ACCOUNTS
of chemical research

Degradation of Glass Artifacts: Application of Modern Surface Analytical Techniques

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RECEIVED ON JULY 11, 2009

CONSPECTUS

A detailed understanding of the stability of glasses toward liquid or atmospheric attack is of considerable importance for preserving numerous objects of our cultural heritage. Glasses produced in the ancient periods (Egyptian, Greek, or Roman glasses), as well as modern glass, can be classified as soda−lime−silica glasses. In contrast, potash was used as a flux in medieval Northern Europe for the production of window panes for churches and cathedrals. The particular chemical composition of these potash−lime−silica glasses (low in silica and rich in alkali and alkaline earth components), in combination with increased levels of acidifying gases (such as SO_2, CO_2, NO_x, or O_3) and airborne particulate matter in today's urban or industrial atmospheres, has resulted in severe degradation of important cultural relics, particularly over the last century.

Rapid developments in the fields of microelectronics and computer sciences, however, have contributed to the development of a variety of nondestructive, surface analytical techniques for the scientific investigation and material characterization of these unique and valuable objects. These methods include scanning electron microscopy in combination with energy- or wavelength-dispersive spectrometry (SEM/EDX or SEM/WDX), secondary ion mass spectrometry (SIMS), and atomic force microscopy (AFM). In this Account, we address glass analysis and weathering mechanisms, exploring the possibilities (and limitations) of modern analytical techniques.

Corrosion by liquid substances is well investigated in the glass literature. In a tremendous number of case studies, the basic reaction between aqueous solutions and the glass surfaces was identified as an ion-exchange reaction between hydrogen-bearing species of the attacking liquid and the alkali and alkaline earth ions in the glass, causing a depletion of the latter in the outermost surface layers. Although mechanistic analogies to liquid corrosion are obvious, atmospheric attack on glass ("weathering") is much more complex due to the multiphase system (atmosphere, water film, glass surface, and bulk glass) and added complexities (such as relative humidity and atmospheric pollutant concentration). Weathered medieval stained glass objects, as well as artifacts under controlled museum conditions, typically have less transparent or translucent surfaces, often with a thick weathering crust on top, consisting of sulfates of the glass constituents K, Ca, Na, or Mg.

In this Account, we try to answer questions about glass analysis and weathering in three main categories. (i) Which chemical reactions are involved in the weathering of glass surfaces? (ii) Which internal factors (such as the glass composition or surface properties) play a dominant role for the weathering process? Can certain environmental or climatic factors be identified as more harmful for glasses than others? Is it possible to set up a quantitative relationship or at least an approximation between the degree of weathering and the factors described above? (iii) What are the consequences for the restoration and conservation strategies of endangered glass objects? How can a severe threat to precious glass objects be avoided, or at least minimized, to preserve these artifacts of our cultural heritage for future generations?

10.1021/ar9002009

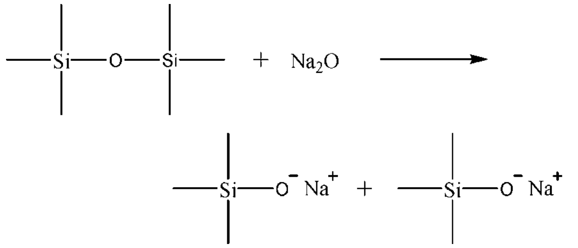
1. Introduction

Although questions concerning the stability and durability of glasses have a history of more than 300 years,[1] this topic is still of great importance for objects of our cultural heritage. To make this obvious, we should have a brief look at the evolution of glass production:[2] While the first man-made glasses were of rather poor quality and were core-formed (a heated mixture of sand (SiO_2), natron (Na_2CO_3), and lime ($CaCO_3$) was wound around a core of clay and dung and formed until it reached its final state when the core was pointed out), the invention of glass blowing (glass pipe) in the second or first century BC made hollow glasses available for a reasonable price and for everyday use as, for example, storage vessels or vases. After the decline of the West-Roman Empire in the fifth century AD mainly less artful glass objects were produced in Europe and the knowledge of the complex ancient glassmaking techniques seemed to be lost until about 1000 AD, when brilliantly colored glasses for windows in churches and cathedrals (for example, St. Denis or Chartres in France) were produced in the Northern part of Europe. These Medieval window panes, often depicting Bible stories, typically consist of numerous smaller glass panels held in their place by lead strips. In contrast to glasses produced in the Mediterranean region, where soda was available as a flux, wood ashes (potash, mainly consisting of K_2CO_3) were added to sand in considerable amounts in order to decrease the melting temperature of the glass batch. The resulting so-called potash glasses became characteristic for Europe north of the Alps. Unfortunately, such glass objects suffer from a poor durability, which, in addition to increased levels of many kinds of air pollutants, causes many of these medieval stained glass objects to perish at present.

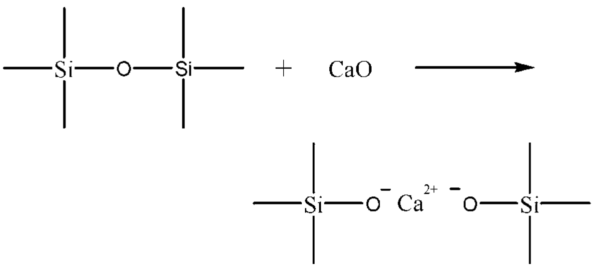
To begin with, we may define the general term *corrosion* as the deterioration of a (glass) material caused by external (e.g., environmental conditions or climatic parameters) or internal factors (e.g., specific chemical composition) leading to a more or less complete loss of its aesthetics, functionality, structure or shape. The *weathering* of glass, which comprises the degradation of glass by atmospheric pollutants, such as acidifying gases (SO_2 or CO_2) or airborne particulate matter, can then be seen as a special type of corrosion and is therefore often referred to as *atmospheric corrosion*. To simplify matters, the term "weathering" will be used synonymously for atmospheric corrosion, while "corrosion" will refer to the attack of liquid substances, such as water, acids, or bases, onto the glass (surface) throughout this Account.

2. Glass: Its Structure and Corrosion Mechanisms

Understanding the physical and chemical phenomena occurring during the aqueous or atmospheric attack onto glass surfaces requires basic knowledge of the structure of silicate glasses. In the 1930s, W. H. Zachariasen[3] developed a structural model for oxide glasses in his famous publication *The Atomic Arrangement in Glass*. He assumed that the linking forces between the atoms in the crystalline substance and in amorphous (noncrystalline) glasses of the same composition are similar and the major difference between them is the absence (glass) or presence (crystal) of periodicity and symmetry in the atomic network. While in the crystalline structure each oxygen atom forms a bridge in the SiO_4 tetrahedra with fixed and defined distances between neighboring silicon atoms, in amorphous silica bonding angles and lengths between O and Si show a more or less wide distribution. Based on geometric considerations, glasses of the formula A_xM_yO basically form a three-dimensional network consisting of cations of type A (the so-called network-forming cations, in the case of silicate glasses type A corresponds to Si^{4+} species), while unbalanced vacancies are "filled" by atoms of type M. For a minimum repulsion between cations of both types, these M ions (so-called network modifiers) must be large and may carry only a small charge, such as Na^+, K^+, Ca^{2+}, or Ba^{2+}. Hence, the introduction of network modifiers into the glass structure breaks up and widens the silicate network and leads to the formation of terminal $-Si-O-M$ groups in the case of the monovalent ions ($M = Na^+$ or K^+, eq 1) or bridging $-Si-O-M-O-Si-$ groups for the bivalent species ($M = Ca^{2+}$ or Mg^{2+}, eq 2). Also, another type of oxygen atom is created, so-called nonbridging oxygen (NBO) atoms, which do not form a bridge between two SiO_4 tetrahedra (Figure 1). As will become obvious, the nature and concentration of these network modifiers in the glass play an important role for the durability of glasses.[4]



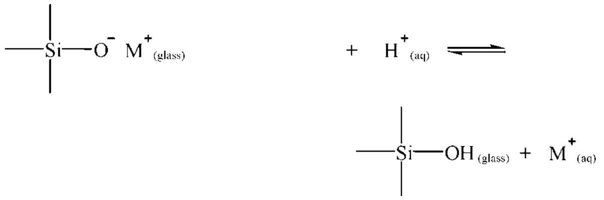
$$-Si-O-Si- + Na_2O \longrightarrow -Si-O^- Na^+ + -Si-O^- Na^+ \quad (1)$$



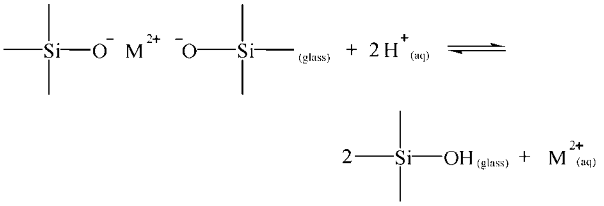
$$-Si-O-Si- + CaO \longrightarrow -Si-O^- Ca^{2+} {}^-O-Si- \quad (2)$$

One of the first systematic investigations on the chemical mechanisms involved in the aqueous corrosion of glasses was published by Douglas and Isard in 1949,[5] who performed leaching experiments on a soda−lime−silica glass (70 wt %

SiO_2, 17 wt % Na_2O, 5.4 wt % CaO, and others) in a temperature range between 20 and 100 °C. They found a linear relationship between the amount of leached sodium ions and the square root of reaction time as characteristic for a diffusion-controlled reaction and proposed the mechanisms in the eqs 3a and 3b. This model is characterized by ion-exchange processes between mono- and bivalent network-modifier ions in the glass (e.g., Na^+, K^+, Ca^{2+}, or Mg^{2+}) on the one hand and hydrogen-bearing species (such as, H^+, H_3O^+, molecular water, or even larger aggregates) of the attacking medium on the other hand. Consequently, the glass (surface) is depleted in alkali and often also alkaline earth ions leading to the formation of a so-called *leached layer* or *hydrated layer*, while the silicate network remains essentially intact ("selective leaching"). The thickness of this depletion layer, the rate of its formation, and hence the degree of glass deterioration depend on numerous factors, such as the glass composition, the properties of the corroding liquid, and the temperature and time of exposure.[6]



$$-\mathrm{Si}-\mathrm{O}^- \mathrm{M}^+_{(glass)} + \mathrm{H}^+_{(aq)} \rightleftharpoons -\mathrm{Si}-\mathrm{OH}_{(glass)} + \mathrm{M}^+_{(aq)} \quad (3a)$$



$$-\mathrm{Si}-\mathrm{O}^- \mathrm{M}^{2+}\ {}^-\mathrm{O}-\mathrm{Si}-_{(glass)} + 2\,\mathrm{H}^+_{(aq)} \rightleftharpoons 2\,-\mathrm{Si}-\mathrm{OH}_{(glass)} + \mathrm{M}^{2+}_{(aq)} \quad (3b)$$

Interestingly, a similar mechanism was also found for the removal of sodium by the reaction with gaseous SO_2, which lead to the formation of Na_2SO_4 deposits on the glass surface. Hence a mechanistic analogy between the aqueous corrosion and the atmospheric weathering process can be assumed.

While alkali and alkaline earth removal by ion exchange is dominant in neutral and acidic environments up to a pH of approximately 9, the reaction between water and glass follows essentially eq 4 in high alkaline media: hydroxyl ions attack the silica network Si—O—Si bonds and form Si—OH (silanol) groups. This second mechanism is also observed for longer reaction times in originally neutral or acidic media due to a consumption of protons in the corrosive medium according to eqs 3a and 3b. In contrast to the ion-exchange mechanism, this network dissolution reaction is characterized by a congruent dissolution of the glass, meaning that the molar ratios of the glass constituents passing into solution per unit time are approximately equal to those of the initial glass.[7,8]

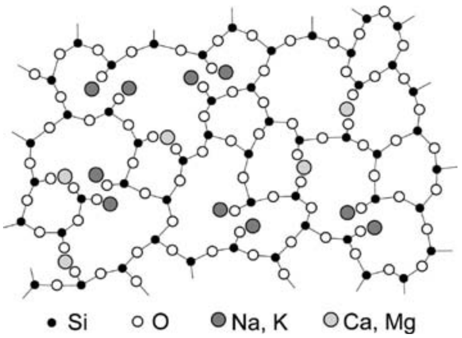
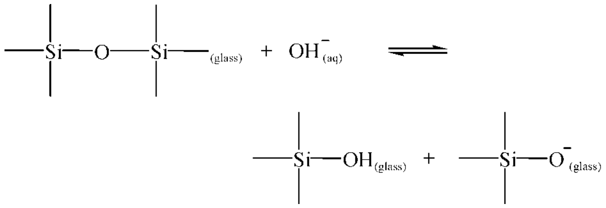


FIGURE 1. Silicate structure widened by the introduction of mono- and bivalent network modifier ions such as Na^+, K^+, Ca^{2+}, or Mg^{2+} in the silicate network creating nonbridging oxygen (NBO) atoms.



$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-_{(glass)} + \mathrm{OH}^-_{(aq)} \rightleftharpoons -\mathrm{Si}-\mathrm{OH}_{(glass)} + -\mathrm{Si}-\mathrm{O}^-_{(glass)} \quad (4)$$

Outstanding contributions to the theoretical background of glass corrosion were made mainly in the 1960s and 1970s by Boksay et al.[9] and Doremus,[10,11] who explained the release of alkali ions due to interdiffusion on the basis of Fick's law. In a simpler version, Douglas and El-Shamy[12] suggested a model equation containing a square-root term (describing the diffusion process), as well as a linear network dissolution term (eq 5):

$$Q = a\sqrt{t} + bt \qquad (5)$$

where Q stands for the amount of alkali ions extracted, t stands for the reaction time and a and b stand for model constants, which are functions of the experimental conditions. Experimental evidence for this model of glass corrosion is huge, and consistent results were derived for a large number of different glass compositions and reaction conditions.[13,14]

The influence of the glass composition and the concentration and nature of the modifying cations on the chemical durability of glasses in the system $K_2O-CaO-MgO-SiO_2$ in water and hydrochloric acid showed that replacing the network former SiO_2 by CaO (or MgO) increases the amount of Ca, Mg, and K passing into solution. Particularly a significant drop of the chemical resistance of the glasses was observed as the silica content decreases below 66 mol %. This can be explained by the fact that above this threshold, the nonbridging $Si-O^-$ sites are isolated by bridging Si—O—Si groups in the glass network and no interconnecting path of neighboring nonbridging oxygen sites exists for a rapid movement of the alkali ions. Notably, potash-based silica glasses were found to be attacked at twice the rate for soda glasses of equivalent composition. In principle, the same poor durability is observed for numerous medieval stained window glasses, which often exhibit silica contents as low as 50 mol % and high concentrations of CaO and K_2O.[15]

As mentioned previously, also the concentration of the attacking liquid may influence the rate of glass dissolution. According to eqs 3a and 3b, an increased rate of alkali extraction is expected in acidic regimes compared with neutral or basic environments. Morphologically glasses leached in acidic/neutral or basic solutions can easily be distinguished in the scanning electron microscope. While the glass surface may show hardly any visual damage when leached in acidic media, the alkaline attack generally produces a severe damage with cracks and detaching pieces on the glass surface.[16] Leaching studies performed on potash−lime−silica as well as soda−lime−silica glasses demonstrated that the alkali and alkaline earth extraction rates also depend on the nature of the acid used, being least in H_2SO_4 and almost equal in HCl and HNO_3.[17,18]

3. Surface Analytical Techniques Applied for the Studies

While up to the middle of the 20th century scientific examinations of the glass degradation processes were carried out using wet chemical analyses requiring sampling of the precious objects, nowadays so-called nondestructive or even noninvasive physical or chemical methods can be applied. Therefore, a short description of the principles of the techniques used for the case studies presented within this Account seems to be appropriate.

3.1. Electron Probe X-ray Microanalysis (EPXMA or SEM/EDX, SEM/WDX). The invention of the electron microscope by Ruska in 1931[19] and the electron microprobe (EMP) by Raymond Castaing in the middle of the last century[20] had a significant impact on all fields of materials science including archaeometric studies.[21,22] The EMP (or synonymously SEM/EDX or SEM/WDX) combines the advantages of simultaneous imaging and analyzing of microdomains of a (glass) sample.[23,24] Its analyzing principle is based on the interaction of a finely focused electron beam emitted by a heated tungsten wire and subsequent detection of the emerging signals produced by elastic and inelastic processes in the material. For example, the detection of the so-called backscattered electrons (BE) as a function of the position of the electron beam on the sample surface yields an image depicting contrasts between regions dominated by low-*Z* and those of high-*Z* elements. Therefore, BE-images enable the characterization of inhomogeneities such as depletions or enrichments of certain elements in the surface domains of weathered or corroded glasses. On the other hand, secondary electrons (SE), which are the result of inelastic scattering processes of the incident electron beam and sample matter, allow for topographical and morphological imaging of the sample surface similar to a light microscope, but with a much better lateral resolution. SE-images can therefore be used for characterizing the morphology of weathering products formed as well as of the glass surfaces attached. Finally, the incident primary electrons also cause ionization of the inner shells of sample atoms resulting in the emission of so-called characteristic X-rays. This secondary radiation, detected either by an energy-dispersive (ED) or wavelength-dispersive (WD) spectrometer, yields a characteristic spectrum from selected microdomains of the specimen enabling rapid qualitative and quantitative analysis and elemental distribution images. A major drawback of measurements in the scanning electron microscope in combination with either EDX or WDX detection is the limited volume of the sample chamber and consequently only small objects such as glass fragments can be analyzed without sampling. SEM investigations presented within this Account were performed on a JEOL JSM-6400 scanning electron microscope equipped with an EDAX Phoenix (EDAX Inc., Mahwah, NJ) energy-dispersive spectrometer.

3.2. Secondary Ion Mass Spectrometry (SIMS). SIMS is based on the bombardment of a sample surface with a high-energy ion beam of, for example, Ar^+, Ga^+, O^{2+}, Cs^+, or O^- and the subsequent detection of the eroded material ions accelerated into a mass spectrometer. This technique is especially suitable for measurements of depth profiles of certain elements/masses (e.g., detection of hydrogen, alkali, or alkaline earth ions in corroded or weathered glasses[25,26]). Outstanding features of SIMS are the capability of detecting all elements of the periodic table and the very low detection limits in the nanogram per gram region. Excellent reviews of the application of SIMS in the field of cultural heritage are given in refs 27 and 28.

SIMS results presented in this paper were achieved using a time-of-flight (TOF)-SIMS (ION-TOF GmbH, Münster, Germany) equipped with a Bi^+ LMIG (liquid metal ion gun) at an energy of 25 keV. For depth profiling, two ion beams operate in the dual beam mode: The first beam (Bi^+) generates the secondary ions (100×100 μm^2 area), which are analyzed in a time-of-flight mass analyzer (Figure 2). During the flight time,

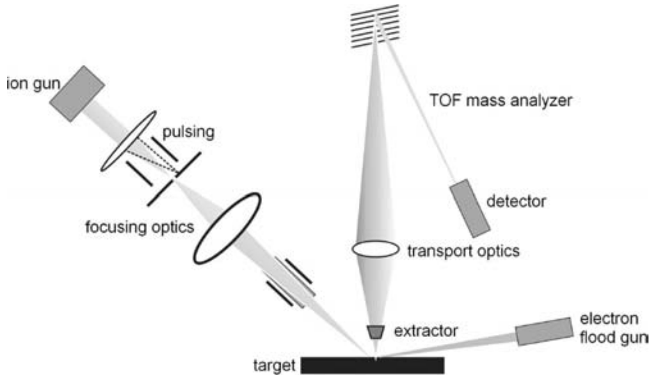


FIGURE 2. Scheme of the experimental setup for the TOF-SIMS investigations consisting of the ion gun, the glass target, and the time-of-flight (TOF) analyzer as main components. For electrically nonconducting materials such as glass, an electron flood gun is used in order to avoid charging effects.

the second beam from a O_2^+ electron impact ionization source (energy 2 keV) for positive secondary ion detection erodes a crater on the sample surface, in this case 300 × 300 μm^2.[29,30] Because glass is an electrically nonconducting material and charging effects can occur during the ion bombardment, sputtering, and secondary ion extraction, an electron flood gun is used to avoid these effects.

3.3. Atomic Force Microscopy (AFM). Since their invention in the mid-1980s, scanning probe microscopy (SPM) techniques and in particular AFM have gained high importance especially for in situ investigations of weathered glasses.[31,32] The principle of SPM techniques is based on scanning a fine tip over a microdomain (typically in the micrometer region) of the specimen and recording the measured signal as a function of its lateral position. In the case of AFM, the deviation of the tip following the surface topography is measured by laser beam deflection and detected with a photodiode. The major advantage of AFM is the possibility of in situ measurements: The topography of glasses can be studied as a function of exposure conditions (varying levels of relative humidity (RH), gaseous pollutants such as SO_2 or NO_2, or even liquids).[33,34] Unfortunately, AFM cannot yield any chemical information about the surface investigated, and its application is limited to the observation of the *initial* stages of (glass) corrosion and weathering as long as the difference in height between the glass surface and the corrosion products formed does not exceed some hundreds of nanometers.

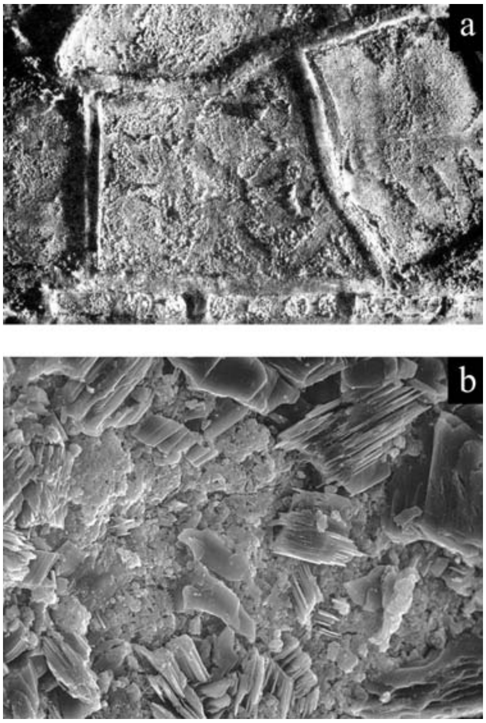


FIGURE 4. Surface of a naturally weathered medieval glass (a) seen in the SEM (b) at a magnification of 1000×.

For the present investigations, an AFM setup as shown in Figure 3 was used. It mainly consists of a NanoScope III system (Digital Instruments, Santa Barbara, CA) equipped with a weathering system enabling examinations of the glass weathering process in situ under (moist) air or atmospheres containing acidifying gases such as CO_2, SO_2, or NO_2.

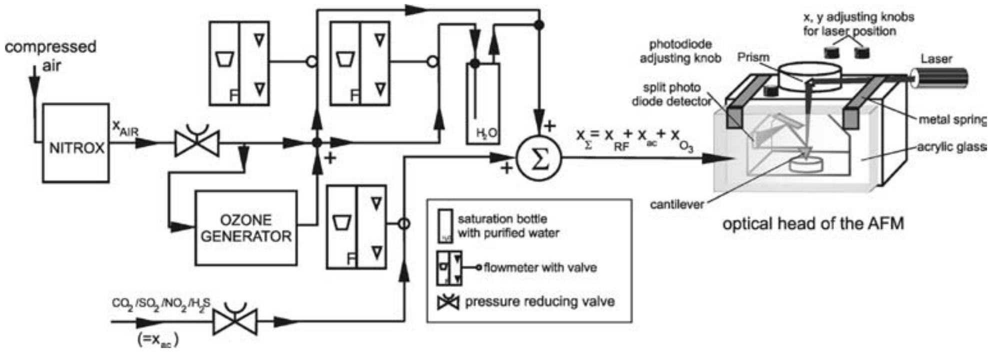


FIGURE 3. Scheme of the experimental setup for in situ AFM investigations depicting the weathering system and the optical head of the AFM as main components.

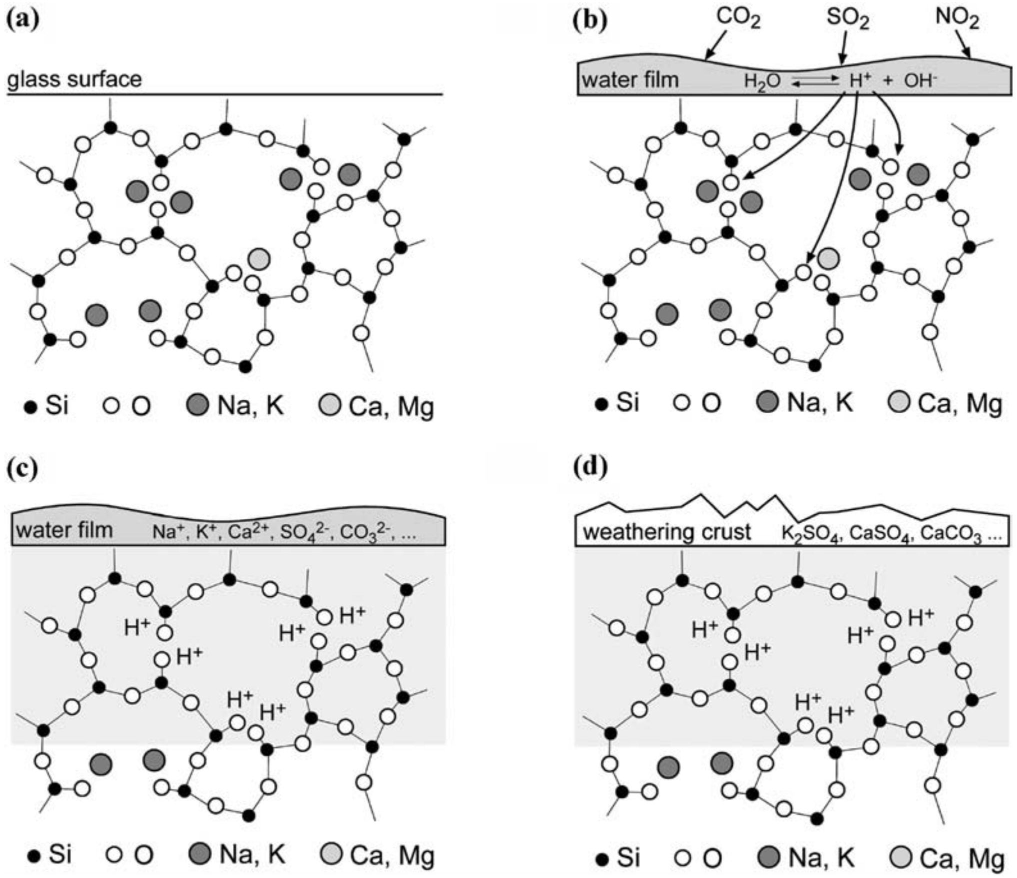


FIGURE 5. Simplified scheme of the glass weathering process starting with a clean and unweathered surface (a). A water film is formed under ambient conditions enabling ion exchange between hydrogen-bearing species and glass constituents, which may further be enhanced by the absorption of acidifying gases (b). A leached layer containing hydrogen is formed (c). Crystalline weathering products finally remain on the glass surface after the evaporation of the water film (d).

4. The Weathering of Medieval Stained Glass Artifacts

4.1. Surface Analytical Investigations of Naturally and Artificially Weathered Glasses. The surfaces of medieval stained glass objects weathered under natural conditions are shown in Figure 4. Usually, a weathering crust consisting of plate-like crystalline weathering products (mainly syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ or gypsum $CaSO_4 \cdot 2H_2O$) and amorphous hydrated silica can be seen. Because the glass itself has a low content of sulfur, these weathering products can only be formed by reactions of the glass constituents (K, Ca) with SO_2 of the ambient atmosphere.[35]

Figure 5 presents a simplified scheme for the physical and chemical processes of the atmospheric weathering of glass surfaces. Under typical ambient conditions, a thin water layer is formed on the glass surface as a result of the condensation of air moisture or by rain causing an ion exchange between hydrogen-bearing species from the water film and the network modifier ions of the glass similar to the aqueous corrosion of glasses. Atmospheric pollutants such as SO_2, CO_2, or O_3 or airborne particulates can dissolve in this water film causing a decrease of its pH and hence an enhancement of the ion diffusion. Increasing temperatures (or a decreasing humidity) may cause evaporation of this film and precipitation of crystalline weathering products on the glass surface. The chemical composition of these weathering products is therefore determined by the glass composition and the atmospheric pollutants.[36,37]

Valuable information on the weathering process can be gained by analytical investigations of the weathering crusts formed on the glass surfaces. Therefore, exposures of two types of potash—lime—silica glass (glass M1, 48.0 wt % SiO_2, 25.5 wt % K_2O, 15.0 wt % CaO, 4.0 wt % P_2O_5, 3.0 wt % MgO, 3.0 wt % Na_2O, 1.5 wt % Al_2O_3, and glass M3, 60.0 wt % SiO_2, 15.0 wt % K_2O, and 25.0 wt % CaO) for periods of 6—72 months at more than 30 European and North American test sites were carried out within the ICP-Materials/UNECE project (International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments within the United Nations Economic Commission for

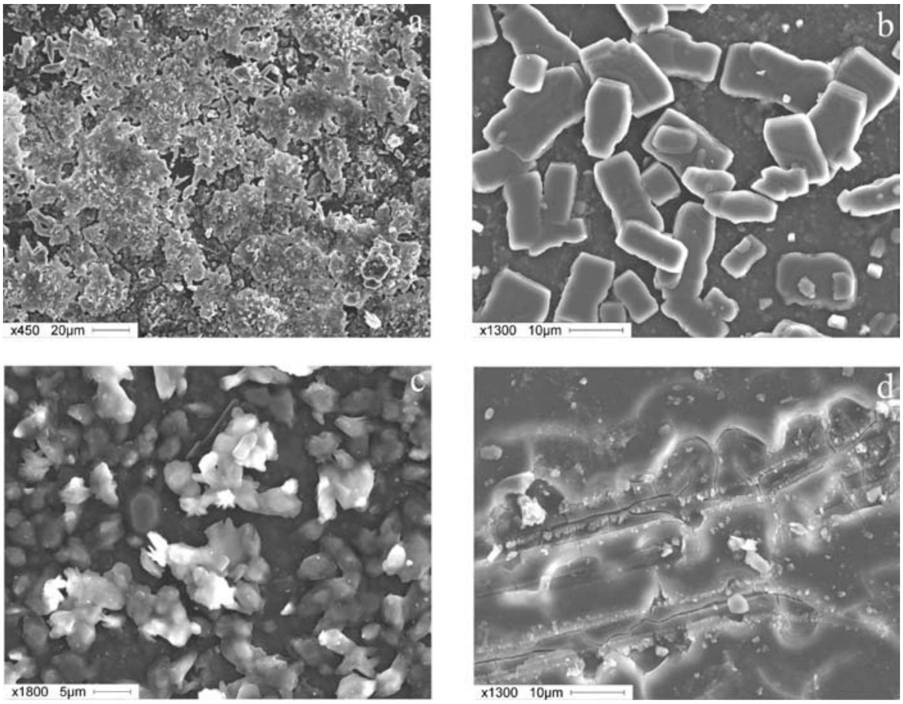


FIGURE 6. SE-images of weathering phenomena on glasses of type M1 after 6 or 12 months of exposure to ambient conditions: weathering crust covering large parts of the surface (a), rectangular-shaped crystalline weathering products (sized approximately 10 μm) consisting of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) (b), increased glass surface roughness (c) and a broken glass surface layer (d).

Europe[38]), dealing with the long-term behavior of various materials of our cultural heritage, such as medieval and modern glass, zinc, bronze, steel, copper, and limestone. SEM/EDX investigations of the weathering products formed during this exposure program revealed that these products mainly consist of K, Ca, and S (Figures 6 and 7). Complementary mea-

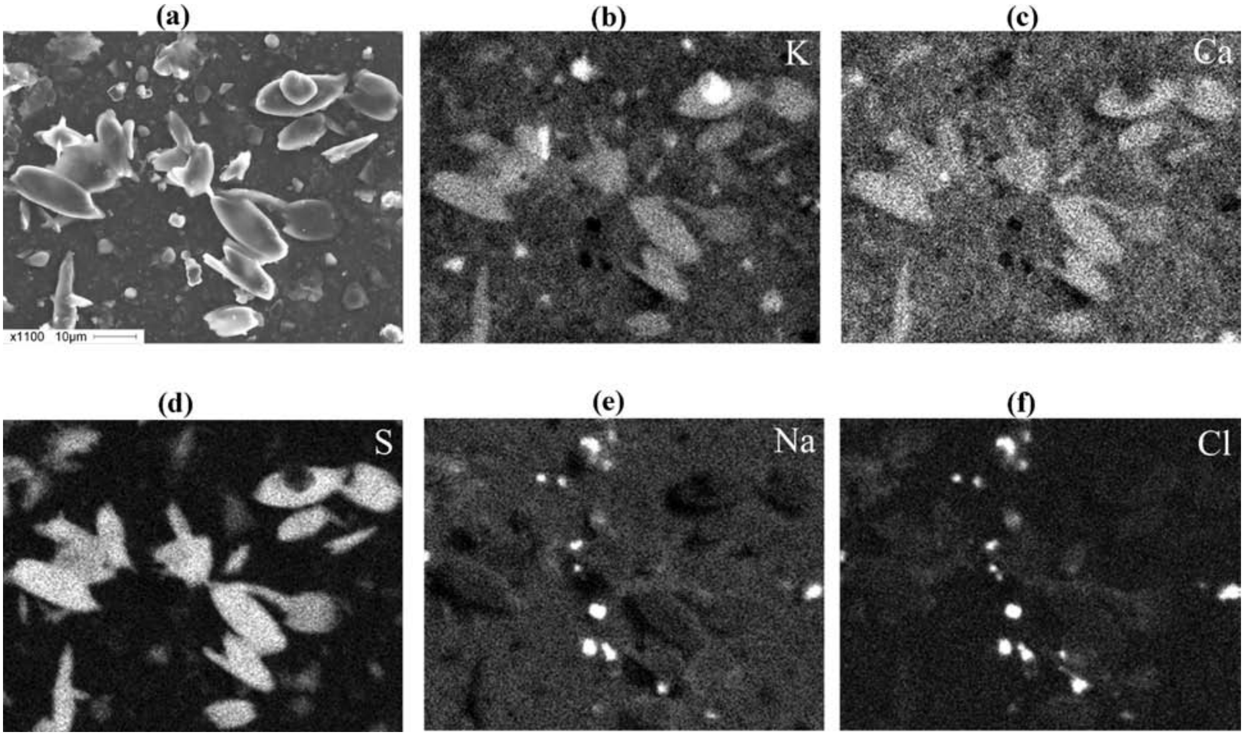


FIGURE 7. SE-image and X-ray mappings of weathering products formed on glass M1 after 12 months of weathering showing the formation of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$). Furthermore, enrichments of K, probably originating from an organic K-compound and the deposition of NaCl particles can be observed, because the sample was exposed in the city center of Athens, Greece, close to the sea.

surements using X-ray diffraction (XRD) showed that mainly syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and, to a much lower extent, also arcanite (K_2SO_4) were present in the weathering crust. The sizes and morphologies of these weathering products show great variations: from 1 to >100 μm and needle-shaped, cubic, rectangular, hexagonal, or shapeless, respectively. Glasses of composition M1 were attacked at a much higher degree due to their higher concentration of network modifier ions and exhibited deep cracks and detached parts of hydrated glass material in some cases.[39,40]

Similar results are also reported by Munier et al.[41] for potash–lime–silica glass, as well as mixed alkali soda–potash–silica glass, which were exposed for times up to 12 months in the polluted urban atmosphere of Paris. Simultaneous measurements of the concentrations of pollutants should enable a correlation with the chemistry of the weathering products. Generally, the formation of sulfates was favored by high contents of SO_2 in the ambient atmosphere and higher humidity. The important role of SO_2 in glass weathering was also demonstrated by investigations of historical glasses from the Cathedral of León, Spain, which were removed during restoration works in the 19th century and stored in the meantime. Interestingly, the weathering crusts consisted mainly of carbonates,[42] which are assumed to be an intermediate product in the degradation mechanism. However, Weigel[43] demonstrated that these carbonates are converted to sulfates as soon as SO_2 is present in the weathering atmosphere.

As mentioned before, also the deposition and reactions of airborne particulate matter onto glass surfaces has to be considered in glass deterioration assessment. In a study on the influence of particulate matter in combination with SO_2 and humidity on the weathering process of potash–lime–silica glass of composition M1 by means of SEM/EDX[44] in the framework of the MULTI-ASSESS project (Model for multipollutant impact and assessment of threshold levels for cultural heritage, project number EVK4-CT-2001-00044[45]) a significantly higher degree of glass deterioration could be observed on samples treated with atmospheric dust in comparison to reference specimens without particulates (Figure 8). Again, the dominant weathering products were syngenite and gypsum. Of special importance was the observation that the weathering rate of dust-treated glass samples was approximately the same when exposed at 50% relative humidity compared with 70% or 100%, whereas for exposures without particulates significantly fewer and smaller weathering products have formed at the lower RH-level. This effect is probably due to the presence of deliquescent constituents in the dust and may be further evidence for the risk potential of dusty urban atmospheres for historical glasses.

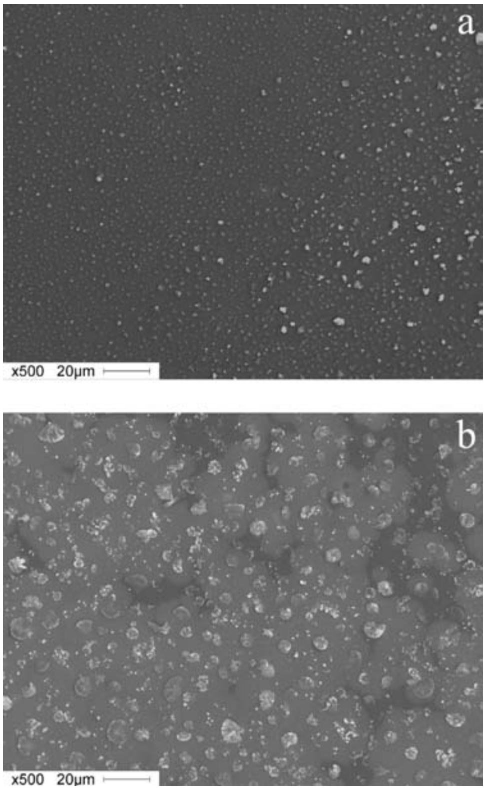


FIGURE 8. SE-images of weathered glass surfaces after 250 h of exposure (glass composition M1, 100% RH, no SO_2) without (a) and with (b) atmospheric dust. A significantly higher degree of weathering and larger weathering products can be observed in the latter case.

Investigations concerning the initial stages of the glass weathering process were carried out using AFM, SIMS, and SEM/EDX[33,46,47] for potash–lime–silica glasses of composition M1. While the glass surface remained unaltered under an inert atmosphere of N_2 for exposure times of more than 1 h, the application of a humid N_2 atmosphere (50% RH) lead to the formation of hydrated and swollen glass material sized approximately 100–200 nm within minutes. Additions of SO_2, NO_2 or both to the humid gas stream showed secondary crystalline phases as additional weathering products, which completely cover the glass surface after typically some 10 h (Figure 9).

Figure 10 depicts the depth distributions of K, Ca, and H in polished model glass M3 (60 wt % SiO_2, 25 wt % CaO, and 15 wt % K_2O). The leached layer, where the mono- and bivalent modifier ions are depleted and hydrogen is incorporated into the silicate structure, can be clearly seen. In comparison to Figure 10, Figure 11 shows the results of leaching experi-

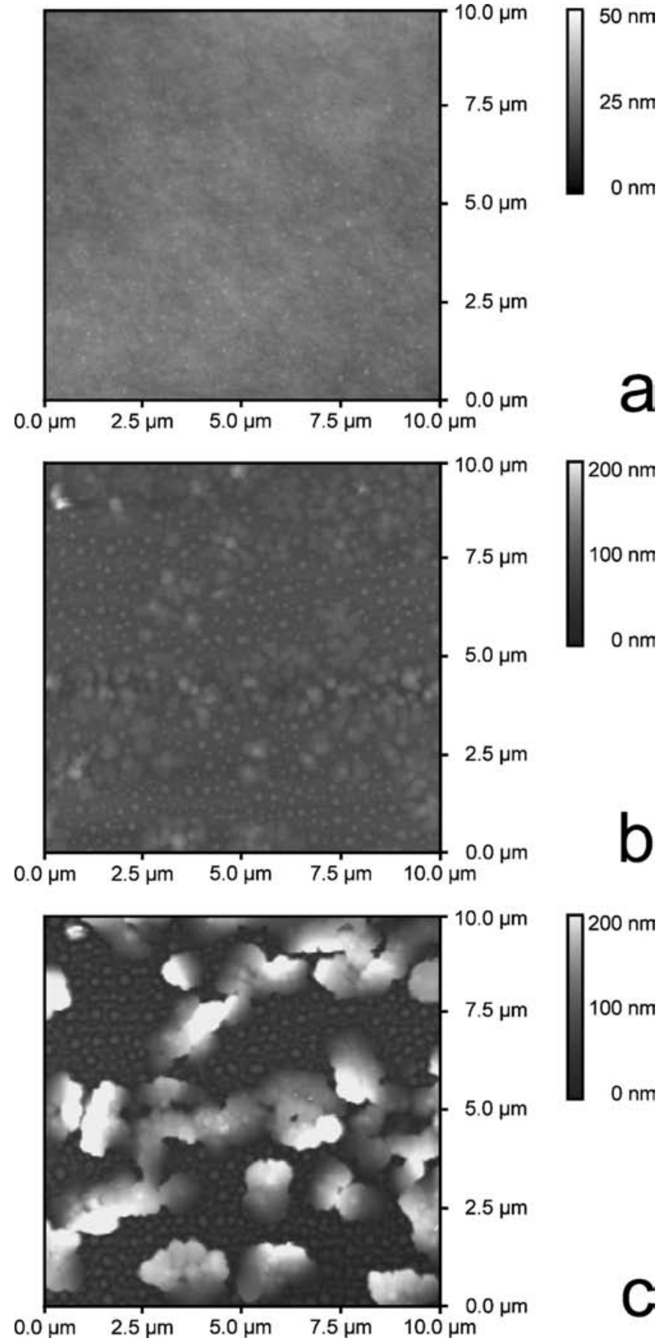


FIGURE 9. AFM images depicting a sketch (10×10 μm^2) of a cleaved glass surface (glass composition M1) under dry nitrogen (image a) and after exposure to humid (RH = 50%) N_2 stream containing 1 ppm SO_2 (images b and c after $t = 14$ and 401 min of exposure, respectively). Within minutes, two kinds of features can be observed: swollen glass material sized in the submicrometer range, as well as crystalline-like features covering large parts of the surface after approximately 6 h of exposure.

ments of glass M3 in 10^{-3} N HNO_3 for 30, 60, and 90 min, which leads to an increase of the thicknesses of the leached layers.

4.2. Quantification of Glass Weathering. A final important question concerns the quantitative estimation of glass deterioration by atmospheric corrosion. As a numerical measure for the degree of weathering of a glass specimen, the leaching depths of the network modifier ions K^+ and Ca^{2+} (determined by linescan measurements of the cross-sectioned specimens using SEM/EDX) proved to be reliable for potash−lime−silica glasses.[48−50] As also the climatic and environmental parameters such as temperature, relative humidity, pH, and amount of precipitation and the concentrations of the acidifying gases SO_2, NO_2, and O_3 were measured at the exposure sites, dose−response relationships could be set up using multiple linear regression (MLR). It is based on the assumption of a relationship between a dependent or response variable, y, and p predictor variables, x_i ($p \geq 1$) of the form

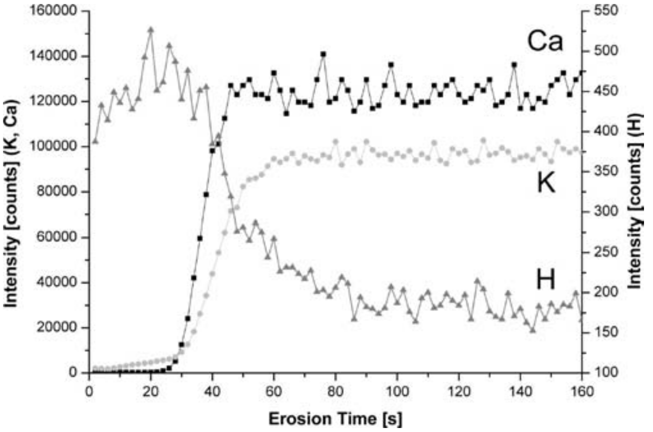


FIGURE 10. Time-of-flight (TOF)-SIMS depth profile of glass M3 (composition 60 wt % SiO_2, 25 wt % CaO, and 15 wt % K_2O) after leaching for 30 min in 10^{-3} N HNO_3. Decreased intensities of the K and Ca signals and increased H intensities (secondary axis) can be observed in the outmost glass layers. The thickness of the hydrated layer is approximately 25 nm.

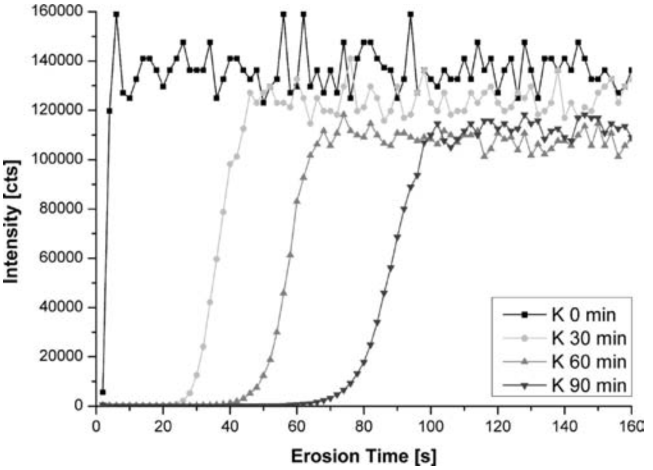


FIGURE 11. TOF-SIMS depth profiles of glass M3 for K: untreated and after 30, 60, and 90 min of leaching in 10^{-3} N HNO_3. An increase of the thickness of the leached layer with leaching time can be observed.

$$y = b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_p x_p + \varepsilon \qquad (6)$$

with a random error component ε and the regression coefficients b_i. Its solution is the so-called least-squares estimator of $\boldsymbol{\beta}$ ($= \hat{\boldsymbol{\beta}}$), which is given in matrix notation by

$$\hat{\boldsymbol{\beta}} = (\mathbf{X}^T \mathbf{X})^{-1} \mathbf{X}^T \mathbf{y} \qquad (7)$$

In the present case, the leaching depths of K and Ca, $d(\mathrm{K})$ and $d(\mathrm{Ca})$, served as response variable y, whereas products of the exposure time and the climatic and environmental parameters were used as predictor variables ("dose"). Results of these calculations for the glass M1 exposed for 6 and 12 months are shown in the eqs 8 and 9. The concentrations of NO_2 and SO_2 (in μg/m^3) as well as the climatic parameters temperature (T, in °C) and relative humidity (RH, %) enter the equation and can be considered as significantly influencing the leaching depths of K and Ca (measured in micrometers) and hence the rate of deterioration of glasses of this composition. Typically, slightly higher values for the leaching depth of K were measured (and are predicted by the eqs 8 and 9) compared with those of Ca. This can be explained by the stronger bonding of the bivalent ion Ca^{2+} to the glass network.

$$d(\mathrm{K}) = -0.64 + (0.03\mathrm{RH} + 0.04c(SO_2))\sqrt{t} - \left(0.05T + 2.03\frac{1}{c(\mathrm{NO_2})}\right)t \qquad (8)$$

$$d(\mathrm{Ca}) = -0.79 + (0.03\mathrm{RH} + 0.03c(\mathrm{SO_2}))\sqrt{t} - \left(0.04T + 1.91\frac{1}{c(\mathrm{NO_2})}\right)t \qquad (9)$$

5. Outlook and Conclusion

The preceding chapters made obvious that estimations of the durability of glasses under ambient conditions are difficult to obtain and are only valid under certain assumptions concerning the glass composition and the exposure conditions. Dose–response relations presented in the previous chapter might therefore be a useful tool for mapping areas of increased risk for glass materials of specific composition. Similar approximations exist for soda–lime–silica glass.[26,51] Hence a first action to be undertaken for an enduring preservation of objects of our cultural heritage must be a substantial reduction of pollutants and particle emissions, as it was the case for SO_2 in the last decades.

It shall be mentioned that today several other concepts for a reduction of deterioration of outdoor glass artifacts caused by weathering are in use. For instance, protective glazings have proved to be an efficient way to reduce the corrosive attack to window panes at Sainte Chapelle in the city center of Paris.[52] A further approach for future protection of endangered glass artifacts are superficial coatings. Promising results were obtained for sol–gel silica coatings, which are transparent, colorless, and low-reflective and which show an effective adhesion to the glass.[53,54]

The authors want to thank Prof. Dr. Gernot Friedbacher and Prof. Dr. Herbert Hutter (Institute of Chemical Technologies and Analytics, Vienna University of Technology) for enabling the SEM/EDX, AFM, and SIMS measurements and Prof. Dr. Johann Wernisch (Institute of Solid State Physics, Vienna University of Technology) for the ESEM investigations. Furthermore, the authors want to thank all partners in the UNECE/ICP-Materials and MULTI-ASSESS projects and the European Union for the financial support.

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Manfred Schreiner studied chemistry at the Vienna University of Technology, where he received an engineering degree. After his Ph.D. in materials science, he was as a postdoctoral fellow at UCSD (University of California, San Diego, CA). In 2000, he became full professor and head of the Institute of Science and Technology in Art of the Academy of Fine Arts in Vienna, Austria. His main research interests are degradation (corrosion) of materials in historic and contemporary art, nondestructive (noninvasive) material analysis, and documentation of objects of art and archaeology using visible, infrared, UV, and X-ray radiations.

FOOTNOTES

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