Glass sickness: Detection and prevention

Investigating unstable glass in museum collections

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INVESTIGATING THE DEPOSITION OF IONS ON THE SURFACE OF ARTIFICIALLY AGED UNSTABLE GLASS
5.1 Introduction

The presence of ions on the surface of unstable glass is a result of its chemical deterioration and a wide variety of ions can be found on the surface of unstable glass. The combination of certain ions on the surface can result in the formation of hygroscopic salts. The attraction of water to the glass surface by these salts can ultimately result in the formation of a moist layer on the surface of the glass – *weeping* – which not only disturbs the appearance of the glass, but also promotes deterioration processes (Chapter 2).

The chemical breakdown of glass of unstable composition may lead to the subsequent deliquescence of salts on the surface, and the presence of the ionic species of which these salts are comprised can be used as an indication of glass instability (Chapter 3). In order to be able to distinguish between stable and unstable glass objects it is of great importance to understand which ions can be attributed to the deterioration of glass and which ions may have a different origin, as discussed in Chapter 3. However, all these ions play a role in the attraction of water to the glass surface through the formation of salts on the surface. Since glass objects in museum collections have a long and often undocumented history of use, storage, display and conservation it is difficult to trace back the source of the ions and the ions may be deposited on the surface of a glass through a process not necessarily related to glass deterioration. Therefore it is of importance to be able to identify those ions indubitably related to glass deterioration. This will be useful for the identification of the sources of the ions, which is not only of relevance to the identification of potentially unstable glass objects, but also plays a vital role in the development of environmental guidelines for storage of these objects.

As a result of ion exchange it is to be expected that cationic species from within the glass will accumulate on the glass surface (Chapter 2). Sodium, potassium, magnesium, calcium ions are the predominant species anticipated, but prior to the research of this dissertation only three analytical studies have been undertaken on historical objects (Robinet et al., 2004; Eremin et al., 2005; Thicket and Pretzel, 2010). The surface deposition of cationic species originates from the glass when it is unstable. SIMS studies have confirmed the depletion of sodium, potassium and calcium from the layer directly below the glass surface (Fearn, McPhail, and
Oakley, 2005), but the relationship between the composition of the leached glass layer and the fate of the cations which migrated from it to the surface has never been investigated. These cationic species can form salts, whose deliquescence relative humidity depends on the anionic counter ions derived from the surrounding atmosphere. Of particular interest is the origin of the anionic species as their source cannot be attributed to the glass, but they find their origin from the surrounding environment.

There are many sources for anionic species which are found on glass surfaces. Acetate and formate can originate from acetic acid, formic acid or formaldehyde emitted by wooden storage cabinets (FitzHugh and Gettens, 1971). Sulfate, if present, would generally be assumed to have derived from sulfur dioxide indoor pollution (Tétreault, 2003; Grzywacz, 2006), if carbonate were to be found on the surface of the glass the proposed origin is from a reaction involving carbon dioxide (Wan Isahak et al., 2015). Chloride may be associated with the deposition of sodium chloride due to handling or its presence in the atmosphere (Nazaroff, 1992).

The use of the ion chromatography (IC) protocol described in Chapter 4 allows for quantitative detection of ions related to glass deterioration. However, the protocol has not been evaluated for samples taken from historical glass surfaces, but only on mock-ups using Melinex as a substrate for ionic solutions (Chapter 4). Before applying the protocol in the study of museum objects, it is relevant to evaluate the suitability of the sampling protocol on glasses aged in controlled environments. This chapter therefore focuses on the identification of ionic species present on the surface of unstable glasses which have been artificially aged in order to study the deterioration of glass with a controlled RH and T. This provides insight into the formation of deterioration products on the surface of unstable glass and the relationship between the ions found on the surface with the deterioration process of the glass under controlled conditions with no atmospheric pollutants present. This is a necessary precursor to the application of the IC protocol to unstable glass surfaces.

Artificial ageing of unstable glass is a valuable method to study the deterioration processes of museum glasses. Researchers have used it to investigate specific
topics relating to glass deterioration, such as the relative humidity at which glasses start to crizzle (Brill, 1975), measuring the alkali depletion depth (e.g. Fearn, McPhail and Oakley, 2004, 2005), measuring the change in chemical structure of the silica network (Robinet et al., 2006). These studies have principally looked at changes in chemical structure of the glass, but none has thoroughly investigated the deposition of ions on the surface of unstable glasses.

An important issue when studying the deposition of ions on the surface of unstable glasses is the rate at which ions are released from the glass structure and become available for formation of salts through interaction with atmospheric molecules. Based on experiments with replica glasses, Fearn (2004) reported that sodium depletion from the glass was linear with the square root of time, meaning that the amount of ions released decreases over time. This suggests that the amount of ions released by unstable historic glass depends on the amount of ions released in the past. The concentration of the ions found on the surface, therefore, is a good indicator for the rapidity of glass deterioration, which is an important parameter to consider for pinpointing those glasses whose instability needs special preventive conservation actions.

The research presented in this chapter adopts a more quantitative approach in the investigation of surface deposits than hitherto reported in the literature. The investigation is designed to provide information on the nature of ions and salts found on the surface of unstable glass, while simultaneously tackling questions related to more fundamental processes of glass deterioration.

### 5.2 Methodology

#### 5.2.1 Information on glasses used

Four different types of unstable glass were used for the artificial ageing studies, their compositions are listed in Table 5.1. Samples XV, XS and GL are pieces of unstable glass of ca. 5x8 cm, whereas sample KVL was a larger piece of glass (ca. 70x50 cm) which was cut up into three large samples (KVL-i, KVL-ii, KVL-iii) and two smaller samples (KVL-iv, KVL-v).
The XS, XV, and GL samples were originally prepared for use in glass deterioration studies at the Corning Museum of Glass (CMOG). Samples XT and XV were part of larger synthetic glass melts designed to have a composition similar to that of unstable historic glass (Brill, 1975). GL has a similar composition to the XS sample, but was melted in a different atmosphere. The pieces of glass used in the present research have not been used for published research at the CMOG, but were stored in the CMOG depots and have thus undergone a natural ageing process of approximately 40 years. A moist film had formed on the surface of all three samples which had been stored in cardboard boxes.

The glass sheet (KVL) was removed from a nineteenth century desk during restoration due to the fact that moisture was accumulating on the surface of the glass and damaging the wood underneath. It was unclear whether or not the removed glass originally belonged to the desk, or if it had been replaced earlier. Visual inspection of the glass confirmed the unstable nature of the glass, as an incipient crizzling pattern had developed.

**Table 5.1**: Composition (wt. %) of the glasses used for the artificial ageing experiments (CMOG = Corning Museum of Glass; KVL is glass removed from a historic desk during restoration). The composition of the KVL samples was obtained through LA-ICP-MS analysis by V.S. Šelih and J.T. van Elteren at the National Institute of Chemistry, Ljubljana, Slovenia. The oxide concentrations of the KVL samples were determined by averaging over 100 samples, the error represents the 95% confidence interval. The compositions of the CMOG samples were published by Brill (1975).

<table>
<thead>
<tr>
<th></th>
<th>CMOG samples</th>
<th>KVL samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XS</td>
<td>XV</td>
</tr>
<tr>
<td>SiO₂</td>
<td>73.5</td>
<td>65</td>
</tr>
<tr>
<td>Na₂O</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>CaO</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>MgO</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>MnO</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
5.2.2 Experimental

Crystallization experiments

Before the first artificial ageing campaign half of the upper surface of glasses XV, XS and GL was cleaned using polyester swabs (Texwipe Alpha® TX761) moistened with 50 µL of deionised water. The collected deterioration products, which had accumulated on the surface during 40 years of storage at the CMOG, were then extracted in a polypropylene vial filled with 1.35 mL of deionised water and these samples were subsequently prepared for IC analysis. The glass samples were then placed inside a desiccator containing 160 gram of dehydrated silica gel in order to dehydrate the deterioration products which had formed on the surface in storage. The RH dropped below 20% within minutes upon which the moist films started to crystallize, no crystals were observed on the cleaned parts of the glasses.

Aging experiments

Treatment before ageing and sampling details

All samples were cleaned prior to each ageing experiment using a mixture of ethanol and deionised water (1:1 volume ratio) and were left to dry in the fume hood before being placed in the climate chamber or desiccator. Samples were taken after cleaning using the protocol developed in chapter 4, but prior to ageing and the sample locations were identified on outlines of the glass samples traced on Melinex. After ageing samples were taken from the same locations as prior to ageing and on new locations, if the geometry of the samples allowed it. Table 5.2 provides an overview of the glass samples included in the different aging experiments. A Heraeus VC0020 climate chamber was used for RH and T control in the artificial ageing experiments. Further details of the ageing experiments are provided in the results section.

Table 5.2: Overview of the samples included in different aging experiments. The numbers represents the number of swabbing samples taken from the surface of the glass samples before ageing (b-a) and after aging (a-a).

<table>
<thead>
<tr>
<th>Unstable glasses</th>
<th>Reference materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>KVL-i</td>
<td>KVL-ii</td>
</tr>
<tr>
<td>b-a</td>
<td>a-a</td>
</tr>
<tr>
<td>Experiment 1</td>
<td>3</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>3</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>3</td>
</tr>
</tbody>
</table>
5.2.3 Analytical methods

**Ion chromatography**

Ion chromatography (IC) was carried out for quantitative analysis of anionic and cationic species in aqueous solutions. Details of the equipment used, chromatographic methods, and standard solutions are the same as described in Chapter 4.

**Charge balance**

The charge balance for each sample was calculated according to equation 5.1:

\[
\frac{[C] - [A]}{[C] + [A]} \cdot 100\% \quad \text{(Equation 5.1)}
\]

In which \([C]\) is the total cationic concentration in meq/L and \([A]\) is the total anionic concentration in [meq/L]. \([C]\) and \([A]\) are determined according to equations 5.2 and 5.3 respectively.

\[
[C] = \sum_{i=1}^{n} c_i z_i \quad \text{(Equation 5.2)}
\]

\[
[A] = \sum_{i=1}^{n} a_i z_i \quad \text{(Equation 5.3)}
\]

In which \(c_i\) and \(a_i\) are the analyte concentrations (mol/L) and \(z_i\) is the corresponding charge number.

The charge balance was calculated for each individual sample and averaged over the replicates. A positive charge balance indicates a surplus of detected cationic species, a negative charge balance indicates a surplus of anionic species and a charge balance of 0% indicates that the total positive charge equals the total negative charge in the samples.

**LA-ICP-MS**

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is an analytical technique used to determine the composition of different materials. During LA-ICP-MS analysis a sample is placed in a chamber where a laser pulse is fired at the surface of the sample, which causes ablation of the material. Particles are released from the sample as an aerosol and transported to a plasma torch.
by a flow of helium or argon, where the ablated material is decomposed and the elements ionised, which allows for the analysis by a mass spectrometer (Giussani, Monticelli, and Rampazi, 2009).

After ageing, samples KVL-iv and KVL-v were sent to the National Institute of Chemistry in Ljubljana, Slovenia, for LA-ICP-MS analysis to determine the composition of the glass. A depth profile of the glass composition was established by consecutively ablating the sample at one point. This allowed for the determination of the composition of the altered surface layer, as well as for the composition of the bulk glass. The estimated depth of each pulse was 100 nm and the laser area was 80 x 80 μm. The composition of the samples was determined by averaging over 100 pulses for the bulk glass and by averaging over 10 pulses for the altered surface layer.

The LA-ICP-MS analysis also allowed for the production of a pseudo cross-section of the glass samples. The laser beam ablated a line on the surface for which ablated material was analysed. By moving the laser over the same line 110 times a pseudo cross-section could be constructed based on the concentration of elements detected. Information on the analytical setup and calibration of the equipment is provided by Van Elteren, Tennent, and Šelih (2009).

5.2.4 X-Ray Diffraction

X-ray diffraction (XRD) was carried out on one sample (XS) using a Bruker D8 Discover equipped with a 2D General Area Detector Diffraction System (GADDS) detector. The measurements were carried out at the Dutch Cultural Heritage Agency (RCE) in Amsterdam by Luc Megens.

5.3 Results and Discussion

Described below are the IC results of the ageing experiments, of the compositional analysis using LA-ICP-MS and of the XRD analysis of salts which had formed upon dehydration of a moist film which had formed on one of the replica glasses. The results are discussed in relation to the three main goals of this chapter: identifying
ions which can indubitably be associated with glass deterioration, evaluation of the analytical IC protocol which was validated in Chapter 4 for samples taken from glass surfaces and making recommendations on storage conditions for unstable glass objects.

### 5.3.1 LA-ICP-MS results

Two aged samples, KVL-iv and KVL-v, were sent to the National Institute of Chemistry in Ljubljana, Slovenia, for compositional analysis using LA-ICP-MS. The samples were aged in a Heraeus VC0020 climate chamber for three weeks at 70°C and 70% RH prior to analysis. The results of the analysis are shown in Table 5.3, they show similar oxide concentrations for both samples. The results indicate that the glass is a mixed-alkali-lime glass, of composition which is generally regarded as unstable due to its low CaO concentration (Brill, 1975). The dominant network modifier is potash, with soda present in lower concentrations.

#### Table 5.3: Composition (wt. %) of glass fragments KVL-iv and KVL-v as determined by LA-ICP-MS. The analytical error is given by the 95% confidence interval (95% c.i.)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>KVL-iv Bulk</th>
<th>KVL-iv Depleted layer</th>
<th>KVL-v Bulk</th>
<th>KVL-v Depleted layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean 95% c.i.</td>
<td>Mean 95% c.i.</td>
<td>Mean 95% c.i.</td>
<td>Mean 95% c.i.</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>68.800 0.154</td>
<td>86.600 0.225</td>
<td>68.900 0.139</td>
<td>87.300 0.228</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>19.800 0.116</td>
<td>5.950 0.136</td>
<td>19.700 0.107</td>
<td>5.810 0.137</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.700 0.037</td>
<td>0.894 0.024</td>
<td>5.600 0.033</td>
<td>0.824 0.015</td>
</tr>
<tr>
<td>CaO</td>
<td>2.930 0.020</td>
<td>3.350 0.065</td>
<td>3.050 0.020</td>
<td>3.000 0.052</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.940 0.010</td>
<td>2.210 0.033</td>
<td>1.930 0.010</td>
<td>2.070 0.043</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>0.406 0.004</td>
<td>0.586 0.011</td>
<td>0.410 0.003</td>
<td>0.571 0.020</td>
</tr>
<tr>
<td>MgO</td>
<td>0.118 0.001</td>
<td>0.141 0.003</td>
<td>0.116 0.001</td>
<td>0.128 0.003</td>
</tr>
<tr>
<td>Sum</td>
<td>99,694</td>
<td>99,731</td>
<td>99,706</td>
<td>99,703</td>
</tr>
</tbody>
</table>

The results highlight the difference in composition between the altered surface layer and the composition of the bulk glass. Of particular relevance is the depletion of sodium and potassium from the glass structure, resulting in the formation of an altered surface layer. Both the sodium and potassium oxide concentration dramatically decreased during ageing, as a result the relative amount of SiO$_2$ increases during aging. The CaO concentration does not seem to be affected by
the ageing process. This could mean that either calcium is not leached from the glass structure, or that the relative amount of calcium leached out is exceedingly small compared to the two monovalent ions.

In order to investigate the leaching of the ions from the glass structure, a pseudo cross-section of the samples was made. The depth profiles of potassium and calcium provide some more insight into the leaching of these elements from the glass. The pseudo cross-sections are shown in Figures 5.1 and 5.2. From these cross-sections, the thickness of the altered layer was estimated to be 2 µm for sample KVL-iv and 2.3 µm for sample KVL-v. For sample KVL-iv the concentration of Ca in the top layer is slightly increased in the altered layer, which is likely to be a result of the decrease in the potassium and sodium concentration. For sample KVL-v the calcium concentration in the altered layer is similar to that of the bulk glass.

![Figure 5.1. Pseudo cross-sections for potassium (left) and calcium (right) of sample KVL-iv as determined by LA-ICP-MS. The colours represent the relative amount of the element. Blue represent low concentration and red represents higher concentrations. Image provided by V.S. Šelih and J.T. van Elteren, National Institute of Chemistry, Ljubljana, Slovenia.](image-url)
5.3.2 Crystallization experiments

Before the CMOG glass samples were artificially aged the deterioration products were sampled from half of the surface and analysed with IC. The glass samples were subsequently placed inside a desiccator containing dry silica gel to dehydrate the solutions on the surface. Upon dehydration crystallization occurred and the crystalline compounds which formed on the surface of sample XS were analysed using XRD.

The deterioration products which were sampled prior to the artificial ageing experiments had accumulated over a period of 40 years and consisted of a thick moist layer. As these glasses are unique and relatively small in size only a single sample could be obtained and no replicates of the measurements could be

![Figure 5.2. Pseudo cross-sections for potassium (left) and calcium (right) of sample KVL-v as determined by LA-ICP-MS. The colours represent the relative concentration of the element. Blue represents low concentration and red represents higher concentrations. Image provided by V.S. Šelih and J.T. van Elteren, National Institute of Chemistry, Ljubljana, Slovenia.](image-url)
conducted. The results of the IC analysis are shown in Figure 5.3. It is evident that the cationic species can be related to the glass composition, sodium is found on the sodium rich glasses GL and XS, while potassium is found on the potassium rich glass XV. The main anionic species detected was formate, suggesting that the main compound found on the surface of the glass is sodium formate or potassium formate. Due to the large amount of sampled material the ion concentrations well exceed the range studied during validation and the exact numbers are therefore not accurate, but the presence of acetate, formate, sodium and potassium in large amounts is demonstrated by these values.

![Figure 5.3](image)

**Figure 5.3.** Ion concentrations present in the layer of moisture present on the CMOG samples prior to any experimental work. Due to the unique nature and limited size no replicate samples could be obtained and therefore n = 1 for each sample.

After IC analysis, sample XS was placed in a desiccator containing dry silica gel upon which the deterioration products left on the surface crystallised. The crystalline material was then scraped together on the glass surface using a scalpel and was analysed using XRD. After the initial analysis the sample was analysed four more times after 30 minutes, 40 minutes, 17 hours and 41 hours to monitor any changes in the crystalline structure. The diffractogram is shown in Figure 5.4. The diffractogram matches that of sodium formate, but two peaks at d = 9.7 and d = 8.3 (Figure 5.5) remain unidentified. They could potentially be related to sodium acetate, which has a peak at d = 9.7. The detail in Figure 5.5 shows the
Figure 5.4. X-ray diffractograms of the crystalline material found on the surface of CMOG sample XS taken at $t = 0$ (black), $t = 0.5$ h (blue), $t = 0.75$ h (green), $t = 17$ h (yellow) and $t = 41$ h (red). The vertical blue and red lines represent the sodium formate peaks.

Figure 5.5. Detail of the X-ray diffractogram of the crystalline material found on the surface of CMOG sample XS taken at $t = 0$ (black), $t = 0.5$ h (blue), $t = 0.75$ h (green), $t = 17$ h (yellow) and $t = 41$ h (red).
transformation of the initially detected phase to another phase or compound as the peak identified at \( d = 8.27 \) is clearly present in the diffractogram taken at \( t = 0 \) (black), while it is completely gone and replaced by another peak at \( d = 9.7 \) in the diffractogram taken 41 hours after the first measurement (red diffractogram). This could be related to the deliquescence of sodium formate, or the formation of another compound which could not be identified in the current research.

5.3.3 Ageing experiments

Experiment 1

For the first ageing experiments samples KVL-i, KVL-iv and KVL-v were aged inside the climate chamber set at 70°C and 70% RH for three weeks. After ageing, six swabbing samples were taken from the surface of sample KVL-i and analysed with IC according to the sampling protocol as validated in Chapter 4. Samples KVL-iv and KVL-v were sent to the National Institute of Chemistry in Ljubljana, Slovenia for compositional analysis using LA-ICP-MS.

Four main ionic species could be identified on the surface of the aged glass: acetate, formate, sodium and potassium, none of these ions were detected prior to ageing (Figure 5.6). Concentrations of other ions (Figure 5.7) were below the associated limit of quantification (LOQ) of the analytical protocol, as determined in Chapter 4.

The high concentrations of sodium and potassium can be explained by the notion that they are leached from the glass structure. It is, however, unclear what the cause of the high concentrations of formate and acetate is. These ions might originate due to off-gassing of formic acid, acetic acid or formaldehyde from wood and paper, which were aged in earlier experiments in the same climate chamber.
Figure 5.6. Major ion concentrations of ions present on the surface of KVL-i and a borosilicate reference glass after ageing experiment 1.

Figure 5.7. Minor ion concentrations of ions present on the surface of KVL-i and a borosilicate reference glass after ageing experiment 1.
Experiment 2

In order to investigate the source of acetate and formate a second ageing experiment was developed in which one sample was placed in a sealed desiccator containing saturated silica gel (Pelsorb) and one sample was placed in the climate chamber. The silica gel was equilibrated for 72 hours at 70°C and 70% RH in the climate chamber used in ageing experiment 1. The saturated silica gel was then placed at the bottom of a large desiccator in which glass KVL-ii and a borosilicate reference glass were placed. The lid of the desiccator was placed on the desiccator and sealed using Vaseline, after which the desiccator was placed inside the climate chamber for temperature control. For comparison, sample KVL-i and a piece of borosilicate glass were placed inside the climate chamber as well at a temperature of 70°C and a RH of 70% for a period of three weeks.

The major ions detected were acetate, formate, sodium and potassium (Figure 5.8). A large difference in the concentrations of these ions was observed between samples KVL-i and KVL-ii and the ion concentrations of sample KVL-i are significantly lower than for sample KVL-ii. Additionally, no formate was detected on sample KVL-i after aging, but carbonate was detected on this sample as well as on the borosilicate reference glass aged in the desiccator (Figure 5.9). Ageing the unstable glass samples in the desiccator did not have the desired effect of removing the sources of acetate and formate from the ageing environment. In fact, based on the results presented in Figure 5.5 it can be argued that the deterioration of the glass was increased significantly by ageing the glass in a sealed desiccator. A possible explanation for this observation is that the silica gel absorbed some of the acetate and formate present in the climate chamber during its saturation, which it released during the aging period in the sealed desiccator, providing an opportunity for these anions to deposit on the surface of the unstable glass. In this way a microclimate could inadvertently have been created containing compounds, acetic and formic acid, which promote glass deterioration (Robinet, 2006), while no microclimate was created outside the desiccator (but inside the climate chamber), in a more open environment. This might suggest that glasses stored inside a closed environment have a higher rate of deterioration. However, these observations may be affected by the fact that sample KVL-i had already been aged in ageing experiment 1, which potentially consumed part of the ions available for release by the glass sample. In order to investigate the above considerations a third ageing experiment was set up.
Figure 5.8. Major ion concentrations of ions present on the surfaces of KVL-i (aged outside the desiccator, but inside the climate chamber, denoted “ch”), KVL-ii (aged inside the desiccator, denoted “des”) and borosilicate reference glasses after ageing experiment 2.

Figure 5.9. Minor ion concentrations of ions present on the surfaces of KVL-i (aged outside the desiccator, but inside the climate chamber, denoted “ch”), KVL-ii (aged inside the desiccator, denoted “des”) and borosilicate reference glasses after ageing experiment 2.
**Experiment 3**

As the source for formate and acetate on the surface of the unstable glasses was still unclear and the differences between ion concentrations detected on the surface of the samples aged in experiment 2 were unexplained, a third experiment was conducted in which the climate chamber was removed as the potential source for the acetate and formate and all samples were aged in the same conditions. Samples KVL-i, KVL-ii, KVL-iii, two quartz slides, a piece of borosilicate lab glass, and the CMOG samples XS, XV and GL were placed inside a desiccator in which a saturated salt solution of ammonium sulfate was placed for RH control. This salt was chosen as both ammonium and sulfate were not detected in significant amounts in earlier experiments. The desiccator was closed and sealed with Vaseline and placed inside an oven at 65°C for three weeks. The RH was regulated by the saturated ammonium sulfate salt solution and had a value of 72% at a temperature of 65°C, which was determined during a test run of 11 days (Figure 5.10). Figure 5.11 and 5.12 show the results for the major and minor ion concentrations for glass samples KVL-i-iii, while Figure 5.13 and 5.14 show the results for the CMOG glasses.

![Figure 5.10. climate conditions of ageing experiment 3, controlled by saturated solution of ammonium sulfate.](image)
Figure 5.11. Major ion concentrations of ions present on the surface of glasses KVL-i-iii, a borosilicate reference glass and quartz slides after experiment 3.

Figure 5.12. Minor ion concentrations of ions present on the surface of glasses KVL-i-iii, a borosilicate reference glass and quartz slides after experiment 3.
Figure 5.13. Major ion concentrations of ions present on the surface of the CMOG glasses, a borosilicate reference glass and quartz slides after experiment 3.

Figure 5.14. Minor ion concentrations of ions present on the surface of the CMOG glasses, a borosilicate reference glass and quartz slides after experiment 3.
The results obtained in the final experiment indicate that there is no increase in the concentrations of formate and acetate during aging. This suggests that the presence of acetate and formate on the aged glasses in ageing experiments 1 and 2 is likely related to the use of the climate chamber. However, formate was detected on sample XS before ageing, but no increase in the formate concentration was observed after aging, suggesting that a residue was left on the surface after cleaning of the sample. Beyond this, no other ions than sodium and potassium were identified in amounts above the limits of quantification. These ions can directly be related to the composition of the aged glasses: sodium is found on glasses with Na$_2$O as an alkali oxide constituent (KVL, XS and GL), while potassium was found on the samples containing K$_2$O as an alkali oxide constituent (KVL and XV).

A comparison of the three different ageing experiments can only be made using sample KVL-i, which was included in all three experiments. Figure 5.15 lists the major ion concentrations detected on the surface of this sample in all three experiments. The cation (sodium and potassium) concentrations on the surface of the glass are the highest after ageing experiment 1 and the two subsequent experiments yield lower ion concentrations. Although the ageing parameters were similar way in experiments 1 and 2 for this sample, the detected concentrations are significantly lower after the second ageing session. This could be explained by the fact that the ion depletion depth increases linearly with the square root of ageing time (Fearn, McPhail and Oakley, 2005), suggesting that the rate of ion release decreases over time. This is in line with the observations made in these experiments. In this respect, it is peculiar that the concentration of sodium and potassium after the third ageing session is higher than after the second. However, this could be a result of the changing ageing conditions, and it is not unlikely that ageing inside a sealed desiccator in the third ageing experiment promotes the rate of deterioration. This would be in line with observations made at the Corning Museum of Glass, where glasses stored in open cabinets, thus allowing air circulation, are less prone to crizzling than objects stored in sealed cabinets (Koob, 2017). Preliminary studies on this type of information have been carried out in the past, and the results indicate that air movement is indeed beneficial for the prevention of ion depletion and subsequent deterioration processes (Fearn, 2004).
5.3.4 Pinpointing the source of the ions

The main question investigated in this chapter is which ions can be attributed to glass deterioration and which ions should be ascribed to another source. The results presented above provide insight in this question. Therefore, this section discusses the potential source of the cations and anions detected in the ageing experiments.

The compositional analysis of the KVL samples, using LA-ICP-MS, demonstrated that sodium and potassium are depleted from the surface layer of the glass. This is in line with the observation that sodium and potassium are detected on all KVL samples analysed with IC which were included in the ageing experiments. This is in agreement with the notion that the source of cations on unstable glass surfaces is the glass itself (Kunicki-Goldfinger, 2008). Since no potassium is detected on the CMOG samples containing Na₂O as the main alkali oxide component (GL and XS), and vice versa the source of these ions can be attributed to the glass itself with confidence.

No other cationic species were identified during the ageing experiments. This
observation is important because SIMS depth profiling of unstable glass has demonstrated that calcium may also be depleted from the top layer of the glass (see e.g. Fearn, McPhail and Oakley, 2004, 2005), but to a smaller depth than sodium or potassium. The compositional analysis of samples KVL-iv and KVL-v indicates that there is limited or no leaching of calcium from the KVL glasses, while the concentration of sodium oxide and potassium oxide is dramatically decreased in the depleted layer (Table 5.3, Figures 5.1 and 5.2). However, it must be noted that the concentration of calcium oxide reported in table 5.3 is an average of the entire altered layer, and it may therefore be that calcium is depleted from part of the alkali depleted layer, but that this is not represented in the LA-ICP-MS analysis.

Anionic species found on the surface of unstable glass are generally thought to originate from the environment in which the glass is stored. All glasses were cleaned before ageing and analysis of samples taken just before ageing show that there are no detectable anions on the surface of the glasses. An exception to this are glass samples XV and XS, where formate was detected before ageing. This may be a result of residues left behind on the surface of the glass after cleaning, which is not unlikely considering the heavy deterioration these objects have undergone in the past 40 years. Otherwise the presence of anions found on the surface of the glass samples can be attributed to the ageing procedure. The main anions found were acetate and formate, but using them as indicators for glass deterioration is problematic because they are not always detected, while sodium and potassium are consistently found on the surface of the aged samples.

Carbonate is an anion which is often related to weeping of unstable glass due to the formation of potassium carbonate (Organ, 1957) and the potential subsequent conversion of carbonate into formate or acetate salts (see Chapter 3). One of the observations made during the proof of principle was that carbonate was only detected in samples where acetate and formate were absent. Similarly, the results presented in this Chapter indicate that the carbonate is only detected in those samples where formate is absent (Figure 5.16). This suggests that there is a chemical conversion taking place, where carbonate is transformed to formate on the surface of the samples. The detection of carbonate on the surface of unstable glass would not be surprising as it can be formed due to the absorption of carbon dioxide from the atmosphere into solution, but there are many factors influencing
the concentration of carbonate is solution, among which is the conversion of carbonate to formate under (Wan Isahak et al., 2015).

The identification of the ions on the surface of unstable glass in controlled environments is a crucial step in the development of an early warning system for unstable glass. In order to understand the nature of the ions found on the surface of unstable glass it is of great importance to understand which processes underlie the release of ions from the glass surface and how they react with ions in the atmosphere. This is reflected by the variety of ions detected with IC, but equally important are the ions that are not detected by IC. Charge balances of the samples show that there generally is a surplus of cationic species detected with IC (Figure 5.17), meaning that the total negative charge of the samples does not equal the total cationic charge in the samples. Two possible explanations for this phenomenon are that the total negative ion concentrations are underestimated, or that there are ions in the sample which are not detected by the used IC method. Examples of the latter are bicarbonate and hydroxide. In addition, carbonate can

![Figure 5.16. Acetate, formate and carbonate concentrations for all samples in which carbonate was detected.](image-url)
be detected in this IC setup, but the quantification limits are quite high compared to other anions (in particular acetate and formate, see Chapter 4). As a result the carbonate concentration could be underestimated.

An important aspect in the development of an analytical protocol for the identification of unstable glass objects is picking out potential marker ions for glass instability. The results from the current study indicate that the cationic species linked to glass deterioration are sodium and potassium. The fact that no other cations were detected indicates that these two alkali ions are the only two suitable for generic identification of unstable glass, the combination of these ions with anionic species results in the formation of hygroscopic salts (see Table 3.3), which is the cause of weeping glass. Extension and replication of the ageing experiments and is necessary to fully understand the mechanisms leading to the formation of specific compounds on unstable glass surfaces and their relation to deterioration mechanisms. Additionally, research on museum objects will indicate whether or not these salts are found on museum objects; this research is described in Figure 5.17.
in Chapter 6. Therefore the presence of these salts on the surface of the glass may be an indication that the glass is unstable. Further experimental work should be aimed at investigating the charge balance in the samples in order to investigate with which anions the cations are associated in solution.

5.3.5 Evaluation of the analytical method and sampling protocol

The analytical protocol described in Chapter 4 was developed for quantitative identification of ions on the surface on glass objects in museum collections. In order to test the efficiency and reliability of a straightforward sampling and extraction protocol a validation was carried out and it was demonstrated that, on mock-up samples, most ions related to glass deterioration gave good analytical results. Translating these validation values to the study of museum glass, however, requires an intermediate step of the analysis of samples taken from the surface of glasses with known compositions and aged in controlled environments. Therefore the results of glasses KVL-i-iii are of relevance for the evaluation of the developed protocol in a situation more similar to the situation in which the protocol will eventually be used.

One of the most important limiting factors of the sampling procedure as encountered during the proof of principle (Chapter 3) was the difficulty of making inter-object comparisons. The results presented in this chapter provide more insight in the effectiveness of discriminating different objects from each other based on the concentration of ions on the surface. Figures 5.8 and 5.11 show the difference in concentration found on different unstable glass samples, and there is a clear difference in ion concentrations between the reference glasses and the unstable glasses. The three different KVL glasses were aged in different environments and ion concentrations indicate that there is indeed a difference in ion concentration between the samples. The application of the sampling and analytical protocol provided significant differences in ion concentrations.

In order to evaluate the reliability of the sampling protocol on the artificially aged samples, the RSD of the samples obtained from the replica glasses is regarded. Although the relative standard deviation (RSD) is larger for the samples taken from the glass surface than the RSD during validation, the major ions do have a
RSD between 10% and 20% (Table 5.4) when detected in high amounts, which is particularly the case for the samples analysed in experiment 2. However, in other instances the RSD is higher than 20% which demonstrates that understanding the cause of this increased error is in need for further investigation, because the RSD values obtained during the validation, also listed in Table 5.4, are much lower.

Table 5.4: Relative standard deviation (RSD) of ion concentrations for all ions with a concentration above the quantification limit, compared to the RSD of the ion concentrations as determined during sampling validation.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Sample</th>
<th>Acetate</th>
<th>Formate</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Chloride</th>
<th>Nitrate</th>
<th>Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KVL-i after ageing</td>
<td>13.05%</td>
<td>30.94%</td>
<td>21.52%</td>
<td>25.27%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>KVL-i (ch) After</td>
<td>16.56%</td>
<td>15.88%</td>
<td>14.00%</td>
<td>14.17%</td>
<td>19.01%</td>
<td>25.83%</td>
<td>22.23%</td>
</tr>
<tr>
<td></td>
<td>KVL-ii (des) After</td>
<td>10.34%</td>
<td>7.66%</td>
<td>7.22%</td>
<td>11.77%</td>
<td>-</td>
<td>17.48%</td>
<td>10.14%</td>
</tr>
<tr>
<td></td>
<td>Borosil (ch) After</td>
<td>1.22%</td>
<td>5.11%</td>
<td>9.66%</td>
<td>-</td>
<td>18.36%</td>
<td>35.87%</td>
<td>17.44%</td>
</tr>
<tr>
<td></td>
<td>Borosil (des) After</td>
<td>9.38%</td>
<td>14.93%</td>
<td>13.35%</td>
<td>-</td>
<td>-</td>
<td>42.09%</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Borosil after</td>
<td>-</td>
<td>-</td>
<td>21.34%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>GL after</td>
<td>-</td>
<td>-</td>
<td>44.06%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>XS before</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>XS after</td>
<td>-</td>
<td>-</td>
<td>47.95%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>XV before</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>XV after</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>66.83%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Validation</td>
<td></td>
<td>2.96%</td>
<td>2.21%</td>
<td>4.20%</td>
<td>4.09%</td>
<td>13.57%</td>
<td>2.87%</td>
<td>10.26%</td>
</tr>
</tbody>
</table>

An explanation for the high RSD of the samples studied in this chapter includes three factors. Firstly, there is a difference in surface from which the samples were obtained. During validation mock-ups of inert materials, polyester, were used to create similar circumstances for each sample, while the samples in the artificial ageing studies were all obtained from unstable glass surfaces. It can be expected that all ions on a polyester surface can be removed by swabbing because the ions are less likely to form a weak ionic bond to the substrate than when ions are present on the surface of unstable glass. If ions are weakly bonded to the surface it is likely that they are not all collected by swabbing, which increases the RSD of the samples. Secondly, the action of swabbing the surface may have an effect on
the altered surface layer of the glass, which in turn influences the amount of ions sampled. Basically, there are two types of ions which could be collected during sampling: the ‘free ions’ on the surface of the glass, present in the form of salts, and the ‘loosely bound ions’ which are present in the altered surface layer. Based on the validation results it is likely that all free ions are sampled from the glass surface, but variations in the amount of ions which are leached from the altered surface layer might explain the increase in RSD. These leachable ions could originate from the glass composition itself, but the increased porosity of the altered surface layer might also result in the presence of ions which were not originally part of the glass in this layer. This hypothesis is in line with the detection of formate on glass XS before ageing, but after cleaning (figure 5.13). This glass is over 40 years old and a thick moist film containing large amounts of sodium and formate had formed on the surface of the glass. The deterioration of glass causes a decrease in density of the top layer of the glass (Kunicki-Goldfinger, 2008; Roemich et al., 2008; Schalm and Anaf, 2016), which potentially results in the retaining of some of the anions that deposited on the surface due to deterioration processes. These ions may have been left behind after cleaning of the samples, after which they were extracted during sampling with a slightly moistened swab. Although this is a single observation, it would be interesting to further investigate the effect of the sampling procedure on the structure of the glass. Thirdly, little is known about the homogeneity in which the deterioration products are distributed across the surface of unstable glass. It has been observed that salts are distributed heterogeneously across the surface of unstable glass (Fearn et al., 2006), but on a much smaller scale (< 0.01 mm$^2$) than the sampling area applied in this study. Therefore, it remains unclear how the deterioration products are distributed across the glass surface on a larger scale, but it could be that local differences in the amounts of ions on the surface exist. This a factor which needs to be taken into account when studying glass deterioration and requires further attention. All these factors need to be included in the study of the formation of deterioration products on unstable glass surfaces and the high RSD of ions present at a high concentration needs to be investigated further.
5.4 Conclusions

The research described in this chapter was aimed at identifying ions on the surface of unstable glass explicitly related to the processes of deterioration by artificially ageing glasses of known unstable composition. Additionally, the results provide insight in the usefulness of IC as an analytical tool in the study of unstable glass and the reliability of the analytical protocol, described in Chapter 4, on actual glass surfaces. Investigation of the results was aimed at better understanding processes of ion release by unstable glass in relation to their composition and providing further understanding on processes of glass deterioration in museum conditions and potential preventive conservation strategies.

The results indicate that the main ions associated with glass deterioration are sodium, potassium, formate and acetate. Sodium and potassium, which originate from the glass itself, were detected on all replica glasses depending on the composition of the glass. Both ions were detected on replica glasses containing both sodium and potassium oxide in its composition, for samples taken from glasses containing sodium oxide and no potassium oxide only sodium was detected and vice versa. This provides confidence that sodium and potassium are the main cations which are found on the surface of unstable glass and could act as marker ions for glass instability. These presence of anionic species could be related to glass deterioration to a lesser extent as their presence largely depended on the environment in which the replica glasses were aged. Moreover, a deficiency of anions was detected in nearly every sample, which is likely due to the fact that certain anionic species, such as hydroxide and bicarbonate, which can form on unstable glass surfaces cannot be detected.

The results of the ageing experiments can be used for the further evaluation of the analytical protocol developed in Chapter 4. We were able to discriminate different glass samples based on the identity and quantity of the ions found on the surface of the aged glasses. However, these observations are based on a limited number of experiments and samples and it is strongly suggested that further research be carried out on the validation of the sampling protocol on glass surfaces in order to investigate the source of the high relative standard deviations determined in several samples in the current study. In this respect it is of great importance to
also investigate the changes in glass composition resulting in the deposition of compounds on glass surfaces. What the results do highlight is the importance of ion chromatography for the study of unstable glass. The fact that the RSD is high for some of the samples is related to deterioration patterns which are imperfectly understood, but which IC may provide a key role in elucidating.

One important aspect of glass deterioration, also relating to its detection in an early stage is the rate at which ions are released from the glass structure. Currently, little is known about the leaching rate of ions from historic glass objects and their deposition on the surface on unstable glasses. The amount of ions deposited on the surface of unstable glass can be monitored by IC, but relating this to the changes in composition has not been possible yet. Extending the ageing time with intermediate sampling and analysis of the composition of the altered glass layer may provide information on the rate of ion release from the glass, which in turn will be of interest in the determination of preferable storage conditions for unstable glasses in museum collections.

Some information on preferable storage conditions can also be derived from the results presented in this paper. The results of the glass which was aged three times (KVL-i) in different conditions suggests that ageing glass in a closed environment increases the rate of deterioration of that glass. This is in line with earlier observations indicating that air movement or storage of unstable glass conditions allowing airflow decreases the glass deterioration rate (Fearn, 2004; Koob, 2017). It will be interesting to follow up these observations with research specifically aimed at studying this effect, as it might greatly change the way in which glass in museum collections is stored. The presence of formate as a main anionic compound is worrying, as its presence is associated with the presence of sodium formate or potassium formate. As already mentioned in Chapter 3, the presence of potassium formate could be particularly problematic as it has a deliquescence relative humidity of 16-17%, which is a non-acceptable RH range for the storage of unstable glass due to the risks of crizzling. This points to the need for preventive conservation strategies for unstable glass which focus on removing organic compounds detrimental to glass objects from the storage environment.
5.5 References


