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A Brief History of Early Silica Glass: Impact on Science and Society

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Abstract. Silicon in the form of silica is the basis of common glass and its uses predate recorded history. The production of synthetic glass, however, is thought to date back to no earlier than 3000 BCE. This glass technology was not discovered fully fashioned, but grew slowly through continued development of both chemical composition and techniques for its production, manipulation, and material applications. This development had become fairly advanced by the Roman period, resulting in a wide variety of glass vessels and the initial use of glass windows. Following the fall of the Roman Empire, glass grew to new heights in Venice and Murano, where improvements in composition and production resulted in both more chemically stable and clearer forms. The quality of this new glass ushered in the development of lenses and eyeglasses, as well as the greater use of glass as a material for chemical apparatus, both of which changed society and the pursuit of science. Finally, glass in the North developed along different lines to ultimately result in a new form of glass that eventually replaced Venetian glass. This Bohemian glass became the glass of choice for chemical glassware and dominated the chemical laboratory until the final advent of borosilicate glass in the 1880s. A brief overview of the early history of silica glasses from their origins to the development of borosilicate glasses will be presented.

Keywords. Soda-lime glass, potash-lime glass, glassblowing, chemical glassware, eyeglasses, windows.

INTRODUCTION

Silicon is one of the most abundant elements of the periodic table, comprising the eighth most common element in the universe by mass and the second most abundant element in the Earth's crust after oxygen (ca. 28% by mass). In nature, silicon occurs almost exclusively in combination with oxygen. Silicon dioxide, SiO_2, occurs in a variety of forms in nature and is known as silica. One form of silica is α-quartz, a major constituent of common sand, sandstone, and granite, as well as the timekeeper in most watches. Silicon also occurs in many minerals as silicates (consisting of compounds in which SiO_4 units may be fused by sharing corners, edges, or faces) or aluminosilicates. For the discussion here, silica also plays a critical role as the major component of common glass.[1-4]

While quartz is a crystalline solid with a regular repeating lattice as shown in Fig. 1,[5,6] glass has no regular repetition in its macromolecular structure and exhibits a disordered structure similar to substances in the liquid state as illustrated in Fig. 2.[3,7] Due to the extent of disorder in amorphous structures, the glass state of a material is higher in energy than its crystalline state and thus glasses can suffer from devitrification (i.e. frosting and loss of transparency as a result of crystallization).[1] As a result, stable glasses are those that can form a highly disordered state that is of comparable energy to the corresponding crystalline state.[8]

Glass as a material shares the properties of both solids and liquids. As such, glass at room temperature is commonly described as either a supercooled liquid or an amorphous solid,[1-3,7-9] although these can both be viewed as oversimplifications.[9] Thus, a glass is a solid, but due to its highly disordered nature, it exhibits properties much like a liquid that is too viscous to flow at room temperature. This dichotomy has led to the commonly cited myth that glass is really a highly viscous liquid and thus observable flow can be detected in objects of a sufficient age. This belief originates from the observation that stained-glass windows of 12th century cathedrals are thicker at the bottom than the top.[2,10-14] It has been verified via theoretical calculations, however, that the compositions used in either medieval or contemporary windows would not exhibit measurable flow at room temperature within the time scales of humanity,[10,12,14] and physical measurements have confirmed that unless sufficient compressive stress is applied, glass does not flow below 400 °C.[11,13] In truth, the uneven nature of medieval windows is the result of the limited technological methods used in their manufacture, and because of the resulting variable thickness, the thicker edges of the panes were logically mounted at the bottom of the window.[10-12]

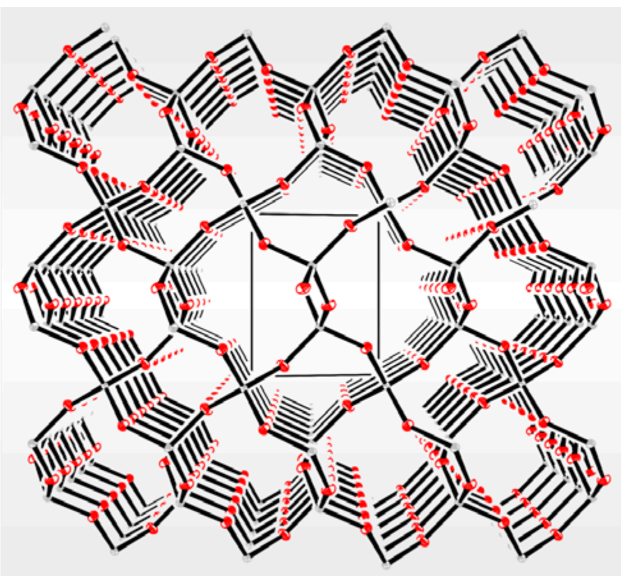

Figure 1. X-Ray structure of quartz viewed down the a-axis.

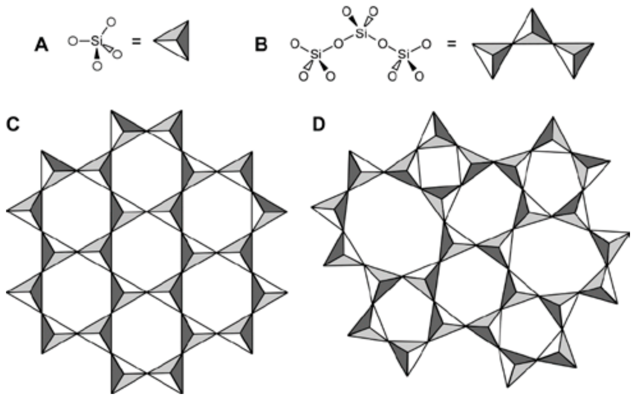

Figure 2. Simplified two-dimensional silicate structures: SiO_4 tetrahedron (A); oligomeric structure (B); crystalline structure (C); amorphous structure (D).

Glass is unlike any other early material and its production required some of the most advanced methods of any of the chemical technologies originating in antiquity. In terms of material properties, the closest modern analogues of silicate glasses are the organic plastics ubiquitous in modern society.[1] Molten glass could be poured into almost any shape and would retain that shape upon cooling. In addition, preformed pieces of glass could be thermally fused together to produce either air-tight seals or more complex structures. Furthermore, chemically stable glasses are relatively inert and can be produced in a wide range of color, opacity, or transparency. As such, this made glass a broadly versatile material for a vast range of applications.

COMPOSITION AND PRODUCTION OF EALRY SILICATE GLASSES

Although it is possible to produce a glass from silica alone, the temperature needed to melt silica (~1710 °C) is too high to have been achieved through methods available during the formative years of glass production.[6,15-19] Sometime during the 3rd millennium BCE,[18] however, it was discovered that the use of a flux (from the Latin *fluxus* - "flow"), such as soda (sodium carbonate, Na_2CO_3), could lower the fusion temperature of silica sources to below 1000 °C.[6,16-19] While this approach successfully reduced the temperature needed to produce molten glass, the sodium contained in the resulting glass is highly soluble and thus susceptible to attack by water. As a result, the glass produced via the application of soda as a flux is of low chemical stability.[1] In order to produce viable glass materials, a third component is thus required that acts as a stabilizer for the final glass product.[17,18] Such stabilizing species generally contribute less soluble cations, with calcium or magnesium compounds the most commonly applied. While potential sources of these ions could be lime, shells, or other mineral additives,[17,20,21] the critical nature of these stabilizing species was not initially recognized and it is believed that calcium was not intentionally added as a major constituent until the end of the 17th century.[20-22] As such, the calcium and magnesium content of all early glasses is thought to have been introduced via impurities in the silica or soda sources utilized.[1,2,21-23] The glasses produced through the addition of soda and calcium species to silica are typically referred to as soda-lime glass and it was these soda-lime formulations that made up the majority of all early glasses in the Western world.[1,2,16,19-24]

Early glass was produced from a silica source (such as beach sand) and a crude source of soda, with both components containing enough lime and/or magnesia to provide some chemical stability.[1,2,23] Heating this mixture would initiate fusion of the soda and other salt species, which would then start reacting with the sand to generate various sodium silicates and initial formation of liquid material. Lime and other basic species would then begin to react with the fusing mixture of silica and silicates to join the growing melt.[21,25] As the melt temperature increased, the viscosity of the mixture was reduced and any remaining silica would be incorporated into the melt.[25] Throughout the generation of the melt, gases would be liberated as the various carbonate, nitrate, and sulfate components were converted to their corresponding oxides,[15] resulting in violent agitation of the fusing mixture and significant bubbles in the final molten glass.[25,26]

In order to minimize the effect of these escaping gases, glass production was often carried out in two distinct stages. The silica-soda mixture would first be heated in shallow pans at a temperature to allow the reaction of the silica with soda and lime, but below that required to achieve homogenous fusion. The majority of the gaseous byproducts would thus be liberated in the process, after which the mixture would be cooled to give an intermediate product commonly referred to as a *frit*.[2,17,21,27] This frit would then be crushed to enhance more intimate mixing and then heated a second time at higher temperatures in order to achieve complete fusion.[17] Via this process, a final glass could be produced that was relatively free of bubbles.[27]

Table 1. Colorants commonly employed in early silica glasses.

Color	Transition or main group metal	Coloring oxides	References
White	calcium/antimony, or tin	$Ca_2Sb_2O_7$; SnO_2	2,7,16,18,28
Yellow	lead/antimony, or iron	$Pb_2Sb_2O_3$; Fe_2O_3	2,6,7,16,18,28
Red	copper and/or lead	Cu_2O; Cu^a; Pb_3O_4	2,7,16,19,29
Purple	manganese	Mn_2O_3	2,6,7,16,19,28
Blue	cobalt or copper	CoO; CuO	2,6,7,15-19
Blue-green	iron	FeO	2,6,7,15-18
Green	chromium	Cr_2O_3	2,6,19,30

[a] Metallic copper nanoparticles can result in a ruby red color.

Although commonly known as soda-lime glass, the chemical composition of these materials was really more complex than suggested by this simple designation. Besides the three primary components (silica, flux, and stabilizer), glasses also contained colorants (Table 1) and/or decolorizing agents, as well as a variety of unintended impurities introduced along with the primary reagents. As a consequence, the composition and structure of the resulting glasses could be quite complex and extremely variable, resulting in a range of physical and chemical properties. Furthermore, the nature of a particular glass depends not only on its chemical composition, but also the manner and degree of heating, as well as the rate the hot glass is cooled (i.e. annealing of the glass).[15,26,27]

ORIGIN AND INTIAL DEVELOPMENT

The origin of synthetic glass is unknown and its discovery has been attributed to the Syrians, the Egyptians, and even the Chinese.[2,31-33] Of course, various legends have developed around the discovery of glassmaking,[2,32-35] the most famous of which was recorded by the 1st century Roman author Pliny the Elder.[32] Pliny's account gives the story of a ship moored along the Belus river in Phoenicia, whose merchants used blocks of soda to support their cooking pots. As the combination of the sand and soda were heated by the cooking fire, it was stated that streams of liquid glass poured forth. While attempts to reproduce this legend have shown that glass cannot be produced in this fashion,[2,33,35] this story continues to be repeated into the present. In contrast, scholars believe glass resulted as either a byproduct of metallurgy, where fluxes were first utilized to convert rock impurities into liquid slag during the smelting of metals, or via an evolutionary sequence in the development of silica-based ceramic materials.[1,2,16,18,31,35-38]

Regardless of the specific developmental path, glass as an independent material is not believed to predate 3000 BCE.[2,39-42] Reports have claimed the analysis of glass beads that date back to as early as 2600 BCE, but at least some of these dates are questionable.[7] Glass objects have been found in Syria that date to 2500 BCE, and by 2450 BCE, glass beads were believed to be plentiful in Mesopotamia.[23,43] Some glass objects were also produced in Egypt during the 3rd millennium BCE,[38,40] but the oldest Egyptian glass of undisputed age is believed to date to only ~2200 BCE.[43] As such, historians have revised the original belief that glass was an Egyptian discovery and current views place the most likely development of the earliest glass in the Mitannian or Hurrian regions of Mesopotamia.[39,44] Furthermore, there is little doubt that glass was made from an early period in both Babylonia and Assyria[45] and routine Mesopotamian glass production is thought to have started ca. 1550 BCE.[41] The first glass objects included beads, plaques, inlays and eventually small vessels,[23,39,40,46] although such glass vessels did not become prevalent until after the middle of the 2nd millennium BCE.[47]

It is generally thought that introduction of glass technology into Egypt occurred during the reign of Tuthmosis III (1479-1425 BCE) via glass objects and ingots being imported as tribute[37,38,40,41] and the import of Mesopotamian glassmakers around 1480 BCE.[37,38,41] As such, this ultimately resulted in the local Egyptian production of glass by the time of Amenophis III (ca. 1388 - ca. 1350 BCE)[40] with evidence supporting onsite glass production in the Egyptian city of Amarna around 1350 BCE. Glass objects exhibiting genuine Egyptian style were made soon after, supporting their manufacture within Egypt. Archaeological evidence further supports this through the identification of several glass workshops in Egypt.[41]

Glass manufacture soon became a major industry and was spread throughout the Mediterranean for the next 300 years.[4] Glass objects of this early period (1500 - ca. 800 BCE) are characterized as a typical soda-lime glass with a high magnesia (3-7%) and potash (1-4%) content,[2,16,24,28,38,40,44,45] which is thought to be representative of glass produced or used throughout the Mediterranean area.[24] These vitreous materials were commonly produced from a mixture of silica and a crude source of alkali. Both the silica and alkali could then act as sources of lime or magnesia to give the resulting glass some chemical stability.[23]

In terms of the specific raw materials used during this early period, crushed quartzite pebbles and sand are usually cited as the two most common sources of silica.[2,21,28] However, the analysis of glasses of this time period reveal very low alumina content (~1.3% or less)[37,38] which is inconsistent with the high alumina content found in the majority of analyzed sands. As such, it is generally believed that these early glasses utilized crushed quartzite pebbles as the source of silica, an interpretation supported by the fact that large angular quartz particles have been found to survive in frits analyzed from Amarna.[38] For the alkali source, the two primary sources for early glassmaking were natron, a naturally occurring mineral source of soda, and various types of plant ash.[7,16,21,27,28,48-52] While both sources were used during this initial period, glass throughout the Eastern Mediterranean, Egypt and Mesopotamia was characterized by high magnesia (3-7%) and potash (1-4%) content.[16,23,24,40] This increased magnesia and potash content has been linked by many authors with the nature of the alkali used in the glass, and as glasses made with natron usually contain less than 1% of either MgO or K_2O,[43,64] this has led to the common view that plant ash was the predominant alkali source during this period.[16,40] In addition to the necessary soda flux, the plant ash also provided calcium and magnesium as chemical stabilizers for the resulting glass.[37] However, sea shells and calcinated corals have been mentioned in Mesopotamian tablets as reagents for glass production, both of which could have acted as additional sources of calcium.[7,27]

Processing methods for the formation of glass objects were fairly rudimentary during this early time period, consisting of either core-molding or cast glass[2]. The first of these dates to ~1500 BCE and was the earliest known technique for the production of hollow glass vessels.[24,46,53,54] As is outlined in Fig. 3, this involved the shaping of a form or core onto the end of a wooden or metal rod,[16,54-56] after which it could then be heated to help set its shape (Fig. 3C), and then glass layers were built up around the central set core. The most commonly cited methods for adding the glass layers involved treating the core with an organic binder (egg white or honey) and then by rolling it in crushed glass (Fig. 3D);[16,56] winding hot strands of glass around the core (Fig. 3D');[40,55,56] or immersing the core in molten glass not much above the softening temperature (Fig. 3D").[7,40,43,54-56] The assembly would then be heated to generate a uniform layer of glass (Fig. 3E), cooled, and another layer applied. Via such a repetitive process, the glass walls would be built up iteratively until the desired thickness was achieved.[54,56] The exterior of the object

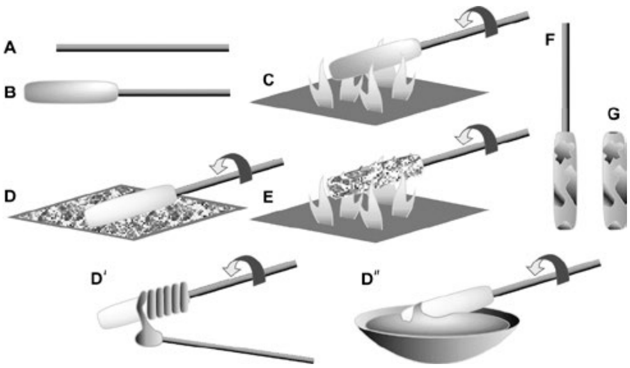

Figure 3. Production of core-molded vessels: (A) metal or wooden rod; (B) formation of core form; (C) firing the core; (D) glass application via rolling in crushed glass; (E) firing of applied layer; (F) completed object; (G) vessel after removal of rod/core. Alternate methods for glass application: (D') coiling strands of softened glass around the mold or (D") dipping the core in molten glass [adapted from reference 42 with permission from Springer Nature].

could then be worked and the object cooled (Fig. 3F), after which the rod was removed from the vessel so that the core material could be carefully dug from its center to give the final hollow vessel (Fig. 3G, Fig. 4).

The next significant advancement in glass forming was then made in ca. 1200 BCE, when the Egyptians learned to press softened or molten glass into open molds,[2,31,54] which allowed the production of simple shapes such as bowls, dishes, and cups not possible via the previous core molding methods. As outlined in Fig. 5, casting involved melting glass pieces into a mold which provided the simple, crude shape of the desired object.[55,57] After the glass had cooled, the mold could then be removed[57] and carved or polished to give the final product.[55]

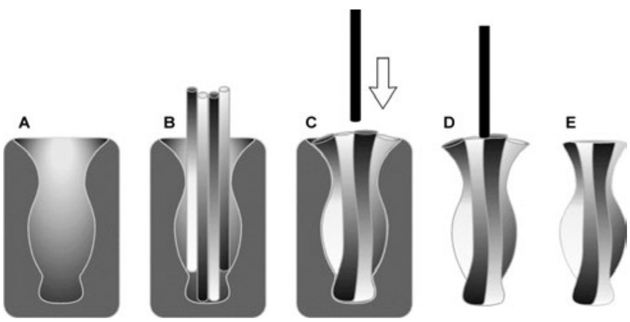

Figure 5. Fuse-casting of glass objects: (A) production of black mold; (B) glass pieces added, heated to fuse and fill mold; (C) metal rod inserted; (D) mold removed; (E) piece ground and polished to finish [adapted from reference 42 with permission from Springer Nature].

Figure 4. Core-formed glass Alabastron (6th - 4th century BCE) [M.88.129.10; Courtesy of the Los Angeles County Museum of Art].

DECLINE AND THE RISE TO ROMAN GLASS

After this period of initial development, the glass industry declined for a time until a revival in production beginning in Mesopotamia during 900-700 BCE.[4,7,16] This was followed by the growth of an apparently independent glass industry in Syria and along the Palestinian coast in 800-500 BCE[7] and a revival in Egypt in ca. 500 BCE.[4] This overall resurgence in glass technology is viewed as part of the Iron Age revival that followed the period of turmoil in the Mediterranean in 1200-1000 BCE. Centers of glass production then continued to develop in Egypt, Syria, and other countries along the eastern shore of the Mediterranean Sea,[9] with the Egyptian industry ultimately becoming centralized at Alexandria.[16,56] During this second period of ca. 6th century BCE to ca. 4th century CE, glass was characterized by lower potassium (0.1-1.0 %) and magnesium (0.5-1.5%) content, along with a consistent high concentration of antimony.[16,24,40] Many authors have linked the decreased magnesia and potash content with a change from plant ash to that of natron as the alkali source.[16,40,50,58] Another major change during this period was a shift in emphasis from opaque to clear glass production, with the move to clear and translucent colored glass thought to be due to a shift in viewpoint as much as any specific new advances in technology.[39]

Colorless glass was produced via the careful selection of a silica source of low iron content, coupled with the addition of antimony as a decolorizing agent.[18,31] The use of antimony as an additive was not new and was previously important for the production of opaque glasses. The colorless glasses achieved via the use of antimony are very similar in composition to the previous white opaque glasses, differing only in higher antimony levels (1.95% on average) for the opaque glasses.[28] Although such colorless glass was relatively transparent, the final object may still exhibit a slight yellow tint depending on the extent of Fe(III) content. In addition, the majority of ancient glass contained various undissolved materials and was therefore not as transparent as modern glass.

The conquests of Alexander the Great (d. 323 BCE) during the 4th century BCE brought the Greeks in contact with the cultures of the Near East as far as India.[39,59] As a result, the Greeks began to amass the technological knowledge of the Middle East, as well as that of the Egyptians, Indians, and Chinese.[42] Rome then conquered Greece in the 2nd century BCE, with the entire Mediterranean basin united under Roman rule by 30 BCE.[39] The culture and natural philosophy of the Greeks was thus absorbed by the Romans, including the collected knowledge and technology of glassmaking.

The term "Roman glass" is used to describe the normal composition of glass of the period 4th century BCE to 9th century CE that was produced throughout Syria, Egypt, Italy, and the western provinces.[24] Such glass consists of a composition similar to that of the previous antimony-rich group, although with a large drop in the amount of antimony and significantly higher manganese content. This has led to the conclusion that the primary distinction between Roman glass and the previous antimony-rich glass is the choice of decolorant used to achieve colorless glass.[16,24,60] However, this is somewhat of an oversimplification as it is generally believed that the Roman period is also distinguished by other changes in the raw materials applied to glass production.[37] The primary alkali source for Roman glass is generally held to be natron, most probably obtained from the Wadi Natrun in Egypt.[16,36,37,40,58,61,62] The Romans extensively imported natron from Egypt and it remained the alkali of choice for glass production for the duration of the Roman Empire.[40] In contrast, the silica source of Roman glass is now thought to consist primarily of sand, based on increased alumina (Al_2O_3, 2.3% average), TiO_2 (0.07% average), and Fe_2O_3 (0.5% average) content.[37,62] Furthermore, Pliny the Elder confirms the use of sand in Roman glass in his *Natural History*[63] and this sand-natron glass formulation remained as the standard glass formulation throughout the Roman and Byzantine periods until ca. 850 CE[37].

In addition to the use of manganese as a decolorant, Roman glass also utilized lead salts and other components as additives to the glass formulation.[7,18,36,63] The primary use of lead was as a colorant in the production of yellow opaque glasses,[28] but lead salts were also sometimes intentionally added to either improve the working properties of the melt[36] or to enhance the brightness of the resulting glass.[18] It has also been claimed by some that the uniform calcium content found in the analysis of Roman glasses is evidence of the intentional addition of lime to glass formulations.[7] To support this reasoning, authors have pointed to passages of Pliny the Elder that mention the addition of shells and fossil sand to glass,[63] as well as suggesting chalk or other forms of limestone ($CaCO_3$) that could have acted as convenient sources of lime in addition to burned shells (primarily a mixture of chitin and $CaCO_3$).[7] Still, it has also been pointed out by others that the distinct lack of substantial amounts of such additives in known glass recipes does not really support such claims.[2] Furthermore, as these potential calcium-based additives are not mentioned in the known glassmaking treatises of the Medieval and Renaissance periods, it is generally believed that the role of lime in glass was not yet recognized during the Roman period.[20] It should be pointed out, however, that analysis of the sands used as the Roman silica sources have shown higher calcium content and thus these sands are believed to have acted as a source of lime as well as silica.[37,60,61]

ADVANCED PROCESSING METHODS AND NEW APPLICATIONS

The Roman Empire presented a ready market for high-quality glass objects, which thus encouraged the development of new methods for the manipulation of glass and a more centralized approach to glassmaking.[2] For the first time, the mass production of similar glass objects became an economic goal and new fabrication methods were required to meet this demand. Such efforts began with bending (Fig. 6), a method also known as sagging or slumping.[2,55] The formation of slumped objects began with pouring hot glass onto a flat surface (Fig. 6A), which was then pressed with a flat,

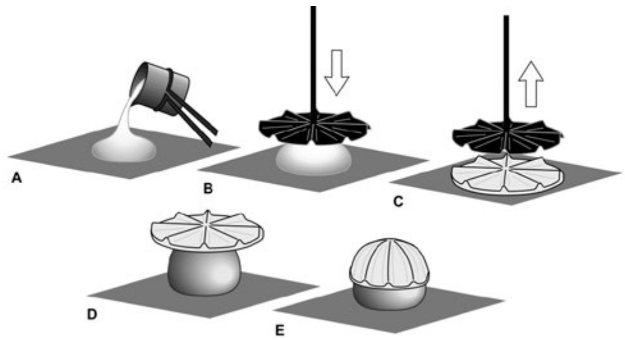

Figure 6. The formation of open-form bowls by sagging glass over convex "former" molds: (A) molten glass is poured onto a flat surface; (B) pressed with a flat, disc-shaped former; (C) cooled to create a glass disc; (D) transferred onto a "former" mold; (E) heated to cause the disc to sag over the mold giving the final bowl shape [adapted from reference 42 with permission from Springer Nature].

Figure 7. Ribbed bowl (1st century CE) [81.10.39; Courtesy of The Metropolitan Museum of Art, www.metmuseum.org].

disc-shaped tool (Fig. 6B) to create a glass disc (Fig. 6C). The resulting disc was then transferred onto a "former" mold (Fig. 6D) and the system was reheated to soften the glass disc to the point that the combination of heat and gravity would cause the disc to sag over the mold to give a bowl-shaped glass object (Fig. 6E, Fig. 7). The formed piece was then finished by grinding and polishing in order to remove mold markings or tool marks.[55,64] The large-scale production of slumped objects has been dated to ca. 400 BCE[39] with one of the most common objects made in this way being the distinctive ribbed bowls often referred to as pillar-molded bowls. Such bowls were popular from the 1st century BCE to the 1st century CE and modern glassmakers have illustrated that this is a viable, easily repeatable, and relatively fast method which reproduces all of the characteristics of Roman-era ribbed bowls.[64]

Of course, the most significant new advancement was the introduction of glassblowing during the 1st century BCE,[2,7,23,31,37,53,56,65] a technique now commonly viewed as synonymous with the general working of glass. Although it has been proposed by some to have been invented as early as 250 BCE, there is far too little evidence to support the application of glassblowing at this earlier date.[65] Sometime after 50 BCE, however, blown glass objects had become common and thus the genesis of glassblowing is typically dated to the time period of 50 BCE - 20 CE.[31,65] The origin and development of this technique is typically attributed to craftsmen somewhere in Syria or Phoenicia,[23,39,54,56,65,66] with many scholars favoring the Phoenician city of Sidon (on the coast of Syria) as its point of origin.[31,66] Glassblowing is then thought to have migrated to Rome via craftsmen and slaves after Roman annexation of the area in 63 BCE.[16] The introduction of the revolutionary technique now made possible the creation of an almost endless variety of hollow glass objects.[56] This method allowed the production of very thin, transparent glass, increased the overall versatility of glass significantly, and opened up potentially new applications for glass.[46] In addition, glassblowing could be combined with previous methods to result in new variants such as mold-blowing (Fig. 8),[65] in which glass was blown into a two- or three-piece hollow mold. The product of this method was a hollow, thin-walled vessel and the molds could be re-used indefinitely to allow the mass production of such objects.[65] As a consequence of such advances, the whole character of glass objects changed, with the heavier forms of earlier periods being gradually replaced by thin-walled vessels.[37] Furthermore, the scale of glass production increased dramatically such that it was now possible for the rapid production of simple utilitarian vessels in large quantities, and glass transitioned from prestige objects to household commodities.[7,37]

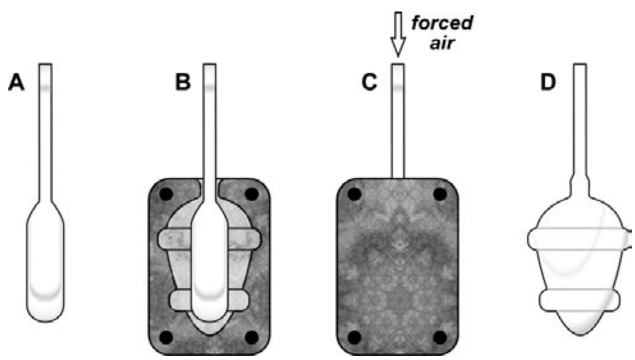

Figure 8. Blow-molding with a two-piece mold: : (A) hollow glass blank; (B) glass blank inserted into mold; (C) mold fastened together and softened glass blown to fill mold; (D) mold disassembled and hollow vessel isolated [reprinted with permission from reference 2. Copyright 2015, American Chemical Society].

One of the new applications of glass introduced by the Romans was the construction of glass window panes as early as the 1st century CE.[67-70] The date of this innovation is supported by window glass in Pompeii structures built or restored after the earthquake of 62 CE, yet preceding the eruption of Vesuvius in 79 CE,[68] with additional examples commonly found in Roman sites in Britain.[69,70] For the most part, however, such early glass windows were quite small, of irregular thickness, and not truly clear or transparent (Fig. 9).[67] Larger glazed windows comprised of multiple glass panes were known, however, such as those used for solar heating of Roman bath houses.[71] Early window panes were fabricated via a variety of different processes,[2,62,67-70,72] the oldest of which was the production of "cast glass" which produced panes of uneven thickness, with one side exhibiting a smooth texture and the other side a pitted, rough finish.[68-70] This seems to have been the prevailing technique up to the 3rd century CE, after which the technique fell into disuse and thus the exact details of making cast glass have been lost.[62,69,70,72] The production of blown window glass (cylinder and crown glass) appeared sometime after the 2nd century CE, with both the cylinder and crown techniques starting to become widespread by the beginning of the 4th century CE.[62,72] It is thought that cylinder-blown glass windows initially existed alongside windows fabricated via the older casting technique.[72]

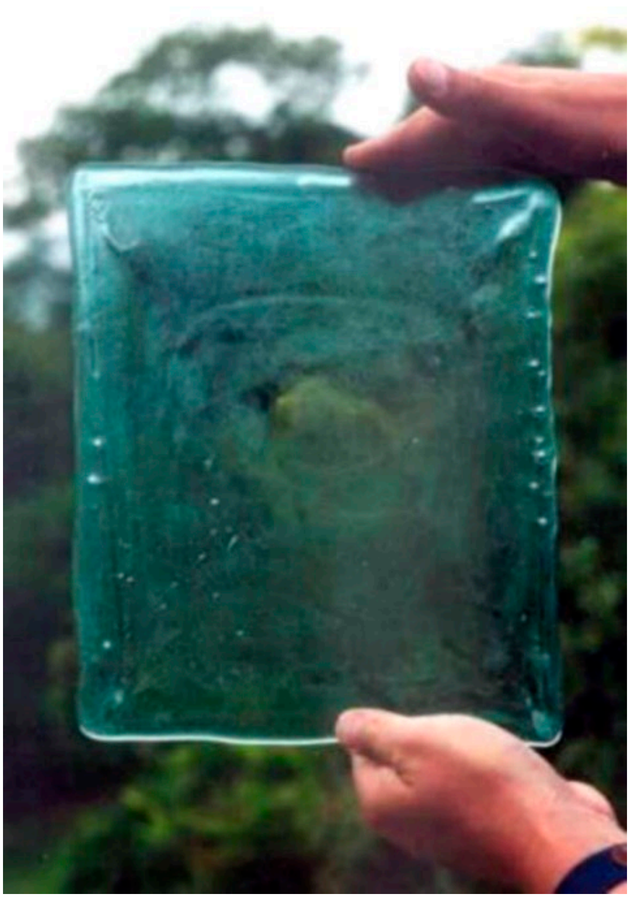

Figure 9. Modern reproduction of Roman window glass (~5 mm thick) [Copyright Mark Taylor and David Hill, used with permission].

It is also during the Roman period that the development of chemical apparatus began sometime towards the end of the 1st century CE.[73-76] Specific known examples at this point in time include the initial distillation apparatus (Fig. 10), the water-bath, and the *kerotakis* apparatus, all credited to the alchemist Maria the Jewess.[73-76] Although glass did find some application in such chemical apparatus, the majority were fabricated from either earthenware (with the interior glazed) or copper.[73,76] Rather, glass was limited to the objects such as the receiving flasks for stills (*bikos*) or other initial types of flasks known as *phials* and *urinals*.[73,76] As glass technology was rising to its initial heights during this time period, it is somewhat surprising that glass-based apparatus for the chemical arts do not seem to have been developed to any significant degree during the Roman period.[22,46,73] The late use of glass for such applications was largely due to the fact that typical soda-lime glasses of this period lacked sufficient chemical durability to be practical for such use.[6] Laboratory glassware must often withstand severe temperature changes in the presence of strong reagents. Thus, for such glassware to be useful, it must not only be resistant to chemical attack, but must also be durable under thermal stress.[22,73] The combination of poor quality, low thermal stability, and the

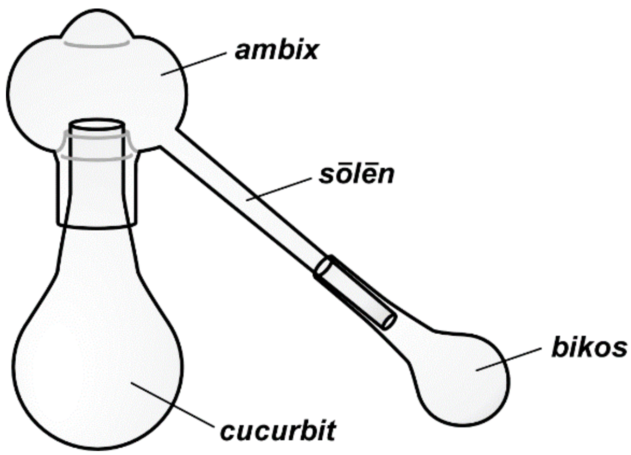

Figure 10. Basic components of the early still [adapted from reference 75 with permission from Springer Nature].

irregular nature of early glasses resulted in the frequent breaking of vessels when used under heat.[77]

VENETIAN GLASS

Centralized glass production came to an end following the fragmentation of the Roman Empire in the 4th century CE, with glassmaking shifting from urban centers to rural locations closer to raw materials and critical sources of fuel. As a consequence, glassmakers became isolated and Eastern and Western glassware gradually acquired distinct characteristics. In addition, this resulted in the loss of more specialized and sophisticated decoration techniques (cutting, polishing, and enameling) and critical techniques such as glassblowing were simplified to their basic essentials.[39] The path of glass in the East continued in the Byzantine Empire long enough to ensure its survival, and aspects of glassmaking that died out in the West were thus kept alive. Furthermore, contact between the Byzantine Empire and the new empire of Islam allowed Islamic glassmakers to add known Roman and Byzantine techniques to their glassmaking activities.[39] As with many chemical arts, this cumulative glassmaking knowledge was then preserved by the world of Islam until the coming of the Renaissance in the West. After the initial Crusades in the 11th century, the center of glass manufacture gradually shifted from glassmakers in the Islamic Empire to the growing glass industry of Venice.[7,56,78]

Venice developed into a city state during the 9th century and grew in importance during the 11th to 13th centuries by exploiting its strategic position at the head of the Adriatic.[39] The strength of the Venetian fleet allowed it to make the most of its advantageous trading position, achieving a virtual dominance of trade with the East. It is believed that the tradition of glassmaking never completely died out in Italy after the fall of Rome and the manufacture of glass had been revived in Venice by the time of the Crusades.[4,46,79] This simple industry was well established by the 9th century and was soon operating on such a remarkably grand scale that it was prospering by 1200.[39,56,80]

It is believed that the Venetians then gained additional glassmaking knowledge via an influx of Eastern expertise, beginning with information transfer from Byzantine glassmakers after the sack of Constantinople in 1204 and enhanced by a critical treaty signed in 1277 between Venice and the Prince of Antioch to facilitate the transfer of technology between the two centers.[39,78,79] This included the transfer of Syrian glassmaking, thus allowing many secrets to be brought to Venice, and a continuous supply of low-cost plant ash for the Venetian glass industry was established in 1366.[81] These factors provided key components that led to the flowering of glass in 14th to 16th century Venice.[78]

As the glass industry grew, the Venetian glassmakers established their own guild in 1268 with a more elaborate guild system to follow in 1279.[39,56] The center of Venice ultimately became dominated by furnaces, the control of which was lost far too often, the resulting fires causing destruction of both critical glasshouses and adjacent neighborhoods. As a solution, the glass industry was ordered to be moved to the island of Murano in 1291, about a mile from Venice.[56,79,80] The glasshouses of Murano are said to have extended for an unbroken mile where thousands of workers toiled to make the glass objects for which Venice became famous (Fig. 11).[56,80]

Until the beginning of the 14th century, the primary source of silica used by the Venetian glassmakers was various local sands.[82,83] In addition to silica, these sands

Figure 11. Venetian wineglass (Murano, 16th century CE) [91.1.1458; Courtesy of The Metropolitan Museum of Art, www.metmuseum.org].

are thought to have provided considerable alumina, as well as iron oxide, lime, magnesia, and small amounts of manganese.[23] However, it had long been known that the cleaner and whiter the source of silica, the clearer the resulting glass. As a result, these sands were gradually replaced with flint pebbles (a form of the mineral quartz) obtained from nearby river beds. Before use, these pebbles were calcined (heated red-hot in an oxidizing atmosphere), ground, and sieved to form a fine quartz powder that was purer than the sands previously used.[23,39,79,82-85] The resulting material was ~98% silica and became the near exclusive silica source of the Venetian glassmakers for the next several centuries.[82,85]

In terms of the alkali source, the Venetians favored the use of plant ashes imported from the Levant (modern Syria, Israel, Lebanon, and the Sinai in Egypt) as discussed above.[21,82-87] The soda ash imported from the Levant originated from the burning of plants thought to have belonged to the large family of the *Chenopodiaceae*, in particular the plant *salsola kali*.[21,82-87] These Levantine ashes, referred to in Venice and Murano as *allume catino*, were in common use by 1285[82] and were used almost exclusively in Murano until the end of the 1600s.[86] Such ash had high soda content (as much as 30-40%), as well as large quantities of potassium, calcium, and magnesium carbonates.[21,82,85-87] The exclusive use of these ashes was even dictated by the Venetian government, with the use of other plant ashes expressly prohibited,[87] thus highlighting the importance of these ashes to the Venetian glass industry. In addition to specific changes in the raw materials utilized, another significant contribution to the success of Venetian glass was the introduction of new processes for the preparation of the alkali raw materials.[86] The plant ash was shipped to Venice as hard pieces of calcined residue, after which it was pulverized and purified by a series of sieving, filtering, and/or recrystallization steps. These methods removed non-fusible material that would act as particulate matter in the resulting glass, as well as removing other unwanted impurities such as iron and aluminum-containing species.[21,23,84]

The choice of raw materials used by the Venetian glassmakers, coupled with their innovative purification methods, resulted in significantly improved glasses that dominated the industry for hundreds of years. The preparation and purification methods utilized removed unwanted colorants, as well as insoluble, non-fusible components from the resulting glass products. Not only did this result in much clearer glass, but this also removed particles that would have acted as stress points during rapid heating. In addition, the reduced soda content combined with the higher amounts of the stabilizing oxides would result in a material that exhibited both higher chemical durability and less thermal expansion.[18,22,73] As a result, the improved Venetian glass would therefore be more resistant to the action of water, acids, and bases, and would be less affected by rapid temperature changes, thus making it much more favorable for laboratory glassware in comparison to the previous Roman glass. As such, it is not surprising that this time period also exhibited a gradual shift of chemical apparatus from pottery and metal to the greater application of glass.[22,73,76]

MIRRORS, EYEGLASSES, AND LENSES

In addition to the production of higher quality glass, the Venetians also introduced a number of innovations for the production of novel forms of glass objects, beginning with advances in glass mirrors.[88] Although the production of glass mirrors was known to the Romans, these were limited to very small sizes and thus polished metal mirrors were preferred.[46] Critical factors that limited the previous development of glass mirrors was insufficient methods for producing flat, smooth glass that was still clear and relatively thin, as well as the fact that the initial metal backing was commonly lead or tin, and the application of hot metal onto glass typically resulted in thermal shock and cracking or breaking of the underlying glass substrate.[46,89]

This latter limitation was overcome with the innovation of metallic leaf, rather than molten metal, a discovery credited to the Venetians.[80] This was then further advanced in the 13th century, when the Venetians started to use a slow grinding process in order to produce highly polished mirrors.[88] The grinding and polishing needed to create a large, distortion-free surface, however, required the mirror glass to be made thicker than possible using conventional methods for the fabrication of windows. As a solution, panels of the desired thickness were typically produced by a modification of the original "cast glass" method of producing glass panes, after which the glass sheets were painstakingly ground and polished. Finally, the reflecting metal foil was then fixed to one surface to give very high-quality mirrors, although prohibitively expensive. A superior method of coating glass with a tin-mercury amalgam was then developed during the 14th-15th centuries, again typically credited to Venetian glassmakers. Venice had become a center of mirror production by the 16th century and was viewed to produce the best mirrors in the world.[89] Of course, mirrors were a crucial feature in the later development of optics and their application had significant effects on the developing sciences of physics, chemistry, and astronomy. It has been said that without mirrors, the Renaissance and the Scientific Revolution might not have occurred.[90]

Once the Venetian polishing techniques became more common, the manufacture of spherical glass surfaces became much easier, ultimately resulting in the production of eyeglasses.[88] Although various people have been credited with their invention over time,[91-93] available historical evidence has shown all of these to be false attributions and the inventor of eyeglasses is still unknown.[91,92] Available sources support their appearance in Italy sometime between 1286 and 1292,[91,92,94,95] with Pisa typically given as the most likely site of origin.[92-94] Eyeglasses were being produced in Venice by 1300 and were repeatedly referenced in guild regulations during the first two decades of the 14th century.[92,93,96] In fact, Venice became such an important production center for eyeglasses that Venetian spectacle makers left the glassmakers' guild to form their own guild in 1320.[93]

The earliest eyeglasses were comprised of two separate lenses and frames, held together with a central rivet (Fig. 12A).[93,94] These initial spectacles utilized convex lenses (Fig. 12B),[95,96] thus improving vision for the farsighted and used primarily for reading.[92,93] Concave lenses, for the nearsighted, were more difficult to work and did not arrive until the mid-15th century.[94-96] It has been stated that eyeglasses are one of mankind's most beneficial material inventions. Without them, people born with poor vision would be illiterate or have insufficient vision for a skilled trade. Even most people born with normal vision typically lose the ability to focus by their mid-40s.[93,95] As a consequence, it is believed that this single invention effectively doubled the intellectual life span of the average person beginning in the 13th century, significantly impacting society as a whole. Of course, as with mirrors, high-quality lenses were critical for the development of optics, as well as allowing later discoveries such as the microscope and telescope.[88]

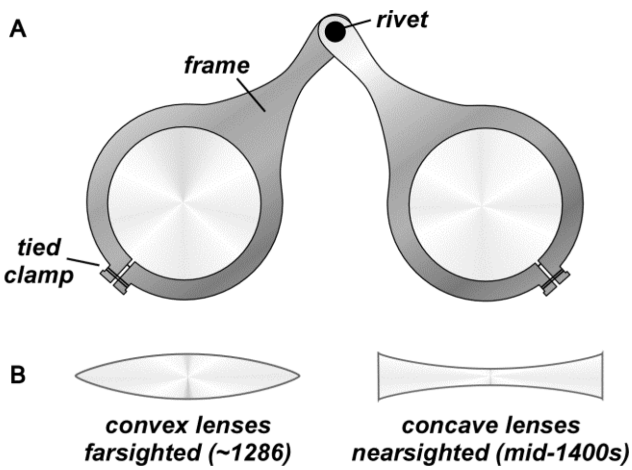

Figure 12. Early eyeglasses design (A) and convex versus concave lenses (B) [adapted from reference 87 with permission from Springer Nature].

FROM WALDGLAS TO BOHEMIAN GLASS

Glass in the West followed a different path following the fragmentation of the Roman Empire.[78] Under Roman rule, glasshouses had been established in the western provinces of Gaul and Britannia prior to the 3rd century CE, including sites at Boulogne, Trier, Cologne, Manchester, and Leicester.[7,16,56] By ~500 CE, the Western Empire fell to German tribes and although glassmaking essentially ceased in the West for a period, the established glasshouses survived and the knowledge of glass production was not completely lost. Reduced access to raw materials unavoidably produced glass exhibiting the character of the local silica and flux used and made it no longer possible to achieve colorless glass.[39] Such northern glass produced in the Middle Ages was sometimes referred to as *Waldglas* (forest glass), and was commonly dark green or brown due to contained impurities.[23,97]

A critical raw material for the production of high-quality soda lime glass was the natron imported from Egypt. However, without suitable access to the previously imported soda, several northern glasshouses started to use the ash of wood logs as the primary flux for glass production as early as 800 CE.[16,18,98,99] Beech was most commonly used for this purpose, although other species such oak, spruce, and birch were also used.[98,100] In comparison to the previously discussed soda-rich ashes obtained from plants grown near the sea or in salty soil, inland species typically provide ash higher in potash (K_2CO_3).[23] Thus, the ash of the various trees used was very low in soda, but all exhibited significant potash content (up to 37%) along with very high levels of calcium.[21,99] Thus by the 10th century CE, glass in the northern glasshouses was produced from a combination of the tree ash and local sands to give a potash-lime formula.[16,18,24,100] Chemical analysis of northern glasses of this time period have revealed high potassium and calcium content (11.8 and 17.9%, respectively) coupled with low sodium (1.63%), although potash-lime glass produced from 780-1000 CE was also quite variable and not as consistent as later glasses.[99]

In comparison to soda-lime glass, potash-lime glasses exhibited significantly different physical properties. For example, the application of potash as the flux could reduce the melting point of the silica to low as 750 °C, compared to the value of ca. 1000 °C achieved with soda.[101] In addition, potash-lime glass was heavier and harder than soda-lime glasses, which made it better for cutting and engraving, although it was also typically not as clear. Due to its lower melting temperature and the simple availability of trees in the Northern European forests, potash-lime glass could be inexpensively mass-produced, making it very desirable, particularly for the production of windows.[99,100]

Such northern potash-lime glass is often viewed as reaching its greatest heights with the material known as Bohemian glass. Although it is named after the Bohemian forests where it was developed, it is typically viewed as a German glass, as its origin stems from efforts by Rudolph II, Emperor of Germany and King of Bohemia, to start an establishment in Prague to make cut glass in imitation of rock-crystal.[97,102] As such, he recruited famous engravers of rock-crystal to Prague in the late 16th century, most critical of which was a German named Lehmann who came to Prague in 1590.[97] Glassworks had been established in the Bohemian and Silesian forests as early as the 15th century, but the glass produced was typical of other northern glasshouses and primarily copied Venetian glass forms.[97,98,102] Lehmann, however, developed a new style of glass-cutting and engraving that served as the basis of Bohemian forms. To facilitate the cut glass, heavier and thicker forms were developed, with the first such Bohemian glasses being white glass cut in facets and engraved with images. At a later period, both colored and colorless glass were also made.[97,102] A new Bohemian glass was then introduced in 1683 under the name of *Kreideglas* (chalk glass), which is the first verified glass that used lime as a significant component. This reputedly improved glass is ascribed to Michael Müller, developed in his factory in southwest Bohemia,[20] and the analyses of Bohemian glasses dated to the end of the 17th century are consistent with the use of lime.[98]

It was not long before Bohemian glass competed successfully with Venetian glass and, by 1730, it had completely supplanted Venetian glass in terms of artistic form.[97,102] Furthermore, it was in the early period of the 19th century that the chemical laboratory underwent what has been described as the "*glassware revolution*".[103] As such, what started with the gradual replacement of other materials (copper and pottery) with Venetian glass had now transitioned to a laboratory consisting primarily of chemical glassware, the majority of which was now produced from Bohemian glass.

CONCLUSION

The introduction of borosilicate glass in the 1880s ultimately ended the reign of the simpler soda-lime and potash-lime glasses, with brands such as Pyrex offering greater thermal and chemical stability and thus dominating most practical applications of glass.[104] Still, many of the everyday innovations commonly associated with glass began with these simpler formulations, including windows, glass mirrors, eyeglasses and lenses, and of course, chemical glassware. Needless to say, silicon in the guise of such silica-based glasses had unimagined impact on science and society, long before the element was ultimately isolated in the early 19th century.

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