ONE

GLASS AS A MATERIAL

A TECHNOLOGICAL BACKGROUND IN FAIENCE, POTTERY AND METAL?

Glass is a thing in disguise, an actor, is not solid at all, but a liquid, that an old sheet of glass will not only take on a royal and purplish tinge but will reveal its true liquid nature by having grown fatter at the bottom and thinner at the top, and that even that it is frail as the ice in a Parmatta puddle, it is stronger under compression than Sydney sandstone, that it is invisible, solid, in short, a joyous and paradoxical thing, as good a material as any to build a life from.

Peter Carey, *Oscar and Lucinda*, 111 chapter 32, 'Prince Rupert's Drops'

1.1 Glass as a Material

Glass was the first man-made translucent 'solid'. Those who first created it must have been impressed and greatly mystified by the way the glowing red-hot liquid cooled and appeared to 'freeze' into a block of 'solid' glossy material that reflected and refracted light. A quintessential characteristic of early glass was its colour, which could be used to imitate semi-precious stones such as lapis lazuli and turquoise, and there was even the potential to modify it. Indeed, the first appearance of glass is likely to have been unexpected in a high-temperature environment, leading inquisitive minds to question how it formed. Even if produced adventitiously, it may have been highly coloured and is likely to have been attributed a ritual significance. Some of the earliest glass, made from plant ash and silica, was certainly intended to imitate semi-precious stones and was attributed apotropaic properties. As the scale of glass production increased and the roles that glass played in society changed over time, the processes of its production became less mysterious and less enveloped in ritual. Nevertheless, even today in Murano, the famous centre for glass production in the Venetian lagoon in Italy, glassmaking families retain closely guarded technical secrets.

Clearly, glass production involved a series of inter-related aspects. The more practical aspects included the selection and use of raw materials; the collection of enough of the appropriate fuel types; the production of bricks and construction and use of particular furnace types; observation of the glass being melted; the production of a range of vessel and bead forms by blowing, moulding and winding; the decoration of vessels and beads and the relationship between glass technology and other industries, with the potential for sharing knowledge and raw materials. The ethnicity of all of the groups of people connected to various aspects of production, whether they were responsible for gathering glass raw materials, preparing them, building furnaces and ancillary structures, making crucibles and moulds and blowing and shaping glass, for example, would have had an impact on the object forms and decorative styles produced and on how they were used. The forms and colours of glass vessels and beads produced were a reflection of the period in which they were made. Depending on the social contexts in which they were used, glass colours may have been significant in a variety of ways. For example, during the sixteenth and seventeenth centuries, native Indians in North America believed that glass properties could be symbolic of the mind, knowledge and life with white glass equating with good things, including peace and a desire for understanding and red glass with war, intense experience, animation and fire heat (Turgeon 2004, 34–5).

Well before the first glass was made, a naturally occurring glass, obsidian, was worked into tools by percussive flaking. Obsidian can be grey, dark green, or apparently black, but the colours do not even come close to the beautiful range that can be achieved in man-made glass, and obsidian could not be worked at the temperatures achieved by ancient man. Man-made glass could also be flaked, but evidence of this is relatively rare (Fig. 1.1). The reason both glass and obsidian can be flaked as if they were stone is that both are amorphous materials. The word *amorphous* has a specific meaning to material scientists; it is a characteristic that helps define a material that lacks long-range structural order and can be described as a state of matter (Brill 1962). Crystalline silica, as opposed to glass, is composed of silicon and oxygen atoms arranged in a regular way; glass is arranged in a far less regular way, with the bridges between atoms being broken and the other components, such as sodium and calcium atoms, distributed in a relatively random way. Most glasses are composed of a network of silica, SiO_2 (the network former) and other metallic oxides. In pure crystalline silica, each silicon atom is bonded with four oxygen atoms, forming what is known as a tetrahedron $(SiO_4)^{4+}$. When arranged into a three-dimensional network, with the adjacent tetrahendra sharing one oxygen atom, it forms pure silica glass (with a melting point of c. 1700°C, unattainable by ancient man). A typical network modifier, such as soda (Na_2O), bonds ionically

1.1. Australian aboriginal arrowheads knapped from bottle glass (photo: J. Henderson; reproduced with kind permission of Håken Wahlquist and the Ethnographic Museum, Stockholm).

with oxygen within the network and disrupts bridging atoms within the silica tetrahedral network. Network stabilisers (such as calcium oxide, CaO), another type of network modifier, increase the durability of the glass: the bond strength of Ca^{+} is twice that of sodium (Na^{+}) and strengthens the structure. Trivalent alumina (Al_2O_3) and iron oxide (Fe_2O_3) can act as either stabilisers or fluxes.

By using techniques such as X-ray diffraction spectroscopy and neutron diffraction spectroscopy a 'structure' of glass can be revealed (e.g. Hannon and Parker 2000), although this in no way approaches the tightly ordered lattice of metal. Greaves *et al*. (1991) have shown that alkalis and nonbridging oxygen atoms are not arranged in a random way but tend to be concentrated in channels, giving rise to the term 'modified random network model'. This model therefore does not quite fit that for a 'liquid'. Indeed, the glassy state does not fit any of the three classical states of matter – solids, liquids and gases (Brill 1962, 129). This has implications for the durability of ancient glass, as has the distribution of pores through the glass (Lester *et al*. 2004).

Because glass is amorphous and assuming that there are no inclusions in it when it is struck, the 'shock waves' will pass through it in an unhindered way. In contrast, when a highly structured material like metal is struck, the 'shock waves' are prevented from being transmitted through it by the presence of ordered crystalline lattices consisting of repeated structural units; this is known as short-range order. When struck, the amorphous property of glass, obsidian and flint produces conchoidal (shell-like) fractured facets (see Fig. 1.1). However, the properties of glass that we are mainly concerned with here are not those that link it to other siliceous materials, like obsidian and flint, but those that come about when it is fused from raw materials, moulded, drawn, blown and wound to create objects and then cooled to a 'solid' state.

The apparently 'solid' property of glass is somewhat deceptive. Material scientists actually refer to glass as a 'super-cooled liquid' (Shelby 2005, 4–5). In 1956, Jones provided the following definition of glass: 'an inorganic product of fusion which has been cooled to a rigid condition without crystallisation' (Jones 1956, 1). Transparency and translucency must have been considered important properties in the past, so it would have been necessary to avoid the formation of crystals as a result of cooling the glass at the appropriate rate. In relation to the clarity of glass, Al-Buhturi (820–897), a celebrated Arab poet, described a glass containing wine in the following way:

> *Its colour hides the glass as if it is standing in it without a container.*

Another property that has been commented on is the brittleness and transitory nature of (some) glass. In his *Pirotechnia*, published in the sixteenth century, Vannoccio Biringuccio used these properties as a metaphor for man's own transitory existence:

> *Considering its brief and short life, it cannot and should not be given too much love, and it must be used and kept in mind as an example of the life of man and of the things of the world which, though beautiful, are transitory and frail.*

However, the numbers of complete Hellenistic and Roman glass vessels that have survived intact are a testament to the durability of glass rather than its brittleness. This piece seems to be more of a commentary on the fragility of human life than on (most) glass! Glass came late to China. In the medieval period the Chinese were fascinated by the transparency of glass and at the same time they were puzzled by the fact that glass could be both hard and fluid. They compared it with ceramics, metal, precious stones (especially jade) and even water 'but were unable to find a satisfactory analogy to further people's understanding of the material'. Moreover glass did not fit their 5 element system (metal, wood, water, fire and earth) (Hsueh-Man 2002a, 72–3).

The appearance of ancient glass, including some of the earliest, was deliberately altered to make it appear more like semi-precious stones, such as the rare mineral lapis lazuli, with a principal source in Afghanistan. This was achieved by rendering the glass *opaque* by adding crystalline materials or developing crystals out of the glass by reheating (striking) the glass.

When glass is cooling, one particular temperature, the *transition temperature* (T_g), is critical to the formation of a glass rather than a crystalline silicate (Henderson 2000, 24, fig. 3.1). At this temperature, the properties of glass pass from those like liquids to those like solids, although 'solidification', as such, does not occur. The crystalline silicate has a lower volume than the equivalent glass, and it is at the transition temperature that an abrupt change of volume occurs in glass and a slowing down of the rearrangements in its structure. When glass cools, its *viscosity* increases, so much so that for a Roman soda-lime natron glass of a typical chemical composition (see Chapters 4 and 8), Brill (1988) showed that the glass could be gathered and marvered (rolled across a flat [metal] surface to regularise the shape of a gather) at between *c*. 1100°C and 1000°C and softened sufficiently at *c*. 1000°C to blow it. Most ancient glass is composed of three major components. The first is silica (SiO_2), which is generally present at between *c*. 65% to 70%; the second is a flux, soda (Na_2O), which reduces the melting temperature of silica from between *c*. 1710°C. and *c*. 1730°C. to *c*. 1150°C; the third is 'lime' calcium oxide (CaO), which provides durability to the glass. Without calcium oxide the glass would dissolve in water. An alternative alkali, potassium oxide (K_2O), was also used. It has been found in glasses dating to as early as the tenth century B.C. in the Mediterranean, western Han Chinese glass and glass dating to the medieval period in northwestern Europe (see Chapter 4).

Wood or plant ashes and alkali-rich minerals are sources of glass fluxing materials (see Chapter 2). By changing the proportions of soda, lime and silica, the melting and working properties of glass also change. Therefore, the chemical composition of glass has a direct relationship to the ways in which it can be worked. Soda-lime-silica glass has a minimum *liquidus temperature* (the absolute melting temperature of the glass above which nuclei and crystals cannot form) at the ternary *eutectic* of 725°C for a composition of 21.9% soda, 5.1% calcium oxide and 73.1% silica (Morey 1964, fig. 20, tables 13 and 33). A eutectic mixture of compounds is one that has the lowest freezing point of all possible mixtures of sodium, calcium and silicon oxides. The wide range of ancient glass chemical compositions that has been found is discussed in Chapter 4. Variations in the balance of each major (and some minor) component in the glass would have had a direct affect on its working properties.

1.2 The Formation of Glass: Of Volcanic Glass, Asteroids, Slags and Scums

When magma is spewed from volcano vents and then chilled, obsidian is formed. Nuclear explosions, such as the first atomic bomb test at the Trinity site in New Mexico in 1945, can lead to glass formation. More recently, the use of another natural glass has been suggested as the material used for the carved scarab that forms the decoration of a breastplate of King Tutankhamen: an asteroid. Asteroid impacts (Mayell 2005) can leave a 'carpet' of glass. One exploded 29 million years ago above the Sahara Desert, turning the sand into glass, with a heat that was equivalent to a 110-megaton bomb (see http://www.sandia.gov/news/publications/technology/2006/0804/glass.html). Impact metamorphism can produce 'diaplectic glasses' from quartz and feldspars (Heide and Heide 2011, 28).

In considerably less dramatic contexts, glassy slags can be produced in virtually any high-temperature environment and it is these that probably constituted the first glassy material seen by ancient peoples. Glassy slags can be produced by burning cereals rich in silica-rich opal phytoliths, which provide rigidity to the plant structure (Dimbleby 1978, 129–30), and the combustion of haystacks (Baker 1968). Folk and Hoops (1982) found 'attractive' twelfth-century B.C. blue-green glass at Tel Yin'am in Israel, which they interpreted as being the adventitious fusion of silica-rich plant ash and silica. Even though vesicular (*ibid*., 460, fig. 14), the chemical composition and colour suggest that it was possibly man-made. Youngblood *et al*. (1978) published scientific analyses of glasses that were formed when the ramparts of Scottish Iron Age forts were ignited, the result of silica in the soil fusing with alkaline-rich materials in the fort ramparts. This actually led to a strengthening of the defences. 'Bone-ash' slags can be produced in cremations, and these also typically have a vesicular appearance (Henderson, Janaway and Richards 1987); Photos-Jones *et al*. (2007) have shown that seaweed known as cramp fused to bone in Bronze Age burials also produced a kind of vitreous slag. Glassy (fuel ash) slags are also often produced in hot furnaces and kilns in which metals are smelted or pots fired; the ashes from the fuel interact with silica present in both the bricks used to build the furnaces and kilns and in crucibles containing hot metals (Biek and Bayley, 1979; Henderson 2000, 53). Indeed *vitrification* in pottery, which results from alkali-bearing minerals interacting with silica in the clay (Kingery *et al*. 1976, 490), can produce hard ceramics such as stoneware and porcelain (Henderson 2000, 133). Pottery wasters from kiln sites often resulted from pots being heated to such high temperatures that the clays became glassy, having started to bloat and the pots then lost their shapes (Henderson 2000, 133). Even glass production generates a range of glassy slags resulting from the interaction of the fuel ashes with the silica-rich bricks used to construct the glass furnace. Glass production can also generate vitreous 'scums' (the nonreactive ingredients of the glass batch) on the surface of glass melts, or they are deposited on the sides and lips of crucibles as the raw materials in the glass batch fuse and the whole melt contracts. Thus these very different formation environments led (and still lead) to the formation of vitreous slags of a range of distinctive chemical compositions, some of which are highly coloured.

This adventitious formation of glass may be regarded as somewhat prosaic in the context of ancient technologies. However, the brilliant red glassy material

1.2. Two faience ushabti figures from Deir el Bahr (c. 1000–900 B.C.; photo: J. Henderson; produced with kind permission of the Museum of Mediterranean and Near Eastern Antiquities, Stockholm).

produced by the presence of reduced copper (Cu I) in metal smelting (Henderson 2000, 54) must have been impressive. Its blood-red colour would undoubtedly have had a ritual significance. Moreover, it is striking that one of the commonest early glass colours in Bronze Age Mesopotamia, Mycenaean Greece and in parts of Europe is the oxidised form of copper (Cu II), which is a turquoise green colour. So although the occurrence of copper in early glasses shows that a copper-rich colourant was available, it does not prove that metallurgy was the driving force behind the emergence of the first glass. As one of the last primary ancient inorganic materials to have been manufactured, it would be obtuse to suggest that only pottery or metal or faience technology led to the development of glass (see Figs. 1.2 and 1.3). Peltenburg (1987, 20–2) has stressed the paucity of solid evidence for the link between glass and metal technologies. Nevertheless, copper-rich minerals did provide the critical colourant that allowed early glassmakers to imitate turquoise, a stone considered to have health-giving properties with ritual playing a dominant part in every aspect of ancient society. Moreover, early stone glazing was achieved by heating copper ore on the powdered surface of talc (Hodges 1970, 62). So the availability of copper can be regarded as one of a number of parameters that played a part in the emergence of early vitreous materials, including glass.

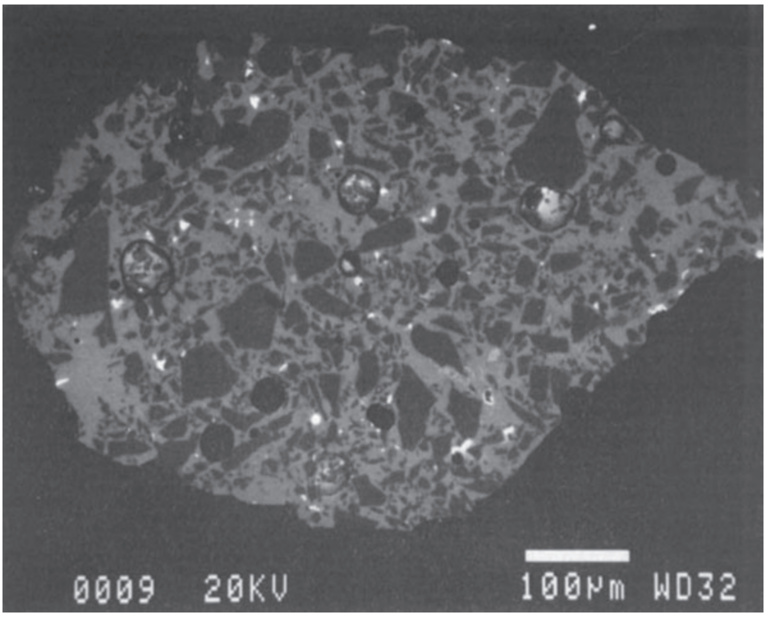
Thus, the adventitious production of glass can be regarded as especially significant in two ways: (1) if brilliantly coloured, it would have made a great impression on those who first observed it, and (2) its very formation would have been striking and almost certainly would have motivated those who saw it to manufacture glass deliberately.

Evidence for an apparent value for early vitreous slag is provided by the discovery of (unpublished) greenish glassy slag placed in an Akkadian *inhumation* burial (c. 2300 B.C.) at Tell Brak excavated by David and Joan Oates. This was characterised by elevated levels of phosphorus and calcium and is therefore probably a bone-ash slag. Although to our eyes it may appear insignificant, given that it was found in an area where the first glasses in the world are likely to have been made and dates to around the time when they were first made, it suggests that such materials may have played a part in the experiments involved in the production of the first glasses. It is, however, difficult to agree with J. B. Lambert's statement (1997, 105) that 'Refinement of slag could have eventually led to glass manufacture' simply because it is difficult to envisage how this could be achieved. Some of the earliest glass known, such as that from Eridu, Iraq (Garner 1956a), dating to c. 2300 B.C., has a chemical composition that is similar to glasses found in archaeological contexts that date to a period covering a further 1,300 years (see Chapter 6). The chemical composition of the block of cobalt blue glass from Eridu indicates that it was made deliberately from a combination of plant ash and silica and coloured with a cobalt-rich material. There is no hint of a compositional link to 'refined' slag, and it is unlikely to be a by-product from an experiment. The technology of ancient glass production may therefore have been 'fully formed' by this time.

1.3 Production of the First Glasses

The first glass appeared c. 2500 B.C. in modern-day northern Syria and Iraq (Moorey 1994). Initially the glass made from plant ash and silica would have been fused in a crucible in relatively small volumes. Most of this early raw glass was then made into beads, and it was not for another 1,000 years or so that larger volumes of raw glass and greater quantities of glass objects, including the first (late Bronze Age) core-formed vessels, were produced. Therefore, there was a period of *c*. 1000 years during which only small quantities of glass were made (see Chapter 5).

The first appearance of glass, and subsequent technological developments, seem to fit Cyril Stanley Smith's contention that 'the discovery of the materials, processes, and structures that comprise technology almost always arose out of aesthetic curiosity, out of the desire for decorative objects and not, as the popular phrase would have it, out of preconceived necessity' (Smith 1981, 347). When seen for the first time, the shiny, coloured, translucent, refractive and smooth properties of glass must have been both exciting and inspiring. As Smith went on to say, 'discovery *is* art, not logic, and new discoveries have to be cherished for reasons that are far more like love than purpose' (Smith 1981, 347). By stating this, Smith, who had a worldwide reputation as an Massachusetts Institute of Technology–trained material scientist, was removing



(a)

(b)

1.3a. A magnified (backscattered electron) image of a faience specimen from Hauterive Champrevèyres, Lake Village, Switzerland c. 1100 B.C. section (pale grey = glassy copper-rich glass matrix, dark grey crystals = silica; white crystals = tin oxide). 1.3b Diagram of 1.3a: hatched crystals = silica, broken lines and stipled areas = pores in sample.

the predictable aspects that characterise much contemporary positivist material science research, consisting of a mechanical and inevitable series of established procedures in the primary manufacture, formation and shaping of materials. For example, the subtle and progressive changes in the colour of glowing iron as a blacksmith works it is a reflection of its changing crystalline structure and something that has little relevance to modern industry. Such characteristics are therefore more connected to the art of creation (and in ancient contexts also to ritual and religion) than to logic.

Although the first glass may not have been deliberately coloured, the process of creating and then modifying the glass eventually led its creators to produce glass opacity, involving the incorporation of masses of tiny crystals (Henderson 2000, 35–8) in imitation of semi-precious stones (Fig. 1.4). Pale blue glass was produced in imitation of turquoise; a deep cobalt blue colour was produced in imitation of lapis lazuli; opaque yellow perhaps in imitation of gold and opaque red in imitation of blood. Most of these colours first started to be made from about the mid-fifteenth century B.C. when the first glass vessels were produced in Mesopotamia (Nolte 1968; Moorey 1994, 193). The Mesopotamian concept of raw material sources was that most had to be imported from specific 'mountains', some more mythical than others (Oppenheim 1970, 9). For example there was a 'cedar mountain', a 'gold mountain', a 'silver mountain' and a 'lapis lazuli mountain'. The wide range of terms used to describe the wide range of shades of lapis lazuli, such as 'beet coloured', 'wild donkey coloured' and 'star-like, starry' [the latter relating to flecks of pyrite in lapis lazuli] is a reflection of how lapis lazuli colours were the most cherished.

There are important questions concerning the manufacture of the first glass that we may never be able to answer adequately. Any evidence for the earliest phases of primary glass production is likely to be on a small scale. It is possible that the first glasses were made deliberately using a range of raw material proportions so as eventually to optimise the process. Perhaps the relatively common production of vitreous slags prompted early glassmakers to somehow establish that plant ash and silica were the primary raw materials. The successful production of glass or glassy materials would, however, be limited by the proportions that could successfully lead to glass production, a ratio of 2:1 by weight of plant ash to silica. Rehren (2000, 15; 2008, 1353) has argued that glass melts follow minimum eutectic troughs, leading to relatively narrow glass compositions. Evidence for experimentation could potentially be shown scientifically if the chemical compositions of contemporary vitreous materials and glasses found on a production site occupy a range or a continuum of *connected* compositions. The compositional continuum would reflect the use of different proportions of raw materials in the glass batch (ideally mixed in a ratio of 2:1 by weight of alkali to sand) and reveal which were unsuccessful. Experiments with different proportions of beech ash and sand have revealed how the all-important melting behaviour of the resulting glasses is affected (Smedley and Jackson 2002). By plotting proportions of one component against another, a mixing line – the 'dilution' of one major component by another – would be produced (see Chapters 10 and 11). The caveats to the possible