

*Second Edition*

# *Conservation and Restoration of Glass*

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*Sandra Davison*

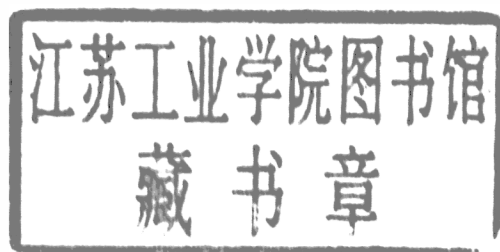


# Conservation and Restoration of Glass

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# About the author

Sandra Davison FICC ACR trained in archaeological conservation at the Institute of Archaeology (London University), and has worked as a practising conservator for thirty-five years. Fourteen years were spent as a conservator at The British Museum, and after a brief spell abroad, she has continued in her own private practice since 1984. Sandra has lectured and published widely, including a definitive work, *Conservation of Glass* (with Professor Roy Newton, OBE), of which this volume is a revised and enlarged edition.

In addition to working for museums in the United Kingdom, France, the Czech Republic, Malaysia and Saudi Arabia, she has taught glass restoration in the UK, Denmark, Norway, the Netherlands, the USA, Egypt, Mexico and Yugoslavia.

In 1979 she was made a Fellow of the International Association for the Conservation of Historic and Artistic Works (IIC), and in 2000 became one of the first conservators to become an accredited member of the United Kingdom Institute for Conservation (UKIC).

# Preface

*Conservation of Glass*, first published in 1989, was intended to serve as a textbook for conservation students, conservators and restorers working on glass artefacts within museums, and those restoring painted (stained) glass windows *in situ*. It was written by two authors with very different, but complementary backgrounds and experience in the conservation of glass. Roy Newton, a glass scientist (now retired), has worked in glass manufacturing, on the archaeology of glass and on the problems concerned with the conservation of medieval ecclesiastical painted windows. Sandra Davison, a practising conservator for over thirty years, has conserved a great variety of glass artefacts, published and lectured widely, and teaches the principles and practice of glass conservation in many countries.

In this edition, written by Sandra Davison, the section concerning painted glass window restoration has been removed, with the intention of producing a separate volume at a later date. However, information concerning the history and technology of glass window-making has been retained as background knowledge for conservators preserving panels of glass held in collections. The revised title, *Conservation and Restoration of Glass*, reflects the closer involvement of conservators in developing conservation strategies for dealing with glass in historic houses and elsewhere in the public arena. The volume includes sections on the historical development and treatment of mirrors, chandeliers, reverse paintings on glass and enamels.

*Conservation and Restoration of Glass* provides an introduction to the considerable background knowledge required by conservators and restorers concerning the objects in their care. Chapter 1 defines the nature of

glass in terms of its chemical structure and physical properties. Chapter 2 contains a brief history of glassmaking, illustrating the changing styles of glass decoration, and the historical development of light fittings (in particular chandeliers), flat glass, mirrors, reverse glass paintings and micromosaics and enamels. Chapter 3 consists of two parts. The first describes the use of the raw materials from which glass is made and the historical development of methods of glass manufacture; the second is concerned with the development of furnaces and melting techniques. The mechanisms by which glass deteriorates, in different environments, are described in Chapter 4, together with an outline of experiments undertaken for commercial/industrial concerns, to determine the durability of glass. The materials used in the processes of conservation and restoration of glass are discussed in Chapter 5. The examination of glass, described in Chapter 6, outlines both simple methods for use by conservators, and those more elaborate techniques which can be of use for analysis, research and the detection of fakes. Finally, in Chapter 7, the details of conservation and restoration techniques, based on current practice in several countries, are described and illustrated. Conservators/restorers should not normally undertake complicated procedures for which they have not had training or experience; but specialized areas of glass conservation are outlined in Chapter 7 in order to identify the problems that will require expert attention. Information concerning developments in glass conservation, which may also include details of treatments that have proved to be unsuccessful, can be found in conservation literature and glass conference proceedings.

# Acknowledgements

There have been significant developments and growth in glass conservation. The author has attempted to reflect this by inviting comments from a number of conservators and restorers (in private practice or museum employment), conservation scientists and experts in related fields, working in Britain, Europe and North America.

In particular, the author is greatly indebted to Professor Roy Newton for undertaking the enormous amount of research for *Conservation of Glass*, of which this book is a development; and to the following colleagues for their valuable assistance (and who, unless stated otherwise, are in private practice):

Chapter 1: Angela Seddon (Professor of Materials Science, University of Nottingham). Chapter 2: Phil Barnes (enamels); Simone Bretz (reverse paintings on glass; Germany); Judy Rudoe (micromosaics; Assistant Keeper, Department of Medieval and Modern Europe, British Museum); Mark Bamborough (painted glass windows); Tom Kupper (plain glazing; Lincoln Cathedral); Eva Rydlova (Brychta glass figurines; Czech Republic). Chapter 3 part 1: Paul Nicholson (Egyptologist, University of Bristol); part 2: David Crossley (industrial archaeologist, The University of Sheffield) and the late Robert Charleston (glass historian and former Curator of the Department of Ceramics and Glass, Victoria and Albert Museum). Chapter 4: Ian Freestone (Deputy Keeper, Department of Scientific Research, British Museum). Chapter 5: Velson Horie (conserva-

tion scientist, Manchester Museum, University of Manchester). Chapter 6: Angela Seddon (University of Nottingham) and Ian Freestone (British Museum). Chapter 7: Victoria Oakley (Head of Ceramics and Glass Conservation, Victoria and Albert Museum) and Patricia Jackson (UK), Rolf Wihr (Germany), Carola Bohm (Sweden), Raymond Errett (retired) and Sharon Smith-Abbott (USA) (glass object conservators); Alison Rae and Jenny Potter (conservators of ethnographic material – beads; Organic Artefacts Section, Department of Conservation, British Museum); Annie Lord (textile conservator – beads; The Conservation Centre, National Museums and Galleries Merseyside, Liverpool).

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# Introduction

The conservation of glass, as of all artefacts, falls into two main categories: *passive conservation*, the control of the surrounding environment to prevent further deterioration; and *active conservation*, the treatment of artefacts to stabilize them. A storage or display environment will consist of one of the following: (i) natural climatic conditions (especially painted glass windows and glass mosaics *in situ*); (ii) modified (buffered) climatic conditions in buildings and cases with no air conditioning; (iii) controlled climatic conditions, where air conditioning has been installed in museum galleries or individual showcases, to hold temperature and relative humidity within carefully defined parameters. Environmental control is a discipline in its own right (Thomson, 1998) and outside the scope of this book. However, conservators need to be aware of the basic facts in order to be able to engage in discussions regarding display and storage conditions, and the choice of materials for display, and packaging for storage and transport. The prevention of further damage and decay by *passive conservation*, represents the minimum type of treatment, and normally follows examination and recording. Reasons for not undertaking further conservation might be lack of finance, facilities, lack of an appropriate treatment or the sheer volume of glass, e.g. from excavation.

*Active conservation*, as the term implies, involves various levels of interference. *Minimal conservation* would include 'first aid', photography, X-radiography (where appropriate), a minimal amount of investigative conservation such as surface cleaning, and suitable packaging or repackaging for safe storage. *Partial conservation* entails the work above but with a higher degree of cleaning, with or

without consolidation. *Full conservation* work would additionally involve consolidation and repair (reconstruction of existing fragments), supplemented by additional analytical information where appropriate. *Display standard conservation* might include cosmetic treatment such as restoration (partial or full replacement of missing parts) or interpretative mounting for display. Restoration of glass objects may also be necessary to enable them to be handled safely. It should only be carried out according to sound archaeological or historical evidence. The level of conservation has to be agreed between a conservator/restorer and the owner, custodian or curator, before work begins.

Historically, glass conservation was not as easily developed as it was for ceramics, for example. The fragile nature of glass made it difficult to retrieve from excavations, and the transparent quality of much glass posed the difficulty of finding suitable adhesives and gap-filling materials with which to work. The use of synthetic materials and improvements in terrestrial and underwater archaeological excavation techniques have resulted in the preservation of glass which it was not formerly possible to retrieve; and continues to extend the knowledge of ancient glass history, technology and trade routes. Early treatments using shellac, waxes and plaster of Paris were opaque or coloured and not aesthetically pleasing (Davison, 1984). Later, rigid transparent acrylic materials such as Perspex (US: Plexiglas) were heat-formed and cut to replace missing areas of glass. Advantages were their transparency and only slight discoloration and embrittlement with age. However, the processes were time-consuming, and the replacements did not necessarily fit well against the original glass. Unweathered glass

surfaces are smooth, essentially non-porous and are covered with a microscopic layer of water, so that few materials will adhere satisfactorily to them. It was only with the commercial formulation of clear, cold-setting synthetic materials, with greater adhesive properties, that significant developments in glass conservation were achieved. Epoxy, polyester and acrylic resins could be polymerized in moulds *in situ*, at ambient tempera-

tures with little or no shrinkage. However, restoration involves interference with the glass in terms of the moulding and casting processes (Newton and Davison, 1989). Recent approaches to glass conservation and restoration have been the construction of detachable gap-fills (Hogan, 1993; Koob, 2000), and the mounting of glass fragments or incomplete objects on modern blown glass formers, or on acrylic mounts.

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# The nature of glass

The term *glass* is commonly applied to the transparent, brittle material used to form windows, vessels and many other objects. More correctly, glass refers to a state of matter with a disordered chemical structure, i.e. non-crystalline. A wide variety of such glasses is known, both inorganic (for instance compound glasses and enamels, and even the somewhat rare metallic glasses) and organic (such as barley sugar); this book is concerned only with inorganic glasses, and then only with certain silicate glasses, which are inorganic products of fusion, cooled to a rigid condition without crystallizing. The term *ancient glasses* is that used by Turner (1956a,b) to define silicate glasses which were made before there was a reasonable understanding of glass compositions, that is before the middle of the seventeenth century (see also Brill, 1962). In this book, for convenience, the term glass will be used to mean both ancient and historic silicate glasses. Understanding the special chemical structure and unique physical properties of silicate glasses is essential in order to appreciate both the processes of manufacture of glass objects and the deterioration of glass, which may make conservation a necessity.

## Natural glasses

Before the discovery of how glass could be manufactured from its raw ingredients, man had used naturally occurring glass for many thousands of years. Natural silica (the basic ingredient of glass) is found in three crystalline forms, quartz, tridymite and cristobalite, and each of these can also occur in at least two

forms. Quartz is the most common, in the form of rock crystal, sand, or as a constituent of clay. Rock crystal was fashioned into beads and other decorative objects, including, in seventeenth century France, chandelier drops. If quartz is free from inclusions, it can be visually mistaken for glass.

Sudden volcanic eruptions, followed by rapid cooling, can cause highly siliceous lava to form natural glasses (amorphous silica), of which obsidian is the most common. In ancient times, obsidian was chipped and flaked to form sharp-edged tools, in the same manner as flint (*Figure 1.1*). Other forms of naturally occurring glass are volcanic pumice, lechatelierite or fulgurites and tektites. Pumice is a natural foamed glass produced by gases being liberated from solution in molten lava, before and after rapid cooling. Lechatelierite is a fused silica glass formed in desert areas by



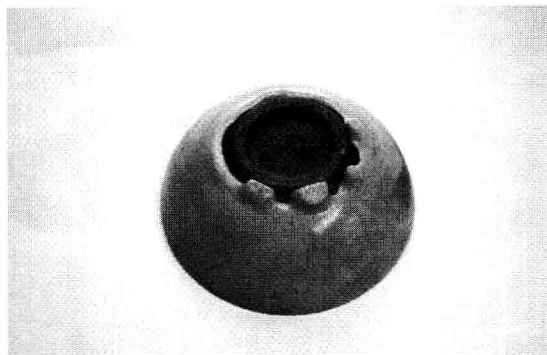
**Figure 1.1** Since prehistoric times, obsidian has been used to fashion tools. The spearhead shown here is a modern example, made in Mexico.

lightning striking a mass of sand. The irregular tubes of fused silica (fulgurites) may be of considerable length. Lechatelierite has also been discovered in association with meteorite craters, for example at Winslow, Arizona. Tektites are small rounded pieces of glass, of meteoric origin, found just below the surface of the ground in many parts of the world, and which appear to have come through the atmosphere and been heated by falling through the air while rotating. Their composition is similar to that of obsidian, but they contain more iron and manganese.

### Man-made glasses

In order to understand the nature of man-made glass, it is first necessary to define several terms for vitreous materials, some of which have previously been used ambiguously or incorrectly (Tite and Bimson, 1987). There are four vitreous products: glass, glaze, enamel and (so-called, Egyptian) faience, which consist of silica, alkali metal oxides and lime. Glass, glaze and enamel always contain large quantities of soda ( $\text{Na}_2\text{O}$ ) or another alkali metal oxide, such as potash ( $\text{K}_2\text{O}$ ), and sometimes both, whereas Egyptian faience contains only quite small amounts of alkali metal oxide. It has formerly been supposed, that because of the difficulty of reaching and maintaining the high temperatures required to melt glass from its raw ingredients, in ancient times, the raw ingredients were first formed into an intermediate product known as frit. However, there is limited evidence for this practice. In the fritting process, raw materials would be heated at temperatures just high enough to fuse them, and in doing so to release carbon dioxide from the alkali carbonates. The resulting mass was then pounded to powder form (the frit). This was reheated at higher temperatures to form a semi-molten paste which could be formed into objects, or was heated at higher temperatures at which it could melt to form true glass.

A silicate glass is a material normally formed from silica, alkali metal oxides (commonly referred to as alkalis) and lime, when these have been heated to a temperature high enough to form them into a homogeneous structure (formerly and ambiguously termed



**Figure 1.2** A thick layer of glaze covering a stoneware bowl.

glass metal). Chemically, glass, glaze and enamel can all be identical in composition, the fundamental difference being their method of use in antiquity. The coefficient of thermal expansion of a glass was not important when it was used alone (unless it was applied on a different glass, as in the manufacture of cameo glass), whereas in a glaze or an enamel any difference in thermal expansion between them and the base on which they were fused could cause the glaze or enamel to crack or become detached from the base material. In practice, glasses and enamels needed to have a low melting point, remain plastic as long as possible while cooling and, apart from the very earliest glasses, be translucent or transparent (in contrast to the early glazing of earthenware where coloured decoration had been important).

A glaze is a thin vitreous coating applied to another material to make it impermeable, or to produce a shiny decorative appearance. Glaze was sometimes applied with the body material before firing, but more often it was applied to the object after it had received a first firing, following which the object was refired to form the glazed surface (*Figure 1.2*).

Faience is composed of fritted silica with about 2 wt per cent of lime ( $\text{CaO}$ ) and about 0.25 wt per cent soda, lightly held together with a bonding agent such as water. The resulting paste was shaped by hand or in an open mould and then heated until the lime and soda had reacted enough (fused sufficiently) to hold the silica particles together. During the formation process, faience objects

formed a glazed surface with a similar composition to the body, usually coloured blue or green with copper compounds. (Strictly speaking the term *faience*, derived from the name of the Italian town of Faenza, should refer to the tin-glazed earthenware made there.) To reduce confusion the material discussed here should be referred to as Egyptian faience, or preferably, glazed siliceous ware (see *Plate 2* and *Figure 3.2*), (Nicholson, 1993; Smith, 1996).

The pigment known as Egyptian Blue, first used in Egypt during the third millennium BC, and during the next 3000 years, in wall paintings, and as beads, scarabs, inlays and statuettes, is the mineral  $(\text{CaO} \cdot \text{CuO} \cdot 4\text{SiO}_2) = (\text{CaCuSi}_4\text{O}_{10})$ . X-ray diffraction analysis has shown that, in addition to this compound, the only crystalline materials were quartz and tridymite (another of the crystalline forms of silica) (Chase, 1971; Tite *et al.*, 1981).

An enamel resembles a glaze in that it is also fused to a body of a different material, in this case, metal (see *Figures 3.33–3.38*, 7 57 and 7.58); however, the term enamel is also used to describe vitreous pigments used to decorate ceramics and glass (see Chapter 3).

### Chemical structure and composition

Zachariasen (1932) established that the atoms and ions in silicate glasses are linked together by strong forces, essentially the same as in crystals, but lacking the long range order which is characteristic of a crystal. Crystalline silica (quartz) melts sharply at 1720°C from its solid state, to a liquid, just as ice melts to form water at 0°C. This melting point is scientifically referred to as the *liquidus*. When the silica liquid (molten glass) is cooled from above the *liquidus*, the randomly distributed molecules will endeavour to adopt a less random configuration, more like those of crystals. However, an alternative three-dimensional structure forms because the crystallization process is hindered by the high viscosity of the glass, and the presence of the network modifiers. The melt becomes more and more viscous as the temperature is lowered until, at about 1050°C it sets to form a solid glass (a state formerly but no longer referred to as a super-cooled liquid). Moreover, the density of that glass is less than that of the original quartz

because there are now many spaces between the ill-fitting molecules.

However, in order to form a usable glass it is necessary to add certain oxides to the silica, which act as network modifiers, stabilizers and colourants, and which also have a marked effect on the structure of the resulting product. When network modifiers are added, they have the effect of considerably lowering the viscosity of the melt (see *Figure 1.8*). Thus there is the potential for a different type of crystal containing atoms from the modifiers, to form in the sub *liquidus* melt, provided the melt has been held at the *liquidus temperature* for long enough. Thus a glass with the molar composition  $16\text{Na}_2\text{O}$ ,  $10\text{CaO}$ ,  $74\text{SiO}_2$  can form crystals of devitrite ( $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ ); which grow at a rate of 17  $\mu\text{m}$  per minute at a temperature of 995°C, the optimum temperature for growth of devitrite in that composition of glass. The total chemical composition of the glass remains unaltered (i.e. no atoms are added or subtracted from those already in the glass), although the composition will change locally as crystals of devitrite separate from the bulk glass.

Ancient glasses have such complex compositions that devitrification occurs much less easily than in modern glasses, so that if crystals of devitrite are present in a sample undergoing examination, there may be doubts concerning the antiquity of the glass. However, the enormous block of glass made in a tank furnace in a cave at Bet She'arim, in Israel, was found to be heavily devitrified (with the material wollastonite,  $\text{CaSiO}_3$ ) as a consequence of containing 15.9 wt per cent of lime (Brill and Wosinski, 1965). The opalizing agent in some glasses may be a devitrification product itself, which forms only when suitable heat treatment is given to the glass. Devitrite does not occur as a mineral in nature.

Early historians and archaeologists have occasionally used the term devitrification in quite a different sense, meaning loss of vitreous structure to describe glass that has weathered with loss of alkali metal ions, of other constituents of the glass and probably a gain in water content. This ambiguous use of the term should be avoided (Newton and Werner, 1974).

### Network formers

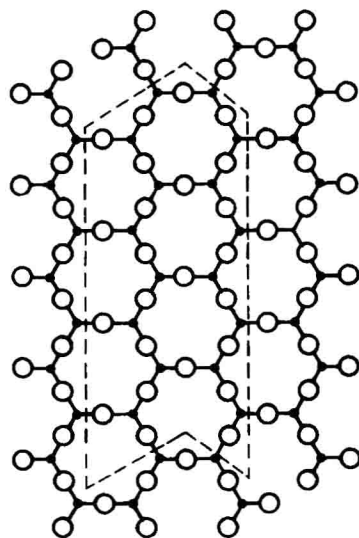
The principal network former in ancient glasses is silica ( $\text{SiO}_2$ ). Silicon and oxygen in

crystalline silica (quartz) are arranged in a definite pattern, the units of which are repeated at regular intervals forming a three-dimensional network consisting of tetrahedra with a silicon atom at the centre and an oxygen atom at each corner; all four of these oxygen atoms form bridges to silicon atoms of the four neighbouring silicon tetrahedra. Other network formers are the oxides of boron ( $B_2O_3$ ), lead ( $PbO$ ) (Charleston, 1960) and phosphorus ( $P_2O_5$ ). The presence of boron is important for clarifying glass compositions. However, it is difficult to analyse and so might easily be missed, especially since ancient glasses typically contained only 0.01 to 0.02 per cent (whereas some Byzantine glasses contained 0.25 per cent boron). Boron entered the glass by way of the ash obtained by burning plants containing boric oxide. The mineral colemanite (hydrated calcium borate) ( $Ca_3B_6O_{11} \cdot 5H_2O$ ) is found in western Turkey, and may have been used in glassmaking.

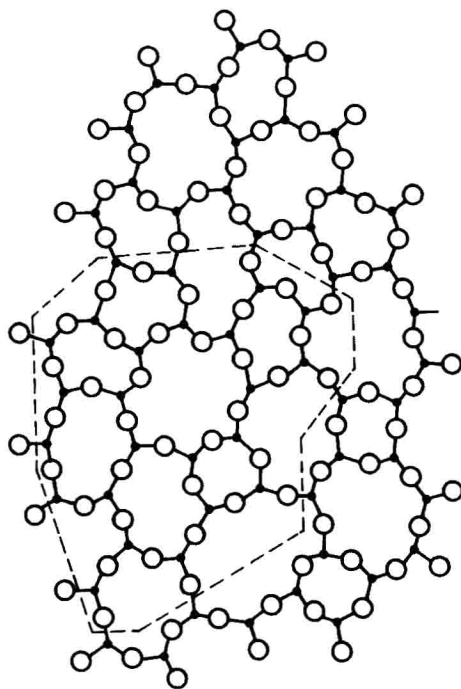
The concept of network-forming oxides is illustrated in *Figures 1.3* and *1.4*. *Figure 1.3* shows the regular structure of an imaginary two-dimensional crystalline material. Within the broken line there are 16 black dots (representing atoms of type A) and 24 open circles (representing atoms of type O); hence the imaginary material has the composition  $A_2O_3$  and its regular structure shows that it is crystalline. If the imaginary crystalline material  $A_2O_3$ , shown in *Figure 1.3*, has been melted, and is cooled quickly from the molten state, the resultant solid might have the structure shown in *Figure 1.4*. Here the broken line encloses 24 black dots and 36 open circles and hence the composition is again  $A_2O_3$  but the structure is irregular and non-crystalline, representing the amorphous, glassy or vitreous state of the same compound. Note that the amorphous structure contains spaces and thus occupies a greater volume than the crystalline one, and hence the crystal has a higher density than the glass, even though the chemical composition is the same.

### **Network modifiers**

*Figure 1.5* shows a structure which is nearer to that of silicate glass. It is again a simplified two-dimensional diagram, and the key to it now mentions the word ion. Ions are atoms that have been given an electrical charge, by

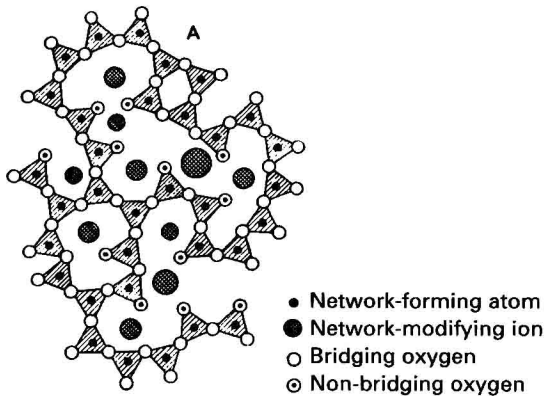


**Figure 1.3** Schematic two-dimensional representation of the structure of an imaginary crystalline compound  $A_2O_3$ .



**Figure 1.4** Structure of the glassy form of the compound in *Figure 1.3*.





**Figure 1.5** Schematic two-dimensional representation of glass, according to Zachariasen's theory.

adding or subtracting one or more electrons; *cations* having lost electrons, have a positive charge, and *anions* having gained electrons, have a negative charge. The network-forming atoms are represented by black dots within shaded triangles (atoms of silicon), and the network modifying ions (positively charged cations) are cross-hatched circles lying in the spaces of the network. Each network-forming triangle (silicon atom) is accompanied by three oxygen atoms (shown by small circles), which can be of two kinds. There are bridging oxygen atoms (shown by plain open circles) which are shared between two triangles, thus joining them together and forming part of the network. There are also non-bridging oxygen ions (shown by circles with a central dot) which belong to only one triangle; each of these thus bears a negative charge which is neutralized by a positive charge on one of the cross-hatched circles (cations). (Strictly, the Si-O-Si bonds are 'iono-covalent'. They are not ionic enough to refer to the oxygen as ions, and the Si as a cation. In the case of the Si-O non-bridging bonds, the Si-O bond is still iono-covalent, but the negative charge on the oxygen gives it the ability to form an ionic bond to a cation in a nearby space.) It should be noted that there is a very small amount of crystalline material in the diagram, near 'A' in Figure 1.5, where four triangles are joined together to form a regular (hence crystalline) area. (This can occur also in ancient glasses,

where micro-crystallites can be detected.) At all other points the triangles form irregular chains, which enclose relatively large spaces (and hence the density of the glass is less than that of a corresponding crystalline form). These spaces in the network have been created by the network-modifying cations which bear one or more positive electrical charges, and which can be considered to be held, by those electrical charges, to be more (or perhaps rather less) loosely bound in those enlarged spaces.

The monovalent cations (which bear only one positive charge, having lost an electron to an adjacent non-bridging oxygen ion) are usually the alkali metal ions, either sodium ( $\text{Na}^+$ ) or potassium ( $\text{K}^+$ ), which bring with them one extra oxygen ion when they are added to the glass as soda or as potash. Because these cations bear only a single positive charge, they can move easily from one space in the network to another (loosely bound). Thus, when the glass is placed in water, it becomes less durable because the cations (the smaller of the cross-hatched circles in Figure 1.5) can move right out of the glass into the water, thus making the water slightly alkaline. In order to maintain the electrical neutrality of the glass, these cations must be replaced by another cation such as the oxonium ion ( $\text{H}_3\text{O}^+$ ).

In the case of the *divalent alkaline earth* cations (the larger cross-hatched circles), each bears a double positive charge (being associated with two non-bridging oxygen ions, the circles with dots inside). These are usually  $\text{Ca}^{++}$  or  $\text{Mg}^{++}$ , added to the glass as lime ( $\text{CaO}$ ) or as magnesia ( $\text{MgO}$ ), but other divalent alkaline earth ions may also be present. The double electrical charge on them holds them nearer (more tightly bound) to their accompanying non-bridging oxygens, making it much harder for them to move from one space to another. Thus divalent alkaline earth cations play little or no part in carrying an electric current through the glass. Because they are associated with two non-bridging oxygen ions, they strengthen the network, thus explaining why they help to offset the reduction in durability produced by the alkali metal cations. However it should be noted that in Figure 1.5 the double ionic linkages (to circles with dots) are not immediately obvious.



It is these linkages which determine the very different effects that the monovalent and divalent cations have on the durability of glass.

Notable advances have been made in the understanding of the structure of glasses. For example, it is now realized that the network is actually loosened in the vicinity of the monovalent cations, channels (rather than merely larger spaces) being formed in which the cations can move even more easily than was formerly realized.

### Phase separation

Despite the essentially homogeneous nature of bulk glasses, there may be minute areas, perhaps only 100 nm (0.1  $\mu$ m) in diameter, where the glass is not homogeneous because phase separation has occurred. These regions (rather like that near 'A' in *Figure 1.5*) can have a different chemical composition from the rest of the glass, i.e. the continuous phase (Goodman, 1987). Phase separation can occur in ancient glasses, and can have an effect on their durability, because the separated phase may have either a greater or a lower resistance to deterioration. The amount of phase separation can be seen through an electron microscope.

### Colourants

The coloured effects observed in ancient and historic glasses were produced in three ways: (i) by the presence of relatively small amounts (about one per cent) of the oxides of certain transition metals, especially cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), etc., which go into solution in the network; (ii) by the development of colloidal suspensions of metallic, or other insoluble particles, such as those in silver stains (yellow) or in copper or gold ruby glasses (red or orange); (iii) by the inclusion of opalizing agents which produce opal and translucent effects. The production of coloured glasses not only depends on the metallic oxides present in the batch, but also on the temperature and state of oxidation or reduction in the furnace. Of course the exact compositions of ancient glasses were complex and unknown, being governed by the raw materials and furnace conditions, so that the results could not be accurately determined.

### Dissolved metal oxides/state of oxidation

Coloured glasses can be produced by metal oxides *dissolving* in the glass (similar to the colours produced when the salts of those metals are dissolved in water), although the resultant colours will also be affected by the *oxidizing* or *reducing* (redox) conditions in the furnace. In the *traditional* sense, a metal was *oxidized* when it combined with oxygen to form an oxide, and the oxide was *reduced* when the metal was reformed. The position can be more complicated when there is more than one state of oxidation. For example, iron (Fe) becomes oxidized when ferrous oxide (FeO) is formed, and a blue colour is produced in the glass (because  $\text{Fe}^{2+}$  ions are present), but it becomes further oxidized when more oxygen is added to form ferric oxide ( $\text{Fe}_2\text{O}_3$ ), which imparts a pale brown or yellow colour to the glass (due to the  $\text{Fe}^{3+}$  ions present). However, the situation is rarely so simple and usually mixtures of the two oxides of iron are present, producing glasses of various shades of green. When a chemical analysis of glass is undertaken, it is customary to quote the amount of iron oxide as  $\text{Fe}_2\text{O}_3$ , but that does not necessarily imply that all of the iron is in that state.

The oxidation process occurs when an atom loses an electron, and conversely, reduction takes place when an atom gains an electron. Consider the two reversible reactions set out in equations (1.1) and (1.2), where  $e^-$  represents an electron, with its negative charge. In equation (1.1) the forward arrow shows that an electron is lost when  $\text{Fe}^{2+}$  is converted to  $\text{Fe}^{3+}$ .



The combined effects of equations (1.1) and (1.2) is equation (1.3), which shows that there is an equilibrium between the two states of oxidation of the manganese and of the iron (Newton in Newton and Davison, 1989).



But the  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  are the more stable states, and hence the equilibrium tends to