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SECRETS AND INNOVATIONS OF VENETIAN GLASS BETWEEN THE 15TH AND THE 17TH CENTURIES: RAW MATERIALS, GLASS MELTING AND ARTEFACTS

From the fifteenth to the end of the seventeenth century, Venice has been the world leader in glassmaking. Murano's primacy was due to the extraordinary quality of its glass (homogeneity, transparency, palette of colours, etc.), the style of Venetian glassware, the skill of glassmasters and the wide range of products. This supremacy could be reached and maintained thanks to the fact that glassmaking in Venice has always been a dynamic craft. Since its beginnings it underwent radical changes and incorporated many innovations along the centuries. The oldest extant document attesting a production of glassware in Venice is a manuscript dating to 982 A.D.; nevertheless archaeological evidence of glassworking since the 7-8th centuries was found in the island of Torcello in the Venetian lagoon.

Since the origins the Venetian glass was (and is still today) of the soda-lime-silica type, that is mainly composed of sodium (Na_2O), calcium (CaO) and silicon (SiO_2) oxides[1]. The reluctance of Venetian glassmakers to change the composition of their glass is rather complex to explain. Any glass represents a combination of properties: thermal (viscosity, workability), optical (colour, transparency), chemical (resistance to environmental attack, …), etc., which cannot be modified separately and vary by changing the composition of glass (type and ratios of the components).

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[1] Other types of glass were created and manufactured in Venice, such as lead silica glass for the production of imitation gemstones, not discussed in this paper.

Glass technology and raw materials

Our present knowledge of the Venetian glass technology is based on the information supplied by historical documents and the scientific investigation of well dated pieces. Scientific analyses are useful to determine the composition of glass, and to identify the raw materials used and colouring techniques. A significant number of analyses of ancient Venetian glass remains is available today[2].

A major source of information on the ancient Venetian glass technology is the chronology drawn up by Luigi Zecchin[3]. Several treatises of Venetian glassmakers dating from the fifteenth to the seventeenth centuries have also been published. They include the 2nd and 3rd books of recipes of the three *Trattarelli* (booklets) lying in the State Archives of Florence (second half fifteenth century, Milanesi 1864), the so-called Montpellier (dated 1536), partially translated and commented by Luigi Zecchin[4], the Anonimous of the fifteenth century[5], the Darduin (16th, early 18th centuries[6]) and the recipe book of the Venetian glassmaker Brunoro found in Gdansk (Poland) dated 1645[7]. The first published book on glassmaking, L'Arte Vetraria by Antonio Neri[8] includes a number of recipes of Venetian origin.

Historical documents describe the use of two basic raw materials to melt glass: quartz (sand or pebbles) as a silica source and plant ash as a fluxer and stabilizer source. The glass technology until the 18th century ignored the use of lime as a stabilizer. It was introduced accidentally into the composition in the form of a plant ash component.

In the Middle Ages and Renaissance period ashes of coastal plants (Salsola kali, Salicornia, etc.) were used in Venice and in the Mediterranean area, while in northern-central Europe ash of

[2] Verità 2013.
[3] Zecchin 1987, 1989, 1990.
[4] Zecchin 1987: 247-76.
[5] Moretti and Toninato 2001.
[6] Zecchin 1986.
[7] Moretti *et al.* 2004.
[8] Neri 1980.

inland plants (fern, beech, oak, etc.) was used. Coastal plant ashes are mainly made of sodium and calcium carbonates (soda ash); chlorides, sulphates, phosphates and small amounts of potassium, magnesium, iron, aluminium and silica are also found.

Inland plants ashes are mainly made of potassium and calcium carbonates (potash ash). In these ashes traces of manganese and of other coloring elements are present and important compositional variations exist, according to plant species, provenance (same species growing in different locations), plant parts (leaves, wood, bark), burning temperatures, etc. These differences caused serious problems to the glassmakers and lowered the quality of the glass. This is why the use of inland plants ash was expressly forbidden to the Venetian glassmakers.

Glass batch and glassmaking

The Renaissance Venetian glass quality was the result of an unceasing improvement of the raw materials selection and of the melting process that began several centuries before. Documents attest since the end of the 13th century and up to the 18th century the import of plant ash from Egypt (*alumen album de Alexandria*), Syria (*allume di Soria*) and later also from Spain (since the 16th c.). Its trade was protected by the Venetian government, with a view to restricting its use to the Venetian glass houses. Efforts to use ashes of local plants (mid-17th c.) gave poor results and were soon abandoned.

Since the mid-14th century, Venetian glassmakers had obtained high quality products by replacing sand (*sablonum ad facendum Vitrum*, from Levant, Sicily, Vicenza, etc.) with quartz pebbles (*cogulo*) from the rivers Ticino and Adige (inferior in quality), and their use continued in the following centuries.

To obtain a finely ground powder suitable for melting, the pebbles were roasted, cast into water, and subsequently ground and sieved. The change from sand to pebbles lead to a decrease of colouring contaminants (iron, chromium).

Glass melting was performed in two steps: the batch of raw materials was preliminary fired in a reverberatory furnace at a relatively low temperature (800 °C) to be transformed in a crystalline intermediate product (the frit). This treatment, eliminates the carbonaceous residual of the ash, transforms the sodium and calcium carbonates into oxides which react with quartz forming low-melting silicates and eliminates CO_2, making the glass fining easier. The frit was then transferred to a pot furnace where it was melted at a high temperature (about 1100 °C). This second stage could last from twelve hours to several days. During melting, the glassmakers would be faced by several problems. The considerable amounts of insoluble salts (sodium sulphates and chlorides) of the plant ash are not reactive with the silica and could not be incorporated into the glass. If not removed, these salts form droplets that cause a dispersion of light resulting in glass turbidity. In Venice transparency was improved by casting molten glass into water and subsequently re-melting it. This procedure, repeated several times, together with the scumming of the salts floating on the molten glass, helped to reduce salt droplets.

Glass colour

The quality of the raw materials was not as high as today and colouring impurities (mainly iron) were introduced into the glass. The iron content depending on its oxidation state produces a more or less intense hue ranging between yellow, green and blue-green. The iron concentration in the best clear Renaissance Venetian glass was 100 times higher (Fe_2O_3 0.2-0.3 wt%) as compared to modern Venetian glass (less that 0.02 wt%).

To obtain a colourless glass, the natural colour was neutralised by adding manganese oxide (first mentioned in a document of 1290); the glass obtained with this process is gray in colour, more intense with increasing iron contents. In Venetian glass furnaces, manganese was added directly to the melt in controlled amounts, until decolouration was obtained. In this way the use of manganese was limited to the lowest amount necessary. Manganese was imported from Catalonia (end of 14th c.), Piemonte, Germany and France.

Until the middle of the 15^{th} century, Venetian clear glass was classified into 2 groups: common glass and Vitrum Blanchum glass. It is not clear which was the distinctive feature of the two glasses; we can reasonably suppose they were different in aspect, common glass with a light natural colour (from green-blue to yellow) and a well decolorized (gray) *vitrum blanchum*.

Cristallo is the term used around the middle of the 15^{th} century in Venice to indicate a transparent glass which had acquired such a clarity (perfect decoloration and high light transmittance) and homogeneity as to be compared to natural rock crystal (quartz). *Cristallo* glass, invented by the Muranese Angelo Barovier, soon was traded throughout the world, and the secret formula was one of the main factors that allowed Venice to maintain its predominance over other European glassmaking sites for about two centuries. For the preparation of *cristallo*, Barovier added a preliminary step to the existing technique, consisting in the purification of the plant ash. The raw ash was ground, sieved, dissolved in boiling water; the resulting solution was filtered, concentrated and dried. The salt obtained was mixed in the right proportion with silica to prepare the frit. The purification process lead to the elimination of insoluble coloring impurities (mainly iron compounds) as well as calcium and magnesium compounds, which are essential to stabilize glass against weathering[9]. The glass obtained thereby (practically sodium silicate) would become coated with an opaque, weathered layer even shortly after being produced, with consequent loss of the brightness and transparency. The good state of preservation of most of the Renaissance Venetian luxury glass attests that Muranese glassmakers searched for and discovered a solution to this problem.

The analyses of Venetian samples dated to the sixteenth-seventeenth centuries allow to identify the new glass. The first analyses identifying the *cristallo* composition are reported in Verità 1985. In fact, despite the lowest level of iron, the Venetian *cristallo* shows also a higher level of sodium than *vitrum blanchum*, and concentrations of calcium, magnesium and phosphorous which are lower by about one half. These compositional differences are

[9] Verità 1985.

in contrast with the *cristallo* recipes in Venetian treatises. In fact, calcium and magnesium carbonates are insoluble also in boiling water and during the purification procedure of coastal plant ash they were completely eliminated. On the other hand, the absence of CaO and MgO would compromise the chemical durability of *cristallo* and objects made with this glass would be rapidly attacked by the atmospheric moisture becoming bloomed and crizzled, with consequent loss of the main characteristics of *cristallo* glass. Most likely, the Muranese glassmakers soon realized that the purification of the fluxing agent removed not only undesired colouring elements but also the components that ensured glass stability. The most easily available source of lime and magnesia readily accessible and controllable was *vitrum blanchum* glass frit (or cullet). The glassmakers probably melt a batch made of equal amounts of *cristallo* and *vitrum blanchum* frits. This process would yield a product of higher quality than *vitrum blanchum*, and assuring a sufficient amount of calcium and magnesium to stabilize the glass (Fig. 1).

The incomparable quality of Renaissance Venetian glass is assessed also in the scientific field. Galileo Galilei made the first «occhiali da veder lontano» (telescope lenses), using selected Muranese mirror glass. No special glass was made for lenses in Galileo's time and the optical quality of the glass produced was affected by several defects: seeds, cords, a certain turbidity and colour (grey). In the attempt to improve this quality, in 1610 Galileo succeeded in persuading the Granduca of Tuscany to make in Florence a furnace where special glass for lenses could be made. This experiment was probably not successful, for in 1618 Galileo asked a Venetian gentleman (Sagredo) to find good quality glass for making lenses in Murano[10]. For Galileo, too, the quality of the Muranese transparent glass was unbeatable.

For the preparation of coloured glass the Venetian glassmasters used the same elements as other glassmaking centers, i.e., cobalt (blue), manganese (purple), copper (green, red and turquoise) and iron. The clarity of their glass clarity and their skill in controlling

[10] Verità 2008.

colours allowed the Venetian glassmakers to make glass in an infinite range of colours. An example of this skill is the production of coloured glasses imitating natural gemstones, which was one of the most successful items of the Venetian glassmaking.

«There is no kind of precious stone which cannot be imitated by the industry of the glass workers …», wrote Sabellico in its *Opera Omnia*, about the town of Venice,1502. In the glassmakers treatises several recipes concern the production of glass for imitation of an incredible variety of precious stones. The most extensively used colours are: blue (recipes for making sapphire, lapis lazuli, aquamarine, turquoise are reported), yellow (amber, topaz), green (emerald, chrysophase), ruby red (ruby, cornelian, coral, garnet balas), purple (amethyst) and clear (rock crystal).

Lattimo

A document dating to 1359 (the purchase in Venice of glass slabs for the mosaics of the Orvieto cathedral) is the earliest written evidence for the production of opaque white glass in Venice. The term lattimo (used in Venice for opaque white glass) appears in the Muranese documents from the 15th century (Fig. 2).

The first opacifier used in Murano was the *calce di piombo e stagno* (lead-tin calx). Prepared by firing a mixture of metallic lead and tin (lead to tin ratio: ½ to 1/1), the lead-tin calx was added to the transparent glass (clear or coloured). Lead dissolved during melting yelding a lead glass in which microcrystals of cassiterite (SnO_2) were dispersed. The *lattimo*, initially used only for mosaic and enamels for glass or metals, from the second half of the 15th century was used also to decorate blown items. In 1527 was invented in Murano a sophisticated decorative technique which used rods of *cristallo* with a core of *lattimo* (*filigrana*).

Lead tin calx continued to be used in Murano until the 19th century, partially replaced by other opacifiers such as calcium antimonate (from middle of the 16th c.), calcium phosphate (bone ash) (second half of the 15th c.) and lead arsenate (from 1693).

Chalcedony

New coloured glasses were created by Venetian glassmakers. Towards the middle of the 15th century a glass called chalcedony was created in imitation of naturally occurring agate and jasper[11]. It is a striped layered glass with green, blue, red, violet and yellow translucent or opaque layers. Moreover, when the chalcedony is illuminated by transmitted light it often displays a deep reddish colour. Fig. 3).

Venetian recipes for chalcedony glass in the Renaissance Venetian texts, dating from the 15th to the 17th century (the Montpellier collection has 17 recipes for chalcedony!) are similar in the respect that they call for a lead-soda-lime-silica glass composition with silver as coloring agent (metallic silver particles of colloidal nature), sometime together with others metals. The instructions in the Darduin recipe call for the silver mixture to be added only 2-3 hours before working the glass to not allow for complete mixing. Once the object had been fashioned, the glassmaker was instructed to return to the furnace hole several more times to heat it until the colours of chalcedony were seen. Some of these recipes are very similar to those used in the furnaces of Murano today.

The use of silver added in very small amounts have antecedents in Islamic lusterware glazes as well as Byzantine glass decoration[12].

Girasole glass

A new glass called *girasole* (sunflower), an imitation of opal gemstone developed from the 17th c. by Venetian glassmakers has been produced with great success up today. The name *girasole* (today raplaced by *opalino*) refers to a translucent, opalescent glass changing its colour from light blue (reflected light) to yellow reddish (transmitted light). This variation in appearance with the light source, is referred to as dichroism (Fig. 4).

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[11] McCray *et al.* 1995.

[12] Gudenrath *et al.* 2007.

The first known literary reference to *girasole* glass appears in Neri's 1612 *L'arte vetraria* (Book 4, Chapter 74)[13], while the first mention in the Ricettario Darduin is dated 1st June 1693 (*Girasole per perleri,* sunflower for beadmakers). Recipes for *girasole* continued to be collected in this treatise until 1711.

The recipes for girasole are quite complex: to the batch of silica (obtained by grinding quartz pebbles) and soda ash, potassium nitrate KNO_3 (a fluxing-oxidizing agent), lead oxide and arsenic (arsenic oxide As_2O_3 prepared by firing a mixture of orpiment (As_2S_3) and sodium chloride) were also added. In this way the traditional Venetian soda-lime-silica glass is replaced by a soda-potash-lead-silica glass.

The opalescence is given by very small microcrystals of lead arsenate [$3Pb_3(AsO_4)_2PbO$] which separate during melt cooling (light scattering). The intensity of this phenomenon depends on arsenic and lead concentrations and on melting and cooling procedures (sizes and concentration of the particles)[14].

Aventurine

Aventurine is a translucent brown glass flecked throughout with sparkling metallic copper particles (Figs. 5a and 5b). *Aventurine* was obtained by chance in a furnace of Murano probably in the second half of the 16th century. Darduin explains that the name *venturina* came from the fact that such a glass, can be obtained sucessfully *più per ventura che per scientia* (more by chance than for the skill of the glassmaker).

This glass is usually worked as a precious stone (grinding and polishing) and only skilful and expert glassmakers can use aventurine in blown artefacts. In fact, if warmed up at a too high temperature or for a too long time, copper-crystals are dissolved and aventurine is transformed into a greenish, transparent glass.

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13 Neri 1980.

14 McCray and Kingery 1996.

The decline of the Venetian glassmaking

Several reasons caused the decline of the Venetian glassmaking in the seventeenth century.

From the second half of the sixteenth century onwards, some glassmakers left Murano to set up glassworks all over Europe, where objects imitating Renaissance Venetian glass were produced (*Façon de Venise*). The same production methods, forms and decoration techniques were used in Venice and in the glasshouses in Europe.

The secrets of Venetian glassmaking were first made public in a printed manual entitled *L'Arte Vetraria* published by the Florentine priest Antonio Neri in 1612. Neri observed and possibly even worked with Venetian masters in Murano, Tuscany and the Low Countries.

This is a well ordered compilation of glass recipes probably taken from an earlier manuscript similar to Montpellier's, which Neri tested personally. The text was translated into numerous languages. Christopher Merret published in 1662 the English translation; from this text to which important observations were added by the translator, the French and German versions were compiled. This text probably inspired some of the experiments carried out by the major inventors of new types of glass in England and Germany

Another cause of this decline was the invention in Bohemia and in England of new glasses more clear and bright and less expensive than the Venetian *cristallo*. In Bohemia, invented by Johan Kunckel in 1676, a potash-lime-silica crystal glass (potash was obtained by lixiviation of the wood ash following the process used in Venice with the soda ash; the glass was probably stabilized by addition of a source of lime like chalk). In England, in the second half of the seventeenth century a lead-silica glass was brought to perfection by George Ravenscroft and the new lead-crystal glass became available on the market.

The Venetian glassmakers reacted to this menace by renovating their traditional *cristallo.* The reasons why these attempts were not so successful as expected are considered in an interesting study of Trivellato, where the decline of Venetian glassmaking is reconsidered[15].

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[15] Trivellato 2007.

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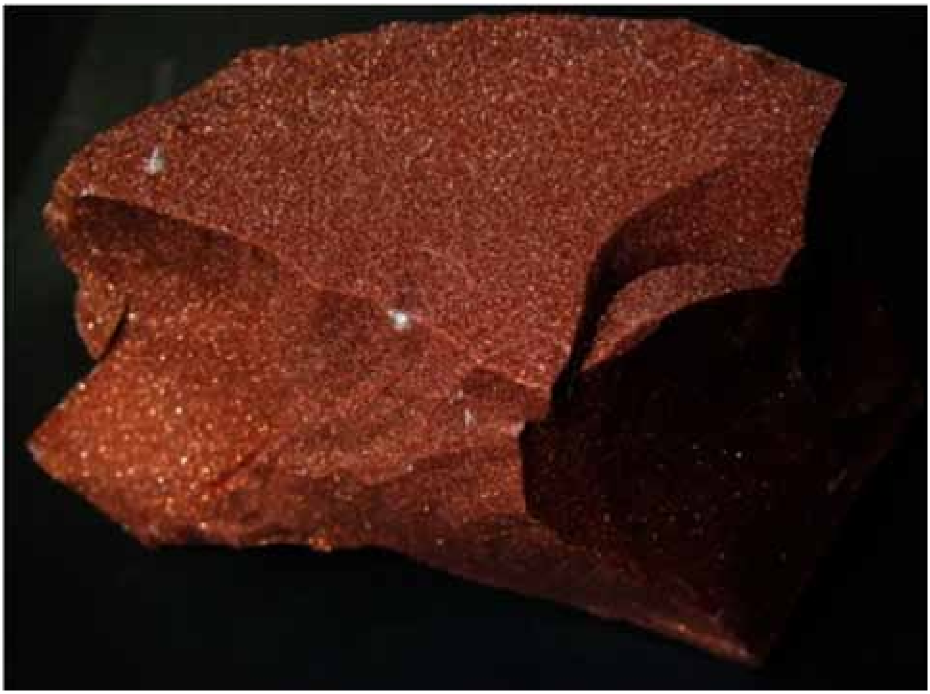
Fig. 1 - *Cristallo* glass. Paris, Musée du Louvre.

Fig. 2 - Cake of *lattimo* glass. Murano, Museo del Vetro.

Fig. 3 - *Calcedonio* glass. Brescia, Museo di Santa Giulia.

Fig. 4 - *Girasole* glass. Brescia, Museo di Santa Giulia.



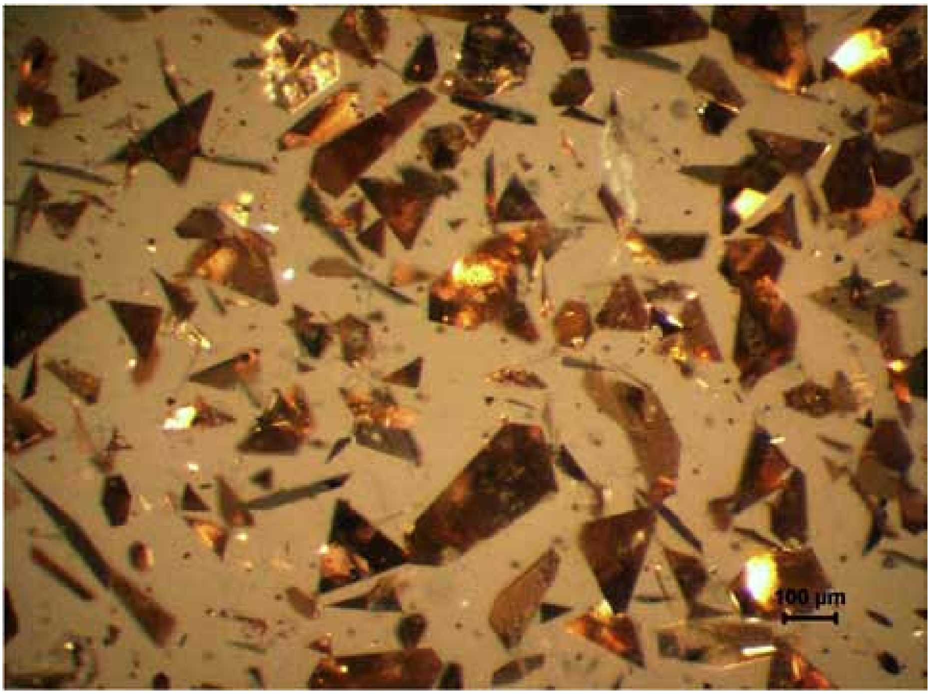


Fig. 5a - Aventurine glass.
Fig. 5b - Sample of aventurine prepared in thin section and observed at the optical microscope.