Journal of Archaeological Science 39 (2012) 1238–1248

Contents lists available at SciVerse ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Chemical analysis of 17th century *Millefiori* glasses excavated in the Monastery of Sta. Clara-a-Velha, Portugal: comparison with Venetian and *façon-de-Venise* production

Augusta Lima [a,b,*], Teresa Medici [b,c], António Pires de Matos [b], Marco Verità [d]

[a] *Department of Conservation and Restoration, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal*
[b] *Research Unit VICARTE – Vidro e Cerâmica para as Artes, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal*
[c] *Department of History, Archaeology and Arts, Faculdade de Letras-Universidade de Coimbra, Largo da Porta Férrea, 3004-530 Coimbra, Portugal*
[d] *LAMA Laboratory, IUAV University, Venice, Italy*

ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form
5 January 2012
Accepted 6 January 2012

Keywords:
Millefiori glass
façon-de-Venise glass
Venetian glass
Provenance analysis
Electron probe microanalysis
Raman microscopy
UV–Visible absorption spectroscopy

ABSTRACT

A set of ten *Millefiori* glass fragments dating from the 17th century, originated from archaeological excavations carried out at the Monastery of Sta. Clara-a-Velha (Coimbra, Portugal), were characterized by X-ray electron probe microanalysis (EPMA), Raman microscopy and UV–Visible absorption spectroscopy. All glasses are of soda-lime-silica type. The use of coastal plant ash is suggested by the relatively high content of MgO, K_2O and P_2O_5, as well as by the presence of chlorine. Tin oxide or calcium antimonate were the opacifiers used in the opaque glasses, cobalt in the blue glasses, copper in the turquoise glasses, iron in the yellow and greenish glasses, and iron and copper were found in the opaque red and aventurine glasses. Based on the concentrations of alumina and silica four different sources of silica were identified, allowing the classification of the glasses into the following compositional groups: low alumina (<2 wt%), which includes a sub-group of *cristallo* samples with $SiO_2 > 70$ wt%, medium alumina (2–3 wt %), high alumina (3–6 wt%) and very high alumina (>6 wt%). Comparison with genuine Venetian and *façon-de-Venise* compositions showed that two fragments are of Venetian production, one of Venetian or Spanish production and the remaining are of unknown provenance. In two fragments the glass of the decoration is probably Venetian or Spanish but the glass used in the body is also of unknown provenance.

1. Introduction

In recent years, there has been a growing interest on glass originating from Portuguese excavations. A large variety of glass objects found in several locations has been investigated in order to distinguish imported glass from Portuguese glass (Ferreira, 2004; Medici et al., 2009; Medici, in press).

The main aim of this work is to study the possible provenance of a set of *Millefiori glass* fragments originating from the Monastery of Sta. Clara-a-Velha based on their chemical composition. In a first step, the type of glass, as well as colourants and opacifiers added, used both in the body and decoration, are identified. An attempt is also made to distinguish compositional groups among the analyzed glasses and establish relations between the chemical compositions and the raw materials used. Finally, the resulting compositions will be compared with those from Venetian and *façon-de-Venise* glasses in order to determine the possible manufacture locations for the *Millefiori* glasses.

With this work we expect to provide important evidence on production and circulation of glass in Portugal during the 17th century.

1.1. The analyzed glass fragments

The glass fragments analyzed in this study originated from archaeological excavations carried out at the Monastery of Sta. Clara-a-Velha in Coimbra, Portugal. The Monastery is located on the left bank of the River Mondego and it was occupied by the Order of *Poor Clares* from 1317 until 1677, when it was abandoned due to frequent flooding. The archaeological excavations carried out by IPPAR, the Portuguese Institute for Architectural Heritage, from 1995 to 2002, yielded an important archaeological record. A preliminary study of the assemblages indicates that the finds

* Corresponding author. Department of Conservation and Restoration, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal. Tel.: +351 212948322.
E-mail address: arl@fct.unl.pt (A. Lima).

0305-4403/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jas.2012.01.006

Table 1
Catalogue number, typology and colour of the analyzed *Millefiori* glass fragments.

Fragment	Object typology	Body colour	Decoration
SCV 171	Small bottle	Turquoise blue	Opaque white and red dots
SCV 173	Cup	Opaque bluish white	Blue and aventurine dots
SCV 174	Vessel	Opaque red	Opaque white trail on the rim, and applied *Millefiori* rods sections in opaque white, blue and opaque red glass
SCV 175	Vessel	Opaque red	*Millefiori* rods sections in opaque white, blue and opaque red glass
SCV 176	Unknown	Opaque white	Opaque red, blue and aventurine dots
V 66	Small flask	Greyish green	*Millefiori* rods sections in opaque white, blue and opaque red glass
V 67	Small bottle	Greenish yellow	Red and light blue dots
V 68	Small jug	Light blue	*Millefiori* rods sections in opaque white and opaque red glass
V 74	Small flask	Green	Opaque white, light blue and opaque red dots
V 108	Goblet?	Blue	*Millefiori* rods sections in opaque white, opaque red and turquoise blue glass

derive mainly from the last 50 years of the Monastery's existence, that is, the second and third quarters of the 17th century (Báez Garzón et al., 2005; Côrte-Real et al., 2002). A large number of glass fragments was collected, most of them very well preserved. Preliminary studies on the glass finds have already been published, and the chemical characterisation of a few glass fragments by micro-EDXRF was also performed (Ferreira, 2004; Medici et al., 2009).

The present work focuses on a set of glass fragments from blown glass objects decorated either with multicoloured scrap glass or slices of *Millefiori* rods, by rolling the parison on them on the marble. A brief description of the analyzed glass fragments is given in Table 1 and the corresponding photographs are presented in Fig. 1.

Based on the decoration, the fragments can be classified into three different groups. The first group includes fragments SCV 174, SCV 175, V 66, V 68 and V 108 decorated with multicoloured rods. This type of *Millefiori* glass is well known, and many well preserved objects are in museum collections. The majority of them are considered of Venetian production and dated between the end of the 15th and the beginning of the 17th century (Theuerkauff-Liederwald, 1994). Others are supposed to be of Spanish origin, Catalan or Castilian (Page, 2004). Some archaeological information is available (Medici, in press), showing not only the wide distribution of this category but also that during the 17th century *Millefiori* glass was being produced in Amsterdam (Gawronski et al., 2010).

The second group includes fragments SCV 173 and SCV 176 and consists of opaque glass vessels, decorated with dots of blue, red and aventurine glass. These fragments belong also to a well-known category of 17th century Venetian glass, including mainly cups, bowls and goblets (Barovier Mentasti et al., 1982; Verità, 2008; Verità and Zecchin, 2009).

The third group comprising fragments SCV 171, V 67 and V 74 is related to objects that are abundant among the 17th century archaeological glass found in Portugal. These objects show some peculiar features: the body is usually made of transparent glass, in a range of sometime intense natural yellow, green or blue hues, decorated with opaque glass flecks of a limited palette of colours, mainly white, blue or red, arranged without any precise decorative pattern. This decorated glass seems to be a simplified and coarser version of the previous groups.

2. Experimental

Small samples of few mm^2 were removed by dry cutting the fragments with a diamond file. The samples were embedded in cross-section in an acrylic resin and polished with abrasive papers and pastes down to 0.5 μm grain size. The glass chemical composition was determined by X-ray electron probe microanalysis (EPMA) using two different equipments: a Cameca SX-50 from *Stazione Sperimentale del Vetro*, Murano, Venice, Italy, equipped

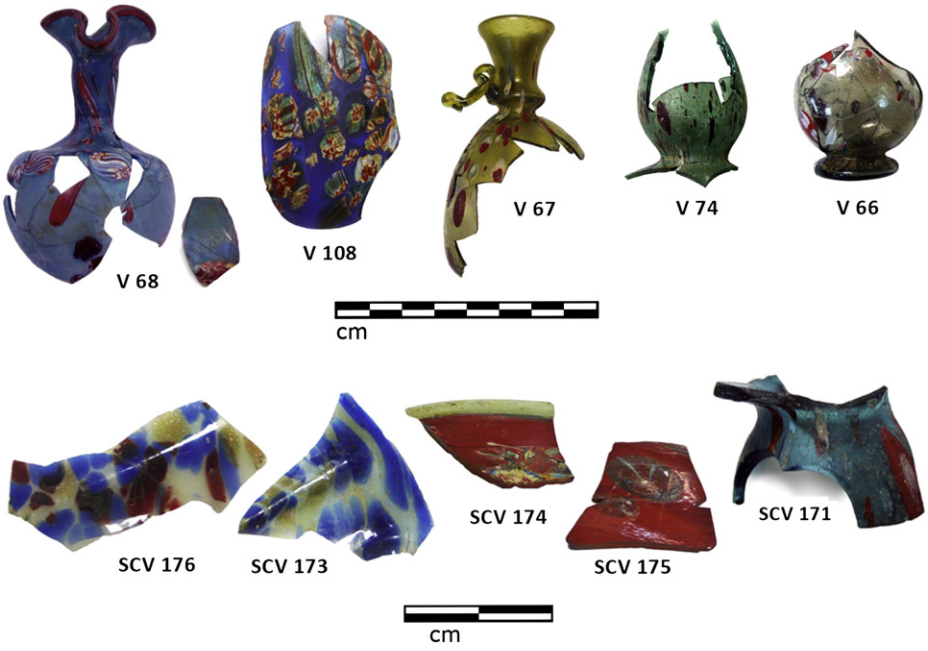

Fig. 1. Analyzed *Millefiori* glass fragments.

with three wavelength-dispersive spectrometers (PET, LiF and TAP crystals) and a Jeol JXA-8500F from *Laboratório Nacional de Engenharia e Geologia*, Oporto, Portugal, equipped with five wavelength-dispersive spectrometers (PET, LiF, TAP and LDE1 crystals). The operating conditions used in the first microprobe were: accelerating potential 15 kV, beam current 20 nA for major and minor components or 100 nA for trace elements, respectively. A 40 × 50 μm scanning electron beam and limited counting time (10 s for major and minor elements, 20–30 s for trace elements) were employed to ensure that no significant alkali drift (ion migration) occurred during the irradiation. The operating conditions of the second microprobe were: accelerating potential 15 kV, beam current 10 nA (major and minor components). An 8–10 μm diameter electron beam and limited counting time (10 s for major and minor elements, 20–30 s for trace elements) was used. Twenty elements were quantified: X-ray Kα lines were analyzed except for lead and bismuth (Mα lines), and antimony, arsenic, and tin (Lα lines). The net X-ray intensities (peak minus background) were quantified by means of PAP correction programs supplied by Cameca and Jeol, respectively.

At least two different areas were analyzed in each glass. The relative standard deviation for SiO_2, Na_2O, K_2O, CaO and MgO is below 1% and for the remaining elements or oxides, Al_2O_3, SO_3, P_2O_5, Cl, Fe_2O_3, MnO, CuO, PbO, SnO_2, CoO, As_2O_5, ZnO and NiO, is below 5%. To verify the accuracy of the method, standard glasses (Corning B, C, D and NBS620) were analyzed under the same experimental conditions as for the samples. The calculated concentration values agreed within 5% with the concentrations of the certified samples (Table 2). The EPMA setting used in this work allows most of the oxides to be analyzed in concentrations as low as 0.02–0.05 wt%. More information on the X-ray microanalysis applied to the glass analysis is fully described elsewhere (Verità et al., 1994).

UV–Visible absorption spectroscopy was used to confirm the presence of the transition metal ions responsible for the colours. An Avantes AvaSpec-2048 fibre optic spectrometer with a 300 lines/mm grating was used. The operational range is 200–800 nm and the instrument has a FWHM resolution of 2.4 nm. The light transmitted was measured using a 200 μm transmission probe (Avantes FC-UV600-2). Raman microscopy was carried out to aid in the identification of the opacifying crystalline compounds. A Labram 300 Jobin Yvon spectrometer, equipped with an Nd:YAG laser 50 mW operating at 532 nm was used. Spectra were recorded as an extended scan. The laser beam was focused either with a 50x or a 100x Olympus objective lens. The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1 and 2).

3. Results and discussion

The study of colourants, decolourants and opacifiers was based on the compositions obtained directly from EPMA analysis, named hereafter as compositions of the "coloured glasses" (Table 3) and on the UV–Vis and Raman spectroscopic analyses. The distinction of compositional groups among the analyzed samples and the comparison of compositions with those from Venetian and *façon-de-Venise* productions, was carried out using the "base glass" composition. The majority of the known analyzed Venetian and *façon-de-Venise* glasses is colourless or slightly coloured. In order to avoid an erroneous distinction of compositional groups, the base glass composition was calculated by subtracting to the composition of the "coloured glasses" the content of colourants, decolourants and opacifiers and then normalizing to 100 wt%.

3.1. Colourants and opacifiers

In the following paragraphs the colour of the glasses will be discussed individually, based on their compositions.

3.1.1. Opaque white glass

The colour and opacity of white glass is due to microcrystals dispersed in the glass matrix. The analytical results revealed that, of the ten white glasses analyzed, cassiterite (SnO_2) was used in eight glasses (Fig. 2), while in the remaining two glasses (SCV 173 and 176), the white opacification can be attributed to crystals of calcium antimonate in its $Ca_2Sb_2O_7$ form (Fig. 3).

The Raman signature of cassiterite are the bands at 633–775 cm^{-1}, and frequently an additional less intense peak is observed at ca. 474 cm^{-1}. These frequencies are almost identical to the signature Raman bands of $Ca_2Sb_2O_7$, at ca. 480 and 633 cm^{-1}, although it is still possible to distinguish the spectra of both through the intensities ratios of the bands and also by the additional bands of $Ca_2Sb_2O_7$ at ca. 318, 367, 781 and 820 cm^{-1}, as described by Gedzevičiūtė et al. (2009) and Ricciardi et al. (2008, 2009).

In the production of opaque white glass, or *lattimo*, the term used in the Venetian documents and in glass recipes from the beginning of the 15th century onwards, the opacifier was prepared by calcining metallic lead and tin and separating the white "calx" (mixture of lead and tin oxides) formed on the surface. This "calx" was added to the batch: the lead oxide dissolved in the melt and

Table 2
Certified and measured composition of the glass standards.

Standards	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	SO_3	P_2O_5	TiO_2	Fe_2O_3	MnO	Sb_2O_3	CuO	PbO	SnO_2	CoO	As_2O_3	ZnO	NiO
Corning B																			
Certified	62.3	4.36	17.0	1.00	8.56	1.03		0.82	0.09	0.34	0.25	0.46	2.66	0.61	0.04			0.19	0.10
Measured SSV	61.9	4.30	17.2	1.02	8.75	1.08		0.82	0.11	0.35	0.24	0.45	2.75	0.38	0.05			0.18	0.10
Measured LNEG	62.2	4.37	17.3	1.03	8.49	0.99		0.81	0.13	0.35	0.27	0.50	2.88	0.90	0.03			0.21	0.08
Corning C																			
Certified	36.2	0.87	1.07	2.84	5.07	2.76		0.14	0.79	0.34			1.13	36.7	0.19	0.18		0.05	
Measured SSV	34.7	0.92	1.05	2.83	4.90	2.85		0.10	0.80	0.33			1.12	37.2	0.20	0.17		0.05	
Measured LNEG	36.4	0.89	1.29	2.81	4.93	2.99		0.09	1.08	0.31			1.16	35.5	0.16	0.19		0.08	
Corning D																			
Certified	55.5	5.30	1.20	11.3	14.8	3.94		3.93	0.38	0.52	0.55	0.97	0.38	0.48	0.10			0.10	
Measured SSV	55.0	5.50	1.25	11.3	14.8	3.90		3.90	0.35	0.50	0.55	0.95	0.36	0.30	0.13			0.10	
Measured LNEG	55.0	5.15	1.35	11.1	14.5	3.93		3.97	0.41	0.48	0.49	1.10	0.42	0.35	0.08			0.12	
NBS 620																			
Certified	72.1	1.80	14.4	0.41	7.11	3.69	0.28			0.04				0.05			0.06		
Measured SSV	72.4	1.81	14.3	0.42	7.31	3.70	0.28			0.05				0.04			0.05		

SSV – Stazione Sperimentale del Vetro (Murano, Italy); LNEG – Laboratório Nacional de Engenharia Geológica (Oporto, Portugal).

Table 3
Composition of the coloured glasses, in weight percent of oxides, obtained by EPMA.

Fragment	Colour		Analyzed area	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	SO_3	P_2O_5	Cl	TiO_2	Fe_2O_3	MnO	Sb_2O_3	CuO	PbO	SnO_2	CoO	As_2O_3	ZnO	NiO
SCV 171	Turquoise blue	Transp.	Body	62.8	1.35	15.2	2.67	6.43	2.41	0.26	0.23	0.82		0.66	0.61		1.09	3.01	2.30				
SCV 171	Red	Op.	Decoration	58.1	1.26	13.3	2.28	8.26	3.19	0.19	0.28	0.73		3.19	0.52		0.92	5.14	3.18				
SCV 171	White	Op.	Decoration	55.5	0.69	11.8	1.93	6.51	2.80	0.11	0.24	0.79		0.39	0.23			11.3	7.75				
SCV 173	Bluish white	Op.	Body	65.1	1.27	14.3	3.30	8.45	3.06		0.25			1.01	0.33	2.67	0.22	0.23			0.09		
SCV 173	Aventurine	Transp.	Decoration	59.0	2.27	14.1	3.11	8.19	2.89		0.34			4.54	0.84	0.14	2.00	2.15	1.76			0.17	
SCV 173	Blue	Transp.	Decoration	65.4	1.61	12.6	2.66	3.32	1.13		0.06			1.84	0.75	0.25	1.09	5.59		0.65	2.84		0.18
SCV 174	Red	Op.	Body	58.5	4.59	15.9	2.47	7.18	4.02	0.13	0.40	0.87	0.19	4.04	0.15		1.11	0.49	0.41		0.13		
SCV 174	Blue	Transp.	Decoration	59.5	3.16	18.2	3.05	7.76	3.26	0.13	0.39	1.06	0.09	1.01	0.74		0.46			0.43	0.69		0.07
SCV 174	Red	Op.	Decoration	57.8	3.83	15.8	2.37	7.46	3.96	0.10	0.44	0.98	0.16	4.53	0.16		0.93	0.63	0.41				
SCV 174	White	Op.	Decoration	36.8	2.63	10.4	1.94	4.41	2.04		0.23	0.95		0.47	0.13		0.22	25.5	14.4				
SCV 174	White	Op.	Trail on rim	44.8	3.27	12.0	2.18	5.38	2.40	0.12	0.26	0.73	0.08	0.68	0.23		0.06	19.1	9.50				
SCV 175	Red	Op.	Body	58.1	5.33	14.1	5.39	8.20	2.81		0.37		0.29	4.34	0.44	0.16	1.12	0.20					
SCV 175	Red	Op.	Decoration	58.6	5.35	13.9	5.43	8.22	2.73		0.33		0.20	4.11	0.38	0.20	0.96						
SCV 175	White	Op.	Decoration	54.0	3.89	12.5	4.71	6.99	2.30	0.09	0.27	0.75	0.19	0.80	0.32		0.78	8.06	3.76		0.15		
SCV 176	White	Op.	Body	63.6	1.11	13.6	1.49	7.97	3.32	0.32	0.20	0.74		0.73	0.24	2.95		3.90				0.18	
SCV 176	Aventurine	Transp.	Decoration	59.4	2.38	13.6	1.80	8.71	3.19		0.30		0.09	3.17	1.23	0.18	1.82	2.50	1.90				
SCV 176	Blue	Transp.	Decoration	70.7	1.53	13.2	2.63	2.91	0.98	0.12	0.14	0.51		1.52	0.47	0.21	0.12	0.97		0.75	2.97		0.09
SCV 176	Red	Op.	Decoration	60.8	2.20	13.9	2.30	8.36	3.06		0.39		0.13	2.91	1.49	1.12	0.95	1.28	0.77		0.15		
V 66	Greyish-green	Transp.	Body	58.2	7.61	16.9	4.12	5.92	2.76	0.15	0.36	0.88	0.20	1.15	1.13								
V 66	Red	Op.	Decoration	60.3	6.27	13.4	3.42	8.78	3.69	0.11	0.36	0.64	0.21	1.68	0.92		1.25	0.48	0.22				
V 66	White	Op.	Decoration	42.1	5.36	10.9	3.01	2.61	1.30		0.46		0.19	0.63	0.18		0.22	29.20	3.00				
V 67	Greenish yellow	Transp.	Body	54.3	7.84	19.2	1.85	4.71	6.61	0.07	0.82	0.88	0.66	2.15	0.95								
V 67	Blue	Transp.	Decoration	66.6	1.22	14.9	2.24	8.42	3.46	0.36	0.33	0.87		0.89	0.10			0.18	0.10	0.11	0.28		0.04
V 67	Red	Op.	Decoration	56.0	1.23	13.2	2.22	8.81	3.06	0.22	0.28	0.63	0.10	3.17	0.70		1.15	5.22	3.16				
V 68	Light blue	Transp.	Body	58.4	3.81	13.2	5.72	11.14	2.97	0.09	0.36	0.46	0.29	1.66	1.34		0.03	0.13			0.15		
V 68	Red	Op.	Decoration	57.8	5.26	15.6	4.31	6.45	2.33	0.10	0.51	0.72	0.62	4.81	0.66		0.36	0.32	0.20				
V 68	White	Op.	Decoration	50.1	3.48	12.2	2.60	5.60	2.28		0.35		0.17	1.58	0.54		0.14	16.3	3.99				
V 74	Green	Transp.	Body	59.8	2.49	15.6	3.13	7.24	2.94	0.22	0.32	0.74		0.94	0.33		0.79	2.83	2.35				
V 74	Light blue	Transp.	Decoration	59.2	1.46	12.5	1.63	9.53	3.61		0.33		0.08	1.63	0.88		0.27	3.92	3.90		0.10		
V 74	Red	Op.	Decoration	58.0	1.34	12.1	1.76	9.23	3.48		0.33		0.09	3.90	0.82		0.69	4.21	4.03		0.14		
V 74	White	Op.	Decoration	51.3	0.83	11.6	1.66	6.00	2.72	0.13	0.26	0.59		0.50	0.72			11.9	11.2				
V 108	Blue	Transp.	Body	60.8	4.57	15.4	5.50	6.54	2.98	0.19	0.29	0.78	0.14	0.81	0.46			0.11	0.06				
V 108	Red	Op.	Decoration	57.0	4.18	14.3	5.18	6.89	3.45	0.19	0.30	0.61	0.15	6.10	0.46		0.53	0.33	0.37				
V 108	Turquoise blue	Transp.	Decoration	58.6	4.69	14.7	4.40	7.32	4.03		0.32		0.21	0.70	0.47	0.11	4.03	0.19	0.06				
V 108	White	Op.	Decoration	38.4	2.75	8.54	3.24	4.42	2.21	0.10	0.14	0.58	0.12	0.52	0.11		0.40	21.5	17.9				

Transp. = transparent; Op. = opaque.

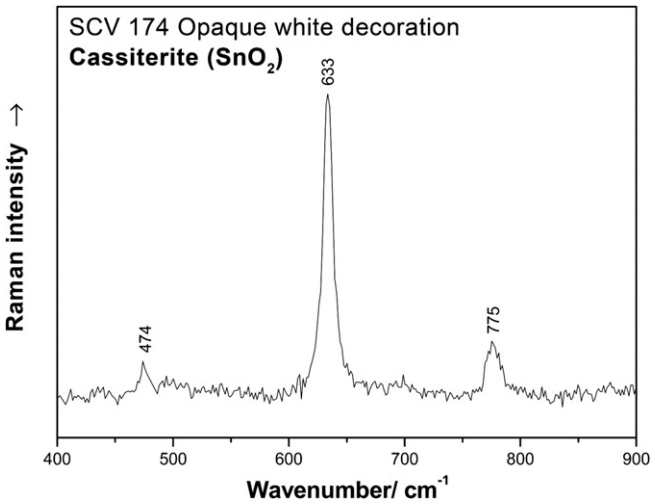

Fig. 2. Raman spectrum of cassiterite (SnO_2), identified in the crystalline phase of the opaque white glass present in the decoration of fragment SCV 174.

crystals of tin oxide (cassiterite) precipitated within the glass matrix (Verità, 2008). Variable amounts of lead (8.06–29.2 wt%) were found in the *Millefiori* tin opacified white glasses indicating that this procedure was used in these glasses. The ratio PbO/SnO_2 varies from 1/1 to 10/1, which indicates that no specific recipe was adopted in all the fragments.

Calcium antimonate was the preferred opacifier of Roman glassmakers but for some unclear reason its use declined in Late Antiquity and early Middle Ages when it was replaced by other opacifiers, including tin oxide. Antimony as an opacifier was reintroduced in Venice in the second half of the 16th century (Verità, 2008). Calcium antimonate may crystallize in two forms: $CaSb_2O_6$ or $Ca_2Sb_2O_7$, the latter was found in a few 16th–18th century Venetian glass vessels analyzed by Raman microscopy (Ricciardi et al., 2008). According to some recipes reported in the *Darduin* manuscript (Zecchin, 1986), a recipe book of a Venetian glassmaker of the first half of the 17th century, the antimony opacifier was prepared by heating soda ash (some of it purified), quartz pebbles, minium (lead oxide, Pb_3O_4) and antimony at relatively low temperatures and for approximately eight hours. As a result of the reaction between calcium oxide (contained in the plant ash) and antimony, crystals of calcium antimonate were formed. This frit was then added to the base glass to produce the antimony opacified white glass (Verità, 2008).

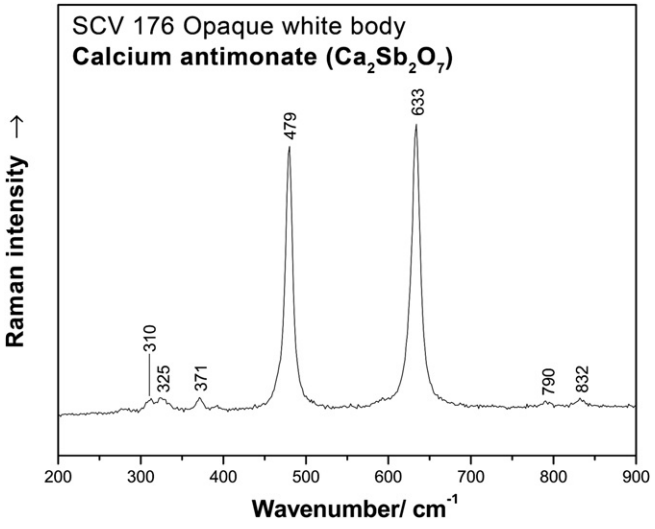

Fig. 3. Raman spectrum of calcium antimonate, in its $Ca_2Sb_2O_7$ form, identified in the crystalline phase present in the opaque white glass of body of fragment SCV 176.

3.1.2. Opaque red glass

According to analytical studies on ancient and historical opaque red glass, red colouration can be produced by nanoparticles of metallic copper dispersed in the glass matrix as well as by dendritic crystals of cuprite (Cu_2O). Batch composition and melting conditions are the key parameters controlling the oxidation state of copper. Iron, antimony and tin oxides have been suggested to act as reducing agents (Brun et al., 1991; Freestone et al., 2003; Gedzevičiūtė et al., 2009; Moretti and Gratuze, 2000). The eleven opaque red glasses analyzed in this study contain CuO from 0.36 to 1.25 wt% and Fe_2O_3 from 1.68 to 6.10 wt%. In a general way, the amounts of CuO and Fe_2O_3 found in our glasses are in agreement with those reported in the literature for some 16th–17th century opaque red glasses (Moretti and Gratuze, 2000; Verità, 2008).

Small amounts of antimony, lead and tin were also found, suggesting that small quantities of tin-lead "calx" and antimony were deliberately added to the base glass to aid in the formation of the colour. Comparison of compositions shows that the red glass of fragments SCV 171, V 67 and V 74 are comparable; in fragment SCV 174 the same red glass was used in the body and decoration, as well as in fragment SCV 175. The red glass of fragment SCV 176 contains a high amount of manganese (1.49 wt%). The average content of this oxide in the other red glasses is 0.52 wt%. Manganese is usually added to the melt to neutralize the colouring effect of iron, which is irrelevant in red glasses; however, in this case it may have been added to change the red hue (Moretti and Gratuze, 2000). In a study of a Venetian polychrome goblet dating from the second half of the 16th century, Verità (2008) has also noted an anomalous content of manganese in the red glass applied in the decoration suggesting that this oxide contributed to the a slight purple hue of the red glass.

As concerns the identification of the exact colouring agent – Cu^0 or Cu_2O –, it was not possible to draw any conclusion using the available analytical techniques. Crystallites of cuprite (0.5–1 μm) were recently identified in Roman opaque red glass by Raman microscopy (Gedzevičiūtė et al., 2009; Ricciardi et al., 2009). In this work, Raman microscopy did not identify this crystallite, which could be due to the poor scattering behaviour of cuprite; or, the red colour being given by nanocrystals of metallic copper, and therefore not rendering a first order Raman spectrum.

3.1.3. Aventurine

The term aventurine refers to a glass with a sparkling gold aspect, invented by the Muranese glassmakers at the beginning of the 17th century, according to Venetian documents. However, aventurine glass had already been used in a Venetian goblet for which a chronology to the second half of the 16th century has been proposed (Verità, 2008).

The characteristic golden sparkling effect is due to the formation of small crystals of metallic copper during the very slow cooling of a melt in a well controlled reducing atmosphere. According to Weyl (1999), the difference between opaque red and aventurine glasses lies in the size of the crystals of metallic copper: a few nm in opaque red glasses and up to 1 mm in aventurine.

In the analyzed *Millefiori* fragments, aventurine is present in the decoration of fragments SCV 173 and SCV 176. The results show that copper, iron, antimony, lead and tin were added to the base glass, similarly to what has been already observed in the

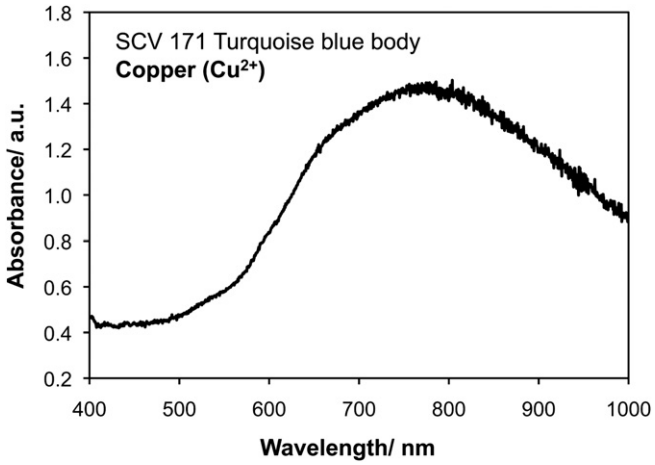

Fig. 4. UV–Vis absorption spectrum of the turquoise blue glass of fragment SCV 171. The broad band with a maximum wavelength at ca. 780 nm is characteristic of divalent copper (Cu^{2+}).

red opaque glasses. Iron plays again the role of reducing agent (3.17 and 4.54 wt%). However, the copper content is higher in the aventurine glass (1.82 and 2.00 wt%) than in the red glasses.

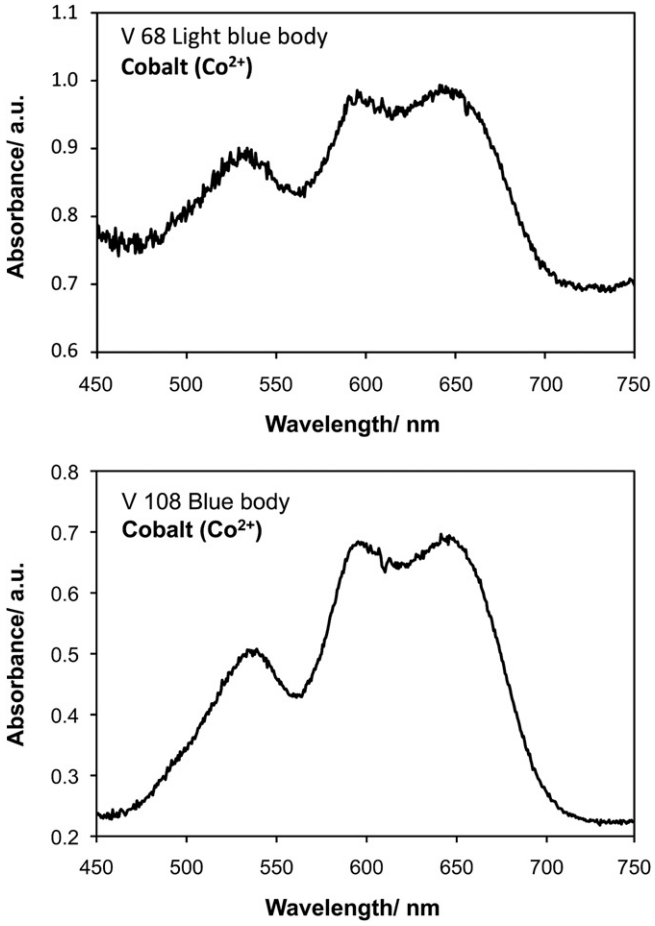

Fig. 5. UV–Vis absorption spectra of the blue glasses of fragments V 68 and V 108. Cobalt was identified through its characteristic triple band at 540, 590 and 640 nm.

3.1.4. Turquoise

Bluish green transparent glass is present in the body of fragment SCV 171 and in the applied sections of canes of fragment V 108. The colour is produced by copper ions in its divalent state, Cu^{2+}, and is obtained by melting the glass in oxidizing conditions (Navarro, 2003; Weyl, 1999). The presence of divalent copper was confirmed in fragment SCV 171 by its characteristic broad band with a maximum wavelength between 780 and 810 nm in the UV–Vis absorption spectrum (Fig. 4). The content of copper oxide in fragment V 108 (4.03 wt%) is about four times more than the amount detected on fragment SCV 171 (1.09 wt%). This difference may be related with the thickness of the glasses: when applying a very thin layer of glass, as in the decoration of fragment V 108, a higher amount of colourant is required to perceive the desired colour.

Small amounts of lead and tin, also present in both turquoise glasses, could be due to the recycling of a certain amount of opaque cullet glass.

3.1.5. Blue

The blue colour of the four samples analysed is given by the cobalt ion Co^{2+} in a tetrahedral environment. Cobalt oxide was detected by EPMA in the blue glasses used for decoration and by UV–Vis absorption spectroscopy in the glass bodies. In the light blue glass of sample V 74 it was not possible to detect cobalt probably due to its low concentration.

It is interesting to note that in glasses used for the decoration the concentration of cobalt oxide is between 0.11 wt% and 0.75 wt%. Contents higher than 0.10 wt%, rarely appear in blown blue glass (Verità, 2008) but, as already stated, a high content of colourant is required when the coloured glass is applied in a thin layer.

In the bodies of samples V 68 and V 108 the ion Co^{2+} was identified by means of UV–Vis absorption spectroscopy (Fig. 5) with its characteristic triple band at 540, 590 and 640 nm (Navarro, 2003). In the glasses where cobalt is present, arsenic, iron and nickel were also detected in small amounts (bismuth was analysed but not detected). These elements coexist with cobalt in the mineral added for colouring the glass. These results indicate that the same cobalt ore was used in all the analysed samples. According to comparative studies by Gratuze et al. (1996), the association of Co, Fe, Ni and As indicates that the mineral used in these glasses was probably from the mines of Schneeberg, in Erzgebirge, Germany.

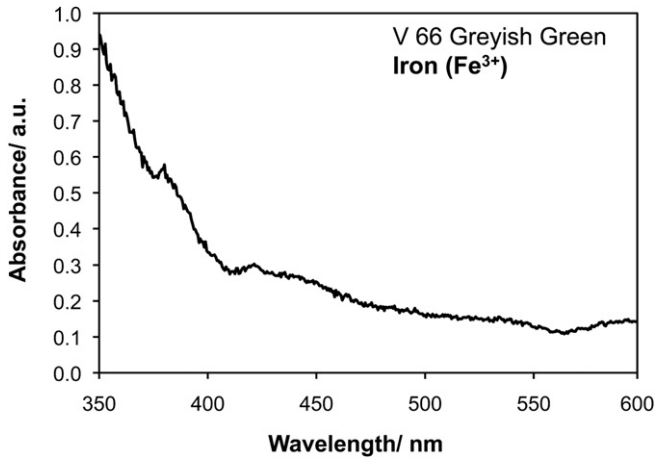

Fig. 6. UV–Vis absorption spectrum of the greyish green glass of fragment V 66. Iron was identified in the glass through its characteristic bands at 380, 420 and 440 nm.

3.1.6. Natural hues

The green to yellow hues observed in the transparent bodies of samples V 66, V 67 and V 74 are considered "natural colours", produced by iron involuntary introduced in the glass through impurities present in the raw materials. The content of iron in these glasses is high, ranging from 0.94 to 2.15 wt%. The manganese concentration from 0.33 to 1.39 wt% indicates that the final colour was the result of a partial decolouration. In a silicate glass, the ferric ion, Fe^{3+}, and the ferrous ion, Fe^{2+}, produce yellow and light blue colours, respectively. The green colour is obtained when both Fe^{2+} and Fe^{3+} ions are present in the glass in certain proportions. The ion Fe^{3+} was identified in the greyish green body of fragment V 66 through its characteristic bands at 380, 420 and 440 nm (Fig. 6) (Navarro, 2003).

According to the resulting compositions manganese oxide is present in all of the analyzed glasses, in concentrations from 0.10 to 1.49 wt%. As referred above, this oxide was in general added (small amounts of manganese may have been introduced through plant ash and recycled glass) either as a decolourant, to neutralize the colour given by iron in the oxidation state II, or as a purple colouring agent (Mn^{3+}) as in the case of the opaque red glass.

3.2. Venetian and façon-de-Venise base glass

Before the discussion of the base glass composition of the analysed samples, a short presentation on the present knowledge of the composition of the Venetian and *façon-de-Venise* base glass is reported.

Table 4
Average chemical compositions, and corresponding standard deviations, of Venetian and *façon-de-Venise* glasses, dating from the 16th–17th centuries, in weight percent of oxides.

Location	Classification	Date	Nr. of samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	PbO
Venice	*Cristallo*[a]	16th–18th c.	*(n = 16)*	17.2	1.81	0.68	70.5	0.15	0.3	1.00	2.93	4.88	0.03	0.32	0.24	
				1.5	0.38	0.14	1.3	0.04	0.07	0.11	0.41	0.69	<0.03	0.14	0.05	
	Vitrum Blanchum[a]	16th–18th c.	*(n = 33)*	13.6	3.35	1.03	66.9	0.31	0.24	0.86	2.97	9.76	0.05	0.47	0.37	
				1.4	0.73	0.37	1.7	0.12	0.08	0.12	1.20	1.18	0.02	0.20	0.08	
	Common[b]	15th–16th c.	*(n = 50)*	12.6	3.65	1.64	65.5	0.30	0.21	0.73	2.84	10.64	0.09	1.00	0.74	
				1.2	0.45	0.35	1.5	0.06	0.07	0.11	0.76	0.86	0.05	0.55	0.15	
Amsterdam[c]																
Waterlooplein		17th c.	*(n = 74)*	13.3	2.85	1.79	65.5	0.28	0.13	0.59	5.02	9.13		0.57	0.51	
				1.4	0.28	0.46	1.6	0.06	0.04	0.08	1.53	1.32		0.21	0.11	
Keizersgracht		17th c.	*(n = 38)*	14.3	3.25	2.12	64.1	0.22	0.12	0.62	4.74	8.83		0.5	0.74	
				1.1	0.38	0.35	1.5	0.07	0.04	0.08	0.88	1.24		0.23	0.24	
Antwerp[c f]																
	Façon-de-Venise	2nd half 16th c.		14.5	2.85	1.45	63.9	0.32	0.14	0.66	5.56	9.63		0.34	0.42	
				1.4	0.45	0.14	2.1	0.07	0.04	0.11	1.24	1.01		0.14	0.07	
	Cristallo	17th c.		15.0	1.68	1.64	69.7	0.35	0.19	0.67	4.51	4.85		0.51	0.32	
				0.9	0.24	0.47	1.9	0.77	0.07	0.14	0.83	0.76		0.16	0.07	
	Mixed Alkali	17th c.		12.0	1.87	1.59	68.9	0.22	0.15	0.48	8.27	5.40		0.50	0.40	
				1.0	0.27	0.10	1.4	0.07	0.06	0.12	0.78	0.53		0.15	0.12	
London[c]																
Old Broad Street		1st half 17th c.	*(n = 32)*	13.1	3.14	1.76	64.7	0.33	0.20	0.57	5.05	9.62		0.68	0.55	
				1.3	0.36	0.21	0.9	0.07	0.04	0.11	1.50	0.56		0.30	0.14	
Aldgate		1st half 17th c. (probably 2nd quarter)	*(n = 40)*	10.1	2.56	1.46	64.3	0.3	0.13	0.47	9.62	9.40		0.38	0.37	
				0.5	0.11	0.16	0.5	0.1	0.03	0.03	0.45	0.47		0.12	0.04	
Spain[d g]																
	Spanish I	end 16th –17th c.		10.2	1.13	1.09	67.1	1.06	0.23		6.87	9.85		1.38	0.59	0.016
				1.1	0.14	0.31	1.4	0.09	0.09		1.05	1.23		0.42	0.13	0.015
	Spanish II	end 16th –17th c.		11.7	3.41	1.72	67.4	0.63	0.31		3.48	9.85		0.62	0.69	0.013
				1.1	0.42	0.54	1.6	0.14	0.08		0.49	1.66		0.25	0.19	0.008
Tuscany[e]																
Gambassi	Tuscany Barilla	Mid 16th c.	*(n = 8)*	14.2	3.4	4.6	59.2	0.4	0.1	0.5	5.7	9.5		1.3	0.7	
				1.0	0.3	0.3	0.5	0	0.1	0.1	0.6	0.4		0.4	0.2	
	Tuscany Levantine	Mid 16th c.	*(n = 1)*	14.4	4.1	4.4	60.9	0.5	0.2	0.5	3.9	9.5		1.3	0.7	
San Giovanni Valdarno																
	Tuscany Barilla	16th c.	*(n = 11)*	14.4	3.1	4.3	59.3	0.4	0.1	0.6	6.0	9.8		1.0	0.6	
				1.5	0.4	0.3	1.6	0.1	0.0	0.1	0.8	1.2		0.3	0.1	
	Tuscany Levantine	16th c.	*(n = 3)*	15.8	4.5	4.1	60.7	0.5	0.2	0.6	3.6	8.2		1.0	0.6	
				0.7	0.3	0.1	1.3	0.1	0.1	0.1	0.1	1.1		0.4	0.1	
	Pebbles Barilla	16th c.	*(n = 1)*	10.3	3.4	1.7	62.7	0.4	0.1	0.5	8.8	10.7		0.7	0.5	
	Pebbles Levantine	16th c.	*(n = 1)*	16.0	1.4	2.1	67.6	0.6	0.1	0.9	3.0	6.1		1.2	0.6	

[a] Verità and Zecchin, 2009.
[b] Verità and Zecchin, 2009a.
[c] De Raedt et al., 2002.
[d] Ulitzka, 1994.
[e] Cagno et al., 2010.
[f] A set of 132 glasses was analyzed but the exact number of glasses included in each group is not indicated by the authors.
[g] The number of glasses included in each group is not provided by the author.

In the 16th and 17th centuries, Venice was the most important European centre of glass production. The style of Venetian glass, allied to its high quality and technique, was greatly admired all over Europe, becoming so successful that Venetian glass began to be imitated by other European countries in the second half of the 16th century, when some glassmakers escaped from Murano to set up glasshouses in France, England, Low Countries (Belgium and Netherlands), Spain and Slovenia (Barrera and Velde, 1989; De Raedt et al., 2001, 2002; Mortimer, 1995; Šmit et al., 2005; Theuerkauff-Liederwald, 1994). As a consequence, the same production methods, forms and decoration techniques were used in Venice and in these glasshouses, and it is still difficult to distinguish genuine Venetian glass from the so called *façon-de-Venise* production (De Raedt et al., 2002; Verità, 2008).

In Portugal, historical documents report the production of glass since the 15th century and in the 17th century several production centres were already active, one of them being in Coimbra (Mendes, 2002). Unfortunately, there is not yet any archaeological evidence of these glasshouses.

Several scientific investigations have been made on Venetian and *façon-de-Venise* glasses, primarily with the aim of establishing the differences and similarities in chemical composition between the two productions (Cagno et al., 2008, 2010; De Raedt et al., 2001, 2002; Mortimer, 1995; Šmit et al., 2005; Ulitzka, 1994; Verità, 1985; Verità and Zecchin, 2009, 2009a). In Table 4 the results of these analyses are summarised.

The nature of the raw materials used, the treatments to which some of these materials were subjected prior to use and the batch formulation are the main factors influencing the chemical composition. In some cases the compositions are so similar that the distinction of manufacture locations was only possible through the analysis of trace elements (De Raedt et al., 2001; Šmit et al., 2005).

The 17th century clear glass was classified in Venetian documents into three groups: *vetro comune* (ordinary glass, slightly coloured), *vitrum blanchum* (intermediate glass, colourless) and *cristallo*, being all the three of the soda-lime-silica type. *Cristallo* was the finest glass produced by the Muranese glassmakers; it was completely clear, free of defects and with high light transmittance, comparable to natural rock crystal (Verità, 1985). In the making of *cristallo*, quartz pebbles of very high purity were used as the silica source and purified plant ashes as the source of fluxing agents. The purification procedure reduced the amount of iron impurities but also the content of Ca and Mg, leading to glasses particularly vulnerable to weathering (McCray, 1998; Verità, 1985; Verità and Zecchin, 2009).

Concerning *façon-de-Venise* glass, some authors adopted the same classification as for Venetian glass (De Raedt et al., 2001, 2002), while others classified the glasses according to the raw materials used (Cagno et al., 2008, 2010). Based on the published data on Venetian and *façon-de-Venise* glass (Cagno et al., 2010; De Raedt et al., 2002; Ulitzka, 1994; Verità and Zecchin, 2009), some conclusions relevant for this work can be drawn. The content of Al_2O_3 in Venetian glass is always below 2 wt% (usually, below 1 wt% for cristallo) and that of Fe_2O_3 is either below 0.5 wt%, in *cristallo* or *vitrum blanchum* glass, or below 1 wt% on common glass. The low amount of these oxides in *cristallo* or *vitrum blanchum* glass is related also with the use of high purity quartz pebbles (Verità and Zecchin, 2009). Regarding *façon-de-Venise* glass the amount of Al_2O_3 is generally also below 2.5 wt%, except for the productions classified by Cagno et al. (2010) as "Tuscany Barilla" and "Tuscany Levantine". These *façon-de-Venise* glasses produced in the Italian region of Tuscany show amounts of Al_2O_3 varying from 4.1 to 4.6 wt % due, according to the author, to the use of local feldspathic silica sand.

The compositions of the French and Slovenian glasses were not included in this Table 4. The former because it is not clear which glasses were imported from Venice and the later because as far as we know major compositions have not been published.

3.3. Base glass of the analysed samples

The base glass of the analysed samples is of the soda-lime-silica type, containing Na_2O from 13.5 to 19.4 wt% and CaO from 3.11 to 11.4 wt%. The use of coastal plant ash is suggested by the relatively high content of MgO (3.31 ± 0.93 wt%), K_2O (3.46 ± 1.32 wt%) and P_2O_5 (0.36 ± 0.13 wt%), as well as by the presence of chlorine.

The blue glass present in the decoration of fragments SCV 173 and SCV 176 can be classified as *cristallo* glass due to the low concentration of CaO, MgO and P_2O_5 and high content of SiO_2 (Fig. 7). These concentrations reveal that a purified ash and a source of silica of high purity were used.

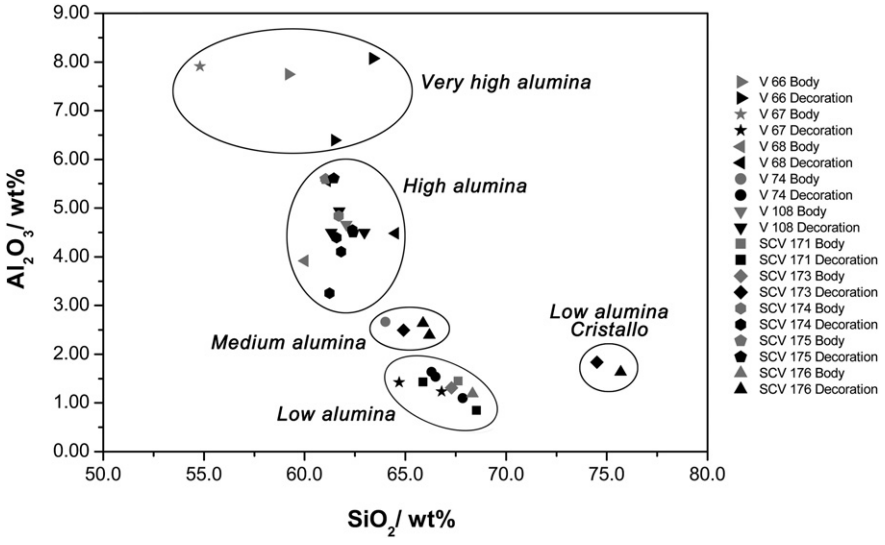

Fig. 7. Concentration of SiO_2 *vs.* Al_2O_3 in the base glasses (body and decoration), in weight percent of oxides.

Table 5
Glasses assigned to each compositional group, distributed by their alumina and silica content, in weight percent of oxides.

Concentration (wt%)	Classification of composition	Fragment and/or glass
$Al_2O_3 < 2$	Low alumina	SCV 171, SCV 173 Opaque bluish white, SCV 176 Opaque white, V 67 decoration, V 74 decoration. A sub-group is constituted by the blue SCV 173 and SCV 176 *cristallo* samples
$2 < Al_2O_3 < 3$	Medium alumina	SCV 173 Aventurine and SCV 176 Opaque red and aventurine, V 74 body
$3 < Al_2O_3 < 6$	High alumina	SCV 174, SCV 175, V 68 and V 108
$Al_2O_3 > 6$	Very high alumina	V 66 and V 67 body

It should be noted that the MgO content in the body of fragment V 67 (6.67 wt%) is unexpectedly high.

The plot alumina *vs.* silica (Fig. 7) suggests that four different sources of silica were used in the manufacture of the analyzed glasses, which allowed their classification into the following compositional groups: low alumina (<2 wt%; a sub-group being the *cristallo* samples with SiO_2 >70 wt%) medium alumina (2–3 wt%), high alumina (3–6 wt%) and very high alumina (>6 wt%).

In Table 5 the samples assigned to each group are identified.

3.4. Comparison with Venetian and façon-de-Venise compositions

As previously mentioned in Section 3.2, the content of alumina in Venetian glass is below 1.5 wt% (except for common glass, below 2 wt%) and in *façon-de-Venise* glass (except for the Tuscan groups) is below 2.5 wt%. The red and aventurine glasses show a higher content of this oxide because iron had to be added to the batch and, therefore, a less pure source of silica was chosen. Thus, according to the amounts of alumina and calcium oxide (Figs. 7 and 8), the glasses included in the low alumina group may be genuine Venetian or, concerning these elements, can belong to the group identified as Spanish II. Nevertheless, samples SCV 173 and SCV 176 have to be considered Venetian production, as they are identical in style and composition to a Venetian goblet recently studied by Verità (2008). Furthermore, as concern potassium oxide, their content is clearly outside the boundaries of Spanish II group. In any case, it must be considered that the number of genuine Spanish glass samples dated to the 16th–17th centuries analysed up to now is still quite small and a final conclusion on the attribution of the glass origin cannot be drown.

The medium alumina group includes the red and aventurine glasses of fragments SCV 173 and 176 (already assigned to Venetian production), and the V 74 body. The latter features a composition showing some discrepancies with the studied *façon-de-Venise* glasses because the amount of alumina is above 2.5 wt% and the amount of potassium oxide is below 3.5 wt%, a relation not found on any of the studied *façon-de-Venise* glasses.

The samples included in the high alumina group – SCV 174, SCV 175, V 68 and V 108 – and very high alumina group – V 66 and V 67 body – show an amount of alumina never found in Venetian and *façon-de-Venise* glasses. The concentration of alumina of fragments SCV 174, SCV 175, V 68 and V 108, as well as the concentration of the other elements, is comparable to the Tuscany production. Finally, fragments V 67 and V 74 are unique and interesting, as the glasses from body and decoration have different compositions: as referred above, the composition of the decoration is comparable to Venetian production and to the group identified as Spanish II, while the glass of the bodies shows very high and medium amounts of alumina, respectively. These results suggest that these objects were locally produced in an unknown glassmaking centre and decorated with slices of glass rods probably imported from a specialised glassmaking centre.

The boundaries of the concentrations of K_2O and CaO in Spanish and *façon-de-Venise* glasses, shown in Fig. 8, were determined based on the average concentrations and respective standard deviations reported in Table 3. The boundaries of Venetian glass were calculated based on data partially published

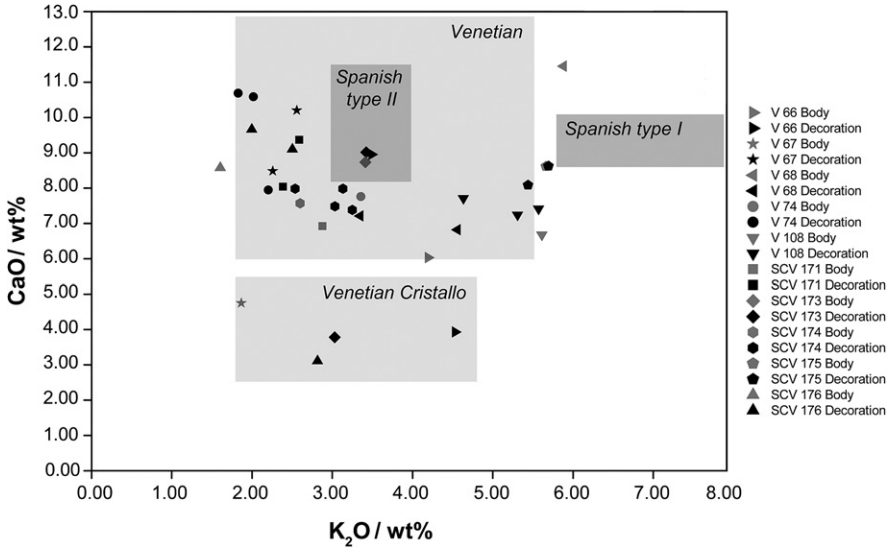

Fig. 8. Concentration of CaO *vs.* K_2O in the base glasses (body and decoration), in weight percent of oxides.

by Verità and Zecchin (2009a) and partially unpublished data of the authors.

4. Conclusions

Chemical analysis, by X-ray electron probe microanalysis, allowed the characterization of both body and decoration of ten 17th century *Millefiori* glass fragments. Some relevant conclusions can be drawn from the obtained compositions. All glasses are of the soda-lime-silica type. The use of coastal plant ash is suggested by the relatively high content of MgO, K_2O and P_2O_5, as well as by the presence of chlorine. Raman microscopy and UV–VIS absorption spectroscopy were also used as complementary techniques in the study of opacifiers and colourants, which allowed the identification of tin oxide (SnO_2, cassiterite) or calcium antimonate ($Ca_2Sb_2O_7$) in the opaque white glasses, and of the colourants cobalt in the blue glass, copper in the turquoise, iron in the natural yellow and greenish hues and iron and copper in the opaque red and aventurine glasses.

Based on the concentrations of alumina and silica, different sources of silica were identified, which allowed the classification of the glasses into four compositional groups. Comparison with genuine Venetian and *façon-de-Venise* compositions showed that fragments SCV 173 and SCV 176 are genuine Venetian production, fragment SCV 171 is comparable to Venetian production, fragments SCV 174, SCV 175, V 68 and V 108, all the glasses of the "high alumina group", are only comparable to Tuscany production. The composition of fragment V 66, included in the "very high alumina group" is not comparable with any composition of the glasses with known provenance. The analyses of fragments V 67 and V 74 show a different origin for the body and decoration. The body of sample V 66 and V 67 may have been produced in the same (unknown) place (the body of sample V 74 shows a composition not comparable to that of the others fragments), while the composition of the glasses used in the decoration indicates Venice or Spain (type II) as a possible site of production.

As a final conclusion, excluding the two fragments attributed to Venetian production (SCV 173 and SCV 176) and fragment SCV 171 whose composition is comparable to Venetian production, the provenance of the remaining *façon-de-Venise Millefiori* glasses from the Monastery of Sta. Clara-a-Velha should be attributed to unknown glassmaking centres. As mentioned above, several glasshouses were active in Portugal in the 17th century, one of them being in Coimbra, and therefore it is possible that some of the studied objects have been locally produced and decorated with imported coloured glass.

Acknowledgements

The authors would like to thank Dr Artur Côrte-Real (Núcleo Museológico do Mosteiro de Sta. Clara-a-Velha) for having supported this project and authorized the loan and sampling of the studied glasses; Fernanda Guimarães from LNEG, for the EPMA analyses; Fundação para a Ciência e a Tecnologia for providing the financial support necessary for the accomplishment of this study and Vânia Solange Muralha for helping in the analysis of the Raman spectra.

References

Báez Garzón, B., Larrazabal Galarza, J., Dórdio, P., 2005. Mosteiro de Santa Clara-a-Velha, Coimbra. Relatório do estudo do subgrupo da cerâmica vermelha de pasta fina decorada a engobe branco, internal report.

Barovier Mentasti, R., Dorigato, A., Gasparetto, A., Toninato, T. (Eds.), 1982. Mille anni di arte del vetro a Venezia.

Barrera, J., Velde, B., 1989. A study of French medieval glass composition. Archéologie Médiévale XIX, 81–127.

Brun, N., Mazerolles, M., Pernot, M., 1991. Microstructure of opaque red glass containing copper. J. Mater. Sci. Lett. 10, 1418–1420.

Cagno, S., Janssens, K., Mendera, M., 2008. Compositional analysis of Tuscan glass samples: in search of raw materials fingerprints. Anal. Bioanal. Chem. 391, 1389–1395.

Cagno, S., Mendera, M., Jeffries, T., Janssens, K., 2010. Raw materials for medieval and post-medieval Tuscan glassmaking: new insight from LA-ICP-MS analyses. J. Archaeol. Sci. 37, 3030–3036.

Côrte-Real, A., César Santos, P., Mourão, T., Pato de Macedo, F., 2002. Intervenção no Mosteiro de Santa Clara-a-Velha de Coimbra. Património-Estudos 2, 23–32.

De Raedt, I., Janssens, K., Veeckman, J., Vincze, L., Vekemans, B., Jeffries, T.E., 2001. Trace analysis for distinguishing between Venetian and *façon-de-Venise* glass vessels of the 16th and 17th century. J. Anal. At. Spectrom. 16, 1012–1017.

De Raedt, I., Janssens, K., Veekman, J., 2002. On the distinction between 16th and 17th century Venetian and *façon-de-Venise* glass. In: Veekman, J. (Ed.), Proceedings of Majolica and Glass – From Italy to Antwerp and Beyond. The Transfer of Technology in the 16th–early 17th Century, Antwerp, pp. 95–121.

Ferreira, M., 2004. Espólio vítreo proveniente da estação arqueológica do Mosteiro de Sta. Clara-a-Velha de Coimbra: resultados preliminares. Revista Portuguesa de Arqueologia 7.2, 541–583.

Freestone, I.C., Stapleton, C.P., Rigby, V., 2003. The production of red glass and enamel in the Late Iron age, Roman and Byzantine periods. In: Entwistle, C. (Ed.), Through a Glass Brightly Studied in Byzantine and Medieval Art and Archaeology Presented to David Buckton. Oxbow Books, Oxford, pp. 142–154.

Gawronski, J., Hulst, M., Jayasena, R., Veerkamp, J., 2010. Glasafval op het achtererf, AAR50 (Amsterdamse Archeologische Rapporten).

Gedzevičiūtė, V., Welter, N., Schüsser, U., Weiss, C., 2009. Chemical composition and colouring agents of Roman mosaic and millefiori glass, studied by electron microprobe analysis and Raman microspectroscopy. Archaeol. Anthropol. Sci. 1, 15–29.

Gratuze, B., Soulier, I., Blet, M., Valauri, L., 1996. De L'Origin Du Cobalt: Du Verre à La Céramique. Revue d'Archéomètrie 20, 77–94.

McCray, W.P., 1998. Glassmaking in Renaissance Italy: the innovation of Venetian Cristallo. JOM 50 (5), 14–19. May 1998.

Medici, T., Revisiting the 'Moura glass treasure': new data about 17th century glass in Portugal, in: annales de l'Association Internationale pour l'Histoire du Verre 18 (Thessaloniki, 21–25 September 2009), in press.

Medici, T., Lopes, F.M., Lima, A., Larsson, M.A., Pires de Matos, A., 2009. Glass bottles and jugs from the Monastery of Sta. Clara-a-Velha, Coimbra, Portugal. In: Janssens, K., Degryse, P., Cosyns, P., Caen, J., Van't dack, L. (Eds.), Annales de l'Association Internationale pour l'Histoire du Verre 17, Antwerp 2006. University Press Antwerp, Antwerp, pp. 391–400.

Mendes, J.A., 2002. História do Vidro e do Cristal em Portugal. Edições INAPA, Lisboa.

Moretti, C., Gratuze, B., 2000. I vetri rossi al rame. Confronto di analisi e ricette. In: Annales de l'Association Internationale pour l'Histoire du Verre 14 (Venice – Milan 1998), Lochem, pp. 227–232.

Mortimer, C., 1995. Analysis of post-medieval glass from Old Broad Street, London, with reference to other contemporary glasses from London and Italy. In: Hook, D.R., Gaimster, D.R.M. (Eds.), Trade and Discovery: The Scientific Study of Artefacts from Post-Medieval Europe and Beyond. British Museum, London, pp. 135–144.

Navarro, José, 2003. El Vidrio, third ed. Consejo Superior de Investigaciones Científicas, Sociedade Española de Cerâmica y Vidrio, Madrid.

Page, Jutta-Annette, 2004. Beyond Venice, Glass in Venetian Style, 1500–1750, with Contributions by Ignasi Domenech, Alexandra Gaba Van Dongen, Reino Liefkes, Maria-Laure de Rochebrune, Hugh Willmont. The Corning Museum of Glass, Corning, New York.

Ricciardi, P., Colomban, P., Tournié, A., Macchiarola, M., Ayed, N., 2009. A non-invasive study of Roman Age mosaic tesserae by means of Raman spectroscopy. J. Archaeol. Sci. 36, 2551–2559.

Ricciardi, P., Colomban, P., Tournié, A., Milande, V., 2008. Nondestructive on-site identification of ancient glasses: genuine artifacts, embellished pieces or forgeries? J. Raman Spectrosc. 40, 604–617.

Šmit, Ž., Janssens, K., Bulska, E., Wagner, B., Kos, M., Lazar, I., 2005. Trace element fingerprinting of façon-de-Venise glass. Nucl. Instrum. Methods in Phys. Res., Sect. B 239, 94–99.

Theuerkauff-Liederwald, A.-E., 1994. Venezianisches Glas der Kunstsammlungen der Veste Coburg. Die Sammlung Herzog Alfreds von Sachsen – Coburg und Gotha (1844–1900). Venedig, À la façon-de-Venise, Spanien, Mitteleuropa. Lingen, Luca Verlag.

Ulitzka, S., 1994. Analysen von historischen Gläsern - Licht im Dunkel der Geschichte? In: Theuerkauff-Liederwald, A.-E. (Ed.), Venezianisches Glas der Kunstsammlungen der Veste Coburg. Die Sammlung Herzog Alfreds von Sachsen – Coburg und Gotha (1844–1900). Venedig, À la façon-de-Venise, Spanien, Mitteleuropa. Lingen, Luca Verlag, pp. 40–53.

Verità, M., 1985. L'invenzione del cristallo muranese: una verifica analitica delle fonti storiche. Rivista della Stazione Sperimentale del Vetro 15, 17–29.

Verità, M., 2008. Scientific investigation of a Venetian polychrome goblet of the 16th century. J. Glass Stud., The Corning Museum of Glass 50, 105–115.
Verità, M., Basso, R., Wypyski, M.T., Koestler, R., 1994. X-ray microanalysis of ancient glassy materials: a comparative study of wavelength dispersive and energy dispersive techniques. Archaeometry 36, 241–251.
Verità, M., Zecchin, S., 2009. Thousand years of Venetian glass: the evolution of chemical composition from the origins to the 18th century. In: Janssens, K., Degryse, P., Cosyns, P., Caen, J., Van't dack, L. (Eds.), Annales de l'Association Internationale pour l'Histoire du Verre 17, Antwerp 2006. University Press Antwerp, Antwerp, pp. 602–613.
Verità, M., Zecchin, S., 2009a. La tecnologia vetraria Veneziana del XV-XVI secolo attraverso le analisi di reperti in vetro d'uso comune. Quaderni Friulani di Archeologia XIX, 237–248.
Weyl, W.A., 1999. Coloured Glasses. Society of Glass Technology, Sheffield, UK.
Zecchin, L., 1986. Il ricettario Darduin: un codice vetrario del Seicento trascritto e commentato. Arsenale, Venice.