Glass sickness: Detection and prevention
*Investigating unstable glass in museum collections*

Verhaar, G.

Publication date
2018

Document Version
Other version

License
Other

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
2

THE CHEMICAL NATURE AND
DETERIORATION MECHANISMS OF HISTORIC GLASS


2.1 Introduction
This chapter describes the chemical nature of glass, mechanisms of glass decay and ways in which the deterioration of glass has been scientifically investigated up to now. Firstly, the development of theories concerning the arrangement of atoms in an amorphous glass structure will be described as a basis for discussions of the research presented in this dissertation. Following this description two main factors that determine the deterioration of historic glass will be described, after which three general theories on glass deterioration will be described. The consequences of the deterioration of glass on its appearance are discussed, leading to an overview of recent developments in the measurement of glass deterioration and the description of methods for the early detection of unstable glass. The emphasis in this chapter lies on research carried out in the field of historic glass, but also discusses studies into glass deterioration in other fields.

Many scholars have published on the production techniques, technological advancements and chemical nature of glass in different contexts (e.g. Morey, 1954; Volf, 1984; Bansal and Doremus, 1986; Henderson, Calas and Stebbins, 2006; Rasmussen, 2008; Axinte, 2011). An excellent overview on analysis of historic glass has been published by Janssens (2013), which provides good insight into the applicability of analytical techniques for glass research.

In particular this chapter seeks to find answers to the following question: What chemical mechanisms are currently associated with glass deterioration in the literature, which analytical techniques are available for the non-destructive investigation of glass deterioration and what are the leading conservation strategies?

2.2 The chemical nature of glass
Glass is best characterized as an amorphous network of oxides whose atoms in the solid state are more randomly distributed than in crystalline materials. This is a result of the transition from the liquid to the solid state upon cooling and vice versa: instead of crystallizing at a well-defined melting temperature upon cooling, the viscosity in glass increases progressively. Verita (2006) provided an excellent
example of this phenomenon by describing the heating and the subsequent cooling of crystalline silica (quartz) to above its melting temperature of 1710°C and evaluating the specific volume of the material against temperature (Figure 2.1). By slowly cooling the liquid silica, the specific volume decreases rapidly and at its melting temperature the atoms will reorder into crystalline form, causing a sudden decrease in specific volume. However, when the molten silica is cooled rapidly, the atoms will not have enough time to crystallize and the specific volume will decrease at the same rate as above its melting temperature, at this point the material is referred to as a supercooled liquid. This continues until the glass transition temperature ($T_g$) is reached, where after the specific volume decreases at the same rate as crystalline silica and an amorphous solid has formed (Faupel et al., 2003; Verita, 2006). In this state, a solid material is formed but with the atomic distribution disorder of a liquid rather than a crystalline solid (for more details on the thermodynamics of this process, see e.g. Angell et al., 2000 and Debenedetti and Stillinger, 2001).

![Diagram of heating and cooling curves](image)

Figure 2.1. General volume changes associated with heating and cooling in systems susceptible to glass formation (from Fulchiron et al., 2015, Figure 1).
When the glass batch is in liquid phase and is cooled down slowly parts of the glass can form crystals, this process is referred to as devitrification (Davison, 2003) and is the cause of physical instability of the glass, resulting in the presence of a whitish layer on top of the glass. For commercial glasses, this is a larger problem than for historic glasses due to the complex composition of historic glasses, which inhibits crystallization of the glass (Davison, 2003). For commercial glasses, the devitrification process is important as the wrong way of annealing the glass or a small error in the glass batch composition can completely ruin a glass (Morey, 1954).

Historic glass generally has three main components: network formers, network looseners and network stabilisers, the latter two are often referred to as network modifiers. The role of these components in the glass network is described below.

### 2.2.1 Network formers

The network formers are the main component of glasses and consist of certain metal oxides with the ability to form vitreous solids as described above. The amorphous structure of glass was first well-described by Zachariasen (1932), and it is often referred to as the random network model (Greaves, 1994). Based on differences between x-ray diffraction experiments on glasses and metals Zachariasen (1932) concluded that there was no long-term periodicity or symmetry in the arrangement of atoms. He drew a two-dimensional representation of glass, which is still used as the basis for a simple schematic depiction of the structure of glass (see for example Figure 2.2). In his following argument Zachariasen postulated four requirements for a certain oxide \( \text{A}_n \text{O}_x \) to exist in a vitreous state, implying that not all oxides are able to form vitreous solids, but also that some unexpected metal oxides can form vitreous solids. The predictions of Zachariasen have been supported by later empirical evidence of different glass-forming oxides such as germanium oxide \( \text{GeO}_2 \), arsenic trioxide \( \text{As}_2 \text{O}_3 \) and vanadium oxide \( \text{V}_2 \text{O}_5 \). The requirements postulated by Zachariasen can be extended to non-oxide glasses and indeed, non-oxide glasses do exist, for example fluoride glasses used for the production of fibre optics (Aggarwal, 1991).

For historic glass, however, the main network former is silicon dioxide \( \text{SiO}_2 \),
also called silica. This compound is found in abundance in nature as the main constituent of sand (Krinsley and Smalley, 1972) and its use in industry is manifold, for example as a desiccant in the form of silica gel (Pramuang and Exell, 2007; San, Ni, and Hsu, 2002) and in food and pharmaceutical industries (Flörke et al., 2008). As mentioned previously, silica can exist as both crystalline (called quartz) and non-crystalline (or vitreous) material. The chemical structure of silica described by Zachariasen (1932) consists of silica tetrahedra (a single tetrahedron is depicted in Figure 2.3), in which each silicon atom is connected to four oxygen atoms by covalent bonds. In quartz these always occur at similar angles so that a crystal structure is created, whereas in vitreous silica these bonds vary within a range of angles to form an amorphous solid, as depicted in a two-dimensional representation of the silica network in Figure 2.2.

**Figure 2.2.** Planar projection of the images of the structure of quartz (a) and quartz glass (b) (from Partyka, Gajek, and Gasek, 2014).

**Figure 2.3.** A schematic representation (not to scale) of a tetrahedral silica unit (from Shamiryan et al., 2004).
In order to be able to make a quartz glass, crystalline silica needs to be heated above its melting temperature of 1710 °C. In order to be able to work with silica to create glasses, this temperature is much too high for regular kilns. Therefore other raw materials need to be added to the glass batch to lower the melting temperature, these materials are referred to as the network modifiers.

### 2.2.2 Network looseners and stabilisers, bridging and non-bridging oxygen

Components added change the properties of the glass batch and the resulting glass are referred to as network modifiers. There are two types of network modifiers: network looseners, mainly sodium and potassium, and network stabilisers, mainly calcium. Addition of these compounds causes a change of the amorphous silica network. The Si-O-Si bonds are partially broken which results in the formation of non-bridging oxygen (NBO): oxygen atoms which are connected to only one silicon atom and therefore carry a single negative charge. In order to balance the charge in the material, modifier ions can connect to these non-bridging oxygens through ionic bonds and fill the gaps in the glass network (Figure 2.4). Monovalent cations (Na⁺ and K⁺) connect to one NBO, while divalent cations (e.g. Ca²⁺) connect to two NBOs. Bridging oxygen (BO) are connected to two silicon atoms and cannot form an ionic bond with modifier ions.

![Figure 2.4](image_url). The glass network including network modifiers and non-bridging oxygen (from Partyka, Gajek, and Gasek, 2014). This is a schematic representation of the glass network in which only the covalent bonds have been drawn. The ionic bonds between the network modifiers and the NBO are not displayed.
The network looseners (sodium and potassium) are added to the glass batch to lower the melting temperature. These ions are introduced into the glass batch in the form of soda (sodium carbonate) or potash (potassium carbonate). After firing and melting the glass batch the carbonate is removed through calcination and the modifiers are introduced as monovalent alkali cations (Na\(^+\) and K\(^+\)), which form an ionic bond with a single non-bridging oxygen. This ionic bond is relatively weak and therefore these ions are quite mobile within the glass network. The mobility of these ions depends largely on the distribution of ions through the glass network. This distribution may not be completely random (as suggested by the ‘random network’ model (Zachariasen, 1932)) but could form high alkali ion concentration channels, as suggested by the ‘modified random network’ model (Greaves, 1985).

Another group of network modifiers is the divalent cations, which are also referred to as the network stabilisers (Davison, 2003; Kunicki-Goldfinger, 2008). Network stabilisers are alkaline earth ions and calcium is the most common network stabiliser, which is added to the glass batch as lime (Brill, 1975; Kunicki-Goldfinger, 2008). As these ions have a double positive charge, they connect to two NBOs and therefore are less mobile than the alkali ions which stabilises the glass network (Kunicki-Goldfinger, 2008).

As explained above, the composition of historic glass is generally described by the three main components: the network former (SiO\(_2\)), the total concentration of network looseners (R\(_2\)O) and the total concentration of network stabilisers (RO). Glasses containing Na\(_2\)O as the main network loosener and CaO as the main network stabiliser are most often denoted as ‘soda-lime-silica glass’, simply ‘soda-lime glass’ or ‘Na\(_2\)O – CaO – SiO\(_2\)’ glass. Of course many other types of glass exist, such as lead silicate glass (PbO – SiO\(_2\)), potash lime glass (K\(_2\)O – CaO – SiO\(_2\)) or potash lead silica glass (K\(_2\)O – PbO – SiO\(_2\)). Many other oxides are included (or arise as impurities) at low concentrations in the composition of historic glass. They generally act primarily as colorants, decolorants or opacifying agents but may have a minor contribution to the glass stability if present in greater than trace quantities. All these components influence the properties of glass and its resistance to deterioration, but the stability of glass is mainly investigated and described in terms of the main constituents of the glass (Brill, 1975). Davison (2003) provides a good overview of main components and additives in glass composition.
2.3 Deterioration mechanisms

Deterioration of the glass structure represents a fundamental change in the glass composition, in particular through the formation of an altered surface layer. Studies of the glass surface are of interest as the altered surface layer can influence the appearance of the glass, through the formation of cracks or a moist surface layer, and partially determines its fragility and long term reactivity. Furthermore, the glass surface is the substrate upon which more complex reactions can occur, such as the precipitation of secondary deterioration products (Pantano and Hamilton, 2000) such as salts (Robinet et al., 2004) or in the form of a corrosion crust (Roemich, 1999; Roemich et al., 2005). The degradation of glass is most often associated with the interaction of the glass with an attacking agent. This attacking agent can be atmospheric water, atmospheric pollution, or soil/liquid water when the glass has been buried in terrestrial, marine or lake environments.

The deterioration of glass has two consequences: the alteration of the chemical composition of the glass itself, but also the formation of new compounds on the surface of the glass (Morey, 1954). These phenomena are related and this section will describe the underlying mechanisms of deterioration of glass, with a focus on mechanisms of relevance for the deterioration of vessel glass in museum collections. The predominant theory used to describe the deterioration of museum vessel glass is the ion exchange model, which will be the first model described in this section. Recent theories originating in the field of radioactive waste storage will also be described, but in less detail. These are the chemical affinity model, the GRAAL (Glass Reactivity with Allowance for the Altered Layer) model and the glass dissolution-silica precipitation model (Geisler et al., 2015). The section will conclude with a description of the surface layer of the glass after it has been altered due to chemical deterioration.

2.3.1 Ion exchange model

One of the mechanisms generally accepted as a prime process in glass deterioration is the extraction of alkali ions from the top layer of the glass and their replacement by hydrogen ions or hydronium ions as a result of the interaction with water. The result of this interaction is the formation of a hydrated surface layer, in literature
referred to as the alkali-deficient, silica-rich, hydrogen glass (Newton and Davison, 1989), leached layer (Anaf, 2010; Kunicki-Goldfinger, 2008), gel layer (Brill, 1998), or hydrated glass (Brill, 1975). In this thesis the more generic term altered surface layer will be used, but a more specific term (i.e. alkali depleted layer) will be used when necessary. The formation of the altered layer may cause a decrease in stability and might subsequently be the impetus for further deterioration of the glass.

The exchange of modifier cations with protons or hydronium ions is generally referred to as leaching. This is the main process associated with glass corrosion, as it causes an alteration of the composition of the surface layer. Chabas (2006) distinguishes between glass corrosion (as being the rupture of the Si-O bonds in the glass network) and leaching (being the process of ion exchange between modifier cations and hydronium ions). As will become clear, however, these processes are strongly coupled, and will therefore both be covered with the term glass deterioration.

Charles (1958) described the interaction of alkali-rich glass with water as a two-step process: the nature of the ionic bond between a NBO and an alkali ion, in the presence of water, allows the diffusion of the alkali ion. The alkali ion can then be replaced by H\(^+\), which is available through dissociation of a water molecule. This is accompanied by the formation of OH\(^-\). In line with this, Ernsberger (1980) argued that it could not be a simple exchange of a modifier cation with a proton as “a bare proton cannot exist in a condensed phase” (Ernsberger, 1980, p. 146). Later, the theory on ion-exchange was refined and included the migration of molecular water into the glass surface and the hydrolysis of the Si-O-Si bonds to form hydroxyl ions. This allows for the transportation of alkali ions out of the glass surface, while electrical neutrality is maintained (Davison, 2003). Three types of interaction between water and glass can be distinguished (Bunker, 1994; Kunicki-Goldfinger, 2008; Kunicki-Goldfinger et al., 2009; Pantano and Hamilton, 2000):

1. Hydration: molecular water enters the glass surface.
2. Hydrolysis: water reacts with the metal-oxygen bonds in the glass to form hydroxyl groups.
3. Ion-exchange reactions: modifier cations are replaced by hydrogen ions. The rate in which these interactions occur strongly depends on the characteristics of the glass, the environmental conditions and the circumstances in which the glass has been stored, as will become clear in the following sections.

**Hydration and hydrolysis of the glass network**

Molecular water can penetrate the glass surface through void spaces between oxygen atoms in the glass structure, resulting in the presence of water molecules in the glass structure (*hydration*). It can also undergo *hydrolysis* and *condensation* reactions with the metal-oxygen (M-O) bonds through the following mechanism (Bunker, 1994):

\[
H_2O + M - O - M \rightleftharpoons M - OH + HO - M \quad \text{(Reaction 2.1)}
\]

The metal atom (M) is the network former of the glass, for historic glasses this is generally silicon (Si). The hydrolysis reaction is reversible and condensation can occur (Reaction 2.1) and an equilibrium is set up, resulting in the presence of both molecular water and hydroxyl groups present in the glass, as shown by nuclear magnetic resonance (NMR) techniques (Kohn, Dupree and Smith, 1989 in Bunker, 1994).

According to Bunker (1994) the rate in which hydration and hydrolysis occur depends on the type of glass. The rate of molecular diffusion is primarily controlled by the presence of voids in the glass network. If the voids are large enough, molecular water can penetrate the glass through these voids. The structure of the interconnected silicate tetrahedra (Figure 2.4) determines the void size. However, the modifier cations can partially block the voids in the silicate tetrahedra rings. If the voids are not large enough to admit molecular water, the dissolution behaviour of glass depends strongly on hydrolysis on the glass surface and condensation reactions within the glass network (Bunker, 1994), as is confirmed by Kohn (2000).

The hydrolysis of the glass network is dependent on two parameters. Firstly, the glass structure determines the rate of hydrolysis of the glass. The tetrahedral silicate, which is common for each type of glass, is susceptible to attack by
hydroxyl ions. This can result in the rupture of the Si-O-Si bonds (Badro et al., 1997; Bunker, 1994; Henderson, Calas and Stebbings, 2006). In pure silica the network rearrangement necessary for the rupture of the Si-O-Si bonds is difficult due to the high connectivity of the glass network. The presence of NBO allows for a more facile rearrangement of the atoms and an increased proportion of NBOs results in a more rapid hydrolysis of the glass network (Bunker, 1994). The second factor determining the rate of hydrolysis is the chemistry of the attacking solution. As the hydrolysis of the Si-O-Si bonds depends on the concentration of hydroxyl ions in the attacking solution, the pH of this solution is crucial. An increase in pH causes a more rapid breakdown of the glass network. For a pH > 10 dissolution of the glass network occurs, whereas the leaching reactions are dominant for a pH < 9 (Kunicki-Goldfinger, 2008).

**Ion exchange reactions**

The leaching of modifier cations from the glass surface is regarded as the most characteristic feature of glass (surface) alteration. It is generally attributed to ion exchange reactions (Bunker, 1994; Kunicki-Goldfinger, 2008):

\[
\text{Si} - \text{O} - \text{Na}^+ + H_2O \rightarrow \text{Si} - \text{OH} + \text{Na}^+ + \text{OH}^- \quad \text{(Reaction 2.2)}
\]

Reaction 2.2 describes a similar process in the presence of a water molecule that penetrated the glass surface during the hydration and hydrolysis mechanisms described above. Again, the rate and extent of ion exchange depend on the glass structure and the chemistry of the attacking solution.

Ion exchange in glass occurs when ion exchange sites are exposed to a high RH or an aqueous environment. The extent of ion exchange can be described by ion exchange equilibrium constants (Harland, 1994). The equilibrium constant is “a measure of how effectively protons compete with sodium ions [or another modifier cation] for occupancy of a given anionic site” (Bunker, 1994, p. 302). The equilibrium constant is the ratio between the concentration of ions in the attacking solution and the concentration of ions in the solid (i.e. the glass). If the concentration of the modifier cation in the attacking solution is high, this should inhibit the leaching of the modifier cation from the glass (Bunker, 1994). If the leaching of a modifier
cation from the glass surface continues, the concentration of this cation in the attacking solution increases, and the ion exchange rate decreases. As hydronium ions migrate from the attacking solution into the glass, the pH of the attacking solution increases, eventually causing the rupture of the Si-O-Si bonds.

The glass structure strongly influences the rate of ion exchange as it determines the distribution of ion exchange sites, which are located at the NBO. If the glass has a large proportion of non-bridging oxygen there are more ion exchange sites and the rate of leaching will be high. It was long thought that the rapidity of leaching was mainly dependent of the diffusion coefficient of cations through the glass (Doremus, 1975). More recently, however, it has been argued that the diffusion of water into the glass surface controls the rate of ion exchange (Bunker, 1994; Pantano and Hamilton, 2000), showing that hydration and hydrolysis of the glass network and ion exchange processes are related. Ion-exchange processes create voids by the leaching of modifier cations and the replacement by smaller hydrogen ions (protons). Hydrolysis opens up the silica structure and makes it possible for molecular water and hydronium ions to enter the glass network. Hydration increases the concentration of molecular water and hydronium ions in the glass, thus increasing the rate of ion-exchange.

2.3.2 Advanced glass deterioration models

Prediction of the stability of glass is not only important in the study of museum objects, but also in the study of the suitability of glass for storage of nuclear waste. Many studies have been devoted into modelling the long-term behaviour of borosilicate glasses in aqueous solutions. As the glasses used for this purpose often are of standardized composition this behaviour can be described using mathematical equations. This model describes the dissolution of glass, which depends on the glass and solution composition, pH, the ratio of sample surface over solution volume, temperature and time in what is called the general dissolution rate equation (Aagaard and Helgeson, 1982; Grambow, 1984). The influence of pH on deterioration is similar to that described above: at neutral and acidic pH the ion exchange processes are dominant, whereas at high pH hydrolysis of the siloxane (Si-O-Si) bonds takes place. Ultimately hydrolysis can lead to the detachment of
silicon atoms in the form of silicic acid (Abraitis, 2000). The rate of deterioration is then determined by the degree of silica saturation in solution, but disregards the role the leached layer has on the kinetic effects of glass dissolution (Geisler et al., 2015). This issue was resolved in the GRAAL model (Frugier et al., 2008). In this model the protective nature of the leached layer is described. It is suggested that this layer develops a dense structure which becomes impenetrable for water and that further alteration of the glass is inhibited (Geisler, 2015). The model was extended and renewed by Geisler et al. (2015), who proposed that the congruent dissolution of silicate glasses is coupled to the precipitation of amorphous silica at the interface between the bulk glass and the altered layer.

2.3.3 The altered surface layer

The initial result of the interaction between glass and water is the formation of an altered surface layer on top of the bulk glass. One of the first to systematically characterize the different types of glass surfaces was L.L. Hench. Using surface analysis tools (see Hench, 1975) he distinguished six different glass surface types (Table 2.1).

Table 2.1: the six types of glass surfaces as described by Hench and Clark (1978) and Hench (1982), see also Davison (2003).

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>A thin (&lt; 5nm) hydrated surface layer. No significant difference between the hydrated layer and the bulk glass.</td>
</tr>
<tr>
<td>Type II</td>
<td>A silica rich protective film due to selective alkali ion removal. No further damage to the silica network occurs.</td>
</tr>
<tr>
<td>Type III a</td>
<td>Two layers of protective surface film of aluminium silica or calcium phosphate on top of a silica rich layer. Addition of Al₂O₃ or P₂O₅ can result in dual surface layers.</td>
</tr>
<tr>
<td>Type III b</td>
<td>Multiple layers of hydroxides or oxides are formed on the surface of the glass when exposed to water. Especially occurs on alkali borosilicate glasses.</td>
</tr>
<tr>
<td>Type IV</td>
<td>Silica rich non-protective film. The silica concentration is not high enough to prevent loss of alkali or destruction of the silica network.</td>
</tr>
<tr>
<td>Type V</td>
<td>The glass is soluble: congruent dissolution with nearly equal loss of alkali and silicate.</td>
</tr>
</tbody>
</table>

Of these six types only type I can be regarded as a stable glass, not likely to deteriorate. In surface types II-V a significant alteration of the glass composition has taken place at the surface. When the environment leads to ongoing alteration of the glass, it can be regarded as unstable.

For historic glass Hench’s type II and type IV are of interest. A type II silica rich
surface layer is formed when a sufficient concentration of network formers is present. A protective surface layer is formed which reduces the glass from further leaching or dissolution and is durable for a pH < 9 (Hench and Clark, 1978). A type IV surface layer is characteristic for glasses with a high soda to silica ratio. A non-protective surface layer is formed and further leaching is not prohibited (Kunicki-Goldfinger et al., 2009). The difference in the surface layers leads to a distinction between stable (Hench’s type II), in which alkali leaching is limited to the formation of a stable surface layer, and unstable glass (Hench’s type IV and V), in which the depletion of alkali progresses also after the formation of an initial surface layer.

Due to ion exchange mechanisms described above, the altered surface layer is often low in alkali and rich in molecular water. Due to the depletion of alkali, the silica content is relatively high compared to the unaltered bulk glass. Therefore the top layer is often referred to as the silica gel layer or gel layer, but the term ‘altered layer’ is used throughout this dissertation. For durable glass the thickness of the altered layer is generally below 10 µm (Hench and Clark, 1978), whereas the altered layer of a less durable glass can become several hundreds of µm’s thick (Brill, 1975). The silica gel layer is thought to consist of two sublayers; a hydrogen glass with a constant thickness and an outer silica gel layer both with a variable thickness depending on the glass composition and the environment in which the glass was stored (Pantano and Hamilton, 2000; Kunicki-Goldfinger et al., 2009).

The hydrogen glass is a layer within the original glass surface that is depleted of alkali and alkaline earth ions. It is named a hydrogen glass as these depleted ions have been replaced by hydrogen ions and molecular water has penetrated the glass structure. The number of water molecules that can be incorporated in the hydrogen glass depends strongly on the size of the leached ion. Different ions leave different spaces, thus determining the rate of diffusion of water molecules (Pantano and Hamilton, 2000). The nature of this barrier between the bulk glass and the altered surface layer determines the deterioration rate (Geisler et al. 2015), but it is hard to predict the behaviour of historic glass of complex composition.

The transformation of the hydrogen glass into the silica gel layer occurs as the silica network is ruptured by hydrolysis of the Si-O-Si bonds (Reaction 2.1).
Condensation reactions within the glass network (Reaction 2.1) lead to a more porous layer than the leached layer which does not limit further leaching of the glass (Pantano and Hamilton, 2000).

The formation of an altered surface layer is typical of Hench’s type IV glass surface and deterioration phenomena observed on unstable historic glass are related to the formation of this layer. These phenomena cannot be observed on glasses with surface type V as, for these glasses, the leaching of alkali is accompanied by the dissolution of the silica network without the formation of an altered surface layer (Kunicki-Goldfinger, 2008).

2.4 Factors influencing glass deterioration

Two main factors affect the deterioration of glass: the glass composition and the environment in which the glass is kept (Newton & Davison, 1989; Koob, 2006). The intrinsic stability of a glass is determined by its composition, but deterioration only occurs when the glass is kept in an unfavourable environment. Environments in which glasses deteriorate often include high relative humidity and acid or alkaline conditions (Schalm and Anaf, 2016). Three general situations in which glasses deteriorate can be distinguished. Firstly, archaeological glass which is buried in the ground or underwater can deteriorate due to interaction with the soil and/or water. Characteristic deterioration patterns of these types of glasses are the development of an iridescent appearance due to the formation of laminated layers (Schalm and Anaf, 2016) and the formation of corrosion crusts (McLoughlin et al., 2005). Secondly, stained window glasses in churches are often exposed to extreme circumstances due to the weather and associated outside and inside changes in climate. Typical deterioration patterns for these types of glass are the formation of corrosion crusts (Perez y Jorba et al., 1980; Schreiner et al., 1999) and the development of cracks through the glass (Roemich et al., 2008). Finally, historic glass stored inside (e.g. in museums) can undergo chemical deterioration in which typical deterioration patterns are the development of a moist surface layer – weeping – and the formation of a network of hairline cracks – crizzling (Kunicki-Goldfinger, 2008). It is the third category that this section will focus on as it is the emphasis of this dissertation.
2.4.1 Glass composition

The composition of the glass determines its chemical structure and its reactivity with the environment. Therefore, it is the most important factor regarding the stability of the glass. Historic glassmakers knew that the composition of their glass batch (and the resulting composition of the solid glass) determined the chemical stability of the glass. An important example of this are the glasses produced by George Ravenscroft.

The movement of modifier ions through the glass structure and their removal from the surface layer of the glass – leaching – is the main process associated with glass deterioration. Glasses of unstable composition have an unsuitable combination of network formers, network looseners, network stabilizers and other oxides. George Ravenscroft recognized the importance of the glass composition for its stability and a change in the glassmaking recipe, by in the raw glass batch replacing part of the alkali salts by lead oxide, resulted in a different composition of the glass, less prone to chemical deterioration (MacLeod, 1987).

Some general remarks on the difference between stable and unstable vessel glass in museums have been made in the past. Brill (1975) observed that historic glasses of the soda-lime type showing extensive crizzling contained a CaO concentration of less than 4 wt. % and a combined alkali concentration of over 20 wt. % and experiments using replica glasses confirmed this hypothesis. El-Shamy et al. (1975) observed similar behaviour in their studies into the extraction of sodium and calcium from Na₂O – CaO – SiO₂ glasses in acid solutions. Their results show that an increase of the CaO to SiO₂ ratio increases glass stability, but when the concentration of CaO exceeds 15 mole % the chemical stability of the glass decreases rapidly, which is in line with the findings by Brill (1975). Other interesting observations are that both calcium and sodium were extracted from the glass, that the ratio of leached sodium and calcium is similar to the ratio of sodium and calcium in the glass and that the absolute amount of sodium leached from the glass depends on the calcium concentration and not as much on the sodium concentration in the glass.

Glasses with a silica concentration of higher than 66.7 mole % and sufficient
network stabilisers are also regarded as stable as the movement of modifier ions in these glasses are restricted (El-Shamy et al. 1975). This is due to the fact that at that critical concentration each silicon atom is associated with a sodium or calcium atom as their second neighbour. In glasses with a silica concentration lower than 66.7 mole % there is always an interconnected path between NBOs, providing the opportunity for movement and exchange of ions. In glasses with a silica concentration higher than 66.7% the NBOs are always isolated by BOs, which inhibits the movement of ions through the glass network.

An important effect of the addition of components to the glass batch is the mixed alkali effect, which is of great influence on the chemical durability of glass. As described above, the prevalent mechanism in the deterioration of glass is ion exchange, preceded by hydration of the glass surface layer. The rate of ion exchange is controlled by the rate of ionic migration. Glasses with a total alkali oxide concentration of over 20% are generally regarded as unstable (Brill, 1975), because the monovalent cations can migrate easily through the glass structure. However, when this oxide is gradually replaced by the other while maintaining the same total molar concentration of the two alkalis, the chemical and physical properties of that glass change. This phenomenon is called the mixed alkali effect (Isard, 1969; Day, 1976; Maass, 1999) and glasses containing both Na₂O and K₂O are generally more chemically stable than glasses containing one of the two (Day, 1976). Of course the chemical stability of the glass depends not only on the proportion of the alkali species in the glass, but rather on the overall composition (Kunicki-Goldfinger et al., 2002).

The visualization of the composition of a glass in a ternary diagram can be a helpful tool to reflect on its stability. Unstable glasses form a cluster in the diagram (Davison, 2003; Fearn, 2004, Figure 2.5), but of course this representation of the glass composition can only be made when it is known. Again, these observations are a generalization and the observations described in this section should be regarded with care. A complication is that experiments which are carried out to study unstable glass often use binary and ternary glasses, whereas historic glass has a more complex composition and other parameters, such as the storage history, are often unknown (Kunicki-Goldfiner et al., 2009).
2.4.2 Environmental factors

The environment in which glass can deteriorate has been studied by many scholars. In particular the effect of atmospheric water and hence the relative humidity has been acknowledged by many (see e.g. Ernsberger, 1980; Ryan et al., 1993; Bunker, 1994; Erhardt and Mecklenburg, 1994; Davison, 2003; Fearn, McPhail, Oakley, 2005; Koob, 2006; Sterpenich and Libourel, 2006). Davison (2003) identifies associated factors that affect the decomposition of glass: temperature, time, pH of the attacking liquid, the ratio of the surface area of the glass that is being attacked to the volume of the attacking liquid, micro-organisms, vibrations and previous conservation methods. The most important factors – relative humidity, pH and the presence of pollutants – will be discussed below.

Brill (1972, 1975) was one of the first to study experimentally the effect of the museum and storage environment, in particular the role of atmospheric water, on the rate of deterioration. Koob (2006) stresses the role of atmospheric water as a

![Figure 2.5. A triangular representation of the composition (mol. %) of crizzled glasses (from Fearn, 2004). RO represents the network stabiliser content, R2O the network modifier content and SiO2 the silica content. The region of instability lies to the left of the dashed line.](image)
catalyser of glass deterioration and the effect of exposure to high relative humidity on the condition of the glass. Analytical studies using artificially aged mock-up samples indeed indicate that a prolonged exposure to humidity increases the depletion depth of sodium as quantified by SIMS (Fearn, McPhail and Oakley, 2004, 2005). The interactions between glass and water are described above in section 2.3.

A crucial factor in the deterioration of glass is the pH of the attacking solution. In acidic solutions the predominant mechanisms of alteration of the glass structure is thought to be ion exchange due to the abundant presence of hydronium ions in the acidic solution. For alkaline solutions, the leading deterioration mechanism will be the dissolution of the silica network due to rupture of the Si-O-Si bonds (Bunker, 1994). The prolonged presence of a layer of moisture on the surface of the glass causes the pH of the attacking solution to increase (Reactions 2.2 and 2.3). Ultimately, continuing deterioration can cause the rupture of the silica network (Reaction 2.1) and the formation of pits in the glass.

The presence of pollutants in the atmosphere may cause the formation of specific salts on the glass surface and affect the rate of deterioration of the glass. Formaldehyde can for example be the cause of a white efflorescence of glass, which has been identified as sodium formate on multiple occasions (Schmidt, 1992; Robinet et al., 2004; Eremin et al., 2005). Generally, in the museum context, carbonyl pollutants can be a main cause of corrosion and the formation of deterioration products (Gibson et al., 1997; Bradley & Thickett, 1999), but other compounds such as carbonates, sulfates and chlorides have also been identified (Tichane, 1966; Roemich, 1999; Eremin et al., 2005). That is why it is difficult to attribute glass deterioration to one specific cause, as often it is likely that it is a combination of factors. The Fraunhofer Institut für Silicatforschung (Institute for Silicate Research) has developed glass sensors, originally designed for assessing stained glass durability *in-situ*, but often used to evaluate the suitability of museum storage environments (Fuchs, Roemich, Schmidt, 1991). The sensors consist of a wafer of potash-lime glass, which is exposed to the storage or display environment; due to the unstable nature of the glass the sensor will react with the environment. Standardized analyses of the glass after a period of exposure then is a measure of the suitability for storage of other glass objects.
2.5  Vessel glass deterioration: changes in appearance

Generally two types of changes in the appearance of historic glass in museum collections can be distinguished: crizzling and weeping. Both can have very dramatic effects for the aesthetic nature of the glass and understanding the causes of these changes is therefore of great relevance to conservators.

2.5.1  Weeping

Weeping is generally associated with the formation of hygroscopic salts on the surface of unstable glasses. Cationic species leached from the glass react with the atmospheric anionic compounds to form these salts. Organ (1956) was the first to describe the formation of salts and in his paper he described that glasses remained dry to the touch at a RH below 42%. This led him to postulate potassium carbonate as the main salt forming on unstable glass surfaces, as it deliquesces at that RH. However, mainly sodium formate has been identified as the predominant salt present on glass surfaces though only as a result of very few (5) analytical studies (Schmidt, 1992; Robinet et al., 2004; Eremin et al., 2005; Fearn et al., 2006; Thickett and Pretzel, 2010). Depending on the deliquescence relative humidity (DRH, the RH at which a crystal will attract water from the atmosphere and form a solution) of these salts they will be present in crystalline form or in solution on the surface. When unstable glasses are stored in a RH above the DRH of the salts present on the surface a moist layer will form.

2.5.2  Crizzling

The visual changes occurring as result of crizzling can be very dramatic. In the most extreme cases the development of full-blown crizzling can lead to the complete disintegration of an object of art (Koob, 2006). The first to study the phenomenon of crizzling comprehensively was Robert H. Brill, research scientist at the Corning Museum of Glass, who used the word “crizzled” to describe “the appearance of certain glasses which have a diminished transparency owing to very fine surface crazing” (Brill 1975, p. 121). In his description of crizzling he identifies the surface crazing (“incipient crizzling”) as the cause, with the effect of a diminished transparency (Brill, 1972). These two factors are most important in
the description of crizzling in conservation publications. In an article about the invention of lead glass by George Ravenscroft, glasses that suffer from crizzling are said to “become opaque and grey through countless hairline cracks” (MacLeod, 1987, p. 777). One to turn cause and effect around is Kunicki-Goldfinger (2008) who described crizzling as a “fine surface cracking which can have a dramatic effect on the appearance of the glass” (p. 47), thus emphasizing that the problem is actually the cracking of the surface, rather than the change of the appearance of the glass.

A more elaborate description of crizzling is provided by Koob (2006), who describes five consecutive stages of crizzling. The initial stage (1) is when a hydrated layer is formed on the glass surface and alkali ions are leached from the surface, resulting in the formation of either a moist layer or crystals on the glass surface, resulting in a hazy appearance. Incipient crizzling is the next stage (2), in this case the glass has undergone a minor irreversible alteration. Cleaning the object will improve its appearance, but incipient crizzling will be visible in certain lighting conditions as tiny silvery lines. The development of clearly visible cracks is the next step (3). Koob (2006) describes this stage as full-blown crizzling. The following stage is when material starts to flake of the surface (4), this can eventually lead to the final stage where the object is fragmented (5), either by impact from the outside or by no interaction with the outside at all. It is clear that in conservation literature the appearance of the glass is discussed more than the chemical and physical principles that underlie the change in the appearance of the glass.

Crizlling is mostly associated with objects with low CaO contents (Brill, 1975; Kunicki-Goldfinger, 2008). There are cases however where it is not only the CaO concentration of the glass, but rather the complete batch formulation that causes glasses to crizzle. It was shown that glasses with a high K/Ca ratio displayed crizzling as well, irrespective of the concentration of CaO (Kunicki-Goldfinger et al., 2002). Only if the surface layer is an unstable hydrated layer (Hench’s Type IV surface) crizzling can develop. The cracking of the gel layer can be attributed to several mechanisms (Kunicki-Goldfinger, 2008): dehydration of the gel layer, network contraction due to the replacement of larger alkali ions by hydrogen ions or the difference between the coefficients of expansion of the bulk glass and
the gel layer. The leading mechanism is in fact thought to be dehydration of the altered surface layer. Before the onset of crizzling, the gel layer of an unstable glass can contain up to twenty per cent by weight in water (Ernsberger, 1972). The loss of water from the gel layer (for example due to a decrease in relative humidity) can cause a major loss of volume in the gel layer causing stress within the layer, ultimately resulting in the cracking of the surface layer.

2.6 Measuring glass deterioration

Scientific analysis of historic glass has played an important role in cultural heritage research, as well as in industry. Handbooks on the properties of glass (e.g. Morey, 1954; Volf, 1984; Bansal and Doremus, 1986) have been published since the first description of the structure of the amorphous glass network (Zachariasen, 1932). These handbooks always contain a section on glass stability and reactivity to its environment. Therefore, chemical alteration of glass is a well-studied topic, but questions relating to its long term stability and dissolution mechanisms still remain and are also under investigation in other fields such as nuclear waste management and clinical studies (e.g. Bunker, Arnold and Wilder, 1984; Geisler et al., 2015; Jones, 2015; Sharmin and Rudd., 2017).

Research into glass deterioration is mainly focused on the long-term behaviour of historic glass objects and depends on many factors such as its often complex composition, manufacturing conditions and techniques and environmental history (Kunicki-Goldfinger et al., 2009). Therefore, the long-term behaviour is much more difficult to predict than that of glass used in industrial applications. However, understanding the long-term behaviour of materials is part of the conservation of cultural heritage and therefore many studies have focused on the identification and understanding of chemical changes and deterioration processes of historic glass. Recently, a comprehensive overview of analytical techniques used in the study of historic glass was published by Janssens (2013). This section provides an overview of those studies concerning the deterioration of historic glass. It focuses on two different ways of looking at glass deterioration: analysis of the changes in glass composition and analyses of compounds which have formed on the surface of the glass. This section concludes with a discussion of previous
work carried out in order to discriminate between stable and unstable glass, a section of particular relevance for this dissertation.

### 2.6.1 Measuring the composition of unstable glass

Compositional techniques provide information on provenance and technological information (Wagner et al., 2008), but also provide information on glass stability. A difference can be made between investigations of quantitative elemental composition and those concerned with molecular bonding and the configuration of atoms within the glass network. Both approaches provide relevant information and the different techniques are often combined.

A much used technique in cultural heritage research is x-ray fluorescence (XRF), as it provides quick and non-invasive analyses of the elemental composition of the studied material (Shugar and Mass, 2013). Without proper calibration of the equipment and laborious sample preparation this technique provides qualitative results of the glass composition. This is often sufficient for the study of glass objects and due to its ease of use, portability and straightforward interpretation XRF has been used in many studies about historic glass and vitreous materials, such as enamels and glazes, for example for the identification of colorants and additives (e.g. Kunicki-Goldfinger et al., 2000; Eremin et al., 2005; Huisman et al., 2008, Girbal and Dungworth, 2011; Casadio et al., 2012; Hložek, et al., 2017). The main disadvantage of XRF however is that it cannot detect elements lighter than potassium due to the absorption of photons by the air between the sample surface and the detector. This can be overcome by flushing this space with helium, but that requires a laboratory setup which defeats the purpose of doing glass analyses in-situ. The use of XRF for quantitative analysis of major and minor elements in glass is possible and would be very useful for the identification of unstable glass in museum collections. However, this is a very difficult procedure, in particular because glass contains so many light elements, and requires extensive calibration and sample characterization (Kaiser and Shugar, 2013).

Other, more accurate techniques to determine the composition of glass include scanning electron microscopy (SEM) coupled with an elemental analysis technique such as energy dispersive x-ray fluorescence (EDX, e.g. Schreiner et al., 1999);
ion beam analysis techniques (e.g. PIXE and PIGE); laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS, see e.g. Van Elteren, Tennet and Šelih, 2009; Panighello et al., 2016); atomic absorption spectrometry (AAS, see e.g. Tennet et al., 1984); and a range of synchrotron radiation (SR) techniques (see Janssens, 2013 for detailed information on the use of these techniques). Though these techniques often provide very accurate compositional information they all require destructive sampling, transportation of the object to the analytical facility or are (micro)destructive in nature.

Extremely valuable work on understanding glass deterioration was carried out using secondary ion mass spectrometry (SIMS) in London at Imperial College and the Victoria and Albert Museum, resulting in several publications on the changes in glass structure due to chemical deterioration in the museum environment (Ryan et al., 1993; Ryan et al., 1996; Fearn, 2004; Fearn, McPhail and Oakley, 2004; Fearn, McPhail and Oakley, 2005; Robinet, Fearn and Eremin, 2005; Fearn et al., 2006a, Fearn et al., 2006b). In these studies, SIMS was used to study the effect of moisture on the chemical structure of glass. The technique is sensitive for all elements and their isotopes in the periodic system (McPhail, 2006) and can detect both organic and inorganic species (Adriaens and Dowsett, 2006), which makes it particularly suitable for the study of glass deterioration. SIMS was mainly used to measure the depletion depth of sodium from replica unstable glass samples, and it was demonstrated that sodium depletion increases with the RH and exposure time. The effects of cleaning techniques and materials were studied as and no interactions between the cleaning agent and glass were observed (Fearn et al., 2006a). These studies indicate that SIMS could be a very good application to study the deterioration of glass. At the moment, however, this is mainly feasible for laboratory experiments as, despite the production of the important results, the disadvantages of SIMS are that it is very hard to do measurements or take samples in-situ due to the restrictions of the analytical equipment (limited sample size due to restrictions of sample chamber) and the damaging effect it has on the studied material (SIMS creates a crater at the location where the ion beam hits the sample).

Besides measuring changes in elemental composition, some studies have focused on the differences in the structure of glass. Raman spectroscopy has been used
to discriminate stable from unstable glass (Robinet et al., 2006) and although it proved to be successful in straightforwardly separating stable calcium silicate and lead silicate glasses from potentially unstable alkali silicate glasses, the further identification of unstable alkali silicate glasses required rigorous spectral peak deconvolution. Confocal Raman spectroscopy has also been used to measure the thickness of the altered surface layer on artificially aged replica glasses (Robinet, Fearn and Eremin, 2005).

### 2.6.2 Measuring deterioration products on the surface of unstable glass

The formation of deterioration products on the surface of unstable glass is a topic which is of great relevance for this dissertation. The identification of the chemical nature of these compounds (often salts) is not only important for the understanding of deterioration mechanisms, it is also essential for the conservation of glass objects. The hygroscopicity of these salts may determine the further interaction with water and are thus of great influence in potential further deterioration.

Heterogeneous distribution of a variety of salts on the surface has identified by ion chromatography (IC), SIMS and Raman. Among the detected compounds are sodium formate (Robinet et al., 2004; Eremin et al., 2005; Fearn et al., 2006), but also sodium carbonate, and sodium hydroxide (Fearn et al., 2006a). In particular, the formation of formate salts is worrying as these salts deliquesce at typical museum RH (ca. 50%). Upon deliquescence these salts will form formic acid which is known to accelerate the leaching of sodium from the glass (Robinet, 2006). The formation of formate salts is generally associated with the off-gassing of formic acid and formaldehyde from wooden storage or display materials (Thickett and Pretzel, 2010). However, in some instances formate salts have also been identified without elevated concentrations of these pollutants (Robinet et al., 2004; Fearn et al., 2006). A possible explanation for this observation is that formic acid may form due to photochemical reduction of carbon dioxide on the glass surface in the presence of water (Fearn et al., 2006a), which was observed on silicate rocks in nature (Ohta, Ogawa and Mizuno, 2000). Other salts detected, albeit rarely, include sodium sulfate (Eremin et al., 2005; Thickett and Pretzel, 2010) and magnesium formate dihydrate (Robinet et al., 2004a). It is peculiar that
there is little mention of potassium salts in the literature. It has been mentioned by Thickett and Pretzel (2010) that potassium salts have formed on the glass, but could not be distinguished by eye, even under magnification.

### 2.6.3 Identification of unstable glass in museum collections

The fact that salts can be present in amounts indistinguishable to the naked eye emphasizes the importance of being able to identify unstable glass before changes in appearance occur. It is therefore surprising that the identification of unstable glass objects in museum collections has received little attention. Ulitzka and Touchard (1991) proposed to use XRF as an analytical tool to distinguish stable glasses from unstable glasses, but no follow-up results of this proposed research have been published. Kunicki-Goldfinger et al., (2002) investigated the use of XRF for the identification of glasses susceptible to crizzling by looking at the ratio of specific element concentrations, but they were not able to identify a specific compositional feature of unstable glasses. With relation to historic vessel glass, there are only three other instances of analytical studies aimed at early identification of unstable glass. First, Neelmeijer and Mäder (2005) used ion beam analysis (IBA) to determine the difference in silicon concentration between the altered top layer using PIXE, and the bulk glass underneath using PIGE. Though successful in examination of replica glasses, the used IBA techniques required analysis of fragments of historic glass, which complicates the analyses *in-situ*, of large amounts of potentially unstable glasses. A second study aimed at identification of unstable glass using Raman spectroscopy (Robinet et al., 2006). As described above the identification of unstable alkali silicate glasses required extensive data processing, which limits the practicality of the technique for the straightforward identification of unstable glass. Thirdly, optical coherence tomography (OCT) has been used as a non-invasive tool for imaging the deteriorated top layer of unstable glass (Sylwestrzak et al., 2009). The ability of the technique to visualize the depth of the crizzled layer was demonstrated. A specific study aimed at using OCT for the identification of unstable glass in museum collection was carried out by Kunicki-Goldfinger et al. (2009). They relied on the ability of OCT to measure the thickness of the altered surface layer based on the difference in refractive index with the bulk glass. The major disadvantage of the technique is the limited axial resolution for portable
application, which yet prevents using OCT for the identification of unstable glass in an early stage.

### 2.7 Preventive conservation strategies

The prevention of advanced deterioration of great importance for those responsible for the conservation of historic glass. Current preventive conservation strategies are mainly based on RH control to prevent the interaction between water and the glass. One of the first to recommend a specific RH for the safe storage of unstable glass was Robert Organ (1957). He suggested to store glasses at a RH below 42% as this is the point at which potassium carbonate remains a crystalline solid. The implications of these recommendations were later further refined by Brill (1975) when he identified the danger of the dehydration of a glass – leading to crizzling – when an object is stored in low RH. His recommendation was to store glasses between 40% and 60% to prevent crizzling from occurring, but keep monitoring the potential development of a moist surface film, in which case it would be recommended to slightly lower the storage RH. Since then, recommendations for the storage of vessel glasses have not changed, although two leading handbooks on glass deterioration quote different preferential RHs: Davison mentions 35-40%, with 42% being the upper limit to prevent leaching of alkali (Davison, 2003), while Koob (2006) about 40-45% to stop weeping/crizzling with a lower limit of 30% to prevent cracking. In both cases, recommendations are aimed at preventing the progression of deterioration, but one focuses on the prevention of moisture coming in contact with glass (Davison, 2003), while the other stresses the importance of preventing the formation of cracks (Koob, 2006).

Another conservation strategy, which has received less attention is the notion of storing glass objects in cases with airflow, as this prevents the establishment of an unfavourable microclimate (Koob, 2006). The use of flowing nitrogen in storage conditions of unstable glass has been investigated and results indicate that this inhibits the formation of salts on the surface of unstable glass, but at the moment there is no corroboratory evidence of these findings (Fearn, 2004; Fearn et al., 2006a).
At the moment it is very difficult to predict the long term behaviour of historic glass in different conditions. Avoiding dehydration and hydration effects simultaneously is a complicated assignment, but generally, it can be concluded that it is important to prevent the contact of the glass with atmospheric water, by reducing the storage RH. Often glass is stored in facilities where many types of objects are stored. In that case, it is most important that the glass is stored in stable conditions, with little RH fluctuations to prevent crystallization and deliquescence cycles of salts, which may cause extra stress and to prevent the development of irreversible cracking (Koob, 2006).

### 2.8 Conclusions

This chapter investigated the nature of glass, the chemical processes underlying glass deterioration and the factors influencing glass deterioration. It also discussed the changes in appearance of historic glass objects as a result of these chemical deterioration mechanisms and finally focused on how glass deterioration has been measured in the past. This provides essential background information for the research presented in the following experimental chapters. Of particular relevance are the principles of glass deterioration and the way in which unstable glass in museum collections has been investigated.

It can be concluded that the deterioration of glass depends on two factors: the composition of the glass itself and the environment in which a glass is kept. Research on the prevention of historic glass deterioration has therefore focused on analysis of the glass composition and on the ideal storage conditions for unstable glass.

Several methods exist for the determination of the glass composition, but many require destructive sampling for a full quantitative analysis of the composition, and for non-destructive methods quantification is often a very laborious task or not even possible. Assessment of glass stability based on the composition is therefore problematic. This is complicated by the very nature of the glass itself: historic glass consists of main components, minor components and trace components, which all affect glass stability. Moreover, glass stability is not dependent on the
presence or concentration of one or two components, but it is rather the overall composition of the glass which determines glass stability. Even if the elemental composition of a glass is fully known, it will only be a clear-cut indication of those glasses with such poor compositions that they will be very unstable anyway, which will be obvious without the analytical information. As the research into nuclear waste glass has demonstrated, all glasses are unstable to a certain extent which further complicates the problem.

Ultimately, it is the combination of the storage environment and the composition of the glass itself which determines the deterioration rate of an unstable glass objects. Therefore, researchers have focused on the changes in the chemical structure of glass as a result of the environmental conditions using various analytical techniques. None were successful, however, in developing a straightforward method for the identification of unstable glass showing unclear or no signs of deterioration.

Associated with the deterioration of glass are conservation strategies of glass applied in museums around the world to prevent deterioration of glass through climate control, as the composition of the glass cannot be changed but the storage conditions can. However, recommendations on storage conditions are mainly made based on observations, rather than on scientific evidence. As it is difficult, maybe even impossible, to establish conditions in which both crizzling and weeping are prevented it is however crucial to better understand deterioration processes and identify unstable glass objects at an early stage.

As ion exchange, and the subsequent leaching of cations, was identified as the main process involved in the deterioration of historic glass, the research in this dissertation is focused on the quantitative identification of leached ions which deposit on the surface of the glass. Few studies have focused on the deposition of compounds on the surface of unstable glass, while it may provide important information on both glass stability and storage conditions.
2.9 References


Brill, R.H., B. Hanson, and P.M. Fenn. ‘Some Miscallaneous Thoughts on Crizzling’. In *Proceedings*. Westerville: The American Chemical Society, 1998.


Fearn, S., D.S. McPhail, B. Hagenhoff, and E. Tallarek. 'TOF-SIMS Analysis of Corroding Museum


