Glass sickness: Detection and prevention

Investigating unstable glass in museum collections

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Publication date
2018

Document Version
Other version

License
Other

7 CONCLUSIONS

7.1 Introduction

The purpose of this dissertation has been to inform the academic and professional field of glass conservation about the identification of unstable glass in museum collections. Although the impetus for the research was mainly of practical nature, the study has sought to enrich the existing body of academic literature on glass deterioration in museum collections in four different ways: by examining what is occurring on the surface of historic glass rather than looking at compositional changes, by investigating preventive conservation strategies based on analytical results, by filling a hiatus of ten years in which no research specifically directed at historic glass was carried out, and by carrying out research which can be translated into the museum practice. The pertinence of these topics is developed in sections 7.1.1-7.1.4.

7.1.1 Analysis of surface deposits

Studies on glass deterioration have predominantly focused on compositional changes inside the glass, rather than looking at what is happening on the surface of the glass. There are two main reasons for this: the notion that analysis of changes in composition provides better insight in chemical processes related to glass deterioration than researching deposits on the surface of the glass may have (Fearn, McPhail and Oakley, 2005; Fearn et al., 2006b) and the related notion that investigating changes in the structure of the glass has a greater impact on the preservation of objects than looking at what is depositing on the surface (Robinet, Fearn and Eremin, 2005). Increased sensitivity of the analytical equipment has indeed enabled the detailed study of glass deterioration and have provided crucial insights into glass deterioration (see e.g. Fearn, McPhail and Oakley, 2005). Yet, processes occurring outside the glass cannot be disregarded in order to fully understand glass deterioration in museum collections. This dissertation therefore focuses on the formation of chemical compounds on the surface of unstable glass. Leached cations from the interior of the glass migrate to the surface of the glass and the nature of the compounds found on unstable glass surfaces can thus be related to the composition of the glass itself. Therefore, the results obtained in this dissertation can be related to studies which quantify depletion of cations from within the glass surface (e.g. Fearn, McPhail and Oakley, 2004).

7.1.2 Preventive conservation strategies

An important part of the literature on historic glass conservation has focused on preventive conservation strategies, particularly the preferred display and storage relative humidity (RH) for unstable glass. A guideline which is often applied for glass collections is a RH of 42% as suggested by Robert Organ (1957), but many other suggestions have been published, ranging from 35% to 55% RH. Kunicki-Goldfinger (2008) provides a good overview of the recommendations in the literature. These recommendations are most often based on the prevention of the dehydration of the altered surface layer (potentially resulting in crizzling), prevention of the further uptake of water in the surface layer through hydration (resulting in increasing thickness of the alkali-leached surface layer), or the prevention of the formation of a moist layer on top of the glass. As the interaction with atmospheric water is the main process in the deterioration of glass (Bunker, 1994), storage of glass in low RH, typically below 40%, is proposed to avoid hydration of the glass structure and moisture accumulation on top of the glass. This low RH might be suitable for glass with an unaltered surface layer, but, depending on the composition of the glass and the storage history, unstable historic glass will have an altered, hydrated surface later and storage in this RH range may lead to crizzling. To avoid dehydration and subsequent crizzling it has been recommended to maintain a RH with minimal fluctuations and similar to the RH the glass is accustomed to (Brill, 1975). Therefore, the safe storage of unstable glass is a balancing act of avoiding hydration and dehydration. This dissertation has the goal of contributing to a better understanding of preferential storage and display conditions for unstable glass from the perspective of avoiding the onset of moisture accumulation on the surface of the glass. Organ (1957) used the deliquescence relative humidity (DRH) of potassium carbonate of 42% to prevent the accumulation of moisture on glass surfaces because he observed that potassium rich glass would dry out at this RH. This recommendation has subsequently been used as guideline for entire glass collections, but little research has been carried out to actually confirm the presence of potassium carbonate on weeping glass objects (Robinet et al., 2004; Eremin et al., 2005). Formates were later detected as a main salt forming on the surface of unstable glass (Schmidt, 1992), but the recommendations for prevention of the onset of weeping have not been changed. A likely partial explanation for this maybe that the identification of multiple different compounds complicates the determination of the DRH of the mixture of salts. This dissertation seeks to identify the ions that make up the salts and investigate the potential of using this information for the specification of preferred target RH to prevent weeping.

7.1.3 Building on existing research

Research into the deterioration of glass has often been motivated by incidental observations. In the 1990s the assessment of the condition of museum glass collections received attention in the UK. This resulted in glass collection surveys at the Victoria and Albert Museum (V&A) (Oakley, 1990, 2001), the National Museums of Scotland (Cobo del Acro, 1999), and at the British Museum, where the results of the survey have remained unpublished. These surveys were the inspiration for collection surveys in the Netherlands at the Rijksmuseum (Lamain et al., 2013) and Museum Boijmans van Beuningen (Burghout and Slager, 2013). The surveys emphasized the need to gain a better understanding of glass deterioration processes in museum collections in order to prevent advanced deterioration of glass objects. These surveys emphasized the need for scientific research into historic glass deterioration, which culminated in several publications between 2004 and 2007 (Fearn, McPhail and Oakley, 2004, 2005; Fearn et al., 2006a,b,c; Robinet, 2006; Robinet et al., 2004, 2005, 2006; Robinet, Fearn and Eremin, 2005; Eremin et al., 2005). Although these publications provided new insights into chemical deterioration of glass, the information provided by the scientists has not been implemented in the conservation practice and as a result most museums have not been able to improve their conservation strategies for the vessel glass collection, other than replacing wooden cabinets. The research carried out over a decade ago has thus had limited impact, and although the outcomes justified future research, no follow-up analytical studies have been specifically directed at investigating glass deterioration in museum collections. The research presented in this dissertation intents to fill this gap.

7.1.4 Translating scientific results into the conservation practice

There appears to be a separation between practical publications and scientific work. To understand the chemical processes of glass deterioration, the problem is simplified by designing experiments in which all conditions are controlled. In this way, specific problems concerning glass deterioration – such as the effect of moisture on glass deterioration (Douglas and El-Shamy, 1975; Fearn, McPhail, and Oakley, 2005), the effect of an acid environment on soda-lime glasses or the effect of the storage environment on the alteration of alkali-lime glasses (Alloteau et al., 2017) – can be investigated and the results are often enlightening on these specific topics. However, it is often difficult to apply the outcomes of this type of research to the daily conservation practice as the museum context consists of many more parameters than simulation experiments can account for. This dissertation has sought to apply a methodology which overcomes this issue by looking directly at what is happening on the surface of museum objects, which means that the analytical data directly provides information on the condition of the objects. The research has thus sought to bridge the gap between the interpretation of scientific data and the needs of conservation practice.

7.1.5 Research questions

The main research question of the dissertation was:

How can unstable glass objects in museum collections be identified using non-destructive, readily-available methods before irreversible changes in appearance occur and how can further deterioration of these objects be prevented?

In order to tackle this problem, five research sub-questions were investigated:

1. What are the main processes indicative of glass deterioration and which analytical techniques are available for the non-destructive investigation of glass deterioration?
2. Which ions are found on the surface of unstable glass? What are potential consequences of their presence for conservation of glass objects?
3. How can ions on the surface of unstable glass be analysed quantitatively?
4. Which ions can be attributed to the deterioration of glass, and which ions have another source?
5. Can the concentration of ions found on the surface of glass objects in museum collections be related to their chemical stability?

The remainder of this final chapter summarises the main findings of each research chapter, in the context of the research questions. Thereafter, the theoretical implications of the dissertation are discussed, also paying attention to the limitations and suggestions for future research. This section is followed by a discussion of the practical implications of the dissertation and finally some recommendations for future research are discussed.

7.2 Answering the research questions

The main research issue in this dissertation concerned the identification of unstable glass objects in museum collections. In this section the achievements concerning this topic are described.

From literature studies it was found that the precise mechanisms of glass deterioration are still a topic of debate, but there is a consensus that the deterioration of glass goes hand in hand with the depletion of alkali ions from the glass structure through ion exchange processes, which occur due to the interaction of the glass with atmospheric water (Doremus, 1975; Ernsberger, 1980; Bunker, 1994; Sterpenich and Libourel, 2006). As a result cations migrate to the glass surface where they may react with atmospheric molecules and form (hygroscopic) salts (Barger, Smith and White, 1989; Schmidt, 1992; Eremin et al., 2005). The presence of these salts on the surface are an indication of glass deterioration and when hygroscopic salts are present in large quantities, enough moisture is attracted to the glass surface to form a liquid film or droplets. Usually, this is a sign for conservators that they are dealing with unstable glass, but since the leaching of ions from the glass structure is an irreversible process, the basic damage has already been done even prior to visible changes at the surface. Identification and quantification of leached cations which denote instability would provide the opportunity to pinpoint unstable glass objects at an earlier stage and thus take precautions to prevent further deterioration.

The proof of principle (Chapter 3) demonstrated the value of IC in the identification of ions found on the surface of unstable glass objects from three different museum collections. A wide variety of ions was found on the surface of unstable glass. The ions generally present in high concentrations were sodium, potassium, chloride, acetate, and formate. Ions detected in lower amounts were magnesium, calcium, nitrate, carbonate and sulfate. Although we speak of 'high' and 'low' amounts, these descriptors of the ion concentrations are relative as quantification of the sampled ions was imperfect at this stage of the research. Furthermore, it was uncertain which ions could be solely and indubitably associated with the deterioration of glass, and which ions could be ascribed to another source, such as the deposition of sodium chloride due to handling or the accumulation of particulate pollutants on the surface.

In order to be able to compare ion concentrations obtained from different objects, an analytical protocol was developed and validated (Chapter 4). The protocol was based on a straightforward sampling procedure in order to allow for the investigation of a large number of objects in a relatively short period and facilitate the sampling by conservators. Specificity, linearity accuracy, precision, and limits of detection and quantification were determined for 6 cationic species and 10 anionic species. It was demonstrated that nearly all the ions associated with glass deterioration could be analysed quantitatively. Chloride and carbonate showed poor validation parameters, which means that less confidence can be ascribed to the analysis of these ions.

In order to investigate the source of ions found on the surface of unstable glass, experiments were designed in which unstable glass was artificially aged in controlled conditions (Chapter 5). The results of these experiments showed that sodium and potassium can be regarded as the main ions associated with glass deterioration. These species likely originate from the glass itself, whereas the anionic species find their origin in the environment in which the glass is kept. Acetate and formate were the main anionic species present on the surface of the glass, but they were not present in all experiments.

Finally, it was demonstrated that the total alkali metal ion concentration found in the samples could be an indicator for chemical instability of glass objects. This conclusion was reached after investigation of museum objects. Conservators had classified all objects under investigation according to their condition and the IC results were compared to this classification. The results presented in the study showed a separation between clearly unstable and stable objects, even when no visible signs of deterioration could be observed. However, some objects from the unstable category showed low ion concentrations, suggesting that they either are "less unstable" than the other objects, or that the applied method is not suitable to determine their stability. In order to investigate the classification of museum objects based on the concentration of ions on their surfaces it is important to study more objects in order to provide better statistics. Nonetheless the current results have demonstrated that the IC protocol is a powerful method to investigate glass stability in museum collections in a relatively quick way, with minimal intervention for the objects. This is the first time that a straightforward method has been devised for the identification of unstable glass in museum collections which allows for the further and rigorous study of glass objects in museum collections.

An important issue in the application of the developed protocol in the study of unstable glass is the high relative standard deviation (RSD) encountered in both the artificially aged samples and the museum samples. During the validation procedure the RSD was below 5% for the ions of interest, except for chloride and carbonate, but the analysis of samples obtained from glass surfaces resulted in a much higher RSD up to 40% in some cases. The fact that the RSD is high for some of the samples is likely related to deterioration patterns and the effect of the sampling protocol on the altered glass layer, which are not very well understood, but for which IC may provide a key role in starting to understand. The distribution of deterioration products on the surface of the glass is an important factor to consider when applying the sampling protocol. It is currently unclear how the distribution of ions on the surface takes place and whether or not this is a result of inhomogeneous glass deterioration or purely of the agglomeration of deterioration products. Another explanation for the high RSD could be found in the nature of the sampled surface. An interaction between the ions on the surface with the surface itself and the potential leaching of ions from the altered surface layer due to the swabbing action could cause an increase in the RSD.

7.3 Theoretical contribution

This dissertation has sought to contribute to the academic literature on historic glass conservation by addressing four research gaps. Firstly, it focused on glass deterioration by looking at what comes out of the glass instead of focusing on structural changes inside the glass network. Secondly, it aimed at providing scientifically-based recommendations for environmental parameters that prevent the onset of weeping. Thirdly, it sought analytical results which are directly related to the museum objects, instead of focusing on simulation experiments. Finally, it aimed at bridging the gap between scientists and conservators.

7.3.1 Researching glass deterioration in museum collections

The choice of focusing on what is happening on the surface of unstable glass objects, instead of looking at changes occurring inside the glass structure, has provided new insights into the deterioration of glass in museum collections. The dissertation demonstrated that the formation of surface deposits is a more complex process than suggested by others (Robinet, Fearn and Eremin, 2005). It provides valuable information on the chemical alteration of glass objects as the formation of compounds on the surface of unstable glass can be directly related to alteration of the glass structure. Generally, the occurrence of ionic compounds on the surface of glass has been associated with *visible* deterioration processes such as the formation of a moist layer or the presence of crystalline products. What this dissertation has shown is that *invisible* products can also be identified and related to the stability of glass objects in museum collections.

One of the main reasons for the study was the development of an analytical protocol for the identification of unstable glass of museum collections. Several efforts to achieve this have been made in the past (Ulitzka and Touchard, 1991, Neelmeijer and Mäder, 2005; Robinet et al., 2006), but none of these methods has been successful in straightforwardly pinpointing unstable glass objects. This dissertation has achieved the development of an analytical method which forms the basis of an early warning system for unstable glasses. It has been established that there is a relationship between the amount of ions found on the surface of glass objects and the chemical stability of these objects. A swabbing protocol in combination with IC analysis has proven to be an excellent approach to determine the amount of ions on the surface. Because of the simplicity of the method it will be possible to investigate large numbers of objects from glass collections around the world, without the need for objects or persons to travel large distances. At this point in the ongoing research threshold ion concentrations of sodium and potassium have been suggested for the identification of glasses at risk of decay, but more research is necessary to refine these threshold values.

7.3.2 Preventive conservation of glass in museum collections

Storage conditions for unstable glass have received much attention in the past. Organ (1957) advocated that glass be stored below 42% RH as he observed that the formation of a moist layer on unstable glasses was prevented. Later, it was recommended to keep historic glass in a stable environment with a RH between 40% and 60% to prevent deterioration (Brill, 1975). In the study of enamel deterioration it was observed that unstable enamels started weeping at a RH slightly above 50%, while they started to crizzle below 40% RH. A RH of 45% was therefore suggested for enamels to prevent both. Although analytical evidence for the cause of the onset of weeping was not provided in these publications, the recommendations were sufficient to prevent visible deterioration consequences (Smith, Carlson and Newman, 1987). Later the role of carbonyl pollutants in the acceleration of glass deterioration was recognized and their presence was taken into account for preferential storage conditions for unstable glass (Robinet et al., 2004). This dissertation gave specific attention to the consequence of pollutants in the museum atmosphere in the selection of a specific RH range for unstable glass

The goal of specifying a RH for the prevention of glass deterioration is twofold. Firstly, it must attempt to prevent crizzling, which may occur due to the dehydration of the altered surface layer in low RH. The proportion of water in this modified top layer of the glass may be as high as 20% (Kunicki-Goldfinger, 2008) and the results of dehydration can be very dramatic, which implies that a high storage RH should be adopted to prevent crizzling. This is, however, in contradiction with the second goal of climate control for storage of glass: preventing the formation of a moist film on the surface of the glass, which consists of a solution of hygroscopic salts. Whether or not the salts form a moist layer depends on the deliquescence relative humidity (DRH). At a storage RH above its DRH a salt will attract water from the atmosphere and form a moist layer or droplets. At a RH below its DRH a salt will dehydrate and crystallise. The recommendations of specific storage conditions are often based on the DRH of specific salts, and as water catalyses the glass deterioration it is often suggested to store glass below the DRH of those salts thought to be responsible for the attraction of water to the glass surface. For examples, 42% is the DRH of potassium carbonate, which was thought to be the salt responsible for the formation of moist films on the surface of unstable glass in the British Museum (Organ, 1957). This dissertation has aimed at identification of salts on the surface of unstable glass, as this is crucial in the determination of preferential storage conditions for unstable glass, but hardly any analytical data exists on the nature of salts forming on unstable glass. The wide range of ions found on the surface of unstable glass suggests that a complex mixture of salts could be present. This complicates the matter of finding a specific RH for storage as the DRH of salt mixtures is different than the DRH of the individual salts. However, the dominance of sodium, potassium and formate in the analytical data suggests that either sodium formate or potassium formate are the main salts forming on the surface of unstable glass. The very low DRH of potassium formate (16-17%) suggests that there may not be a RH which prevents the onset of weeping on all objects in a museum collection. It does, however, stress the necessity of identifying those specific objects on which the highly hygroscopic salts form in order to take specific measures to prevent further deterioration of these objects.

7.3.3 Bridging the gap between the scientist and conservator

The literature on historic vessel glass deterioration has focused mainly on two topics: practical guidelines for conservation and analytical research into the chemical and physical mechanisms underlying glass deterioration. Although the latter is often aimed at providing helpful information for the conservation of glass, the scientific data produced in these studies is often not directly beneficial for conservation. This observation is not surprising as the deterioration of glass is a many-facetted problem and understanding it requires extensive study. This leads, however, to a gap between the resultant scientific data and the needs of a conservator for the preservation of glass. Handbooks on glass conservation have tried to merge these two topics (see for example Davison, 2003), but this leads to a summary of scientific research alongside conservation strategies. Scientific research targeting the conservation community is rare and limited to research reports, such as the Leverhulme Research Project 2001-2004 Report (Fearn, 2004) which was intended only for limited circulation. In this way the gap between the scientist and conservator remains wide.

A major goal of this dissertation has been bridge this gap by providing new insights into glass deterioration while catering to the needs of conservators in their responsibility for the preservation of historic glass collections. This goal was achieved by developing methods to which conservators can relate and by interpreting the results in relation to problems glass conservators face in their work. By involving conservators in the development of, for example, sampling methods the analytical results become more meaningful for the conservation practice as they can be related to conservators' experiences of processes occurring on actual museum objects. The next section discusses the relation between analytical outcomes and their implementation in the conservation practice.

7.3.4 Translating analytical results into the conservation practice

Two main conservation problems were tackled in this dissertation. Firstly, the identification of unstable glass objects using analytical techniques was investigated. For the preservation of glass collections it is necessary to identify unstable glass objects, but currently conservators can only assess glass stability based on visual examination of the objects, which is insufficient for the identification of unstable glass objects not showing clear signs of deterioration. This dissertation has made the first steps in the early identification of unstable glass objects based on the presence of ions on the surface of unstable glass. An important future step in the development of an early warning system for unstable glass is the determination of threshold ion concentrations and extension of the collaboration with conservators in order to refine the sampling and analytical methods.

A second conservation problem tackled in this dissertation is the prevention of the formation of moist layers on unstable glass objects. Preventive conservation of glass is an imperative for conservators, but little is known about the parameters which influence the condition of glass objects. It is widely acknowledged that the deterioration of glass is accelerated by the presence of pollutants in the atmosphere (Robinet, 2006). Extensive evidence of the presence of these pollutants on the surface of unstable glass was found, showing a direct link between the condition of the object and the environment in which it is kept. The most important parameter for preventive conservation, however, is the relative humidity in which a glass is kept. Although this is recognised in the conservation community, no definite preferred storage RH has been rigorously formulated. This dissertation has shown that it is unlikely that such a value exists, in particular because often the storage history of objects is unknown. The results suggest that there are two requirements for the implementation of a preferred storage RH to prevent weeping: setting a benchmark condition of the glass objects by removing accumulated surface deposits and ascertaining that there are no extraneous sources of pollutants in the storage environment. That being said, it was observed that residues of formate remained on the surface after cleaning of the very unstable CMOG samples in the artificial ageing research (Chapter 5). It is therefore recommended to investigate the long term effect these compounds can have on the condition of the glass, and the success of removal of undesirable surface deposits during cleaning of unstable glass objects.

7.4 Practical implications

Analytical studies on glass deterioration in museums, limited in number though they are, stem from practical problems of conservators. The aims of these studies often develop into questions of understanding glass deterioration, such as measuring the depletion of sodium from glasses in different atmospheric conditions (Fearn, McPhail, and Oakley, 2005), which are often very hard to relate to the practical problems conservators are facing. This dissertation has attempted to ensure that the results of the analytical studies can be linked directly to the situation in museums. The following discussion concentrates on how the research may be incorporated into conservation practice.

7.4.1 Storage conditions

The problem of safe storage of unstable glass is a central topic in glass conservation. Conservators around the world are searching for the proper storage conditions and materials for their glass collections. The results of this dissertation, supplemented by observations and personal communications with conservators, provide four suggestions for good practice concerning storage of unstable glass.

Firstly, the selection of suitable storage materials is essential in order to prevent deterioration. Materials which off-gass volatile organic compounds can result in damage to glass objects. In a particular instance it was observed that glass stored on a sheet of paper was deteriorating progressively from the bottom upwards and that materials used for the construction of display cases led to the formation of deterioration products on the glass surface (De Corneillan, 2016). It is therefore advised to omit all materials potentially off-gassing volatile compounds from the storage environment. An example of the effectiveness of this approach is Museum Boijmans van Beuningen where all glass objects were removed from wooden cabinets and placed inside metal cabinets. Prior to this change in environment unstable glasses showed deterioration effects, in particular weeping, but after cleaning and five years of storage in metal cabinets no new signs of deterioration occurred. Future monitoring of this collection will provide more long-term information on the effectiveness of this preventive conservation measure.

Secondly, relative humidity control is crucial in the storage of unstable glass. This dissertation has not found a specific RH in which unstable glass will not deteriorate, but observations confirm that it is vital in delaying deterioration phenomena (De Corneillan, 2016). A choice for a suitable RH depends largely on risk assessment: to store glass in a dry environment leads to crizzling, but a moist environment results in the advancement of alteration of the glass structure. It can be argued that crizzling is the more worrisome of the two processes as it results in an irreversible change in appearance and a decrease in the physical strength of the object, whereas the slow formation of a hydrated surface layer possibly in conjugation with the accumulation of moisture on the surface poses a less drastic threat to the integrity of unstable objects. However, the invisible advancement of deterioration processes may ultimately lead to larger problems. As water is the main agent of deterioration of unstable glass a RH higher than 50%, the DRH of the most abundant compound – sodium formate – lies just above this value (Peng and Chan, 2001), would be undesirable. Evidence exists that a moist film forms on unstable glass at this RH (Smith, Carlson and Newman, 1987). It is therefore recommended to store unstable glass at a stable RH in the range of 45-50%, in line with suggestions made by Brill (1975).

Thirdly, it is recommended to clean glass objects regularly and schedule regular condition surveys. This reduces the potential detrimental influence of compounds already present on the surface of unstable glass. Regularly inspecting glasses for signs of deterioration prevents the accumulation of surface deposits and allows for timely changes of the environmental conditions in which the glasses are stored when necessary.

A final suggestion for the storage of unstable glass is to allow air movement inside the storage cabinets. It has been observed that deterioration processes of glass progress more slowly when air movement is allowed (Fearn, 2004; Koob, 2017). Similar observations were made in the artificial ageing experiments described in this dissertation; lower ion concentrations were determined on the surface of those glasses stored outside of desiccators than on the samples stored inside desiccators in the same conditions. This is also related to the prevention of microclimates, for which it is recommended to allow airflow underneath the objects as well, also when the glasses are stored in metal cabinets.

7.4.2 The investigation and monitoring of glass condition

The methodology for the investigation of glass objects described in this dissertation was aimed at providing a novel means of assessing the condition of glass objects. Although the early warning system needs further refinement, analysis of the ion concentration on the surface of glass objects can still be important in the assessment of applied conservation strategies. The investigation of the ion concentrations on the surface of unstable glass is therefore recommended alongside visual inspection. This will provide information on the deterioration rate of the glass objects and complement the visual examination of the condition of glass objects. When it is observed that significant amounts of ions are leached from the glass, further research on that specific object can be carried out in order to avoid the occurrence of dramatic deterioration phenomena. The placement of a reference material, such as a quartz slide or stable piece of borosilicate lab-glass, inside the storage cabinet is recommended as this will provide the opportunity to identify species that are depositing on the glass surface due to factors unrelated to glass deterioration.

When applying the IC protocol it is important to account for some effects that influence the outcomes of the analyses. It has been demonstrated that the sample location is crucial: samples taken from the bottom, foot, outside of the main body or inside of the main body may yield significantly different ion concentrations. In order to be able to compare the analytical results between objects it is suggested that several samples be taken from the outside of the main body of the objects, where the sampling surface is easily accessible and the influence of microclimates is as minimal as possible. Although the RSD of the samples is still high in some cases, this has proven to be the best method to make inter-object comparisons.

7.4.3 Exposing glass deterioration in museum collections

This dissertation has focused particularly on the deterioration of vessel glasses. However, there are many more instances where glass is incorporated in museum objects. Limoges enamels from the first quarter of the 16th century are notorious for their chemical instability (Smith, Carlson and Newman, 1987), deterioration of cover glasses on early photographs is a serious problem (Barger, Smith and White, 1989), cover glasses of miniature paintings may be unstable (Beiner-Büth, 2015), deterioration of glass may lead to the formation of exotic metal corrosion products (Eggert, 2010; Eggert et al., 2008, 2010, 2011) and, even in paintings, glass deterioration occurs with the pigment smalt (Robinet et al., 2011).

When questions of glass stability arise in other instances than on vessel glass, the research described in this dissertation is also relevant. The advantage of the method developed in this dissertation is that it is easily applicable to the above-mentioned objects and may provide important information for their conservation.

7.5 Recommendations for future research

The outcomes of this dissertation invite further research on glass deterioration. It is suggested to continue research in four directions.

Firstly, it is recommended to extend the experimental work on replica glasses. This is of particular importance to investigate the origin and amount of cations on the surface of unstable glass. There are many parameters affecting the deposition of cations on the surface of unstable glass, and it has not been possible to investigate those parameters within the framework of this PhD project. In particular the relation between the glass composition and the release of ions from the glass structure should be investigated further. Subsequently, it is relevant to investigate if and how ion release changes with progressive glass alteration. Hench and Clark (1978) and Hench (1982) identified six types of chemical glass surface structures, of which two progressively deteriorate in unfavourable conditions and three inhibit the progression of glass alteration after an initial formation of an altered surface layer. Therefore, the chemical structure of the glass surface affects the release of ions from the glass structure and thus the release rate of ions might change when glass deterioration progresses. Long-term experiments should be designed to investigate the rate of ion depletion from the glass structure over time, for example through SIMS depth profiling, and compare this to the amount of ions detected on the glass surface.

In particular, the amount of ions that are leached from the glass structure should be directly related to the amount of the same ion found on the surface of the glass. This is particularly relevant for the determination of the depletion rate of ions from the glass structure, which is a crucial parameter in determining threshold values for assessing the deterioration of glass objects. Some research has been carried out on determining the depletion rate of sodium from replica glasses (Fearn, McPhail and Oakley, 2004; Fearn et al., 2006b) and it was suggested that the depletion depth followed a $t^{0.5}$ behaviour. The amount of ions found on the glass surface largely depends on the composition of the glass and the environment in which the glass is kept. Therefore, before an early warning system can be fully established it will be important to get more insight into the relationship between the amount of leached ions and the amount of ions actually detected on the glass surface. Related to this, the nature of cations found on the surface of unstable glass remains a topic in need of investigation. The main cations found in this study are sodium and potassium.   Other studies have suggested the leaching of calcium as well (Fearn, McPhail and Oakley, 2004, 2005; McPhail, 2006), but this has not been observed in the IC data. Brill (1975) reported that calcium contents in the altered layer are unaffected by leaching processes. A final important aspect in the suggestions for future research on the development of an early warning system for unstable glass is the necessity to be able to determine the stability of glass using other methods than IC or visual examination. The corroboration of the IC-assessment of glass stability by means of another analytical technique is a desirable feature for future research.

Secondly, it is important to expand the sample database of museum objects and include another method of assessing glass stability, besides visual inspection and IC analysis. The observations made in this dissertation provide confidence in the applied method, but for the development of an early warning system the incorporation of more data to the existing datasets is essential to improve statistical analysis. The implementation of a technique to assess glass stability might be problematic for museum objects due to potential need for destructive analysis, but is essential as a feedback mechanisms for determination of glass stability when interpreting the IC results.

Thirdly, it is proposed to further investigate the effect of atmospheric molecules, such as carbonyl pollutants (e.g. acetic acid, formic acid or formaldehyde), on the deterioration of glass and the modes of formation of salts on unstable glass surfaces. Although in many cases it is evident that formate salts form on the surface of unstable glass objects, the role of other anions, such as carbonate and acetate, remains unclear. The chemistry of formation of salts on the surface of unstable glasses and the precise identity of salts which form on crystallisation of ionic solutions is now worthy of further investigation. For example, the results presented in this dissertation suggest that there is a relationship between the amount of carbonate and the amounts of acetate and formate. It can be argued that when carbonate is detected, little acetate or formate is detected and vice versa. This is an important topic as the determination of the preferential storage conditions depends on the identity of compounds found on the surface of unstable glasses;

future research is now timely as a result of this dissertation. Additionally, the conditions in which certain salts form on unstable glasses require more research. It has, for example, been suggested that the presence of formate and acetate on unstable mosaic glass is a result of parts per billion concentrations of ambient acetic and formic acid (Tennent and Carthy, 2016), which could be essential in the determination of preferential storage conditions for unstable glass.

Fourthly, the further investigation of the homogeneity of the deposits of ionic compounds on the surface of unstable glass is recommended. Currently, no research has assessed the way in which droplets or moist films agglomerate on the surface of unstable glass. Although the analytical protocol in this study provides confidence in the quantification of ions from the sampled surface, it is advised to extend the validation of the protocol to investigate the potential differences in the amount of ions present on different locations of the same unstable glass surface. We don't know if the deterioration of the glass itself is an inhomogeneous process, but the accumulation of ions might be increased on specific places, for example due to the formation of droplets in different sizes.

The pursuance of these research lines will certainly advance understanding of historic glass deterioration mechanisms, aid conservators in identifying glass deterioration in an early stage and form a framework for the development of improved storage guidelines for unstable glass.

7.6 References

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