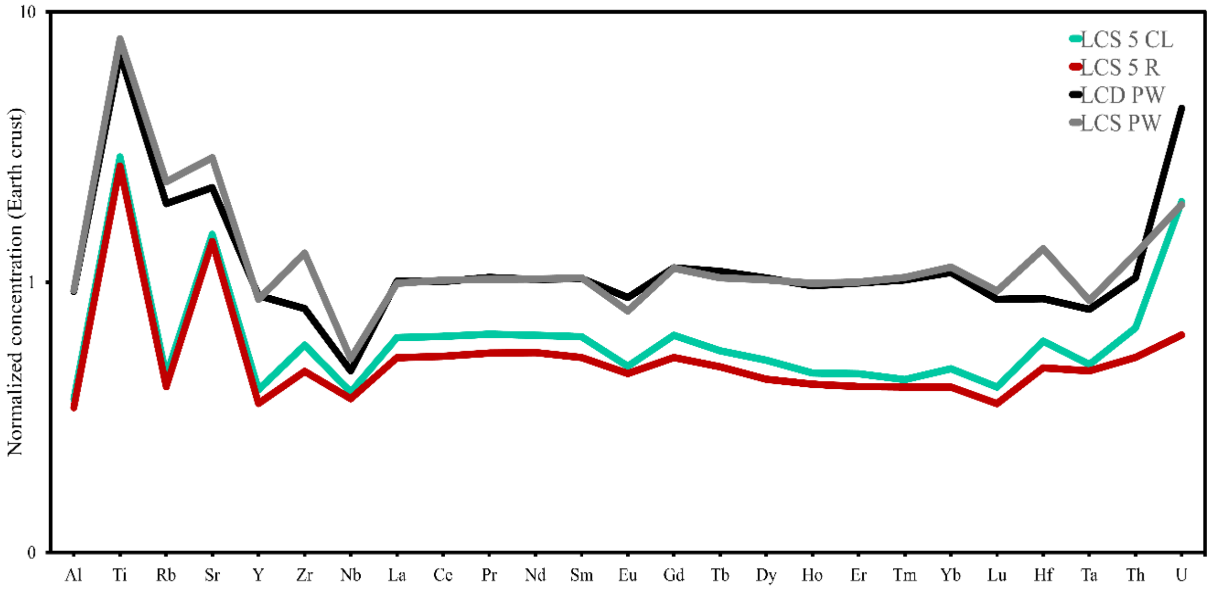


Fig. 4.14: Selected elements associated with silica sources of the samples normalized to the Earth crust presented in logarithmic scale. *cl= Clear; r= Red; pw= Production waste.

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 & Karklins 2016).

The analysed red glass layers used to decorate pick-up artefacts 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 & Willmott 2006, Verità & 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 1wt% (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 & Zecchin 2008, p. 111).

4.2.1.5.3 Turquoise

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 & 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) and in some beads of the Nueva Cadiz type unearthed in Lisbon (Veiga & Figueiredo 2002).

4.2.1.5.4 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 & Hreglich 2007). Although this opacifier does not belong to Venetian tradition, its presence in Venetian glassware was already detected (Veritá & 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 & Hreglich 2007, Verità, Zecchin and Tesser 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 & 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 & Rohanová 2015).

Tab. 4.4: Chemical composition of the oxides that have been associated to white recipe in wt%.

	P_2O_5	CaO	SnO_2	Sb_2O_3	PbO
LCD_54	0.18	3.38	16.65	0.01	21.04
LCS_01	0.43	5.60	6.69	0.02	13.04
LCS_02	0.41	5.36	10.87	0.02	10.89
LCS_04	0.33	3.84	13.85	0.01	17.46
LCS_05	0.29	4.95	11.45	0.02	21.92

The two oxides that are increased, when compared with the other glass layers, are SnO_2 and PbO (Tab. 4.4). 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 & Zecchin 2008).

4.2.1.7 Production waste/ Slag:

The chemical composition of PW has an amount of Na_2O between 1.5-5.6 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% (Tab. 4.1).

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. 4.7a and 4.7b) and those associated with silica sources (Fig. 4.8).
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 ºC, there are a sever loss of sodium by its volatilization (Rodrigues, Fearn & Vilarigues 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 (Rehren 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, Varela Gomes & Varela Gomes 2020).

On the contrary, despite the pronounced dark hue of the PW glass fragments, discernible streaks of lighter tones (Fig. 2.3 and 2.5) 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 (Fig. 4.7 and 4.8), 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. 4.7, 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%) (Appendix A.6).

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) (Fernández 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. 4.15).

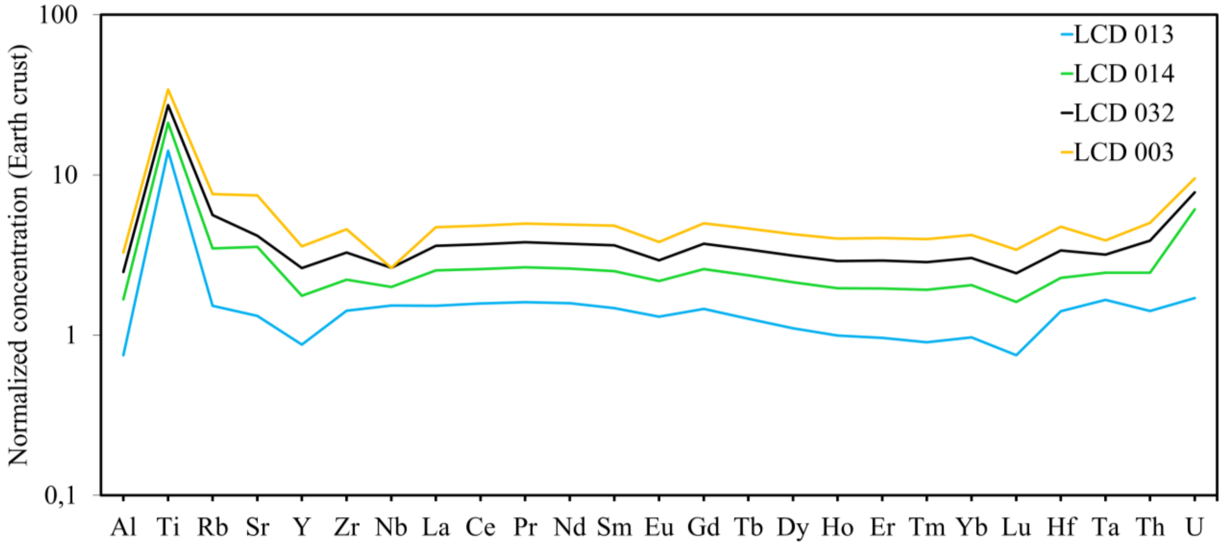


Fig. 4.15: Selected elements associated with silica sources of the samples normalized to the Upper Earth crust presented in logarithmic scale. *cl= Clear; r= Red; pw= Production waste.

Moreover, the geochemical patterns associated with PW appears in higher position when compared with the analysed glass artefacts (Fig. 4.11 and 4.14), this observation reinforce the idea that PW are less pure (less refined or selected) than the *millefiori* fragments (Lazar & 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.

4.2.1.8 Provenience summary

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 production waste 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 production waste 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.

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 a different content of these oxides was observed from the already known Venetian or *façon de Venise* production centres. Moreover, the tendency line of Al_2O_3 verses TiO_2 of Lisbon glass samples is also different from the already known Venetian or *façon de Venise* production centres.

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

All the analysed LCS glass samples were made with *barilla* as a 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 can reflect an improvement of recipe.

By looking at the coloured glass layers, it 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 having been made by using the flashed technique (to the author 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 in the glass matrix.

The production waste is also an interesting case study because the blue/amber colours 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 colour.

Looking at the provenance study, none of fragments can be considered of genuine Venetian production nor can be attributed to any known *façon de Venise* production centres. This result raises the possibility of Lisbon or Portuguese 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 time, by the original *rosette* patterns found in LCD (cross and *rosette* pattern) and LCS (caravel, concentric circles and flower), and by the geochemical patterns that group all pick-up glass fragments and production waste together.

4.2.1 SCV and SJT Contexts

4.2.1.1 Clear glass and base glass

As in previous Lisbon contexts, this part of thesis will begin by examining clear and base glass of *Santa Clara-a-Velha Monastery* (SCV) and *São João de Tarouca Monastery* (SJT). The analysis of glass colorants will be discussed subsequently.

To achieve the base glass of coloured glass, the oxides associated with colorants (such as cobalt, copper, iron, and manganese), opacifiers (including antimony and tin), and other relevant elements (such as arsenic, bismuth, lead, nickel, etc.) were subtracted from the main composition and then normalized to 100% (Tab. 4.5).

Tab. 4.5: 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%.

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2
SCV_044	Blue	Cane	17.4	2.8	7.0	59.2	0.37	0.88	4.57	7.51	0.29
SCV_232		Body	11.0	3.1	2.1	67.8	0.27	0.72	4.77	10.17	0.07
SCV_245		Cane	15.5	3.3	4.4	60.9	0.34	0.77	5.60	8.98	0.19
SCV_250		Cane	14.5	3.6	1.5	66.8	0.31	0.90	2.22	10.18	0.06
SCV_329		Body	11.5	3.0	3.4	63.7	0.34	0.68	7.46	9.77	0.09
SCV_357		Body	18.7	3.1	4.1	31.3	0.32	1.11	3.55	7.62	0.14
SCV_360		Body	15.7	3.0	2.2	66.0	0.30	0.99	3.95	7.69	0.11
SCV_360		Cane	16.2	2.9	2.3	65.9	0.34	1.00	4.27	7.02	0.11
SCV_364		Cane	12.4	3.0	1.1	69.5	0.28	0.83	5.83	7.06	0.05
SCV_365		Body	17.6	2.0	3.4	66.9	0.43	1.10	3.83	4.53	0.23
SCV_365		Cane	16.3	2.7	3.3	65.5	0.46	0.93	3.91	6.80	0.15
SCV_366		Cane	13.0	3.6	1.2	70.0	0.22	0.72	2.30	8.93	0.07
SCV_368		Body	15.8	2.7	3.4	65.8	0.48	0.85	3.97	6.79	0.15
SCV_368		Cane	17.4	2.0	4.5	66.9	0.43	1.11	3.89	4.53	0.23
SCV_369		Body	18.0	3.1	4.1	61.1	0.35	1.03	4.79	7.32	0.16
SCV_369		Cane	17.7	3.2	4.2	61.1	0.33	1.00	4.76	7.47	0.16
SCV_375		Body	18.6	2.8	4.0	62.5	0.30	1.17	3.03	7.35	0.15
SCV_388		Body	18.8	2.9	3.9	62.5	0.37	1.19	3.32	6.87	0.18
SCV_394		Body	17.3	1.9	0.9	68.4	0.37	1.28	3.95	5.90	0.06
SJT_001		Body	12.7	3.6	4.4	59.1	0.42	0.69	7.34	11.52	0.14
SJT_009		Body	14.0	3.7	3.5	60.6	0.33	0.65	7.48	9.73	0.08

Tab. 4.5: 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% (Continued).

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2
SCV_044	Clear	Body	21.3	2.9	7.2	58.7	0.35	1.19	4.19	3.87	0.34
SCV_046		Body	15.0	3.1	7.2	64.6	0.32	0.80	0.73	8.22	0.08
SVC_235		Body	14.9	3.0	3.6	64.3	0.23	0.70	5.13	8.01	0.18
SVC_236		Body	14.2	3.1	5.5	60.1	0.26	0.72	6.89	8.99	0.24
SVC_245		Body	15.6	3.6	4.8	60.3	0.35	0.86	5.68	8.63	0.21
SVC_250		Body	15.6	3.1	5.7	62.9	0.31	0.97	3.83	7.43	0.21
SCV_272		Body	19.1	7.1	7.7	57.0	0.84	0.99	1.89	5.09	0.30
SCV_275		Body	16.4	5.4	5.4	66.4	0.38	0.99	1.38	3.33	0.29
SCV_394		Cane	17.3	1.9	1.6	67.2	0.70	1.30	3.47	6.11	0.07
SCV_232	Green	Cane	11.1	3.2	2.2	66.7	0.26	0.85	5.01	10.48	0.08
SCV_368	Purple	Cane	15.9	2.7	3.4	65.8	0.48	0.88	3.92	6.74	0.15
SCV_044	Red	Cane	17.6	3.0	7.4	58.1	0.57	0.86	4.88	7.19	0.35
SCV_216		Cane	17.9	3.2	4.3	61.6	0.42	1.04	3.97	7.39	0.18
SCV_232		Cane	11.1	3.1	2.3	67.1	0.28	0.80	4.98	10.25	0.08
SCV_235		Cane	14.5	3.9	1.5	65.5	0.34	0.78	2.72	10.66	0.08
SCV_245		Cane	15.4	3.3	4.1	61.7	0.36	0.72	5.37	8.87	0.18
SCV_250		Cane	14.6	3.6	1.3	66.9	0.38	0.75	2.40	9.99	0.06
SCV_275		Cane	14.9	3.7	1.3	66.6	0.37	0.75	2.38	9.86	0.06
SCV_329		Cane	11.9	3.3	1.9	67.6	0.36	0.75	4.59	9.56	0.09
SCV_357		Cane	17.8	3.7	4.7	60.8	0.41	1.03	3.59	7.88	0.16
SCV_360		Cane	16.0	3.0	3.1	65.6	0.38	0.84	3.92	7.04	0.14
SCV_364		Cane	12.5	3.0	1.2	69.1	0.31	0.80	5.79	7.17	0.05
SCV_369		Cane	17.1	3.6	4.4	60.8	0.46	0.95	4.29	8.32	0.18
SCV_375		Cane	17.7	3.6	4.4	61.0	0.41	1.09	3.73	7.82	0.16
SCV_388		Cane	17.4	3.6	4.7	61.8	0.44	0.98	3.32	7.62	0.19
SCV_394		Cane	15.6	2.7	2.1	67.9	0.52	0.90	3.42	6.73	0.11
SJT_001		Cane	14.6	3.3	4.1	60.6	0.41	0.72	6.76	9.25	0.12
SJT_009		Cane	14.3	3.7	3.6	60.3	0.36	0.62	7.52	9.61	0.08
SCV_216	Turquoise	Body	15.0	3.5	2.5	65.5	0.35	0.82	2.94	9.29	0.10
SCV_250		Cane	18.4	2.9	3.9	62.9	0.38	1.10	3.91	6.41	0.18
SCV_329		Cane	10.0	2.2	5.2	65.8	0.36	0.63	6.73	8.99	0.16
SCV_364		Cane	12.4	3.0	1.0	68.8	0.28	0.82	5.62	7.99	0.04
SCV_365		Cane	15.6	2.9	3.0	66.4	0.43	0.96	3.61	7.01	0.13
SCV_366		Cane	14.4	2.0	2.1	70.1	0.29	0.91	3.15	6.96	0.04
SCV_368		Cane	15.4	3.0	3.0	66.3	0.43	0.92	3.58	7.26	0.13
SCV_369		Cane	18.1	4.6	4.6	62.3	0.36	1.17	4.58	6.22	0.17
SCV_388		Cane	18.5	3.9	3.9	63.1	0.37	1.18	3.71	6.26	0.17
SJT_001		Cane	12.9	3.7	5.1	58.4	0.38	0.78	7.29	11.29	0.17
SCV_044	White	Cane	15.8	2.3	5.9	62.5	0.41	1.81	4.53	6.50	0.25
SCV_216		Cane	11.2	2.9	1.8	68.7	0.30	0.81	4.90	9.33	0.07
SCV_232		Cane	15.5	3.0	4.8	61.7	0.39	0.86	5.67	7.85	0.20
SCV_245		Cane	14.8	3.5	0.9	67.2	0.39	0.71	2.27	10.17	0.05
SCV_250		Cane	17.3	2.6	3.7	64.4	0.40	1.66	3.42	6.31	0.16
SCV_329		Cane	12.7	3.5	1.4	67.1	0.31	0.72	4.43	9.79	0.06
SCV_360		Cane	15.7	3.0	2.1	66.8	0.37	1.13	3.43	7.43	0.10
SCV_364		Cane	12.1	2.9	1.6	69.9	0.29	0.92	5.59	6.63	0.04
SCV_365		Cane	18.0	2.2	2.9	66.2	0.60	1.34	3.64	4.94	0.20
SCV_368		Cane	18.6	1.9	2.8	66.4	0.80	1.57	3.47	4.21	0.24
SCV_369		Cane	18.9	3.3	4.0	61.4	0.44	1.39	3.68	6.77	0.15

Tab. 4.5: 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% (Continued).

Sample	Color	Part	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2
SCV_375	White	Cane	17.7	3.1	3.5	64.0	0.34	0.74	3.34	7.18	0.13
SCV_388		Cane	19.4	2.7	3.3	63.4	0.40	1.54	3.10	5.88	0.16
SCV_394		Cane	18.9	1.6	1.1	66.1	0.90	2.22	3.73	5.32	0.08
SJT_001		Cane	15.0	3.7	2.7	62.6	0.34	1.06	6.03	8.47	0.09
SJT_009		Cane	13.9	3.5	3.1	61.9	0.38	0.87	7.35	8.93	0.07

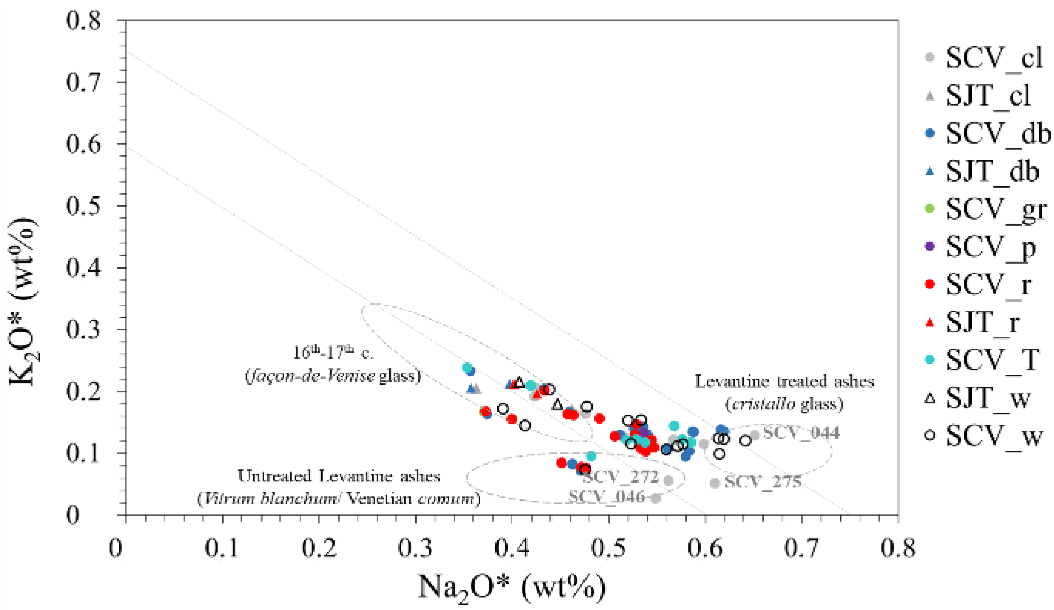
The reduced composition was used as representative of the original clear glass, enabling a comparison of the main oxides with coeval Venetian and *façon de Venise* glass data published in the literature (e.g., Biron and Verità 2012, p. 2710; Lima et al. 2012, p.1240; Thornton et al. 2014, p. 6; Verità 1986, p. 243; Verità and Biron 2015, p. 180). In clear glass the considered composition was the total of oxides (without the normalization) as it was considered that the presence of colorants, opacifiers and related elements were intentionally added to decolorize or were introduced unintentionally throughout the raw materials.

4.2.1.2 4.2.3.2 Alkali source

The values of Na_2O between 10.0-21.2 wt%, K_2O of 0.7-7.5 wt% and CaO of 3.33-11.52 wt% are consistent with soda-lime-silica glass type. This type of glass was made by using halophytic plant (that grow in salty soils) ashes as fluxing agent (Lima et al. 2012).

To distinguish and predict different kind 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, Coutinho et al. 2016, Janssens et al. 1998). Na_2O^* and K_2O^* are calculated 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).

As expected, due to the results of previous studies where SCV glass fragments were chemically investigated (Coutinho et al. 2016 and 2017, Lima et al. 2012), this glass fragments appeared dispersed throughout the different sodic alkali sources profusely used in 16^{th} and 17^{th} centuries (Fig. 4.16 (up)). In this context, glass composition comparable to Venetian and *façon de Venise* production were already detected in *splashed* and *millefiori* (Lima et al. 2012), *filigrana* (Coutinho et al. 2016), gourd-shape vessels (Coutinho et al. 2017), amongst others.



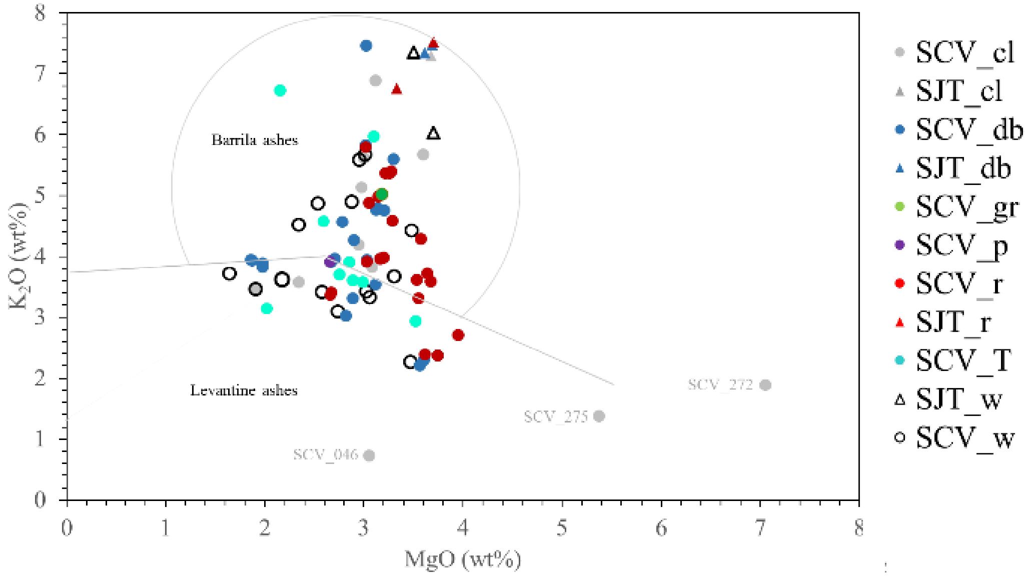


Fig. 4.16. (Up) Normalized Na2O* (Na2O/(MgO+P2O5+K2O+CaO)) and K2O* (K2O/ (Na2O+ MgO+P2O5+CaO)) are plotted with the correlation lines Na2O*+K2O*=0.6 and 0.75 indicating the use of, respectively, unpurified, and purified ashes. (Down) K2O and MgO content to identifies what kind of plant ashes was used in the glass making: "Levantine" or "Barilla" (Occari, Freestone and Fenwich 2021). *cl= Clear; db= Dark Blue; gr= green; p= purple; r= Red; t= Turquoise; w= White; pw= Production waste

As mentioned earlier in the second chapter, the SCV Monastery holds significant historical and cultural importance due to its association with Holy Queen Isabel, who was canonized by Pope Urban VIII in 1625. This canonization event likely attracted numerous pilgrims, resulting in the potential donation of objects as offerings. Additionally, it is possible that some of the high-quality glassware discovered at the site could have belonged to noble women who joined the monastery.

According to our data, clear glass from SCV 044, 046, 272, 275 and 394 (*murrine*), dark blue glass layer from SCV 250, 365 (body), 366 and 368 (body), red glass from SCV 235 and 275, turquoise glass from SCV 250 and white glass from SCV 250, 365, 368, 388 and 394 were produced by using Levantine plant ashes. The underlined glass layers represent the analysed glass samples which exhibit a composition compatible with *cristallo* glass (purified Levantine ashes). Moreover, clear glass from SCV 235, 236, 245 and 364 (*millefiori* cane), blue glasses from SCV 232, 329 (body) and 364, green glass from SCV 232, red glasses from SCV 232, 245, 329 and 364, turquoise glasses from SCV 329 and 364 and white glasses from SCV 245, 250, 323, 329 and 364 are in the 17th century *façon de Venise* glass region (fig. 4.16 up). The other part of glass fragments are distributed between the two correlated lines that represent the use of unpurified and purified ashes.

While the presence of tin and lead oxides constitutes approximately 20 wt% of the total composition of the white glass, which may impact the reduced composition, the observation about its fluxing agents was here discussed.

Fig. 4.16. down is an adaptation of Occari, Freestone and Fenwich (2021) work to align its information with the results obtained in the left graph. Interesting to note is, when comparing both graphs the number of glass layers made with *Levantine* plant ashes increase in the right graph (SCV_216T and W, SCV_250cl, r, SCV_357b, SCV_360db, body and w, 365db and t,SCV_366T, SCV_368db, t and p, SCV_369r, SCV_375dbBody and w, all the glass layers of SCV_388 and SCV_394r), in this chart the difference between treated and untreated ashes are not identified.

While SCV glass fragments are dispersed in both graphs of Fig. 4.16, all the coloured glass layers belonging to SJT and some SCV *millefiori* fragments are located in the "16th and 17th century *façon de Venise* glass" (up) and “*Barilla*” (down) regions. This observation suggests that

Levantine ashes were not used as flux agent in the production of the analysed SJT glass fragments. It is worth noting that the potassium enrichment observed can also be attributed to different factors such as the use of silica sources rich in feldspars or intentional addition of calcined tartar (*gripola di vino*, k-carbonates), which was widely used in glass production since the 15th century (Moretti & Hreglich, 2013, pp. 27-30; Verità et al., 2018, p. 243).

According to available literature, it has been stated that the stability in composition of raw materials used in the production of Venetian glass has been considered essential for ensuring the production of this high-quality glass material (Veritá, 2013, p. 533). This observation makes improbable a Venetian attribution of SJT and a major part of SCV glass based on its fluxing agents.

Barilla plant ashes are sodic plant ashes of lower quality compared to the ashes imported from the Levant region. *Barilla*, also known as *salicorn* or *kali* grows in various regions, including the Iberian Peninsula, along the Lido, Venetian coast, and the Po River. Different sources of sodic plant ashes can contribute to variations in the composition and quality of glass produced (Moretti & Hreglich 2007, 30).

To highlight, in Fig. 4.16 (up), the "clear" glass falling within the "*Levantine plant ashes*" region displays distinct intense natural hues: 1) amber in SCV 394 *murrine*, 2) greyish in the body glass of SCV 44 little flask fragment, 3) greenish in the body glass of SCV 46 gourd-shape vessel fragment, and 4) yellowish in the body glass of SCV 272 and 275 fragments. Additionally, the clear glass within the *façon de Venise* region appears more discoloured (e.g., SCV 235, 236, and 245). More decolorized and transparent is SCV 250 body glass which falls between the two correlated lines. These observations open some questions such as: 1) can this observation indicate that "clear" glass, which was produced with *Levantine* ashes composition, based on its fluxing agent, is a result of glass recycling instead of intentional production? 2) If the answer is yes, why? 3) Is it linked to aesthetic issues or the preservation purpose of its content?

Interesting to note is the clear body glass of SCV_046 which presents a significant amount of lead (2.4 wt%), copper (0.7 wt%) and tin (2.3 wt%) but can still be classified as "*vitrum blanchum*". Its hue can be a consequence of the unintentional addition of small amounts of coloured/ opaque glass **presented in cullet** (Cagno et al. 2012b). Comparable amount of PbO in clear glass fragments found in SCV were already detected in previous studies: (1) 2.83 wt% of PbO in the clear body glass of V_74 plashed glass fragment (Lima et al. 2012) and (2) 1.89 wt% of PbO in the body glass of the SCV_210 gourd-shape vessel fragment (Coutinho et al. 2017) (Fig. 4.17).

Fig. 4.17: Image of the glass fragment V_74 analysed by Lima and co-authors (2012).

Can this observation be strictly justified by glass recycling?

In an investigation focused on "*trace element analysis in provenancing on Roman glass-making*" the authors (Brems & Degry 2014 p. 120) pointed that concentrations of trace elements associated to (de)colorants (Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, In, Sn, Sb, Au, Hg and Pb oxides) over 0.1 wt% "suggest that they were deliberately added to the glass batch to influence the colour" while the content of these oxides between 100 and 1000 μg/g can be interpreted as glass recycling.

Note that the yellowish body glass fragments, SCV_272 and SCV_275, which employed Levantine ashes as a fluxing agent (as indicated by the results shown in Fig. 4.16), exhibit low concentrations of CoO, CuO, SnO_2, Sb_2O_3, and PbO, all below 10 μg/g while, MnO and Fe_2O_3 are present at approximately 1 wt% and 1.5 wt%, respectively. This observation suggests two possibilities: either no cullet was used, or a carefully selected cullet was incorporated into the glass batch along with purer alkali sources.

Bering in mind that for decolorised soda plant ash the ratio between MnO and Fe_2O_3 should be greater than 2 (i.e. $MnO/Fe_2O_3>2$) and, for clear glass, this ratio is lower than 0.94, one can infer that yellowish hue of SCV_272 and SCV_275 body glass are the result of a partial discoloration.

Furthermore, the UV-visible spectrum analysis of the colourless body glass fragments (Fig. 4.18) revealed the distinct influence of Co^{2+} and Fe^{2+} and Fe^{3+} ions within the glass matrix. It is evident that the final colour of clear body glass of SCV_235, SCV_236, and SCV_245 (made with barilla ashes) is influenced by cobalt (bands at 540 nm, 590 nm, and 640 nm) and iron (bands at 380 nm, 420 nm, and 440 nm) (Coutinho 2016, p. 72; Fernández 2003, p. 457).

The presence of cobalt oxide in clear glass is not common however, it has been reported in a few contemporaneous *façon de Venise* glass found in Portugal (Coutinho et al. 2016, p. 446).

Based on Fig. 4.19, it is possible to note that both yellowish body glass of SCV_272 and SCV_275 (made with Levantine ashes) fragments are more influenced by iron ions than the colourless body glass of SCV_250 (which seems to be made by a mixture of ashes).

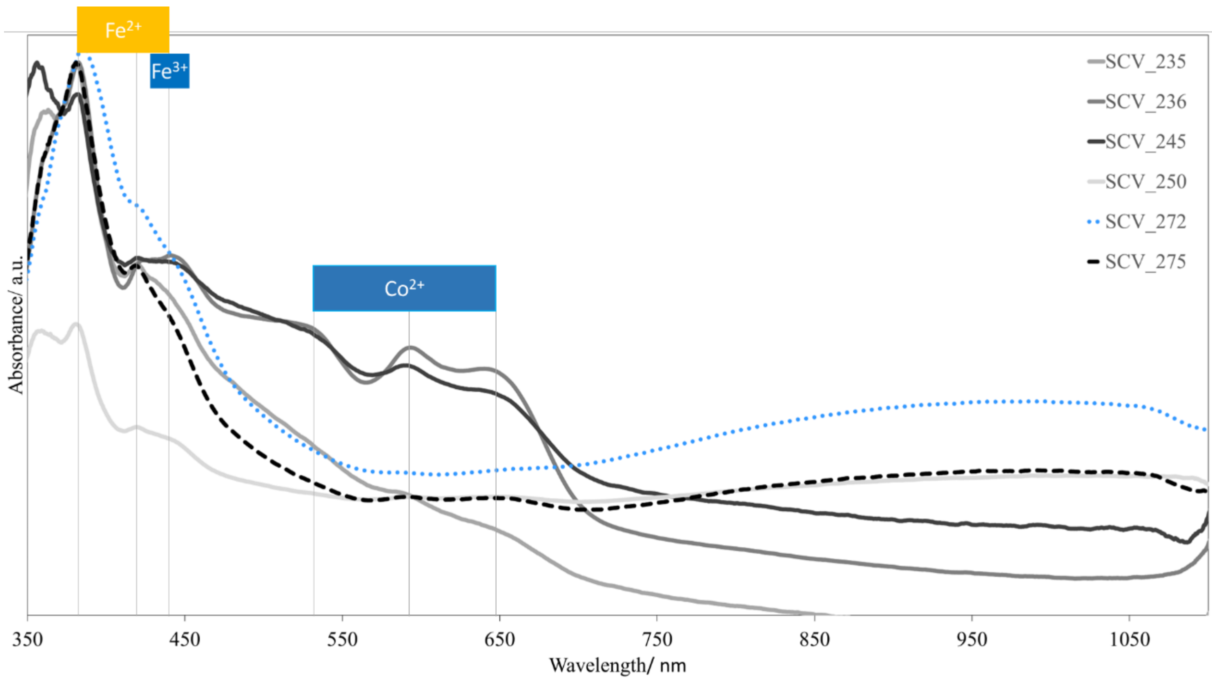


Fig. 4.18: UV-Vis absorption spectrum of the clear body glass performed on SCV (235, 236, 245, 250, 272 and 275) fragments revealing the discernible influence of Co^{2+} and Fe^{2+} and Fe^{3+} ions within the glass matrix.

Moreover, based on fluxing agents, the clear body glass of SCV 250 exhibits a distinct composition when compared with blue, turquoise, and white colours of *murrina* canes that decorate it and which are made by using unpurified Levantine ashes. This evidence was already noted by Lima and co-authors (2012) for some SCV *millefiori* glass fragments and by Verità and Zecchin (2008) on a Venetian splashed glass goblet dated to the 16th Century, where the canes' composition does not match the one of the object's bodies.

SCV_329 is a small flask/ bottle where the chemical composition of body glass and *murrina* all fall in the *façon de Venise* region of the graph and *barilla* seems to be used in its production due to its high amount of K_2O.

Regarding *millefiori* canes it is interesting to note that although all the layers of SCV 364 cane are situated in *façon de Venise* of 16th and 17th centuries region, the blue layer of SCV 366 falls within the *cristallo* region but the turquoise colour is positioned between the two correlated lines on left graph. These results indicate that glass from different origins and/ or with different recipes could have been combined to create the intricate designs that can be observed in *millefiori* decorated glass objects.

4.2.1.3 4.2.3.3 Silica sources

Historical documents attest that Venetian glassmakers were using quartz pebbles from the Ticino and Adige rivers as silica sources (Verità 2013, Verità & 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).

For this part the reduced composition (of the base glass) was used to compare our data with the reported data on the literature as the base glass has been considered most closer with the original glass before the addition of glass colourants (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 1986, p. 243).

The content of SiO_2, TiO_2, and Al_2O_3 have a paramount importance in tracking the origin of raw material 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 pebbles of quartz) and its geological setting (Occari, Freestone and Fenwick 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 & Degryse 2014, Verità & Zecchin 2009).

In Fig. 4.19 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).

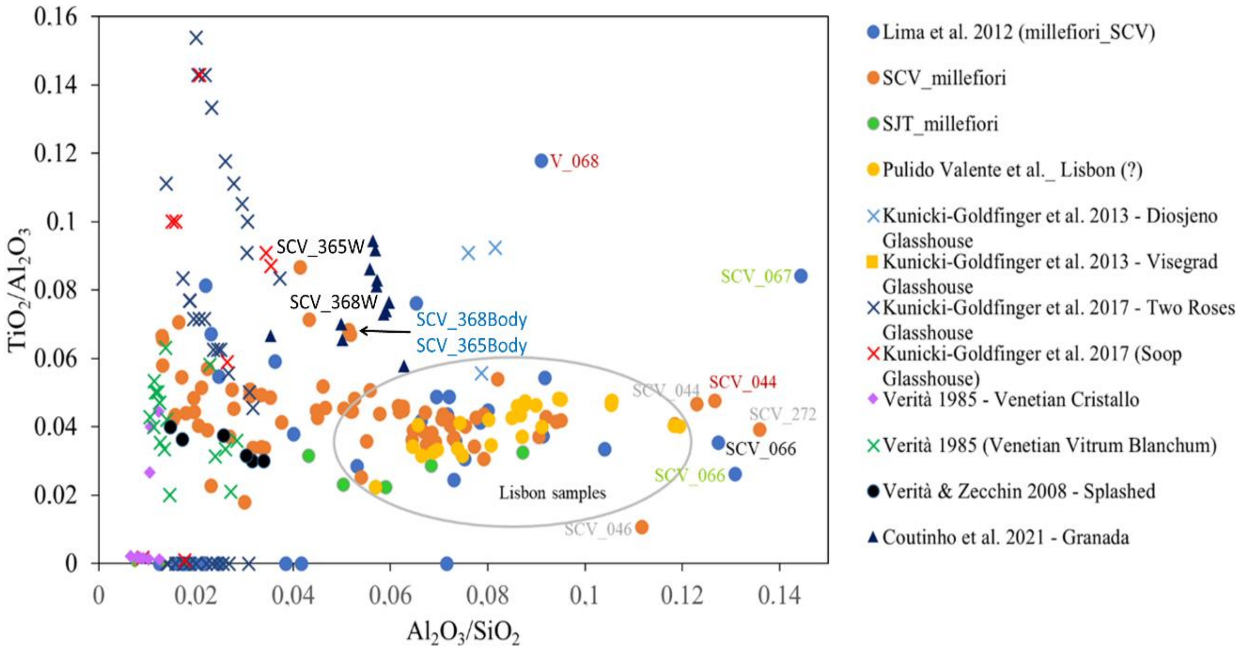


Fig. 4.19: Binary plot of TiO_2/Al_2O_3 and Al_2O_3/SiO_2 of SCV (orange circle) and SJT (green circle) glass fragments treated in this thesis and some contemporary glass fragment reported on the literature. The clusters are grouped based on the mineralogy of the glass making sands.

Fig. 4.19 shows that both SCV and SJT contexts are spread and mixed with the different considered contexts: Lisbon (Pulido Valente et al. 2023), Low Countries (Kunicki-Goldfinger et al. 2017), Spain (Coutinho et al. 2021) and Venice (Verità 1985, Verità and Zecchin 2008).

When comparing the alkali source with the information taken from Fig. 4.19, it is interesting to note that the previously considered *cristallo* glass of SCV_044cl, SCV_275cl and SCV_394cl and previously considered "*untreated Levantine ashes*" of SCV_272cl and SCV_275cl, falls in Lisbon samples region of the graph.

Moreover, SCV_368bBody and SCV_368w, both probably made with purified Levantine ashes (*cristallo*) are located, respectively, in Granada and between Granada and De Twee Rozen glasshouse area of the Fig. 4.19.

Based on the available data, it appears that only SCV_275r and SCV_360w glass fragments may have been produced using raw materials compatible with Venice. It is worth noting that the *splashed* SCV_275 glass fragment exhibits a yellowish body glass, which was made using purified Levantine ashes. Additionally, the blue *millefiori* SCV_360 glass fragment displays a delicate pattern of a four-petal flower, which is particularly unique and not found outside of Portugal, to the authors knowledge (Fig. 4.20).

Fig. 4.20: Flower pattern of SCV_360 glass fragment.

The hypothesis that the red and white colours of those fragments (respectively, SCV_275 and SCV_360) may have been imported from Venice and subsequently worked to create the corresponding decoration patterns must be taken into consideration.

Zirconium (Zr) and hafnium (Hf) have been extensively utilized for distinguishing different glass sources (e.g., Cagno et al., 2012b; Coutinho et al., 2016; De Raedt et al., 2001). It is widely accepted that Venetian glass exhibits the lowest Zr content (< 30 μg g–1), whereas glass production centres of *façon de Venise* display higher levels of these elements (De Raedt et al., 2001; Lazar & Willmott, 2006; Šmit et al., 2005). This observation is linked to the fact that Venetian glassmakers enhanced the clarity of their glass by utilizing superior-quality raw materials, which include purer quartz sands (Brems & Degryse, 2014).

By consolidating all the available data, including the information provided thus far and referring to Fig. 4.21, it becomes evident that the number of glass layers associated with the Venetian production region on the graph is actually lower than initially anticipated:

- Clear: SCV (364 and 394).
- Blue: SCV (250, 364, 366 and 394).
- Red: SCV (235, 250, <u>275</u>, 329 and 364).
- Turquoise: SCV_366.
- White: SCV (232, 250, 329, <u>360</u>, 364 and 394), SJT (01 and 09).

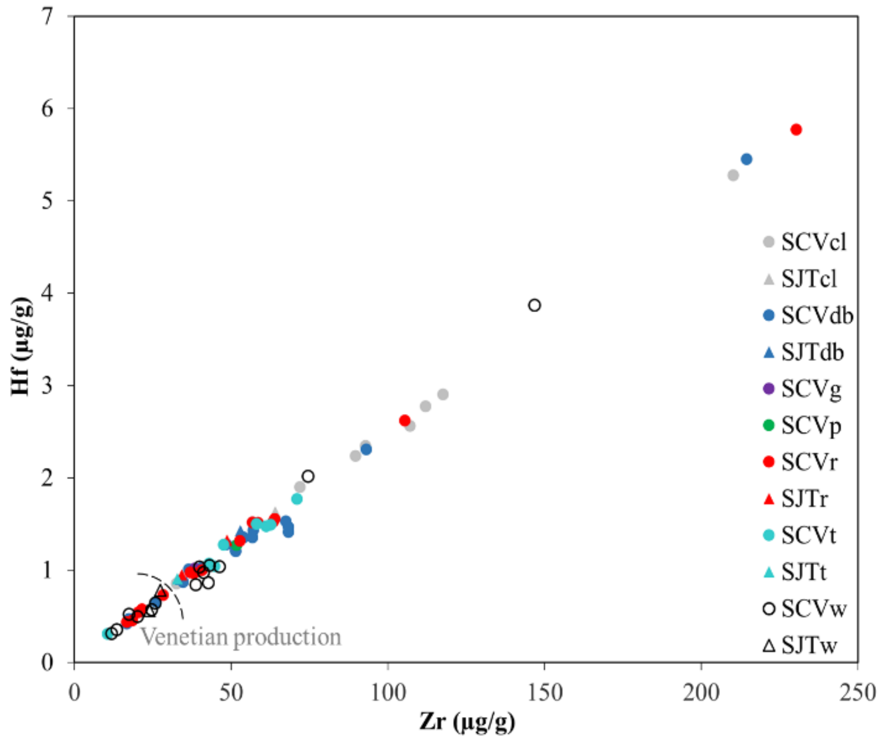


Fig. 4.21: Binary chart of zirconium vs. hafnium (Cagno et al. 2012b, De Raedt et al. 2002). *cl= Clear; db= Dark Blue; g= green; p= purple; r= Red; t= Turquoise; w= White

However, SCV_275r and SCV_360w remains compatible with Venetian production. All data seems to indicate that all clear glass and the main-coloured glass layers of *pick-up* fragments belonging to SCV and SJT assemblages were produced outside Venice.

4.2.1.4 4.2.3.4 Glass colourants

Concerning the coloured glass, LA-ICP-MS, µ-PIXE and µ-RAMAN provided information about the colourants 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 & Hreglich 2007, Verità & Zecchin 2008, Verità et al. 2018).

As mentioned in the previous chapter, iron and manganese oxides can be unintentionally introduced in the glass matrix through raw-materials or deliberately added by glassmakers to make clear or coloured glass.

To understand how MnO and Fe_2O_3 influence each colour a binary chart was built (Fig. 4.22).

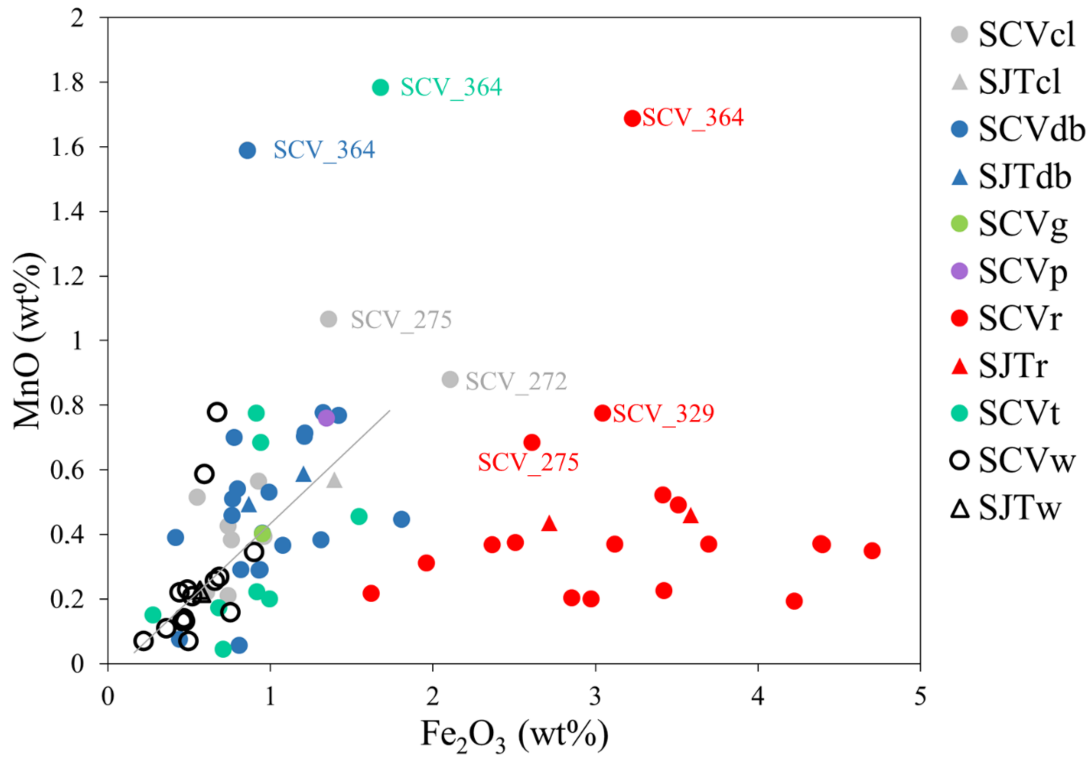


Fig. 4.22: Binary chart of MnO vs. Fe_2O_3. *cl = Clear; db = Dark Blue; g = Green; p = Purple; r = Red; t = Turquoise Blue; w= White.

Fig. 4.22 illustrates a positive correlation between Fe_2O_3 and MnO in most clear, blue, green, purple, and white glasses. This evidence suggests that their presence in the glass matrix is probably unintentional.

The yellowish body glass fragments of SCV_272 and SCV_275 exhibit the highest concentration of both oxides in clear glass (considered as natural hues). Combining this observation with previous findings (Levantine ashes as fluxing agent, high content of feldspars, the absence of glass recycling evidence) it is possible to infer that the raw material used in their production was probably enriched in iron and manganese oxides. Other possibility for this positive correlation (Fig. 4.22) can be viewed as a recipe improvement whereas, the higher content of Fe_2O_3 in the glass batch requires an increased addition of MnO to oxidise the ferrous ion (Fe^{2+}) into ferric ion (Fe^{3+}) and thus convert MnO_2 into MnO (almost colourless) (Lima et al. 2012; Volf 2011, p. 343).

Manganese oxide exhibits a strong colouring ability and can impart a deep purple hue, even at concentrations as low as 1.1 wt% (Coutinho, 2016, p. 281). However, its effects are highly dependent on the redox conditions within the furnace and the composition of the glass batch. Therefore, the addition of this element should be approached with caution. Blue, red and turquoise colours observed in SCV_364 sample (*millefiori* cane) exhibit an MnO enrichment (around 1.7 wt%) when compared with the other samples (Fig. 4.22). This evidence suggests that MnO was intentionally added into the glass batch to either reduce the hue of the clear base glass or to intensify the final colour.

As observed to the other red samples, the intentional addition of Fe_2O_3 is evident when compared SCV_364 red glass layer with blue and turquoise colours of the same sample. Furthermore, traces of PbO (between 250 and 3938 µg/g) and SnO_2 (between 111 and 5707 µg/g) detected in these coloured layers may be attributed to: (1) glass recycling, (2) deliberate addition to achieve opacity in the glass or (3) by the diffusion of these oxides from adjacent white layers.

The presentation and discussion of each colour is made in the following parts.

4.2.3.4.1 Blue

Blue colour observed in *millefiori* glassware is attributed to the presence of CoO within glass matrix. The analysed assemblage reveals that all blue body glass from SCV context and SJT_01 sample, contain CoO values lower than 0.11 wt%. This content of cobalt oxide aligns with blue blown glassware reported on literature (Veritá & Zecchin 2008).

In contrast, SJT_09 body glass (0.19 wt% of CoO) and all blue glasses used in the decorations display CoO levels ranging from 0.1 to 0.45 wt%. These values are comparable to those found in beads (Costa et al., 2019), enamels (Biron & Verità, 2015), and Portuguese glazed tiles (Coentro et al., 2014). As pointed in a Venetian splashed vessel by Marco Verità and Sandro Zecchin (2008, p. 111), the CoO content detected in decorations is typically higher than that found in the blue body glass because the original colour of the decoration must be preserved, even if it is applied thinly.

A limited number of samples underwent compositional analysis. However, the UV-vis absorbance spectroscopy analyse was performed in all blue layers of the samples to determine the ions that contribute to the final colour of the blue and bluish glass layers.

Besides cobalt (Co^{2+}), the ions of copper (Cu^{2+}), iron ($Fe^{2+/3+}$) and manganese (Mn^{3+}) also influence the blue colour of the examined artifacts, as illustrated in Fig. 4.23 for SCV_357, SCV_365, and SCV_400 samples.

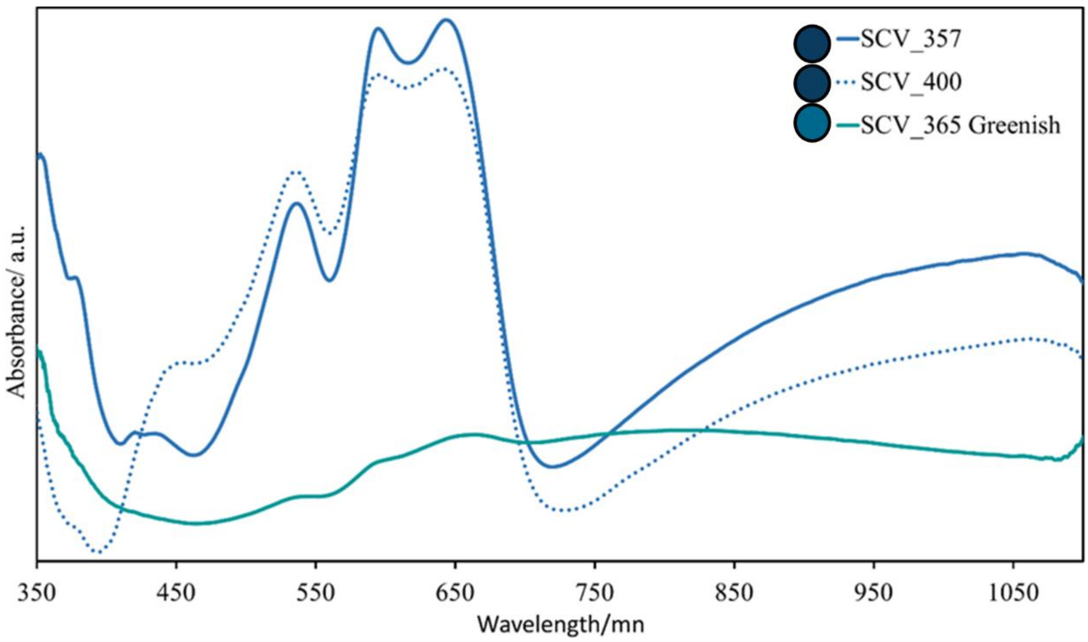


Fig. 4.23: UV-Vis absorption spectrum of blue glass layers performed on SCV_357, SCV_265 and SCV_400 fragments revealing the discernible influence of cobalt (Co^{2+}), copper (Cu^{2+}), iron ($Fe^{2+/3+}$) and manganese (Mn^{3+}) ions within the glass matrix.

In Fig. 4.23 one can observe the blue body glass of SCV_357, apart from the triple band attributed to Co^{2+} located at 530, 590 and 640 nm. The triple band of cobalt characterizes the cobalt ions in $3d^7$ electronical configuration with a tetrahedral coordination. This configuration of cobalt ions have a high extinction coefficient and, for that reason, is well detected in UV-Vis analysis that is able to detect the cobalt ions presence even at very low concentration, when compared with other techniques as, for instance, XRF, EDS or PIXE (Arletti et al. 2011, p.83; Coutinho et al. 2016, p. 446; Lima et al. 2012, p. 1243; Fernández 2003, p. 450-451).

The characteristic absorption bands of ferric ion (Fe^{3+}) at 380, 420 and 440 nm and, again the 440 nm peak, plus the broad band around 1100 nm typically attributed to ferrous ion (Fe^{2+}) were detected (Lima et al. 2012, Fernández 2003). Interesting to note is that, in SCV_400 sample, the band located at 450/500 nm can be associated to Mn^{3+}.

At necked eye, SCV_357 and SCV_400 blue tones are quite similar. Can the difference in the UV-vis absorption spectrum be linked with (1) different origins of raw materials added to the batch glass, (2) different recipes used in the production of these blue glasses, (3) attributed to glass recycling or (4) linked redox equilibrium acquired in the furnace atmosphere?

For bluish colour of SCV_365 fragment, apart from the triple band attributed to Co^{2+} and the bands associated to iron irons, the presence of divalent copper ion was confirmed by the observation of its characteristic broad band with a maximum wavelength located between 780 and 810 nm (Lima et al. 2012, Fernández 2003).

In all SCV and SJT samples, MnO is lower than 1 wt%, ranging from 0.02 to 0.78 wt%, this observation can indicate that this oxide was not intentionally added to the batch glass (Cagno et al. 2012b, p. 1544).

As pointed in the previous chapter, some oxides as NiO, ZnO, As_2O_3 and Bi are used to track either the origin of cobalt ore and as time indicator (e.g. Gratuze at al. 1996, Thornton et al. 2014 and Zucchiatti et al. 2006).

Apart from SCV_394 fragment, all the blue sample have contents of NiO (0.009-0.12 wt%), ZnO (0.004-0.02 wt%), As_2O_3 (0.05-0.52 wt%) and Bi (0.01-0.51 wt%) associated with CoO. These results indicate that these objects were produced after 1520/30 decade and that the cobalt ore was imported from Schneeberg (Gratuze at al. 1996, Thornton et al. 2014, Zucchiatti et al. 2006).

In contrast, SCV_394 blue body glass has an absence of As_2O_3. This observation has been viewed as a timeline indicator (before 1520/30) because is attributed to a calcination process of cobalt ore before the addition of glass batch because arsenic is a volatile oxide (Gratuze at al. 1996, Zucchiatti et al. 2006). Due to this As_2O_3 absence, it is possible to predict that this glass object was produced before 1520/30 or, by using the oldest recipe.

4.2.3.4.2 Green

Green glass of SCV_232 fragment is the consequence of an equilibrium between Fe^{2+} and Fe^{3+} which is almost 1 wt% (of Fe_2O_3) along with the presence of Co^{2+} (CoO = 0.016 wt%).

The content of MnO at a concentration of approximately 0.4 wt% does not provide sufficient evidence to conclude that manganese was intentionally added to the glass batch.

However, the content of PbO (0.35 wt%), and SnO_2 (0.42 wt%) suggests that cullet may have been used in this glass layer. Additionally, it is possible that these oxides have been diffused from the adjacent white layer during the working time, when the glassmaker fused the decoration to the body glass and manipulated the object being created.

In Fig. 4.24, the first band of Co^{2+} triple band, located at 540 nm is nearly imperceptible at first glance. However, upon closer examination, a slight shoulder around 540 nm can be seen. This "anomaly" could potentially be attributed to the presence of Mn^{3+} as their characteristic broad band, located at 450/500 nm, may mask the first Co^{2+} band (Fernández 2003). CuO represents 0.23 wt% of the total oxides but its broad band with a maximum wavelength located between 780 and 810 nm is almost imperceptible.

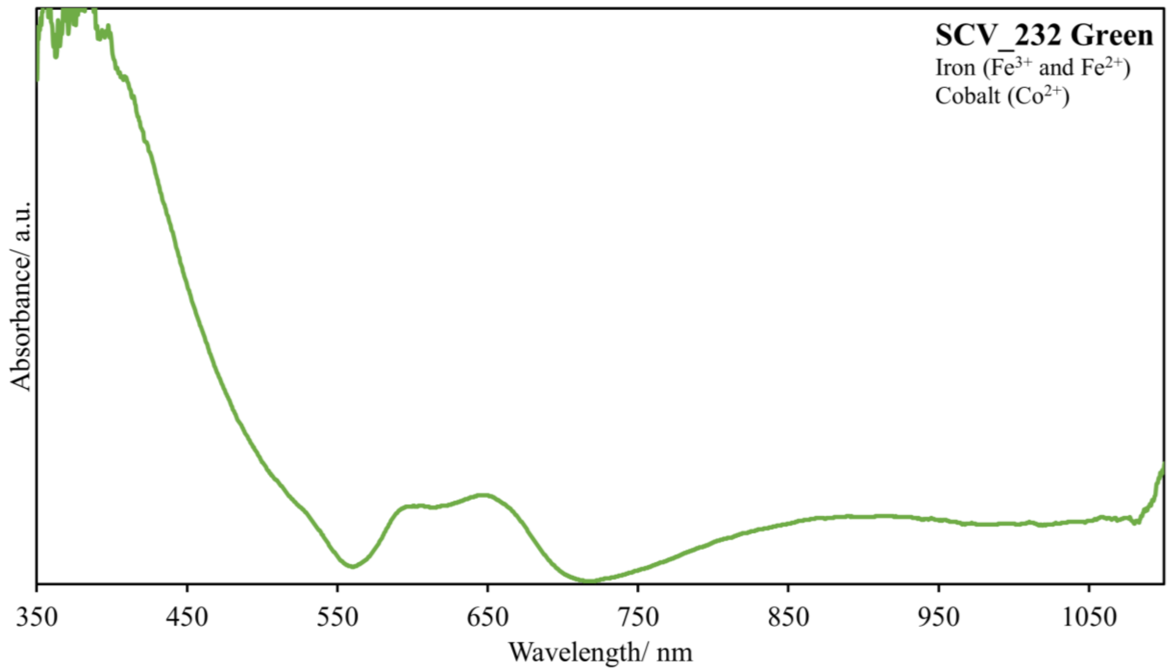


Fig. 4.24: UV-Vis absorption spectrum of green glass layer performed on SCV_232 fragment revealing the discernible influence of cobalt (Co^{2+}) and manganese ($Fe^{2+/3+}$) ions within the glass matrix.

4.2.3.4.3 Purple

The analysed purple glass layer of SCV_368 sample is almost black (Fig. 4.25) and have the following amount of coloured oxides: MnO = 0.76 wt%, Fe_2O_3 = 1.34 wt%, CoO = 0.30 wt%, CuO = 0.05 wt%, SnO_2 = 0.07 wt% and PbO = 0.05 wt%.

As noted in the previous green color, the broad band of Mn^{3+} at 450/500 nm, can be masking the triple band of Co^{2+} located at 530, 590 and 640 nm by considering the sum of all the bands. It is worth noting that both MnO and CoO exhibit a strong colouring effect, even at low concentrations in the range of a few hundred parts per million (ppm). In contrast, iron oxide is present in higher amounts within the glass matrix compared to MnO and CoO. While iron oxide contributes to the final colour of the purple glass, its effect may not be as visibly pronounced due to its relatively weaker colouring ability.

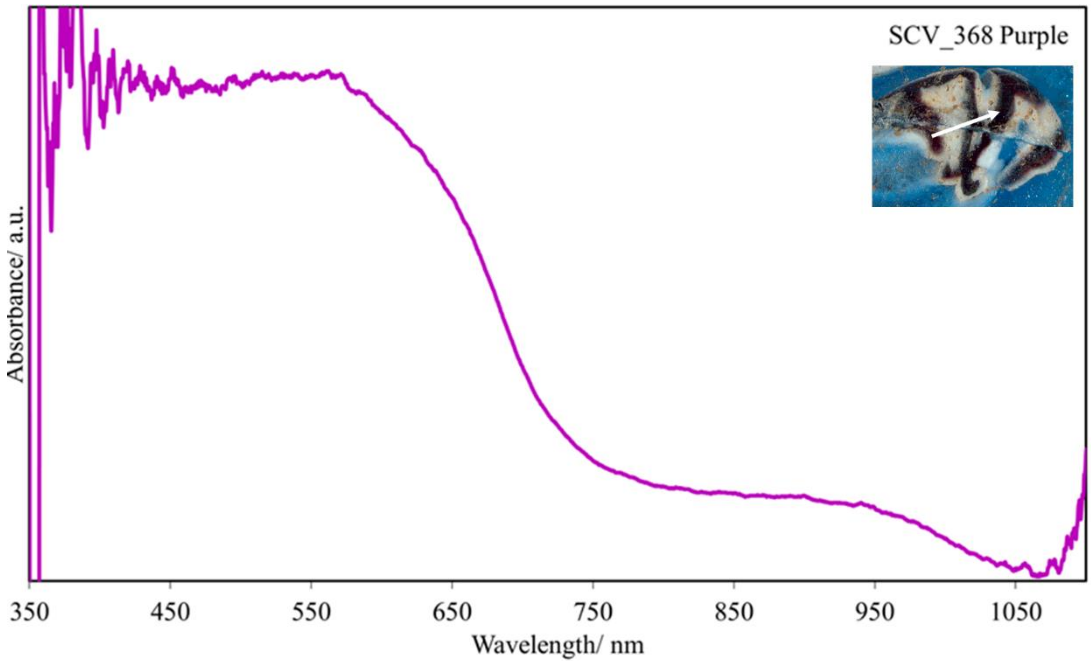


Fig. 4.25: UV-Vis absorption spectrum of purple glass layer performed on SCV_368 fragment revealing the discernible influence of cobalt (Co^{2+}) and manganese ($Fe^{2+/3+}$) ions within the glass matrix.

4.2.3.4.4 Red

Copper red glass is tricky to produce, however this colour has been used since the Roman times, (Bandiera et al. 2020, Moretti & Gratuze 2000). In reduced 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 & Gratuze 2000; Verità & Zecchin 2008).

The analysed red samples show amounts of CuO (0. 59 – 2.41 wt%), Fe_2O_3 (0.98 – 4.70 wt%), SnO_2 (0.048 – 4.71 wt%), Sb_2O_3 (0.003 – 0.014 wt%) and PbO (0.05 – 6.06 wt%) compatible with those reported in the literature (e.g. Lima et al. 2012, Moretti and Gratuze 2000, Verità & Zecchin 2008).

This type of glass is characterized by having a broad band between 330 and 770 nm in UV-Vis absorption spectrum (Fig. 4.26) as noted in all red glass analysed in this project (Fernández 2003).

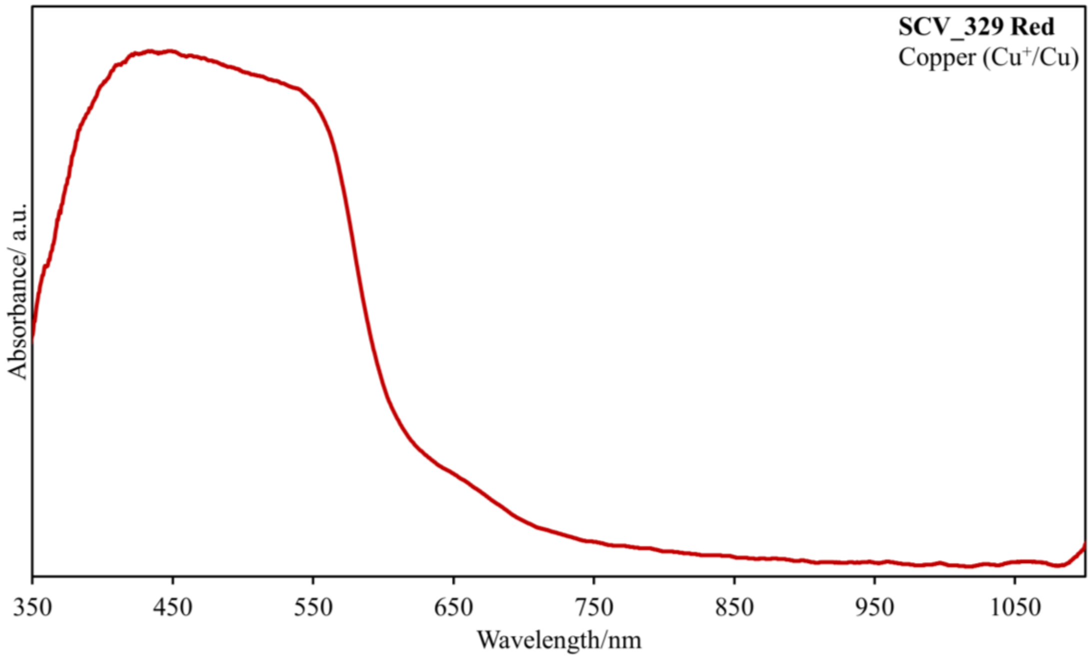


Fig. 4.26: UV-Vis absorption spectrum of red glass layer performed on SCV_329 fragment revealing the discernible influence divalent copper.

In SCV and SJT fragments only the red decoration belonging to SCV_245 sample presents several layers of red, turquoise, white and clear glass under the cross-section (Fig. 4.27). Under the surface it is possible to note that this decoration has several hues which can indicate that these layers were intentionally produced. This observation may indicate that SCV_245 fragment, initially attributed to a splashed glass have *millefiori* decoration although the drawing of pattern is impossible to determine.

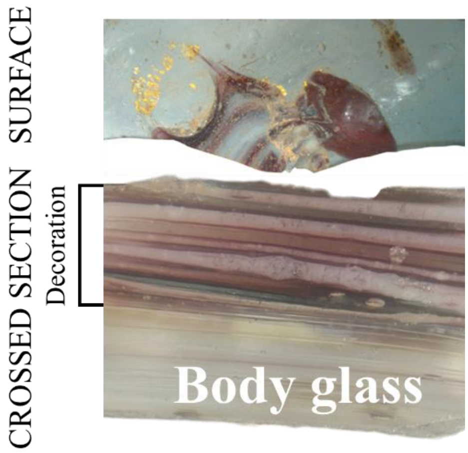


Fig. 4.27: close-up of the SCV_245 fragment under surface and crossed section.

4.2.3.4.5 Turquoise

Turquoise blue colours belonging to the selected SCV and SJT fragments have CuO content between 0.19 and 7.97 wt%. This amount of cooper oxide is in line with what has been reported on the literature for *millefiori* glass (Lima et al. 2012) and glass beads (Loewen & Dussubieux 2021) of the 15th-17th centuries.

This colour, produced by the presence of Cu^{2+} ion is obtained under oxidizing conditions and the characteristic broad band of UV-Vis absorption spectrum is located between 780 and 810 nm (Fig. 4.28) which corresponds to octahedral coordination with a $3d^9$ electronical configuration (Arletti et al. 2011, Bandiera et al. 2020, Lima et al. 2012, Moretti & Gratuze 2000, Fernández 2003).

As pointed by Mafalda Costa and co-authors (2019), the amount of PbO has a significant impact on the final turquoise colour. Most of the analysed fragments have low contents of lead oxide, ranging between 0.09 and 1.86 wt%, while the turquoise glass colour of SCV_366 (*millefiori* cane) have 8.16 wt% of PbO. Although this particular turquoise colour may not appear visibly distinct from the others, a simultaneous detection of SnO_2 (8.50 wt%) suggests that both lead and tin oxides were likely added to the glass batch for opacification purposes, as was also observed in some tubular blue glass beads of the Nueva Cadiz type unearthed in the Lisbon city centre (Veiga & Figueiredo 2002). The other fragments have SnO_2 content that range between 0.06 to 2.07 wt%.

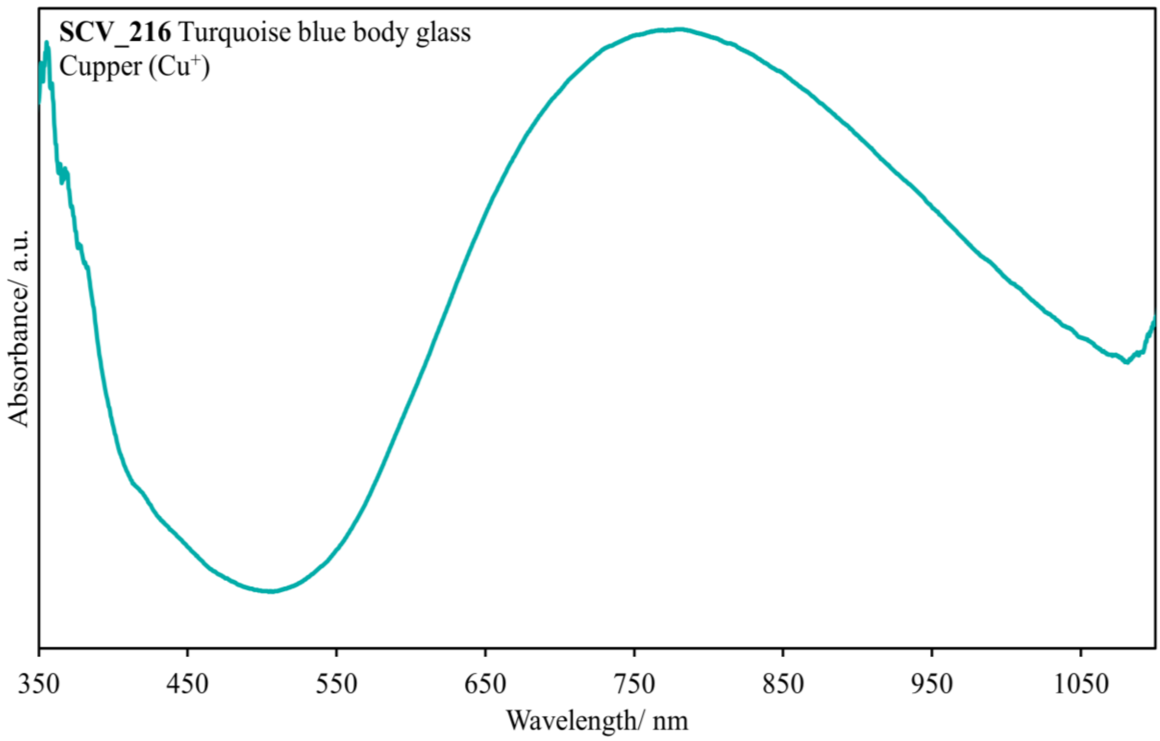


Fig. 4.28: UV-Vis absorption spectrum of turquoise body glass of SCV_216 fragment revealing the discernible influence Cu^{+} ions into the glass matrix.

4.2.3.4.6 White

The oldest known opacifier is the calcium antimonate dating to the 15th century B.C. and was profusely used by the roman glassmakers (Moretti & Hreglich 2007, p. 167). For unknown reasons, in Antiquity and early Middle Ages it was replaced by calcinated tin and lead oxides compounds and in the second half of the 16th century it was reintroduced in the Venetian glass making (Gedzevičiūtė et al. 2009 p. 22; Lima et al. 2012, p. 1240; Verità & Zechin 2008, p. 110).

White glass layers of the suited pick-up glass fragments of SCV and SJT archaeological contexts have SiO_2 (19.35 – 56.43 wt.%), SnO_2 (4.34 - 30.57 wt.%), and PbO (7.73 – 22.04 wt.%) as major components.

White opaque glass displays a notable heterogeneity, characterized by the presence of white opaque clusters of diverse sizes dispersed within the glass matrix (Fig. 4.29).

The study of this opaque white particles dispersed in the glass matrix were carried out by Raman microscopy.

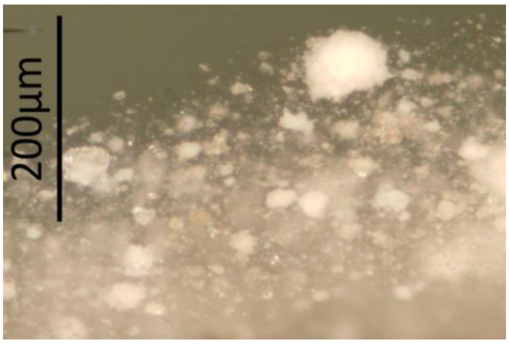


Fig. 4.29: Optical microscope image of the SCV_250 glass sample where it can be observed the coarse white particles.

Raman spectrums performed on these white clusters allowed to identify the presence of cassiterite in all analysed samples and, for SCV_245 and SCV_250 samples, some malayaite crystals were also detected (Fig. 4.30).

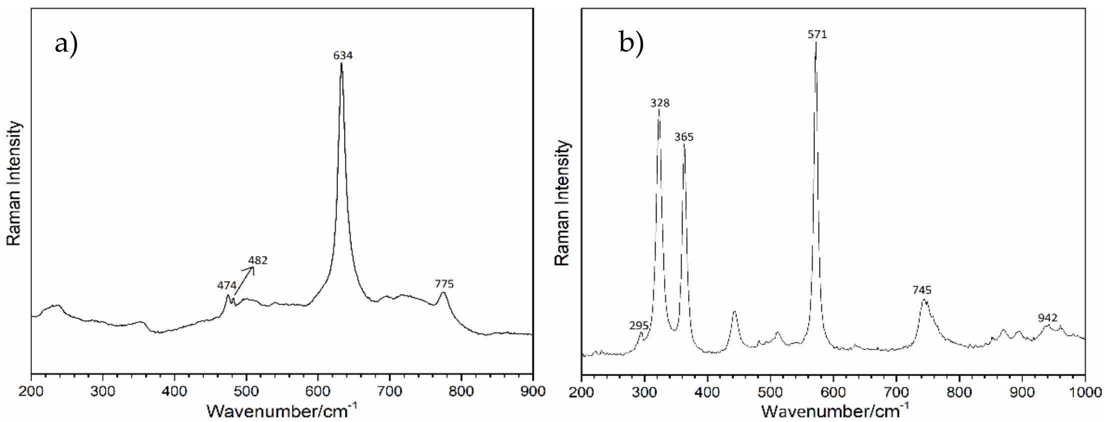


Fig. 4.30: Raman spectrum of (a) cassiterite (SnO_2) and (b) malayaite ($CaSnOSiO_4$).

Cassiterite (tin dioxide) was introduced in the Venetian glass recipes at the beginning of the 15th century[7] and, being the preferred opacifier of Venetian glassmakers in the Renaissance period, it was used to make the white threads in *filigrana* glass canes, enamels, and to make Chinese porcelain imitations (see for example Lima et al. 2012, p. 1240; Medici 2014, p. 112; Moretti & Hreglich 2007, p. 167; Verità & Zecchin 2008, p. 110). This compound has a characteristic Raman signature at 635 cm^{-1} and 775 cm^{-1} and, frequently, a less intense pike at 474 cm^{-1} can be observed (Coutinho 2016, p. 154; Lima et al. 2012, p. 1240; Ricciardi et al. 2008, p. 607) (Fig. 4.30.a).

Cassiterite clusters were also detected in contemporaneous white glaze of Portuguese tiles (Coentro et al. 2014), beads found in Africa and America's continents (respectively, Costa et al. 2019 and Loewen & Dussubieux 2021), enamels (Thornton et al. 2014, Verità & Biron 2015) and *mosaic* tesserae (Verità, Zecchin and Tesser 2018).

The presence of malayaite ($CaSnSiO_4$) in SCV245 and SCV_250 sample (Fig. 4.30.b and 4.31) is confirmed by its characteristic Raman bands at: 571, 365 and 322 cm^{-1} (Muralha et al. 2014). The formation of this tin mineral is a consequence of the presence of equimolar parts of CaO, SiO_2 and SnO_2 and its development can be favoured in the presence of transition metal ions (Coentro et al. 2014; Muralha et al. 2014). The proximity of the opaque white layers to, respectively, red and blue layers suggest that its formation of was likely unintentional.

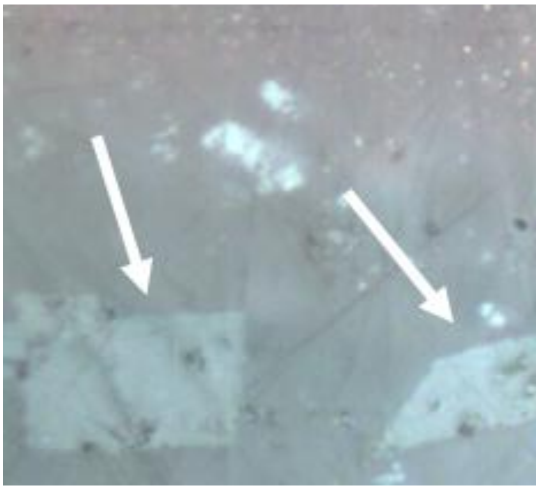


Fig. 4.31: Morphology of malayaite crystal found in SCV_245 sample in-between cassiterite clusters.

White layers of SCV_245 and SCV_250 samples have, respectively, a content of 35 and 46 wt% of SiO_2, 6 and 8 wt% of CaO and 10 and 7 wt% of SnO_2.

[7] Recipes written by *Anonimus*, *Neri* and *Darduin* (Moretti & Hreglich 2007, p. 167) and the *Liber diversarum arcium*, well known as Montpellier (Clarke 2011, p. 1).

Although calcium antimoniate was not detected in the analysed samples, this compound was observed in contemporaneous glass fragments in two *millefiori* glass samples from SCV context with an attributed genuine Venetian production (Lima et al. 2012) and in a genuine Venetian glass goblet with *splashed* decoration (Verità & Zecchin 2008). This observation provides evidence that during the Renaissance period, although tin dioxide was the favoured opacifier among Venetian glassmakers, they were also capable of utilizing the ancient opacifier in the production of contemporary glass objects.

4.2.3.4.7 μ-PIXE map

Through μ-PIXE analysis some elemental maps were performed to understand the different distribution of the elements through the layers (Fig. 4.32).

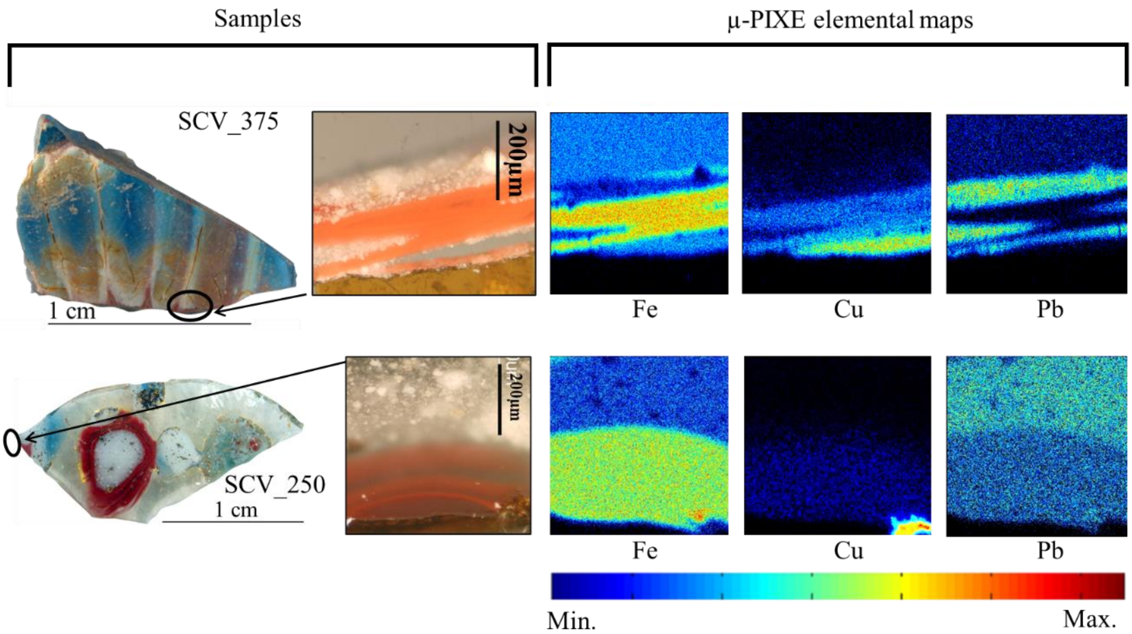


Fig. 4.32: Elemental maps of SCV_ SCV_375 and SCV_250 glass fragments acquired by using μ-PIXE.

The elemental maps have shown that the elementary diffusion is not significantly high as one can distinguish the different concentrations of each element across the glass layers.

Moreover, it is interesting to note that, in red coloured layers of SCV_375, iron and copper present different concentrations: the lower layer has a higher content of Fe, while the upper layer has a higher content of Cu (Fig. 4.32). This observation reinforces the theory that the same cane can be made with glasses that were produced following different recipes.

For red glass of SCV_250 fragment it is curious that while, under crossed-section, different hues of red colour can be distinguished the μ-PIXE elementary maps does not provide any compositional distinction between them. This observation may be justified by the low size of cuprite crystals. This evidence may be linked to the diminutive size of copper crystals that lacks sufficient dimensions to exhibit coloration.

4.2.1.5 4.2.3.5 Geochemical patterns

Geochemical studies have been profusely used in provenance projects because they are able to link the relative abundance of trace and rare-earth elements (REE) attributed to a certain region with the mineral's origins of the silica sources used in glass production (e.g. Cagno et al. 2012a, Costa et al. 2019, Coutinho et al 2021, Kunicki-Goldfinger et al. 2008 and Šmit et al. 2005).

Trace and rare earth elements (REE) analyses have also been employed in coloured glass as its REE contents in colouring and fluxing agents does not significantly influence the geochemical patterns due to their insignificant amounts (Costa et al. 2020, Wedepohl et al. 2011, p. 293).

To obtain the geochemical pattern of a certain material, different normalisations can be made, in this case the normalisation of the considered trace and REE elements were performed to (1) the upper Earth crust by using the values reported in Wedepohl, Simon, and Krons (2011) work and (2) carbonaceous chondrite normalisation by using the values reported in McDonough and Sun (1995) work. The first normalisation has been profusely used in contemporary glass provenance studies (e.g. Cagno et al. 2012a, Coutinho et al. 2021, Kunicki-Goldfinger et al. 2008, Šmit et al. 2005) being useful for comparison while the last normalisation may provide complementary information about redox conditions of the mineral formation (Costa et al 2020).

Looking to SCV and SJT analysed samples normalised to upper Earth crust, it was possible to identify nine different geochemical patterns (GP). This division was made by observing some deviations presented in the tendency line that represents each glass sample (Fig. 4.33

and Tab. 4.6). The first five patterns exhibit a notable similarity and are exclusively composed of SCV samples (Table 4.6). Nevertheless, slight deviations can be observed in the trend line between Zr and Ce (Fig. 4.33). Furthermore, patterns 4 and 5 demonstrate additional variations in the elements Lu, Hf, and Ta when compared to the preceding patterns (1-3). These elements are highly likely to be attributed to silica sources (Brems & Degryse, 2014). Moreover, the 7th to 9th patterns exhibits significant similarity among themselves encompassing SJT and some SCV glass samples (Tab. 4.6). However, some deviations can be observed between Ti and Zr elements and positive anomalies in Tm and Yb were detected in 8th and 9th paters, respectively (Fig. 4.33). Although we are unable to elucidate the mineralogical significance of these anomalies, distinct trends in line profiles have been attributed to the utilization of different silica sources.

7th pattern is quite similar to the REE (from La to Lu elements) geochemical pattern found in three Islamic beakers decorated with Arabic inscriptions found in Brno (Czech Republic) and dated to the 13th/ 14th centuries (Wedepohl, Simon and Krons 2011, p. 91). However, these Islamic glass fragments have low amount of alumina and iron oxides which seems to be not compatible with the understudied pick-up samples (Wedepohl 2007). This observation may indicate that different but related silica sources were used in both glass production.

Tab. 4.6: Attribution of each analysed sample to its geochemical pattern (GP).

GP	Nº	Analysed glass layers
1	4	SCV_365 (Body db/ w), SCV_368 (Body db/ w)
2	1	SCV_368 (t)
3	1	SCV_365 (t)
4	5	SCV_216 (w), SCV_365 (db), SCV_368 (db/ p), SCV_388 (w)
5	2	SCV_388 (Body db/ t)
6	35	SCV_044 (cl/ db/ r/ w), SCV_216 (r/ t), SCV_232 (gr), SCV_235 (cl), SCV_236 (cl), SCV_245 (cl/ db/ r/ w), SCV_250 (cl/ tb), SCV_275 (cl/ r), SCV_329 (Body db/ tb), SCV_357 (db/ r), SCV_360 (Body db/ db/ r/ w), SCV_369 (Body db/ db/ r/ t/ w), SCV_375 (Body db/ r/ w), SCV_388 (r), SCV_394 (Body db)
7	16	SCV_235 (r), SCV_250 (db/ r/ w), SCV_364 (cl/ db), SCV_329 (r), SCV_364 (cl/ db), SCV_366 (db/ t), SCV_394 (cl), SJT_01 (Body db/ r/ t/ w)
8	3	SJT_09 (db/ r/ w)
9	9	SCV_046 (cl), SCV_232 (db/ r/ w), SCV_272 (cl), SCV_329 (w), SCV_364 (r/ t/ w)

GP - geochemical patterns/ Nº - number of different glass layers

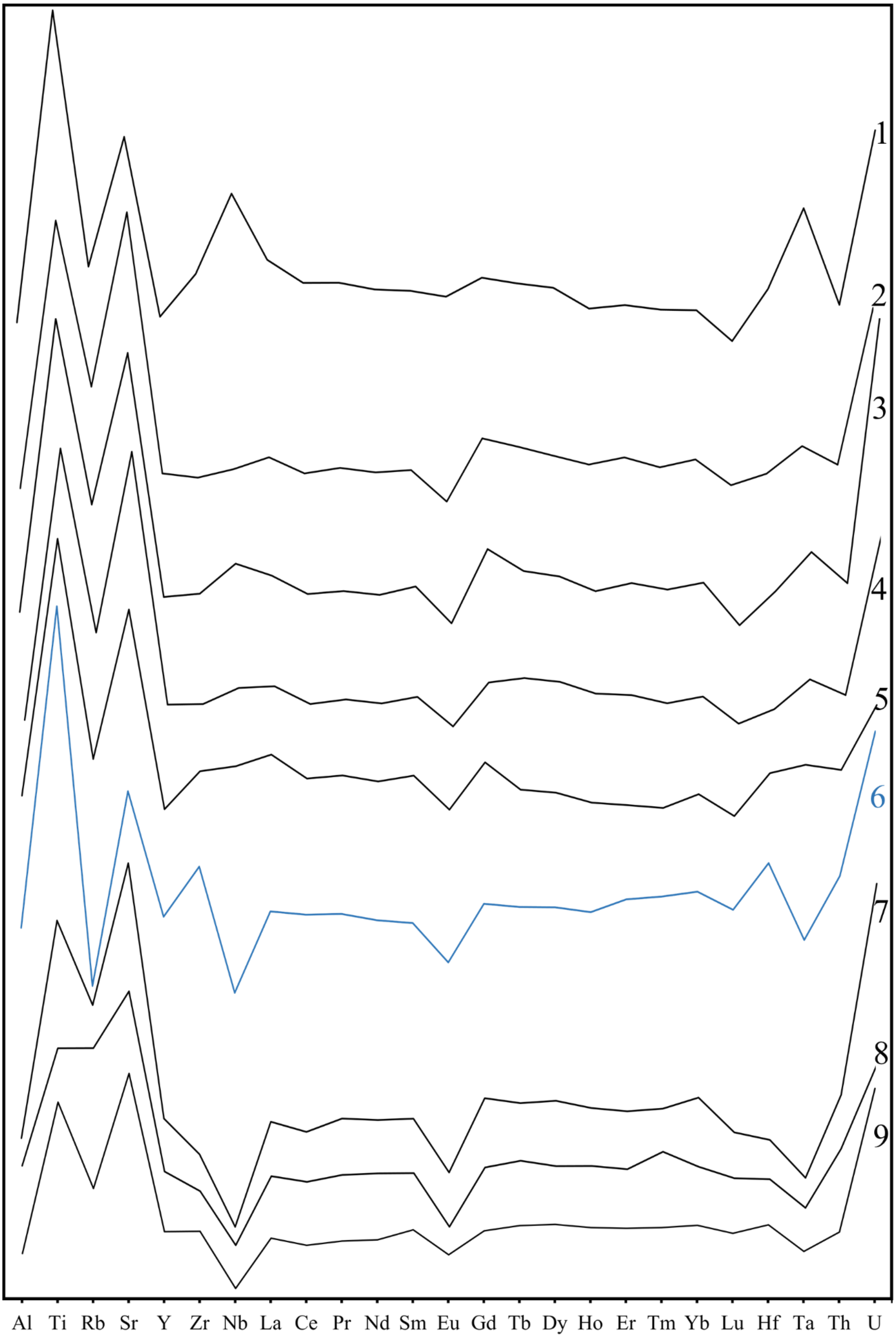


Fig. 4.33: Representative geochemical patterns presented in logarithmic scale, of trace and rare-earth elements (REE) found in SCV and SJT glass samples, normalized to Earth's upper crust, in logarithmic scale.

It is noteworthy that more than 45% of the analysed samples (35 out of 76) exhibit a geochemical pattern comparable to 6th. This specific geochemical pattern was previously identified in LSC_03 sample (a glass production waste) recovered from Santana Convent in Lisbon and has also been observed in other contemporary Portuguese contexts, such as the Rua do Arsenal site (Coutinho, 2016), Largo do Chafariz de Dentro site in *filigrana* glassware (Varela, 2018), and in some glass vessel with a gourd shape found in SCV (Coutinho et al., 2017). These gourd-shaped vessels have been attributed to Portuguese production due to their distinctive morphology (Medici et al. 2009). This characteristic indicates that all these glass fragments were probably made in the same glass production centre or, at least, were made with the same silica source.

Less than 15 % of the considered glass samples (10 out of 76) shared the same geochemical pattern in all layers (including body glass): SCV_044, SCV_245, SCV_275, SCV_357, SCV_360, SCV_366, SCV_369, SCV_ 375, SJT_01 and SJT_09. Being interesting to note that, excepted SCV_366 sample, all other SCV samples exhibit the 6th geochemical pattern. While SJT_01 and SCV_366 belong to 7th and SJT_09 to 8th patterns.

Note that, although 9 different geochemical patterns were observed, almost all the analysed samples are characterized by the presence of a clear negative Eu anomaly. This evidence is being attributed to the separation of Eu^{2+} from Eu^{3+} in melts under low oxygen pressure forming plagioclase minerals, substituting calcium (Wedepohl, Simon and Krons 2011).

In the provenance study of European glass beads recovered in Angola (Africa) and dating from the 14th to 19th Centuries, Mafalda Costa and co-authors (2019) employed chondritic normalization for Rare Earth Elements (REE). This normalization technique was utilized to emphasize the variations in sand composition used in the production of these artifacts. Chondritic normalization of SCV and SJT glass fragments was conducted using the values reported by McDonough and Sun (1995, p. 238). This normalization approach provides insights into the elemental composition of these samples, revealing an enrichment in light rare earth elements (LREEs) compared to heavy rare earth elements (HREEs) and exhibiting negative Eu-anomalies (Fig. 4.34). While the range of the negative Eu element anomaly ($Eu/Eu^* = 0.14 - 0.93$) may be considered substantial in the analysed samples, it is significant notable because is in consonance with the dispersed values observed so far. The presence of this Eu anomaly, coupled with the concurrent enrichment of LREEs relative to HREEs, suggests that the silica sources used in the glass production originated from the weathering of granite-type rocks within the upper continental crust (Costa et al., 2019; Taylor & McLennan, 1985). Moreover, weathered granite-type rocks with Eu/Eu* values ranging between 0.61 and 0.76 and, have been attributed to Venetian glass production (Costa, 2019; Wedepohl, Simon, & Krons, 2011).

Around 40 % of samples from SCV and SJT archaeological contexts (28 out of 67) present values of Eu/Eu* compatible with Venetian production (Apendix A.8): SCV_044 (cl), SCV_216 (t), SCV_235 (cl), SCV_236 (cl), SCV_245 (cl/ db), SCV_250 (db/ r), SCV_272 (cl), SCV_275 (cl/ r), SCV_357 (db/ r), SCV_364 (db/ r), SCV_365 (db), SCV_366 (t), SCV_368 (db/ t), SCV_369 (db Body/ db), SCV_375 (db/ r), SCV_388 (db/ r/ t), SCV_394 (r) and SJT_001w.

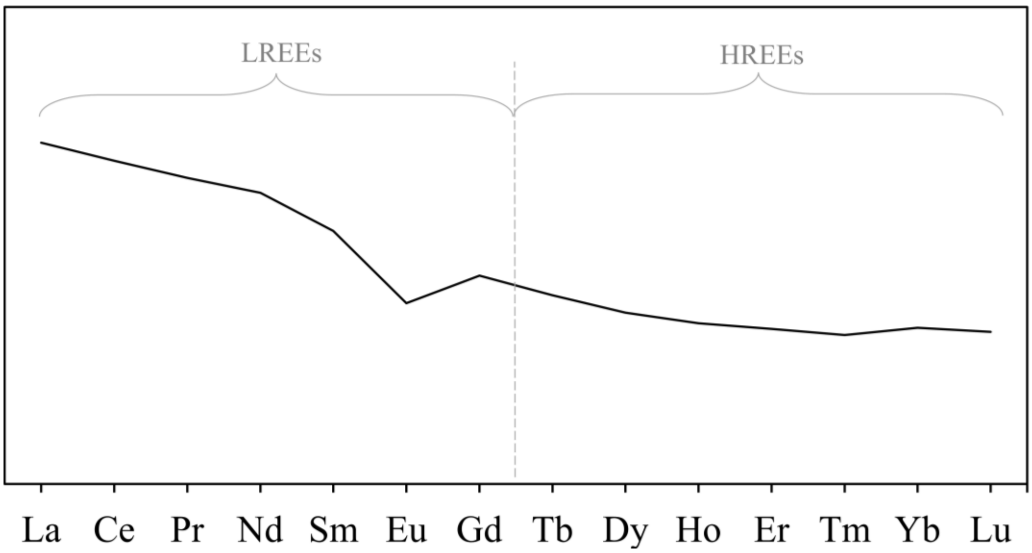


Fig. 4.34: Pattern representation of the chondrite normalisation to REE of SCV and SJT glass fragments.

By reproducing glass from sands and pebbles obtained from sedimentary deposits close to Coimbra and Côvo (Portuguese sites with documented glass production), Inês Coutinho and co-authors (2021) obtained the geochemical patterns of those synthetic glass to compared them with historical samples. In that project three historical SCV glass samples previously studied presented geochemical pattern comparable with that synthesized glass however, no SCV nor SJT pick-up glass fragments studied in this project presents those characteristics. In that work the classification of silica sources as having granitic origin was also pointed by the authors (Coutinho et al. 2021).

Based on the available information, it is noteworthy that the identified geochemical pattern, represented by the 6th pattern, appears to be exclusive to Portugal. While historical documentation suggests that certain Portuguese glass productions attained a level of quality comparable to Venetian production, the absence of archaeological evidence regarding the production furnaces and associated artifacts hinders a definitive attribution of the 6th geochemical pattern to Portuguese glass production. Further investigation and analysis are necessary before conclusive assertions can be made.

4.2.1.6 4.2.3.6 Provenience summary

The 21 selected glass fragments decorated in pick-up technique gave a total of 76 different glass layers analysed, presenting in addition to the clear glass, a wide range of different colours: blue, green, purple, red, turquoise and white.

This range of colours were profusely used by both Venetian and *façon de Venise* glass makers: (1) blue glasses were coloured by CoO, (2) green glass layer of SCV_232 sample is the consequence of the coexistence of three different transition metals within the glass matrix (Fe_2O_3, CoO and CuO), (3) purple is the mixture of MnO and CoO, (4) red and turquoise glass by CuO (plus iron, tin, and lead oxides to create a reduced environment within the red glass matrix) and (5) white by the precipitation of cassiterite (SnO_2) clusters in all the studied white layer and malayaite ($CaSnOSiO_4$) in SCV 245 and SCV 250 fragments.

In all clear glass layers, the presence of Fe_2O_3 was detected, in addition to this oxide, only the SCV_272 clear body glass does not present the coexistence of CoO and, in SCV_236 and CVS_245 the presence of MnO were also detected by UV- Vis absorbance spectroscopy, showing that the final hues of different clear glass are influenced by these oxides.

According to the existing literature, it is evident that Venetian glassmakers were exclusively permitted to use Levantine ashes, both in purified and non-purified forms, in their glass production. On the other hand, glassmakers working outside Venice were producing *façon de*

Venise glassware employing various types of fluxing agents, including Levantine ashes, particularly in the production of high-quality artworks.

Compositional analyses performed in the selected samples show that, considering their major components (e.g. Na_2O, K_2O, CaO, Si_2O, TiO_2, Al_2O_3, MgO), they can be considered as soda-lime-silica type and, at least *Levantine* and *barilla* ashes were used as alkali source. Considering the major components attributed to silica sources (Si_2O, TiO_2, Al_2O_3); while SCV fragments are dispersed thought the binary chart that relates TiO_2/Al_2O_3 and Al_2O_3/SiO_2, SJT fragments are closely related with the cluster attributed to Lisbon origin as they are grouped together while different content of these oxides was observed from the already known Venetian or *façon de Venise* production centres.

The analysed sample were divided into 9 distinct geochemical patterns by the normalization of its trace and REE to the Earth's upper crust, being interesting to note that, more than 85% of the analysed samples (66 out of 76) were made by a mixture of different silica sources in the same object as noted by Augusta Lima and co-authors (2012), implying that the base glass and the canes used for the decoration were made using different silica sources and probably in different production centres.

Apendix A.8 gathered all the relevant information related with decoration pattern, alkali sources, silica sources, geochemical patterns (GP) and Eu/Eu* values of each analysed layers.

Most of fragments that exhibit a composition consistent with the use of barilla as an alkaline source and a silica source located in the Lisbon area of Apendix A.8, display a geochemical pattern compatible with the 6^{th}. The 6^{th} pattern is consistent with the glass production remain unearthed at Santana Convent in Lisbon (LCS_03). This observation suggests that all those glass fragments were produced in the same unknown production centre or in different close production centres using the same source for raw materials.

For SJT samples, Venetian production is quite impossible because nor alkali sources (barilla), silica sources or Eu/Eu* values are consistent with what is reported on the literature for genuine Venetian production. All the analysed layers from SJT_01 and SJT_09 fragments are compatible with, respectively, 7^{th} and 8^{th} geochemical patterns. Furthermore, the unique pattern observed in SJT_09 (Crist's cross) suggests that this specific glass object was ordered from a *façon de Venise* glasshouse, potentially of Portuguese origin, given its significant symbolic importance.

According with the results taken from (Apendix A.8, all the glass fragments compatible with Venetian production (highlight in green colour) displays different geochemical patterns (1st, 6th, 7th and 9th) this result open some possibilities:

(1) Venetian glassmakers were using more alkali and/or silica sources than the ones been mentioned so far in the literature.

(2) *Façon de Venise* glass production made glassware by using pure and similar raw materials to produce their glassware (as pointed by De Raedet et al. 2002) and different glass production centres can only be traced by geochemical patterns investigation.

(3) Glass recycling.

Further studies are still required for a deeper understanding of European glass production of modern period.

5

FINAL REMARQUES

The present thesis encompasses the foremost comprehensive investigation of early modern *pick-up* decorated glass artifacts discovered in Portuguese archaeological contexts. This project enabled a thorough morphological and chemical characterization of *pick-up* glass fragments dating back to the late 16th and 17th centuries, which were discovered in Lisbon (Largo do Chafariz de Dentro (LCD) and Santana Convent (LCS)), Coimbra (Santa Clara-a-Velha monastery (SCV)) and Lamego (São João de Tarouca Monastery (SJT)) regions. The selected fragments were compared with contemporary glassware mentioned in the literature (in both archaeological and museological contexts), providing a comprehensive understanding of their characteristics.

One of the primary findings presented in this dissertation is that, based on the literature review, less than 10% of the studied pick-up fragments have a chemical glass composition compatible with the Venetian glass produced between the end of 15th and 17th centuries. This result is much lower than we expected once that pick-up fragments found in archaeological contexts are frequently attributed to a venetian production.

The survey pointed that in coloured glass cobalt is responsible for the blue colour, copper for the *aventurine*, red and turquoise colours (in different oxidizing stages) and iron and manganese for black colour (plus CoO in very low amounts). For the white colour two opacifiers were detected: Cassiterite (latimo) profusely used by the Venetian glassmakers and Calcium antimonate that was more used by the Roman glassmakers but was also detected in Venetian glass objects. The analysed glass fragments in our work show the same tendency, while malayaite crystals were also detected in SCV_240 and SCV_250 white glass layers. As mentioned previously, its formation in glass matrix is a consequence of the presence of equimolar parts of CaO, SiO2 and SnO2 and favoured in the presence of transition metal ions.

Concerning the colours choice, it is interesting to note that turquoise, greenish, opaque red and greyish body glass were only observed in some *millefiori* fragments found in two Portuguese archaeological contexts: Santana Convent in Lisbon and Santa Clara-a-Velha Monastery in Coimbra, although the most popular colour present in *millefiori* body glass is blue (about 75%), followed by clear glass (around 9%). This colour choice is not consistent when compared them with museological artefacts, where clear glass is the most popular on the body glass, followed by blue. Moreover, in the case of *splash* glass fragments, an expanded range of colour variations is observed within the body glass, encompassing hues such as green, clear, turquoise, opaque white, blue, amber, light blue, greyish, and red (listed in order of popularity, from most encountered to less frequently observed).

Additionally, it was noted that the presence of *aventurine* glass, characterized by its luxurious appearance of sparkling gold due to the inclusion of minute copper particles within the glass matrix, was exclusively observed in splash fragments.

Concerning morphological characterization (Chapter 4.1), the decorative patterns observed in *millefiori* glass fragments were categorized into eight distinct motifs. These include: (1) indefinite pattern, which constituted more than 50% of the total considered fragments (108 out of 213 fragments); (2) *rosette* (40 out of 213); (3) flower (37 out of 213); (4) cross (15 out of 213); (5) hybrid (9 out of 213); (6) *rosette* with a central cross (5 out of 213); (7) caravel (3 out of 213); and (8) concentric circles (1 out of 213) (Fig. 5.1). Among these patterns, certain types such as specific flowers, crosses, caravels, and hybrid motifs have not been documented in the literature available to us. This observation indicates the possibility that these unique decorative patterns were either commissioned (as happened for certain Chinese porcelains), or produced in Portugal, showcasing the aesthetic preferences of Portuguese society.

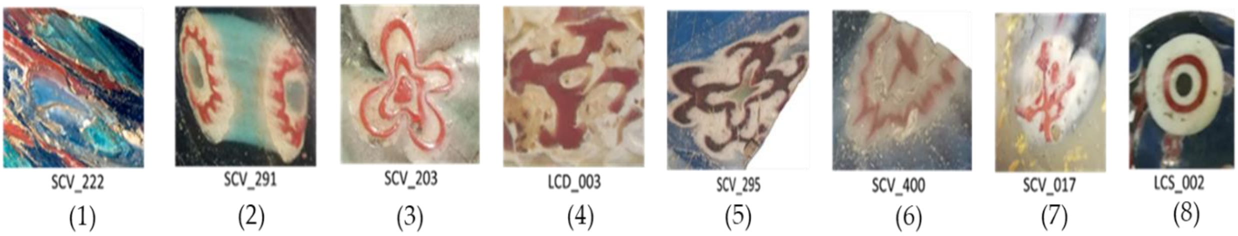


Fig. 5.1: Examples of different decorative patterns observed in the understudied *millefiori* glass fragments.

Through this investigation, we have successfully demonstrated, for the first time, that Portugal possesses the highest studied number of *millefiori* and *picked-up* glass fragments, as well as the largest published concentration of archaeological sites where this type of artifacts was unearthed, surpassing other European regions as Venice.

The compilation of this information, coupled with the notable diversity in manufacturing quality, renders this subject an intriguing and noteworthy case study worthy of investigation.

Furthermore, we advocate for the standardization of nomenclature of this subject matter, as we identified a significant discrepancy regarding terminologies in the literature we consulted, posing a substantial challenge to comprehension and scholarly discourse:

- *Splashing* for the glass objects that were decorated by picking up sliced coloured glass without any regular pattern.
- *Millefiori* for the glass objects that were decorated by picking-up *murrine*.
- *Mosaic* glass for the glass objects which are made by fusing side by side sliced canes in order to form a plaque that was then slumped over a mould.
- *Murrine* for sliced glass canes that have a decorative pattern which can be seen in cross-section.
- *Pick-up technique* for the glassware that was decorated by picking-up (by rolling a molten glass bubble over them) *murrine* or sliced glass without decorative motifs.
- *Rosette* for the pattern that is similar to the image present in Fig. 5.1 (2).

The comprehensive survey of chemical compositions associated with glass artifacts of this nature, as documented in existing literature and historical sources, has significantly enhanced our understanding of the evolutionary trajectory of production techniques and glass compositions. This investigation extends beyond Venice to encompass other notable glass manufacturing centres, and it holds great significance for attributing the production of Portuguese *millefiori* and *splash* glass fragments.

The meticulous selection of Portuguese archaeological pick-up glass fragments, comprising 31 glass fragments along with 4 glass fragments categorized as glass production remains, yielded a total of 105 distinct glass layers for our comprehensive compositional study.

All the analysed pick-up glass fragments can be classified as soda-lime-silica type, which indicates that their production involved the utilization of halophytic plant ashes as alkali source. *Levantine* and *barilla* ashes were probably used as fluxing agent and, it is quite possible that, while all the analysed LCS and SJT glass samples were probably made with *barilla* as fluxing agent, most of the LCD glass samples were produced through *Levantine* ashes. This information suggests that, at least, two different recipes were used and can mean that they were produced in different furnaces or can reflect an improvement of recipe.

Looking to SCV glass fragments they are dispersed through the alkali study graphs, this result may suggest that, as previously pointed by Augusta Lima and co-authors (2012) and Inês Coutinho and co-authors (2016), they have different origins.

Note that, according with the existing literature, it is evident that Venetian glassmakers were only allowed to use Levantine ashes (both purified or non-purified), in their glass production. On the other hand, glassmakers working outside Venice were producing *façon de Venise* glassware employing various types of fluxing agents, including Levantine ashes, particularly in the production of high-quality artworks.

An interesting result is related with the major components associated to silica sources (SiO_2, Al_2O_3 and TiO_2) from Lisbon contexts (LCD and LCS) as they are grouped together while different content of these oxides was observed from the already known Venetian and *façon de Venise* production centres. Moreover, the tendency line of Al_2O_3 verses TiO_2 is also different from the already known Venetian and *façon de Venise* production centres, suggesting a utilization of distinct sources of silica, leading to the observed variations in the composition of Lisbon glass samples as the balance of both oxides are different. This observation is interesting because two different correlation lines associating alumina and titanium oxides were never mentioned before perhaps because the content of TiO_2 is not profusely mentioned for contemporaneous glass studies, while has been widely used in Roman glass provenance studies. While SCV fragments are dispersed thought the binary chart that relates TiO_2/Al_2O_3 and Al_2O_3/SiO_2, SJT fragments are closely related with the cluster attributed to Lisbon origin.

Geochemical patterns allowed us to group all the analysed glass samples by its mineralogical origin using their relative abundance of trace and rare-earth elements (REE) with a normalisation of those elements present in glass composition to the values of upper Earth crust.

The analysed sample were divided into 9 distinct geochemical patterns by the normalization of its trace and REE to the Earth's upper crust. The first five geochemical patterns exhibit a notable similarity and are exclusively composed of SCV samples. However, some deviations between Zr and Ce elements and some variations in Lu, Hf and Ta elements can be identified when compared 1st to 5th geochemical patterns. To the authors knowledge, these patterns do not have any parallel outside Portugal.

Considered the SCV and SJT glass assemblages, more than 85% of the analysed samples (66 out of 76) were made by a mixture of different silica sources in the same object as noted by Augusta Lima and co-authors (2012), implying that the body glass and the canes used for the decoration were made using different silica sources and/ or were probably produced in different production centres and/or are the consequence of the usage of glass recycling.

In 1st geochemical pattern are included all *cristallo* glass (purified Levantine ashes) silica sources associated with Granada and the samples that are located in between Venetian and De Twee Rozen glasshouse (Appendix A.8).

The 2nd and 3rd geochemical patterns belong, respectively, to the turquoise body glass layer of SCV_368 fragment and this fragment and turquoise glass layer of SCV_365 fragment. These fragments are characterized by having a mixture of *Levantine* and *barilla* ashes as alkali sources and having the major components associated to silica sources (SiO_2, Al_2O_3 and TiO_2) located between Venetian production and De Twee Rozen glasshouse.

4th geochemical patterns belong to SVC 216 white, SVC 365 blue, SVC 368 blue, SVC 368 purple and SVC 388 white glass layers. These glasses are characterized by having a mixture of *Levantine* and *barilla* ashes as alkali sources and (1) for the first glass layers, the major components associated to silica sources (SiO2, Al2O3 and TiO2) is located in De Twee Rozen glasshouse region while, the last four samples, the major components associated to silica sources (SiO2, Al2O3 and TiO2) are located in Lisbon region.

5th geochemical patterns belong to SVC 388 blue and turquoise glass layers. These glasses are characterized by having a mixture of *Levantine* and *barilla* ashes as alkali sources and the major components associated to silica sources (SiO_2, Al_2O_3 and TiO_2) are located in Lisbon region.

Can those first five geochemical patterns be a consequence of glass recycling as they have a same tendency line with some small deviations?

For SJT samples, Venetian production is quite impossible because neither alkali sources (barilla), silica sources or Eu/Eu* values are consistent with what is reported on the literature for genuine Venetian production. All the analysed layers from SJT_01 and SJT_09 fragments are compatible with, respectively, 7^{th} and 8^{th} geochemical patterns. Furthermore, the unique pattern observed in SJT_09 (Crist's cross) suggests that this specific glass object was ordered from a *façon de Venise* glasshouse, potentially of Portuguese origin, given its significant symbolic importance.

An intriguing observation is that despite the general deviation of waste production in Lisbon from the reported compositions in the literature, indicating a disparity between observed and published data, approximately 60% of the analysed pick-up glass samples (61 out of 105, only from Lisbon and SCV contexts) exhibit a geochemical pattern consistent with LCD_03 production waste. Notably, among these pick-up glass fragments are the gourd-shaped vessels SCV_044 and SCV_329, as well as the SCV_360 fragment adorned with an original flower drawing. Furthermore, most of fragments that exhibit the 6^{th} tendency line have a glass composition consistent with the use of barilla as an alkaline source and the major components associated to silica sources located in the Lisbon area. This observation aligns with historical documentation, which extensively mentions the utilization of barilla ashes by Portuguese glassmakers.

Moreover, all the glass fragments compatible with Venetian production (concerning the alkali and silica source and Eu/Eu* values) displays different geochemical patterns (1^{st}, 6^{th}, 7^{th} and 9^{th}). This observation opens some possibilities to considerate:

(4) Venetian glassmakers were using more alkali and/or silica sources than the ones that have been mentioned in the literature (pebbles from the Ticino River – Veritá 2013, 528).

(5) *Façon de Venise* glass production made glassware by using pure and similar raw materials to produce their glassware (as pointed by De Raedet et al. 2002) and different glass production centres can only be traced by geochemical patterns investigation.

(6) Glass recycling.

Gathering all this information we can open the possibility of Lisbon glass production centres being here disclosed for the first time, although further studies are still required to confirm this attribution.

This work allowed us to identify the knowledge gaps about the study of pick-up glass decorative techniques and aims to encourage the development of further research that will help to raise awareness and the value of these objects.

6

FUTURE WORK

To enhance the valorisation and comprehensive understanding of Portuguese glass, we deem it crucial to gain access to the glass furnaces in Portugal, particularly those situated in Lisbon, as we strongly believe that the geochemical patterns specific to Lisbon have been revealed through our research. Additionally, we intend to explore the synthesis of glass using silica sources from the Tagus River region in Lisbon, with the aim of corroborating our hypotheses.

Furthermore, there are unresolved questions that necessitate further investigation, as continued research endeavours have the potential to shed light upon these unresolved aspects:

- Why this type of glass objects preserved in Museums do not follow the same tendency (e.g. form, colours choice, decoration) of those which were found in archaeological contexts?
- Can this observation be related with the fact that only the considered master pieces were preserved by the collectors and, consequently, are preserved in the museums?
- Can it be linked with different production centres (only the Venetian glassware or the best *façon de Venise* glass are in the museums)?
- Was the colourless *millefiori* glass considered more luxurious than the *millefiori* that have a coloured body glass?
- Were the different hues of colourless observed mainly in the body glass of archaeological artefacts deliberated (greyish/ greenish)?
- Was it a matter of taste and fashion?
- Or, could the above observation imply different (local?) production places?

Another crucial aspect to emphasize is that, in the realm of provenance studies, there exists a greater advancement in the analysis of Roman glass compared to that of Modern glass.

Therefore, we propose the necessity of further promoting investigations into the composition of more recent glass, with the aim of recovering vital information pertaining to the pinnacle of Portugal's historical development. These artifacts form an integral part of collective memory, serving as reflections of the ancestral Portuguese community from which we have descended and as a testament to the consequences of an evolution.

| 7

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A

Appendix

A.1 Nomenclature

NOMENCLATURE USED IN THE LITERATURE APPLIED TO THE DIFFERENT PERIODS

Period	Terms	References
Roman	*Millefiori*	Barber et al. 1990; Gedzevičiūtė et al. 2009; Revi 1958; Truman 1979
	Millefiori or Mosaic glass	Richter 1919
	Mosaic glass	Whitehouse 1993; Eisen 1919; Moretti 2012
	Murrina	Loewental et al. 1949
	Murrhine	Loewental et al. 1949
	Murrino	Moretti 2012
Renaissance (glass objects decorated with multi-coloured sliced canes)	*Millefiori*	Baart 2002; Barber 1915; Barovier Mentasti 2012; Baumgartner 2010; Bruhn 1995; Charleston 1984; Whitehouse 1993; Grawronski et al 2010; Gros-Galliner 1970; Gudenrath 2012; Henkes 1994; Hollister 1981; Holl-Gyürky 1986; Lima 2010; Lima et al. 2012; Marquis 1972; Medici 2012; Newman 1977; Page 2004; Reynolds 1992; Tait 1979; Tait 2012; Taylor 1992; Whitehouse 2012; Zerwick 1990
	Murrine	Moretti 2005; Uboldi 2015
Renaissance (glass objects decorated with monochromatic glass slice)	*Blobbing*	Gudenrath 2012; Medici 2014
	Dotted glass	Baart 2002
	Flecked glass	Henkes 1994
	Gevlekt glas	Grawronski et al 2010
	Macchie	Medici 2010
	Decoratted with pastilles	Gratuze & Janssens 2004
	Nailsea	Dungworth et al. 2006
	Picchietato	Medici 2010
	Splashed/ Splashing	Dungworth et al. 2006; Lazar & Willmott 2006; Medici 2014; Willmott 2003

A.2 Technological development - making canes

INFORMATION ABOUT HOW MANY AUTHORS HAVE CITED EACH STEP OF *MURRINE* PRODUCTION.

Step	References
1	Marquis 1972; Moretti 1982; Moretti 2005; Moretti 2012; Selman 1983; Taylor 1992
2	Gros-Galliner 1970; Moretti 1982; Moretti 2005; Moretti 2012
3	Barber 1915; Gros-Galliner 1970; Gudenrath 2012; Marquis 1972; Moretti 1982; Moretti 2005; Taylor 1992; Theuerkauff-Liederwald 1994
4	Marquis 1972; Moretti 1982; Moretti 2005; Selman 1983; Taylor 1992;
5	Moretti 1982; Moretti 2005; Revi 1958; Selman 1983
6	Barber 1915; Marquis 1972; Moretti 1982; Moretti 2005; Revi 1958; Selman 1983; Taylor 1992;
7	Barber 1915; Barovier Mentasti 2005; Bruhn 1995; Charleston, 1984; Gudenrath 2012; Hollister 1981; Moretti1985; Moretti 2005; Moretti 2012; Selman 1983; Taylor 1992
8	Hollister 1981; Marquis 1972; Moretti 2005
9	Barber 1915; Gudenrath 2012; Hess 1997; Moretti 2005; Moretti 2012; Revi 1958; Selman 1983; Taylor 1992
10	Barber 1915; Bruhn 1995; Gudenrath 2012; Hess 1997; Marquis 1972; Moretti 1982; Moretti 1985; Moretti 2005; Moretti 2012; Revi 1958; Selman 1983; Taylor 1992
11	Barovier Mentasti 2005; Barovier Mentasti 2012; Bruhn 1995; Gedzevičiűtè et al. 2009; Gros-Galliner 1970; Gudenrath 2012; Moretti 1982; Moretti 1985; Moretti 2005; Moretti 2005; Moretti 2012; Perran 2000; Reynolds 1992; Selman 1983; Theuerkauff-Liederwald 1994
12	Barber 1915; Eisen 1919; Gedzevičiűtè et al. 2009; Gros-Galliner 1970; Hess 1997; Perran 2000; Revi 1958; Taylor 1992; Theuerkauff-Liederwald 1994; Wood 2000; Zerwick 1990
13	Cambril Campaña & Marinetto 2016; Gedzevičiűtè et al. 2009; Gros-Galliner 1970; Perran 2000; Revi 1958; Selman 1983; Zerwick 1990
14	Gedzevičiűtè et al. 2009; Gros-Galliner 1970; Revi 1958; Zerwick 1990
15	Barber 1915; Cambril Campaña & Marinetto 2016; Eisen 1919; Gedzevičiűtè et al. 2009; Hess 1997; Selman 1983; Zerwick 1990

A.3 Technological development - making objects

INFORMATION ABOUT HOW MANY AUTHORS HAVE CITED EACH STEP OF *MILLEFIORI* OR *SPLASHING* TECHNIQUE.

Step	References
1	Bruhn 1995;
2	Bruhn 1995; Gudenrath 2012; Theuerkauff-Liederwald 1994
3	Gudenrath 2012; Medici 2012; Moretti 2012; Theuerkauff-Liederwald 1994
4	Barovier Mentasti 2012; Bruhn 1995; Helmut 1995; Henkes 1994; Gudenrath 2012; Lima et al. 2012; Medici 2012; Moretti 2012; Tait 2012; Taylor 1992; Whitehouse 2012
5	Bruhn 1995; Charleston 1984; Gudenrath 2012; Moretti 2012; Newman 1977;
6	Helmut 1995; Henkes 1994; Moretti 2012; Theuerkauff-Liederwald 1994

A.4 Different types and categories of the consulted references

DIFFERENT TYPES AND CATEGORIES OF THE CONSULTED REFERENCES

Type of literature	Categories	Exclusive	Language	References
Book section	Al	No	English (Eg)	Tyson 1996
	Al	No	Italian (It)	Medici 2010
	Al	No	It	Uboldi 2015
	Al / H	No	Eg	Charleston 1984
	Al/ Am/ H	No	Eg	Gratuze & Janssens 2004
	Al/ Am/ H	No	Eg	Lazar & Willmott 2006
	Am/ H	No	German (Gr)	Theuerkauff-Liederwald 1994
	H	No	Gr	Helmut 1995
	H	No	Gr	Minutoli 1827
	H	No	Eg	Tait 1979
	H	No	Eg	Zerwick 1990
	H	No	Eg	Hills 1999
	H	No	Eg	Tait 2012
	H	No	Eg	Whitehouse 2012
	H	No	Gr/ Eg	Spenlé 2014
	H / T	No	Eg	Bruhn, 1995
	H/ T	No	Eg	Gros-Galliner 1970
	H / T	No	Eg	Wood 2000
	T	No	Eg	Pellatt 1849
	T	No	Eg	Gudenrath 2012
	T	No	Eg	Schmid 1997
	T	Yes	Eg	Selman 1983
Catalogue	Al/H/T	No	Spanish (Sp)	Campaña & Marinetto 2016
	Al / H	No	French (Fr)/ Gr	Baumgartner 2015
	H	No	Eg	Hess & Husband 1997
	H	No	Eg	Page 2004
	H	No	Eg	Barovier Mentasti 2005
	H	No	Fr	Baumgartner 2010
	H	No	It	Tonini 2011
	H	No	It	Barovier Mentasti 2012
	H	Yes	Eg	Taylor 1992
	H / T	No	It	Moretti 2012
Conference proceedings	Al/ Am/ H	No	Eg	Baart 2002
	Al/ Am/ H	No	Eg	Mendera 2002
	Al/ Am / H	No	Gr	Gradmann et al. 2013
	Al / H	No	Eg	Medici 2012
	Al/ H	No	Sp	Beltrán de Heredia & Miró i Alaix 2006
	Al / H / T	Yes	Eg	Pulido Valente et al. 2019
	H	Yes	Eg	Hollister 1981
Dictionary	H / T	No	Eg	Newman 1977
	T	No	Eg	Whitehouse 1993

Al – archaeological
Am – archaeometric
H – historic
T – technologic

DIFFERENT TYPES AND CATEGORIES OF THE CONSULTED REFERENCES (Continued)

Type of literature	Categories	Exclusive	Language	References
Journal article	Al	No	Eg	Barber et al. 1990
	Al	No	Portuguese (Pt)	Ferreira 2004
	Al / H	No	Hungarian (Hg)	Gerevich 1952
	Al / H	No	Eg	Holl-Gyürky 1986
	Al/Am/H/T	No	It	Verità 1985
	Al/Am/H/T	No	Eg	Dungworth et al. 2006
	Al/Am/H/T	No	Eg	Gedzevičiūtė et al. 2009
	Al/Am/H/T	Yes	Eg	Verità & Zecchin 2008
	Al/Am/H/T	Yes	Eg	Lima et al. 2012
	H	No	Eg	Eisen 1919
	H	Yes	Eg	Richter 1919
	H	Yes	Eg	Loewental et al. 1949
	H	No	Eg	Charleston 1967
	H	No	It	Zecchin 1968
	H	No	It	Zecchin 1990a (1983)
	H	No	It	Zecchin 1990b (1980)
	H	No	It	Zecchin 1990c (1984)
	H	No	It	Zecchin 1990d (1952)
	H	No	Eg	Truman 1979
	H	Yes	Eg	Hollister 1983
Journal article (Continuation)	H	Yes	Eg	Reynolds 1992
	H	No	Eg	Kos 1994
	H	Yes	Eg	Bloom 1995
	H / T	No	Eg	Revi 1958
	H / T	Yes	Eg/ It	Moretti 1982
	H / T	Yes	It	Moretti 1985
	H / T	No	Eg/ It	Moretti 2005
Poster	Al /Am /H/T	Yes	Eg	Pulido Valente et al. 2019
	T	Yes	Eg	Pulido Valente et al. 2017
Report	Al	No	Gr	Henkes 1994
	Al	No	Dutch (Dt)	Willmott 2009
	Al	No	Dt/ Eg	Gawronski et al. 2010
	Al	No	Eg	Kunicki-Goldfinger & Dzierzanowski 2010
	Al	No	Eg	Willmott 2003
Thesis	Al	No	Pt	Medici 2014
	Al/Am/H/T	Yes	Eg	Lima 2010
	Al/Am/H/T	No	Pt	Teixeira 2014
	H	No	Eg	Trowbridge 1922
	T	No	Eg	Marquis 1972

Al – archaeological
Am – archaeometric
H – historic
T – technologic

A.5. Samples presentation:

Context	Nº.	Type	Part preserved	Gold	Cane colours	Patterns
LCD	LCD_03	Undetermined	Part of wall with rim	No	Clear, Red and White	*Rosette*
	LCD_31	Undetermined	Part of wall	No	Red	Undefined
	LCD_54	Undetermined	Part of wall	No	Clear, Amber and White	*Rosette*
LCS	LSC_001	Undetermined	Part of wall	Yes	Blue, Turquoise, Red and White	Flower/ cross and Caravel
	LSC_002	Undetermined	Bird head	No	Blue, Red and White	Flower/ cross
	LSC_004	Undetermined	Part of wall	No	Blue, Red and White	Undefined
	LSC_005	Undetermined	Part of wall	No	Blue, Turquoise, Red and White	*Rosette*
	LSC_006	Small flask/ jar	Neck	No	Blue, Turquoise, Red and White	*Rosette*
SCV	SCV_044	Gourd-shaped flask	Neck and rim mouth	Yes	Blue, Greenish, Red and White	*Rosette*
	SCV_046	Flask in gourd shape	Neck and rim mouth	No	Red and White	Dots
	SCV_216	Undetermined	Part of wall	No	Red and White	*Rosette*
	SCV_232	Bowl	Part of wall with rim	No	Blue, Greenish, Red, and White	Undefined
	SCV_235	Undetermined	Part of wall	No	Blue, Red, Turquoise and White	*Rosette*
	SCV_236	Small flask (?)	Part of wall	No	Red	Dots
	SCV_245	Small flask (?)	Part of wall	Yes	Red, Turquoise and White	Undefined
	SCV_250	Small flask (?)	Part of wall	Yes	Blue, Red, Turquoise and White	Undefined
	SCV_272	Undetermined	Part of wall	No	White	Undefined
	SCV_275	Undetermined	Part of wall	No	Red	Dots
	SCV_329	Flask in gourd shape	Neck	No	Red, Turquoise and White	Cross
	SCV_357	Bowl	Part of wall	No	Blue, Red and White	*Rosette*
	SCV_360	Undetermined	Base/ foot	No	Blue, Red and White	Flower
	SCV_364	*Millefiori* cane (?)	Cane	No	Blue, Greenish, Red and White	Concentric
	SCV_365	Undetermined	Base/ foot	No	Blue, Turquoise, Red and White	Flower
	SCV_366	*Millefiori* cane (?)	Cane	No	Blue, Turquoise and White	Concentric
	SCV_368	Undetermined	Part of wall	No	Blue, Purple, Turquoise and White	Flower
	SCV_369	Bowl	Base/ foot	No	Blue, Turquoise, Red and White	*Rosette*
	SCV_375	Undetermined	Part of wall	No	Blue, Red and White	*Rosette*
	SCV_388	Undetermined	Part of wall	No	Blue, Turquoise, Red and White	*Rosette*
	SCV_394	Undetermined	Part of wall	No	Clear, Blue, Red and White	*Rosette*
SJT	SJT_001	Bowl	Part of wall with rim	No	Red and White	*Rosette*
	SJT_009	Small flask	Neck, part of wall and part of base	No	Turquoise, Red and White	Cross

N/a – Non applicable; Gold= Gold Leif

APENDIX A.6: Composition of the analysed production waste 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_03	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_31		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_54		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_54		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_02		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_04		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_06		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_03	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_01		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_02		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_05		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_31	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_54		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_01		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_02		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_04		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_05		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_01	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_06		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_03	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_54		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_01		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_02		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_04		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_05		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_14	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_14	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_32	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_32	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_03	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_03	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_03	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

APENDIX A.7: Composition of the analysed production waste 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. The chemical composition of red and clear glass presented in body glass of LCS_05 are highlighted.

			Wt%											µg/g											
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	SnO_2	SrO	ZrO_2	BaO	PbO	Bi
SCV_044	B	Cane	17.0	2.5	6.4	57.9	0.36	0.86	4.48	7.34	0.28	0.65	1.11	1430	291	226	75	2617	565	577	75	457	537	658
SCV_232		Body	10.4	3.0	2.0	64.5	0.26	0.68	4.53	9.68	0.07	0.38	1.31	4544	1514	1202	159	6268	6261	534	49	221	5308	5131
SCV_245		Cane	14.4	3.1	4.1	56.7	0.31	0.71	5.21	8.35	0.18	0.45	1.81	839	662	5906	96	2066	12489	496	126	312	2.32	809
SCV_250		Cane	14.3	3.5	1.5	65.7	0.31	0.89	2.18	10.02	0.06	0.06	0.81	1361	338	313	67	2773	444	700	24	134	532	456
SCV_329		Body	11.4	3.0	3.4	63.2	0.34	0.67	7.40	9.69	0.09	0.07	0.44	358	85	36	47	1119	<10	598	66	138	25	124
SCV_357		Body	18.2	3.0	4.0	59.8	0.31	1.09	3.45	7,42	0.14	0.40	0.95	1689	576	938	69	2695	2018	455	77	194	1819	1029
SCV_360		Body	15.9	2.9	2.3	64.9	0.33	0.99	4.20	6,92	0.11	0.29	0.82	456	148	202	59	500	772	733	55	456	521	409
SCV_360		Cane	15.3	3.0	2.2	64.5	0.29	0.97	3.86	7.50	0.11	0.37	1.08	3214	367	213	108	2194	482	656	47	200	466	343
SCV_364		Cane	11.9	2.9	1.0	67.2	0.27	0.81	5.64	6.83	0.05	0.02	1.23	5118	1460	2036	76	6556	138	489	24	75	258	3338
SCV_365		Body	17.1	1.9	3.4	65.3	0.42	1.07	3.73	4,42	0.23	0.70	1.21	606	204	190	113	720	1191	382	92	290	731	547
SCV_365		Cane	15.7	2.6	3.2	63.3	0.45	0.90	3.78	6.58	0.14	0.78	1.32	2639	799	350	171	2938	1304	542	70	445	904	1312
SCV_366		Cane	12.8	3.6	1.2	68.8	0.22	0.71	2.27	8.79	0.06	0.50	0.61	1038	332	53	62	1385	66	654	23	194	52	898
SCV_368		Body	17.0	1.9	3.4	65.3	0.42	1.09	3.80	4.42	0.23	0.71	1.21	603	202	145	111	717	1011	533	92	467	3125	1568
SCV_368		Cane	15.2	2.6	3.3	63.3	0.46	0.82	3.82	6.53	0.15	0.77	1.42	2991	910	461	197	3104	2514	385	70	290	610	524
SCV_369		Body	17.4	3.1	4.1	60.0	0.32	0.98	4.66	7.33	0.16	0.54	0.80	821	302	196	66	1347	483	480	77	238	6531	550
SCV_369		Cane	17.4	3.0	3.9	59.0	0.34	1.00	4.63	7.07	0.15	0.70	0.78	1242	387	5461	77	2108	1745	487	73	215	4623	425
SCV_375		Body	18.1	2.7	3.9	60.7	0.29	1.14	2.94	7.14	0.14	0.46	0.76	1021	354	460	61	1746	6168	413	77	208	1732	683
SCV_388		Body	18.4	2.8	3.8	61.0	0.36	1.16	3.24	6.70	0.18	0.53	0.99	1044	326	465	81	1527	1347	450	91	93	238	455
SCV_394		Body	17.0	1.8	0.9	67.3	0.37	1.26	3.88	5.81	0.06	0.29	0.93	1142	440	689	115	<10	231	206	35	94	220	n.d.
SJT_001		Body	12.4	3.5	4.3	57.7	0.41	0.67	7.17	11.26	0.14	0.59	1.20	627	82	55	55	1806	187	971	71	12	210	109
SJT_009		Body	13.7	3.6	3.4	59.2	0.32	0.64	7.30	9.50	0.08	0.49	0.87	1853	689	246	246	2887	745	737	46	<10	692	506
SCV_044	Cl	Body	20.2	2.8	6.8	55.8	0.33	1.14	3.99	6.88	0.32	0.55	1.06	148	49	50	74	250	363	634	284	443	386	88
SCV_046		Body	14.3	2.9	1.8	61.4	0.31	0.76	2.70	7.82	0.07	0.27	1.07	185	92	8833	63	544	29433	484	44	131	26083	88
SVC_235		Body	14.7	2.9	3.5	63.5	0.23	0.69	5.07	7.91	0.18	0.51	0.55	10	<10	12	39	<10	<10	652	126	384	10	<10
SVC_236		Body	14.0	3.1	5.4	59.0	0.25	0.70	6.77	8.83	0.23	0.56	0.93	73	41	310	71	127	130	477	145	374	207	26
SVC_245		Body	15.4	3.5	4.7	59.4	0.35	0.84	5.59	8.50	0.20	0.38	0.76	36	25	145	55	67	913	660	121	338	907	27
SVC_250		Body	15.4	3.0	5.6	62.0	0.31	0.95	3.77	7.31	0.21	0.39	0.96	12	11	16	53	20	<10	536	159	276	22	<10
SCV_272		Body	18.5	6.8	7.5	55.2	0.81	0.95	1.83	4.93	0.29	0.88	2.11	20	27	31	132	<10	<10	490	97	318	11	<10
SCV_275		Body	15.9	5.2	5.3	64.7	0.37	0.97	1.35	3.24	0.29	1.07	1.36	20	18	14	90	<10	<10	365	151	368	<10	<10
SCV_394		Cane	17.5	1.8	1.4	64.5	0.67	1.26	1.34	5.89	0.07	0.22	0.61	11	12	9500	121	<10	5295	240	33	148	10877	<10
SCV_232	G	Cane	10.8	3.1	2.2	65.1	0.25	0.83	4.88	10.21	0.07	0.40	0.94	163	69	2287	65	264	4236	551	54	231	3489	178
SCV_368	P	Cane	15.4	2.6	3.3	63.6	0.47	0.85	3.79	6.52	0.15	0.76	1.34	2998	847	473	189	3220	735	528	70	458	533	1489
SCV_044	R	Cane	15.6	2.9	7.1	55.4	0.55	0.82	4.69	6.88	0.34	0.41	2.83	97	46	4640	120	154	6743	475	311	354	6076	73
SCV_216		Cane	16.7	3.0	4.1	57.5	0.39	0.97	3.70	6.90	0.17	0.37	4.40	221	102	6025	84	432	4721	408	86	178	5639	136
SCV_232		Cane	10.2	2.9	2.1	62.1	0.26	0.74	4.61	9.48	0.07	0.35	4.70	179	83	14154	85	310	4584	511	50	210	3811	194
SCV_235		Cane	12.6	3.4	1.3	56.7	0.30	0.68	2.35	9.23	0.07	0.19	4.22	313	143	7413	62	907	34758	620	29	119	44990	192

SCV_245		Cane	14.5	3.2	5.4	57.3	0.38	0.80	5.26	8.36	0.22	0.52	0.98	121	74	7067	78	223	484	714	151	312	516	94
SCV_250		Cane	13.9	3.2	1.1	58.7	0.33	0.66	2.10	8.77	0.06	0.52	3.42	305	133	6537	82	782	37183	522	25	100	36597	102
SCV_275		Cane	12.8	3.2	1.1	56.6	0.31	0.64	2.02	8.37	0.05	0.68	2.61	399	105	7587	106	750	47149	560	23	137	60600	113
SCV_329		Cane	16.8	2.8	1.6	58.5	0.31	0.65	3.98	8.27	0.07	0.77	3.05	741	363	17776	107	1696	36317	510	38	200	37104	1039
SCV_357		Cane	12.6	3.5	4.5	57.7	0.39	0.98	3.40	7.47	0.15	0.22	3.42	110	66	9859	66	195	1453	444	79	159	1297	92
SCV_360		Cane	10.3	2.8	2.9	61.2	0.35	0.78	3.66	6.57	0.13	0.37	3.12	81	85	21440	130	188	3231	615	55	212	2170	135
SCV_364		Cane	11.5	2.8	1.2	63.9	0.29	0.74	3.36	6.63	0.05	0.02	4.62	20	29	24732	32	52	1697	466	466	76	2016	11
SCV_369		Cane	15.0	3.4	4.2	57.6	0.43	0.91	4.07	7.89	0.17	0.22	1.62	27	30	12749	64	70	1466	417	79	149	17504	22
SCV_375		Cane	16.2	3.3	4.0	55.2	0.38	0.99	3.37	7.08	0.15	0.20	2.85	58	47	9785	66	113	22619	423	75	148	30072	48
SCV_388		Cane	16.0	3.3	4.4	58.2	0.42	0.93	3.12	7.17	0.18	0.37	3.70	178	121	7758	76	359	3930	445	86	197	4052	135
SCV_394		Cane	14.8	3.5	2.0	64.4	0.50	0.85	3.24	6.39	0.10	0.37	2.36	57	87	15183	2158	69	2255	286	52	212	3014	<10
SJT_001		Cane	13.9	3.2	3.9	57.7	0.39	0.69	6.44	8.80	0.11	0.44	2.71	68	31	13316	69	217	629	582	66	253	691	17
SJT_009		Cane	13.5	3.5	3.4	57.3	0.34	0.59	7.15	9.13	0.08	0.46	3.58	59	28	6488	50	97	714	692	46	267	651	36
SCV_216	T	Body	17.7	2.7	3.7	60.4	0.37	1.60	3.75	6.15	0.17	0.20	1.00	36	55	24845	62	92	682	444	85	150	973	39
SCV_250		Cane	14.0	3.3	2.3	61.4	0.33	0.77	2.75	8.70	0.10	0.45	1.55	229	91	1916	76	530	20708	549	64	147	18647	72
SCV_329		Cane	9.0	1.9	4.7	59.5	0.32	0.57	6.09	8.13	0.14	0.17	0.68	38	114	79704	113	207	3028	508	96	267	2682	20
SCV_364		Cane	12.2	2.9	1.0	67.3	0.27	0.81	5.50	6.80	0.04	0.02	0.52	5153	1483	1185	77	6805	123	490	24	75	276	3197
SCV_365		Cane	15.1	2.8	2.9	64.2	0.42	0.93	3.49	6.78	0.13	0.77	0.91	30	33	12617	115	50	887	573	61	279	905	25
SCV_366		Cane	10.6	1.6	0.7	55.4	0.23	0.72	2.43	5.52	0.03	0.40	0.01	73	60	29622	51	119	11.93	588	15	110	88852	24
SCV_368		Cane	14.8	2.9	2.9	63.7	0.41	0.88	3.44	6.97	0.12	0.68	0.94	33	41	19306	126	66	1513	592	58	274	1054	32
SCV_369		Cane	16.6	2.4	4.2	57.2	0.33	1.08	4.20	5.71	0.15	0.04	0.71	<10	74	71156	53	103	592	319	79	105	1574	15
SCV_388		Cane	17.6	2.6	3.7	60.1	0.35	1.12	3.53	5.96	0.17	0.22	0.92	46	84	32668	78	148	1119	424	83	145	1689	60
SJT_001		Cane	12.6	3.6	5.0	56.9	0.37	0.76	7.10	11.0	0.16	0.57	1.39	777	70	480	22	1942	212	915	87	251	446	79
SCV_044	W	Cane	10.5	1.6	4.0	41.5	0.27	1.10	2.99	4.33	0.17	0.17	0.67	23	39	965	75	55	13.2	354	199	181	19.59	60
SCV_216		Cane	10.9	1.6	2.3	40.4	0.25	1.04	2.15	3.96	0.10	0.14	0.47	28	47	754	52	92	15.8	240	58	137	20.66	27
SCV_232		Cane	8.0	2.1	1.3	49.1	0.21	0.58	3.51	6.68	0.05	0.27	0.69	247	132	601	78	678	16.4	359	35	252	10.79	395
SCV_245		Cane	12.5	2.4	3.9	49.7	0.31	0.69	4.56	6.32	0.16	0.26	0.66	46	41	1309	74	487	4.3	601	101	88	13.89	75
SCV_250		Cane	12.4	2.9	0.7	56.4	0.33	0.60	1.91	8.54	0.04	0.78	0.67	75	51	1361	54	242	6.6	484	18	98	7.73	34
SCV_329		Cane	9.7	2.6	1.0	51.1	0.24	0.55	3.37	7.45	0.04	0.59	0.60	82	48	224	51	319	10.1	513	24	109	12.40	141
SCV_360		Cane	10.7	2.1	1.4	45.7	0.26	0.78	2.35	5.08	0.07	0.21	0.52	14	38	115	57	248	15.0	491	33	116	15.57	10
SCV_364		Cane	8.7	2.1	0.6	50.1	0.21	0.65	3.98	4.72	0.03	0.09	0.33	63	59	372	21	84	12.1	349	16	73	16.12	59
SCV_365		Cane	13.2	1.6	2.1	48.4	0.44	0.98	2.66	3.61	0.15	0.35	0.90	24	46	931	75	37	15.6	279	63	149	9.82	19
SCV_368		Cane	10.4	1.1	1.5	37.2	0.45	0.88	1.94	2.36	0.13	0.16	0.75	22	73	1697	72	39	30.6	177	56	97	12.10	17
SCV_369		Cane	12.4	2.2	2.6	40.2	0.29	0.91	2.41	4.43	0.10	0.07	0.50	12	43	22723	41	47	13.5	249	52	77	18.02	14
SCV_375		Cane	13.4	2.3	2.7	48.4	0.26	0.56	2.53	5.43	0.10	0.23	0.49	31	42	3436	48	52	12.3	343	54	117	10.83	25
SCV_388		Cane	11.9	1.7	2.1	39.0	0.25	0.95	1.91	3.62	0.10	0.22	0.44	33	53	7089	61	71	18.3	250	58	97	18.72	30
SCV_394		Cane	14.9	1.3	0.9	52.1	0.71	1.75	2.93	4.19	0.06	0.13	0.47	<10	22	2259	99	37	6.8	168	27	63	13.46	74
SJT_001		Cane	11.5	2.8	2.1	47.9	0.26	0.81	4.61	6.47	0.06	0.22	0.58	42	30	4406	36	190	7.77	455	37	143	14.37	17
SJT_009		Cane	10.3	2.6	2.3	45.9	0.28	0.65	5.45	6.62	0.05	0.23	0.57	52	47	113	47	221	12.12	481	32	144	12.70	43

B = Blue; Cl= Clear; G = Green; P = Purple; R= Red; T= Turquoise; W= White;

Apendix A.8:

Summary of all the information taken from SCV and SJT pick-up samples: pattern, alkali sources, silica sources, geochemical pattern (GP) and Eu/Eu* values.

Patterns	Samples	Alcaly Sources	Silica Sources	G P	Eu/Eu*
Splashed + rosette	SCV 044 cl	*Cristallo*	Lisbon (?)	6	0.48
	SCV 044 db	*Barrila*	Lisbon	6	0.45
	SCV 044 r	*Barrila*	Lisbon (?)	6	0.49
	SCV 044 w	*Barrila*	Lisbon	6	0.43
Splashed	SCV 046 cl	Untreated Levantine ashes	Lisbon (?)	9	**0.63**
Rosette	SVC 216 r	*Barrila*	Lisbon	6	0.33
	SVC 216 t	Mix (*Barrila* and *Levantine*)	Lisbon	6	**0.62**
	SVC 216 w	*Levantine* (+ Bar (?))	De Twee Rozen	4	n/d.
Indefinite	SVC 232 db	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	9	0.57
	SVC 232 gr	*Barrila*	Venetian Splashed glass (Veritá & Zecchin 2008)	6	0.56
	SVC 232 r	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	9	0.56
	SVC 232 w	*Barrila*	Venetian/ De Twee Rozen	9	n/d.
Splashed	SVC 235 cl	*Barrila*	Lisbon	6	**0.62**
	SVC 235 r	Untreated Levantine ashes	Between Venetian *blanchum* and De Twee Rozen	7	0.28
Splashed + rosette	SVC 236 cl	*Barrila*	Lisbon	6	**0.72**
Indefinite	SVC 245 cl	*Barrila*	Lisbon	6	**0.69**
	SVC 245 db	*Barrila*	Lisbon	6	**0.61**
	SVC 245 r	*Barrila*	Lisbon	6	0.51
	SVC 245 w	*Barrila*	Lisbon	6	0.29
Splashed + rosette	SVC 250 cl	Mix (*Barrila* and *Levantine*)	Lisbon	6	0.52
	SVC 250 db	Untreated *Levantine* ashes	Lisbon	7	**0.70**
	SVC 250 r	*Levantine* (+ Bar (?))	Between Venetian *blanchum* and De Twee Rozen	7	**0.62**
	SVC 250 t	Untreated *Levantine* ashes	Between Venetian *blanchum* and De Twee Rozen	6	0.60
	SVC 250 w	Untreated *Levantine* ashes	Venetian/ De Twee Rozen	7	0.14
Splashed	SVC 272 cl	Untreated *Levantine* ashes	Lisbon (?)	9	**0.70**
Splashed	SVC 275 cl	*Cristallo*	Lisbon	6	**0.61**
	SVC 275 r	Untreated *Levantine* ashes	Venetian Splashed glass (Veritá & Zecchin 2008)	6	**0.70**
Splashed + cross	SVC 329 db	*Barrila*	Lisbon	6	0.53
	SVC 329 R	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	7	0.47
	SVC 329 TB	*Barrila*	Lisbon	6	0.43
	SVC 329 W	*Barrila*	Venetian Splased glass (Veritá & Zecchin 2008)	9	n/d.
Rosette	SVC 357 DB	Mix (*Barrila* and *Levantine*)	Lisbon	6	**0.62**
	SVC 357 R	*Barrila*	Lisbon	6	**0.62**

Flowers + hybrid	SVC 360 db	Mix (*Barrila* and *Levantine*)	De Twee Rozen	6	0.57
	SVC 360 db	Mix (*Barrila* and *Levantine*)	De Twee Rozen	6	0.55
	SVC 360 r	*Barrila*	Lisbon	6	0.59
	SVC 360 w	*Levantine* (+ *Bar* (?))	Venetian Splashed glass (Veritá & Zecchin 2008)	6	n/d.
millefiori cane	SCV 364 cl	*Barrila*	Venetian/ De Twee Rozen	7	0.58
	SCV 364 db	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	7	**0.68**
	SCV 364 r	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	9	**0.64**
	SCV 364 t	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	9	0.58
	SCV 364 w	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	9	0.93
Flowers	SVC 365 cl	*Cristallo*	Between Venetian blanchum and De Twee Rozen	1	0.78
	SVC 365 db	Mix (*Barrila* and *Levantine*)	Lisbon	4	**0.72**
	SVC 365 t	Mix (*Barrila* and *Levantine*)	Between Venetian *blanchum* and De Twee Rozen	3	0.65
	SVC 365 w	*Cristallo*	Between Granada and De Twee Rozen	1	n/d.
millefiori cane	SCV 366 db	Untreated *Levantine* ashes	Between Venetian *blanchum* and De Twee Rozen	7	0.77
	SCV 0366 t	Mix (*Barrila* and Levantine)	Between Venetian *blanchum* and De Twee Rozen	7	**0.67**
Flowers	SVC 368 db	*Cristallo*	Granada (Coutinho et a. 2021)	1	0.78
	SVC 368 db	Mix (*Barrila* and *Levantine*)	Lisbon	4	**0.65**
	SVC 368 t	Mix (*Barrila* and *Levantine*)	Between Venetian *blanchum* and De Twee Rozen	2	**0.61**
	SVC 368 w	*Cristallo*	Between Granada and De Twee Rozen	1	n/d.
	SVC 368 p	Mix (*Barrila* and *Levantine*)	Lisbon	4	0.59
Splashed + rosette	SVC 369 db	*Barrila*	Lisbon	6	**0.67**
	SVC 369 db	*Barrila*	Lisbon	6	**0.66**
	SVC 369 r	Mix (*Barrila* and *Levantine*)	Lisbon	6	0.54
	SVC 369 t	*Barrila*	Lisbon	6	0.50
	SVC 369 w	*Barrila*	Lisbon	6	n/d.
Rosette	SVC 375 bd	*Levantine* (+ *Bar* (?))	Lisbon	6	**0.69**
	SVC 375 r	*Barrila*	Lisbon	6	**0.65**
	SVC 375 w	*Levantine* (+ *Bar* (?))	Lisbon	6	0.33
Indefinite + rosette	SVC 388 db	*Levantine* (+ *Bar* (?))	Lisbon	5	**0.70**
	SVC 388 r	Mix (*Barrila* and *Levantine*)	Lisbon	6	**0.66**
	SVC 388 t	Mix (*Barrila* and *Levantine*)	Lisbon	5	**0.66**
	SVC 388 w	*Levantine* (Left)	Lisbon	4	0.18
Indefinite	SVC 394 cl	*Cristallo*	Lisbon	7	0.49
	SVC 394 db	*Barrila*	Between Venetian *blanchum* and De Twee Rozen	6	0.49
	SVC 394 r	Mix (*Barrila* and *Levantine*)	De Twee Rozen	9	**0.65**

	SVC 394 w	*Cristallo*	Venetian/ De Twee Rozen	9	n/d.
Rosette	SJT 1 db	*Barrila*	Lisbon	7	0.44
	SJT 1 r	*Barrila*	Lisbon	7	0.52
	SJT 1 t	*Barrila*	Lisbon	7	0.56
	SJT 1 w	*Barrila*	Lisbon (?)	7	**0.61**
Splashed + Rosette + Cross of Crist	SJT 9 db	*Barrila*	Lisbon	8	0.50
	SJT 9 r	*Barrila*	Lisbon	8	0.48
	SJT 9 w	*Barrila*	Lisbon (?)	8	0.17

(Underlined) – The glass layer belonging to the body glass appear underlined.
Green – The glass layers that have a compatible composition with Venetian production.

Yellow – The glass layers that were probably produced in Lisbon or, at least, in Portugal.

Blue – The glass composition which the geochemical pattern was only found in the glass fragment that are decorated with the cross of Christ decorative pattern.

UNIVERSIDADE NOVA DE LISBOA

OMNIS CIVITAS CONTRA SE DIVISA NON STABIT

2023

Maria Francisca Vasconcelos Raposo Pulido Valente Monteiro Cabral

Decoding the past through *Pick-up* decorated glass: glass fragments unearthed in Portugal dated to 16th-17th centuries.