Chapter 2
Origins of Glass: Myth and Known History

Where and when glass production began is uncertain. It is thought by some that the first glass was probably developed in the Mitannian or Hurrian region of Mesopotamia, possibly as an extension of the production of glazes (~5000 BCE) [1]. Around this same time, a new material called *faience* was developed, which was produced by utilizing a variety of techniques to create a glaze layer over a silica core [2, 3]. It may have been invented in either Sumeria or Egypt, but its full development was accomplished in Egypt, and it is therefore commonly referred to as Egyptian faience [2]. Although this material was used to craft beads during the third and fourth millennia BCE, it involved sintering (fusion below the melting point), rather than the complete melting of the silica mixture [4]. As such, faience can be thought of as an intermediate material between a glaze and glass [4]. Glass as an independent material is not thought to predate 3000 BCE, with the first glass objects including beads, plaques, inlays and eventually small vessels [1, 5–7]. Glass objects dated back to 2500 BCE have been found in Syria, and by 2450 BCE, glass beads were plentiful in Mesopotamia [4]. Glass came later in Egypt, with its manufacture appearing as a major industry around 1500 BCE [4, 8–11]. The oldest glass of undisputed date found in Egypt dates from ~2200 BCE [12].

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2.1 Myth and Legend

Many legends have attempted to explain the discovery of glassmaking. The most famous of these was recorded by the first century historian Pliny the Elder[1] in his *Naturalis Historia* (*Natural History*) [13]:

> In Syria there is a region known as Phœnice, adjoining to Judæa, and enclosing, between the lower ridges of Mount Carmelus, a marshy district known by the name of Cendebia. In this district, it is supposed, rises the river Belus, which, after a course of five miles, empties itself into the sea near the colony of Ptolemaïs. The tide of this river is sluggish, and the water unwholesome to drink, but held sacred for the observance of certain religious ceremonials. Full of slimy deposits, and very deep, it is only at the reflux of the tide that the river discloses its sands; which, agitated by the waves, separate themselves from their impurities, and so become cleansed. It is generally thought that it is the acridity of the sea-water that has this purgative effect upon the sand, and that without this action no use could be made of it. The shore upon which this sand is gathered is not more than half a mile in extent; and yet, for many ages, this was the only spot that afforded the material for making glass.
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> The story is, that a ship, laden with nitre,[2] being moored upon this spot, the merchants, while preparing their repast upon the sea-shore, finding no stones at hand for supporting their cauldrons, employed for the purpose some lumps of nitre which they had taken from the vessel. Upon its being subjected to the action of the fire, in combination with the sand of the sea-shore, they beheld transparent streams flowing forth of a liquid hitherto unknown: this, it is said, was the origin of glass.

Pliny's account places the discovery of glass in the north of modern Israel, just south of Lebanon (Fig. 2.1). The Belus river is identified with what is now known

[1] Pliny the Elder or Gaius Plinius Secundus (23–79 CE) was a Roman officer and encyclopedist. He was born in late 23 or early 24 at Novum Comum (modern Como), a small city in the region known as Transpadane Gaul (or Gallia Transpadana). Introduced to the city of Rome at an early age, he studied there before going on to become a military tribune at age 21. As an army officer, he held three posts, at least two of which were served in Germany. Best known as a writer and encyclopedist, he wrote his first treatise in 50–51, followed by a two-volume biography of the senator *Pomponius Secundus* and the twenty-volume *History of Rome's German Wars*. Following this, his writing shows a change in direction, thought to be associated with his final return to civilian life. He is most well-known for his encyclopedia, *Naturalis Historia*, published in 77 CE. This massive work resulted from years of collecting records, both from his reading and from personal observations, or anything and everything that seemed to him worth knowing. He died in late August of 79 during the evacuation around the erupting volcano Vesuvius. The exact cause of his death is unknown, but it has been said that he was asthmatic and overcome by sulfurous fumes. It is reported that he was still recording the personally observed marvels of nature to the last hours of his life [14].

[2] Alkaline carbonate, typically soda (sodium carbonate or Na_2CO_3). The word '*nitre*', which most recently refers to sodium nitrate, has only acquired that meaning within recent centuries. Originally it meant carbonated alkali, something that effervesced with vinegar or other acid, and when dissolved in water was a cleansing agent. The ancient Egyptians obtained native soda called '*nitrike*' from lakes such as those in Nitria. The Greek word became '*nitron*' and in turn became the Latin '*nitrum*' and the European '*nitre*'. Thus, the Greek '*nitron*' used by Hippocrates in the fifth century BCE, the Latin '*nitrum*' of Pliny in the first century CE, and their English equivalent '*nitre*', all apply to the soda obtained from either evaporitic lakes or plant ash [16].

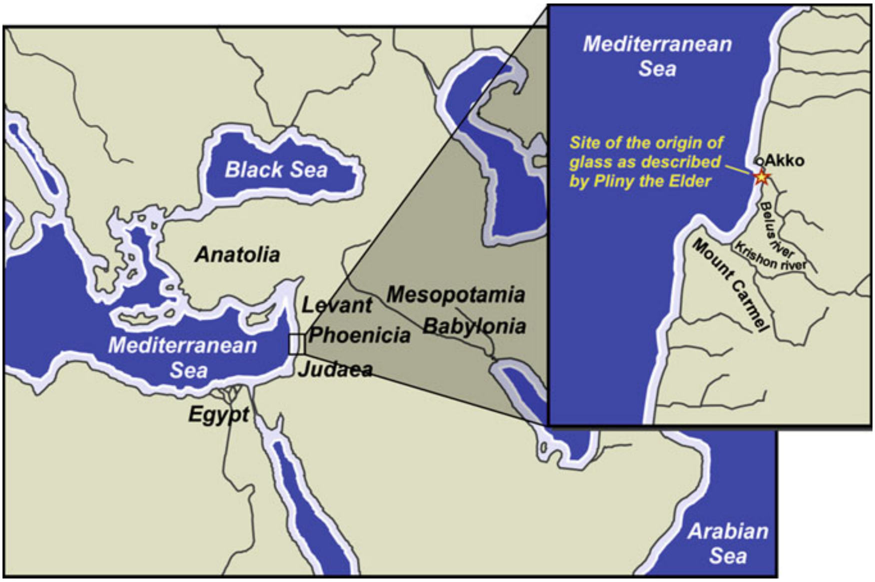

Fig. 2.1 Site of the discovery of glass as described by Pliny the Elder

as the Na'aman river, and the mouth of the Belus resided just south of the city of Akko (modern Acre). Analysis of the sand at the mouth of the Belus has revealed that it indeed is a high silica sand containing sufficient quantities of calcium components, yet with little other measureable impurities [15]. In addition to Pliny, the Belus sand has been referred to by a number of classical writers and is thought to have served as a long-time silica source for glassmakers working along the Syrian coast. Its exportation to other glassmaking centers has also been proposed [15].

In *The Art of Glass*, seventeeth century glassmaker Antonio Neri[3] gives a slightly different account, although again occurring at the mouth of the Belus river. Neri credits this tale again to Pliny the Elder [17]:

> Pliny saith, that Glass was found by chance in Syria, at the mouth of the river Bellus, by certain Merchants driven thither by the fortune of the Sea, and constrained to abide there and to dress their provisions, by making fire upon the ground, where was great store of this sort of herb which many call Kali, the ashes whereof make Barilla, and Rochetta; This herb burned with fire, and therewith the ashes & Salt being united with sand or stones frit to be vitrified is made Glass.

[3] Antonio Neri (d. 1614) is the author of the Italian manuscript *L'Arte Vetraria* (*The Art of Glass*). Initially published in 1612, it is considered to be the world's most famous book on glassmaking. Little is actually known about Neri, but he has been generally referred to as a Florentine monk and the tone of this writing is consistent with this profession. He was but one of several monks who, over a period of several centuries, were important contributors to the knowledge of glass [25].

To investigate the possibility of the discovery of glass as described in these accounts, William L. Monro of the American Window Glass Co. attempted to recreate the conditions described during a series of experiments in the 1920s [18]. Over a bed of glass sand mixed with an equal quantity of carbonate of soda, he built an open wood fire which he kept burning for two hours. As the fire burned, he monitored the temperature generated using a standard pyrometer couple inserted into the bed of the fire. He determined that a maximum temperature of 2210°F (~1210°C) was obtained when the fire had been reduced to a mass of burning charcoal. After the fire had completely burned itself out, the ashes were removed and a portion of the bed was found to be fused into a vitreous mass.

He then repeated the process, this time using a bed of glass sand mixed with an equal quantity of nitre.[4] As before, a portion of the bed mixture was found to have undergone fusion [18]. Finally, he carried out the process a third time, now using only the bed of glass sand, unmixed with any other ingredients. In this last case, examination of the sand bed after removal of the ashes revealed no evidence of even the slightest trace of fusion.

While Monro felt that these results confirmed the plausibility of the Pliny's story [18], others have pointed out some important considerations. The first consideration is that in Munro's recreation, a large quantity of soda was mixed throughout the sand, rather than the relatively limited interface of soda and sand described by Pliny [19]. As such, Munro's conditions were much more favorable for the production of the fused products and are not truly an accurate recreation of Pliny's story. The second point made is that it can be assumed that the merchants were interested in a fire hot enough to cook, not necessarily the extreme temperature achieved by Monro [18]. In fact, it has been reported by multiple sources that an ordinary campfire does not reach much higher than 600–650°C [20], with a possible maximum of 700°C [21–23]. As such, the temperatures claimed by Monro are significantly high and it is unclear exactly how these extreme temperatures were achieved. In fact, as the fusion temperature of a one-to-one mixture of sand and soda is typically below 1000°C [24], the claimed temperature of 1210°C should have resulted in fusion of a greater portion (if not all) of the bed. Nevertheless, even with the conditions tipped in his favor, Monro did not observe the free-flowing liquid glass described by Pliny.

Munro goes on to mention that seaweed ash contains a large amount of sodium carbonate and has been used in glassmaking to produce what has been called 'kelp glass'. He thus states [18]:

> It requires no great stretch of the imagination to think that at some time there had been kindled along a sandy shore a great bonfire of dry seaweed, with perhaps a lot of driftwood, which left amid its charred embers the vitreous mass we now call glass.

While such conditions proposed by Munro are speculation, they do follow fairly closely with Neri's account above.

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[4] While it is unclear, it appears that sodium nitrate ($NaNO_3$) was used in the second attempt. It may be that Munro is interpreting Pliny's use of '*nitre*' in its modern sense here.

2.2 Current Historical Knowledge

While the accounts discussed so far make entertaining stories, they are not commonly accepted as historically accurate and currently scholars believe that glass was discovered either as a byproduct of metallurgy or from an evolutionary sequence in the development of ceramic materials [11, 21]. These two hypothetical origins are deemed plausible as both early technologies had procedures that could be considered precursors of glass [4]. Considering the possibility that glass arose from metallurgical operations, a brief discussion of the history of metallurgy is required. It is known that the smelting of copper began as early as 6000 BCE in Anatolia (modern Turkey) [4]. Others, however, credit the Sumerians in southern Mesopotamia with the origin of copper smelting. By 3700 BCE, copper was being produced in the Sinai Peninsula and a little later ($\sim$3000 BCE) on Cyprus, from which the word copper is derived [21].[5]

The smelting of copper consisted of heating the ore malachite ($Cu_2CO_3(OH)_2$) in the presence of charcoal at temperatures of $\sim$1200°C [20]. The incomplete combustion of the charcoal would result in a strong reducing atmosphere of carbon monoxide, which would reduce the Cu(II) of the ore to metallic copper. At the temperatures employed, the metallic copper produced would become molten (Cu mp = 1084°C) and could be isolated and cooled to generate pure copper cakes [20, 25]. Of course, a complication in this process is that in collecting the ore, a good deal of rock was unavoidably collected as well. Common rock is comprised of various silicates and aluminosilicates which do not easily melt at the temperatures applied for the smelting of copper. Thus their presence would result in the isolation of a solid heterogeneous mixture of rock and raw metal, which would then have to be broken up and the metal removed, making its isolation cumbersome [25].

To overcome this complication, a flux would be added to assist with the melting of the residual silicate and aluminosilicate species. Early common fluxes for copper smelting were easily fusible pyrites and evidence has been found confirming such iron ores as flux in copper smelting [20, 25]. However, the types of species utilized as fluxes were quite diverse and in addition to various metal ores, also included a number of simple carbonate, sulfate, and nitrate salts. Known examples of such fluxes include soda (Na_2CO_3), potash (K_2CO_3), saltpeter (KNO_3), and vitriols (metal sulfates) [26]. Application of the flux would then result in a combination of molten metal and a fused mixture of rock and flux, commonly referred to as the *slag*. As the molten metal and slag were not miscible, they would form two separate molten layers within the smelting furnace. The two layers could be separated from one another via a process called *liquation*, in which the layers were poured or drained off one layer at a time (Fig. 2.2).

[5] The modern term '*copper*' derives from the Old English '*coper*' with its respective origin in the Latin '*cuprum*'. Cuprum in turn is a Roman contraction of '*aes cyprium*', meaning "metal of Cyprus".

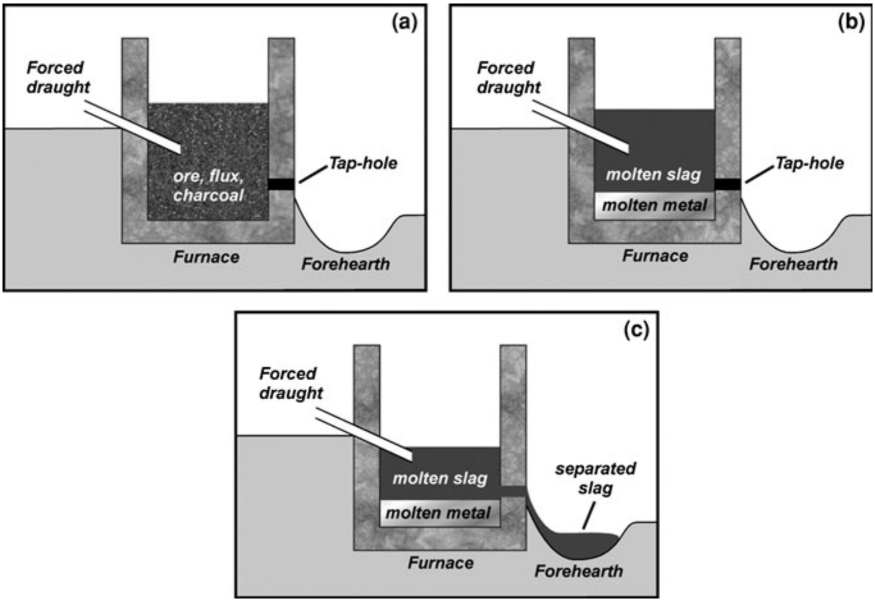

Fig. 2.2 Smelting process: ore, flux, and charcoal are mixed in the smelting furnace and fired (**a**); heating produces immiscible layers of molten metal and slag (**b**); the tap-hole is removed, allowing the slag to drain off into the forehearth (**c**)

When the molten slag was allowed to cool, it produced a rigid, glassy solid similar to obsidian. It is easy to imagine that experimentation with such siliceous slags (variation in types and source of rock, variation in flux, etc.) might well have led to the direct formation of colored vitreous silicate objects [11, 27]. Support for this proposed origin for glassmaking has also included the fact that many early glazes and glasses were colored blue by the addition of copper [21, 27]. However, the most significant evidence for a relationship between ancient glassmaking and metallurgy comes from archaeological finds. The Ramesside Egyptian site of Qantir (late second millennium BCE), contains evidence for both the preparation of red opaque glass ingots and bronze casting in a single site. Thus, this provides a clear example of the production of colored glass taking place at the very site where metallurgical byproducts were being generated [27].

Additional support for this connection comes from the analysis of second millennium BCE light blue opaque Malkata glasses, which revealed the presence of tin oxide [27]. As these glasses are colored with copper species, the presence of tin indicates the potential use of bronze dross, scale, or corrosion products as the source of copper(II) ions to color the glass. Similar relationships have also been observed between the copper and tin contents of blue New Kingdom glasses, the ratio which is compatible with the compositions of New Kingdom bronzes [27].

Of course, it has also been pointed out that slags from copper smelting actually contain only a little copper and are much richer in iron than either the early glazes or glasses [21]. It must be remembered, however, that only very small amounts of copper would be needed to provide the blue color. In addition, the high amount of iron is not surprising considering the common flux for copper was iron pyrites. The move to another flux via experimentation could easily have resulted in early blue glass with low iron content.

The second possible origin for the discovery of glass is thought to be due to an evolutionary development of a family of highly siliceous ceramics coated with alkali glazes originating in either Sumeria or Egypt [2, 11, 21]. The immediate predecessor of glass in this developmental sequence is the material known as faience [11, 21]. Faience was used mostly to make small objects such as beads and is found in profusion at archaeological sites in Egypt and elsewhere [4, 21]. It is produced utilizing a variety of techniques to create a glaze layer over a silica core [2, 3]. The resulting surface of faience is a transparent glass, usually blue or green, encapsulating a body consisting of crystalline grains of quartz loosely bound together by a glassy phase. In some specimens a thin layer of powdered material lies between the glaze and the body [20].

Chemical analysis has shown that the body of faience consists primarily of silica with small amounts of soda and other impurities [11, 21]. The study of several specimens by X-ray diffraction has revealed that the grains of silica consist of α-quartz, indicating that the material was heated to a temperature no higher than 870°C. The application of higher temperatures would have produced domains of tridymite in the body [21]. The formation of faience objects has been easily duplicated in the laboratory. Finely powdered quartz is combined with aqueous sodium carbonate to produce a firm paste, which can then be formed and fired. During the heating, the sodium fuses with the surface of the quartz grains, giving rise to both a glass exterior and an interior glassy phase that binds together the domains of α-quartz. In this case, the crystalline domains predominate, with only a small amount of glassy material and a large proportion of empty space [21].

From this knowledge, it is clear that the initial discovery of glass could have occurred via a few simple variations in the production of faience. Such variations could easily have occurred accidentally due to poor compositional or temperature control (i.e. excess soda or heat), or else as a result of investigating the effect of variable conditions on faience production [21, 28]. For example, if the ratio of sodium carbonate to powdered quartz had been increased in the initial paste, or if the formed paste had been fired at either a higher temperature or for an elongated period of time, the fusion of quartz and soda could have proceeded to a greater extent. Under such modified conditions, the domains of α-quartz would have been fewer in number and of smaller size, so that the material would have been mostly glassy. Having once made such a crudely formed glass, the faience makers could readily have gone on with a little additional experimentation to produce a true glass without any crystalline domains [21].

Such a path to the discovery of glass is supported by the fact that there is a known type of faience known as glassy faience. The structure of glassy faience is intermediate between the structure of ordinary faience and that of true glass and could thus be a logical intermediate in the path from faience to glass [21].

Unfortunately, the time period for the introduction of such glassy faience is not well documented and thus it is not certain that it was made before the invention of glass itself [21]. An inconsistency that should also be considered with this theoretical path is that while the full development of faience was accomplished in Egypt (and thus commonly referred to as Egyptian faience) [2], glass is thought to have originated in Mesopotamia and Syria, with its spread to Egypt at a later date [1, 6–10]. As the more advanced and significant faience production occurred in Egypt, it would be logical that the transition from faience to glass would also take place among these Egyptian artisans. Of course, this does not eliminate the possibility that the less advanced faience artisans of Mesopotamia accomplished the more significant advance to glass, while the Egyptian craftsman continued to perfect the production of faience without the transition to the new material.

In attempting to explain the delay of more than 2000 years between the production of faience and that of glass, it has been suggested that an important factor was that the production of faience involved only cold-working and reduced temperature sintering of the raw materials [4, 28]. In contrast, the routine production of glass vessels and other objects involved the manipulation of hot, viscous fluids, a process that was more akin to metal working. Therefore, although the production of glazed stones, faience, and glass all involved the same combination of essentially identical raw materials, the change from cold-working for glazes and faience to hot-working for glass may not have been a logical progression or an easy transition [28].

Such a transition would most likely have required input from metal workers who were more familiar with such high temperature manipulations. Thus, it can be argued that the discovery of the techniques necessary for hot-working glass was the result of interaction between the workers of glazed stone and faience and metal workers [27, 28]. Further, it is possible that such interactions were a result of the changing control over and organization of artisans following the political upheavals occurring in Egypt and the Near East during the sixteenth century BCE. As a result, artisans skilled in different crafts could have been brought into close proximity in workshops and production centers. In such an environment, the transfer of technologies between crafts would have been facilitated, paving the way for the eventual discovery of glass production [28].

While arguments can be made for either of the two commonly proposed pathways to the origin of glass, it is clear that either path is not completely independent of the other. In the first case, metallurgy is thought to originate in the pottery kilns, potentially as a consequence of using metal ores in glazes. In the second case, the high temperatures required for the production and working of glass is thought to have required input from metal workers. As such, it is quite reasonable to propose a combined path in which transfer of knowledge and observation between the two groups of craftsmen resulted in the discovery of glass with origins in both metallurgy and siliceous glazes.

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