

Scientific Examinations of Historical Stained Glass

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This article is the first of two dealing with historical stained glass. The aim of this article is to provide an overview of the composition of historical glasses, to discuss the ensuing problems when attempting to restore medieval church windows, and to illustrate how scientific examination of glass surfaces can be used to select an appropriate cleaning method. The second article, which is to appear in the next issue of *Structure*, will deal with the materialographic preparation and examination of historical glasses and modern copies produced for test purposes.

Stained glass

Stained glass is composed of three basic materials: coloured, mouth-blown flat glass, the dark-brown vitreous enamel that is painted onto the glass and the lead used to hold the pieces of glass together. The glass is cut into segments to match the cartoon (a full-size working drawing). A suspension of the dark vitreous enamel is applied to the glass with a brush and worked to give the desired effect. Once dry, the glass is fired at a temperature of 600–700 °C. Usually the glass is subjected to repeated paint-fire cycles. Finally, the coloured glasses are assembled to create the desired form by mounting the edges of the individual segments in flexible leaden comes (H-section lead strips) which themselves become part of the picture being created. To improve the mechanical stability the glass and lead are cemented together using a putty. Medieval and contemporary techniques differ only in detail (see Figure 1).



Fig. 1. Medieval stained glass from the Marienstern Cistercian Monastery, Panschwitz-Kuckau (1370/1380)

In medieval Europe, glass was essentially made by melting sand and wood ash. The chemical composition of this glass can be determined by examining minute fragments of the original material using electron probe microanalysis (EPMA) and energy dispersive x-ray spectroscopy (EDS). The chemical composition of these historical glasses is found to vary widely, depending not only on the age of the glass and the region from which it came, but also on the type of glass examined. The smelting and processing techniques used in the glass-making huts of the Middle Ages necessitated the use of relatively large amounts of ash and lime, so that the chemical composition of these historical glasses is very different to the coloured glass manufactured today (Figure 2).

Corrosion phenomena and corrosion-induced crusting

In contrast to glasses manufactured in the 19th and 20th centu-

ries, the chemical composition of the colourless and coloured flat glasses produced in the Middle Ages made them highly susceptible to weathering. Contact with high levels of humidity, precipitation and harmful gases emitted from domestic, industrial and traffic sources have meant that the coloured glasses have suffered considerable chemical transformation especially on their exterior surfaces. The medieval stained glass in church windows, which was exposed

unprotected to the weather for centuries, often exhibit a hard crust on the exterior surface. As stained glass windows display their full splendour only in transmitted light, the presence of this crust, which absorbs incident light, can impair the visual appreciation of the window to such an extent that cleaning is essential if the work of art is to be enjoyed as it was meant to be seen.

Many types of glass have become visibly thinner over time due to a process of dissolution, and in many cases the original painted layer on the exterior surface has also been lost completely. Viewed in cross-section normal to the surface, badly weathered glass of this type displays three distinct layers: an unweathered glass core (1 to 4 mm thick), followed by a thin gel layer with a thickness of between 0.01 and 0.1 mm, and, finally, the outermost corrosion-induced layer. This layer, which may have a depth of several millimetres, is frequently highly inhomogeneous in

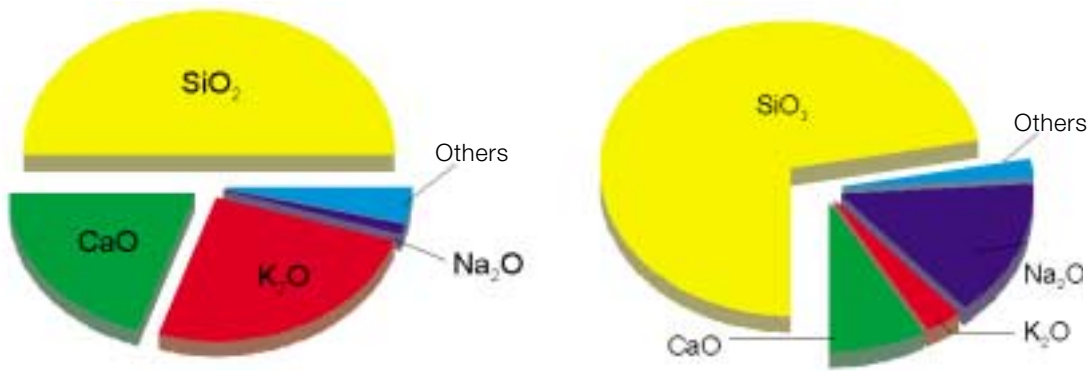


Fig. 2. Typical composition ranges for medieval glasses (left) and glasses from the 19th century (right)

structure; it may, in parts, have already flaked off, but in many cases it adheres very firmly to the substrate (see Figure 3).

The exterior crust is composed of the corrosion products gypsum and syngenite, i.e. it consists of calcium sulphate, potassium calcium sulphate as well as amorphous silica. The gel layer which forms by potassium, calcium and other components leaching from the glass whilst water penetrates into the glass is thus almost solely composed of silica and water. As this porous layer of corrosion products absorbs water and harmful substances as well as marring the beauty of the stained glass window, it should be removed, at least in part.

However, in removing this layer one runs the risk of penetrating

too far into the glass, thus damaging the unweathered core layer.

Experimental investigations into the cleaning of the glass surface

By recording an electron micrograph at a particular location on the edge of a glass segment before and after cleaning, one can establish whether the corrosion products were removed safely or whether the cleaning procedure was too intense, resulting in damage to the gel layer or even to the intact glass core. Typically, an edge that is normally concealed under the lead came is chosen. The edge of the glass segment is prepared by grinding off a few tenths of a millimetre normal to the surface of the edge and then polishing the ground cross-section to yield a smooth surface. The grinding and polishing stages must be done in the absence of water in order not to alter the corrosion-

sensitive glass any further. This is the main difficulty of the method; the preparation of an undamaged sample demands a great deal of experience.

The effects of the various cleaning regimes can be systematically compared with one another by dividing the sample into several zones, each of which has been uniformly cleaned with a different tool or with a different degree of intensity, and each of which extends to the edge of the glass segment. A cleaning method is regarded as acceptable if it succeeds in reducing the thickness of the corrosion-induced crust without damaging the glass core. The gel layer should also remain undamaged, as it acts as a diffusion barrier for ion transport processes that cause further weathering. The gel layer can thus be regarded as a natural protective layer that guards the unweathered glass core.

ESMA-Analysis on medieval glass (main components)

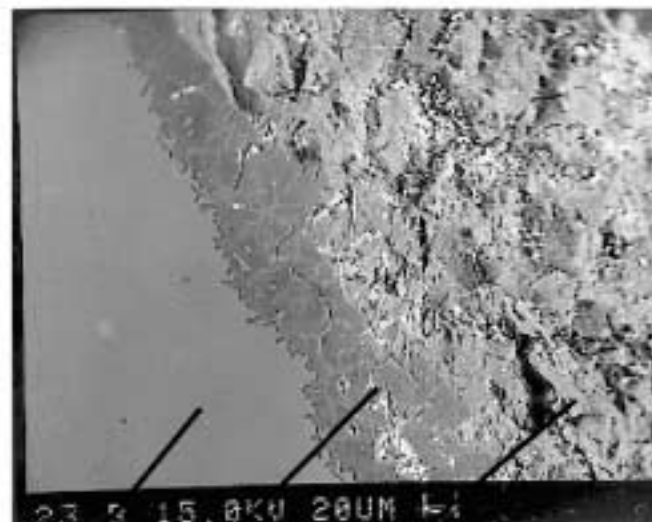
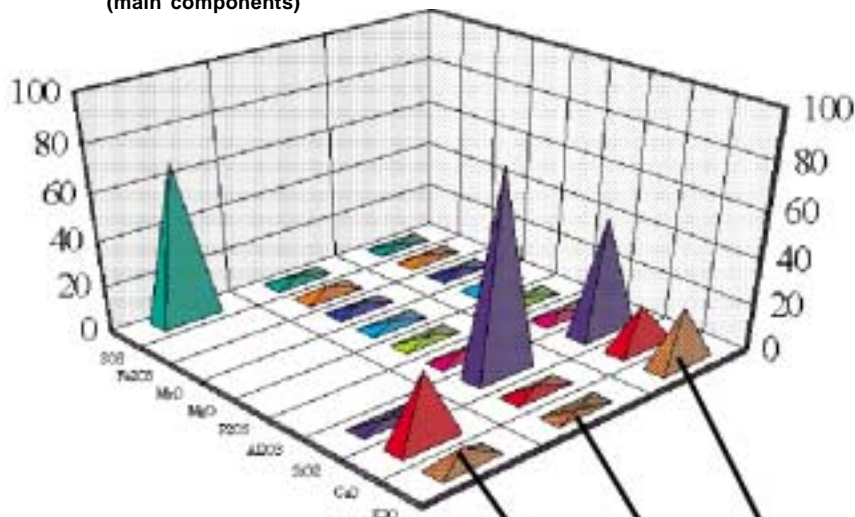


Fig. 3. Electron micrograph of the cross-section of a sample of weathered medieval glass and the composition of the different regions

Glass core

Gel layer

Corrosion-induced crust

¹ Römich, H.; Jägers E.; Torge, M.; Müller W.; Adam K.; Reinigung - eine Gratwanderung [Walking the tightrope - cleaning historical stained glass. In German] In: Restaurierung und Konservierung historischer Glasmalereien [Cleaning and Conserving Historical Stained Glass]. In German] Verlag Philipp von Zabern Mainz, 2000 ISBN 3- 8053-2648-3 S. 101-127

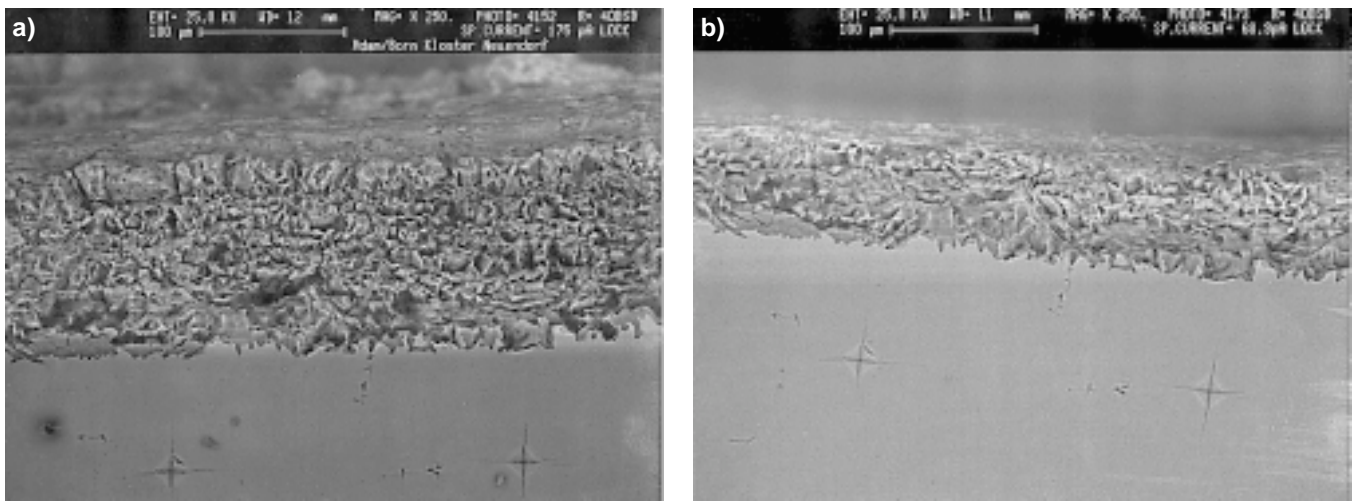


Fig. 4a/b. SEM image of the marked cross section of a sample of medieval glass:

a) left: original state

b) right: after partially removing the corrosive crust with a scalpel

Corrosion-induced crusts can be removed with a variety of tools and techniques depending on their composition and the strength to which they are bonded to the glass. If the layers are loose, a brush or similar soft implement is sufficient to remove them. More tightly bound layers are very carefully removed by experienced restorers using a scalpel whilst monitoring progress under a stereo microscope.

The scanning electron micrographs in Figures 4a/b show the reduction in the thickness of the exterior crust achieved using a scalpel and without damaging the gel layer. The preparation (grinding and polishing) of the edge of the glass segment was performed prior to the cleaning process. In addition, a force of 1 N was applied to a Vickers diamond indenter (monitored under a microscope) to make pyramid-shaped indentations in the glass core close to the gel layer. The marks enable reliable assessments of the various cleaning procedures to be made as the state of the surface can be recorded at exactly the same location before and after cleaning¹.

Fig. 5. Glass sample from Window n III, Cologne Cathedral showing the test cleaning zones



In England (Canterbury), good results have been achieved by using a microblast jet machining technique (Airbrasive) to remove corrosion-induced crusting. The effectiveness of the cleaning process (or, in unsuccessful attempts, the severity of any damage done) depends not only on the jet parameters (pressure, distance, type and grain size of the abrasive, etc.), but also to a large extent on the structure of the original sample, specifically on the structure of the corrosion-induced crust. It is therefore important to select glass samples that cover a range of different structures when carrying out comparative testing. In Germany, the removal of the exterior crust using this microblast jet abrasion method has only been tested under laboratory conditions. The main results and the conclusions reached have been published elsewhere² and will only be mentioned in the following for the purposes of illustration.

Figure 5 shows a sample of red glass from the window n III (triforium, tracery) in Cologne Cathedral, Germany. The glass has a relatively uniform, light coloured corrosion crust on its exterior surface. The corrosion layer on this sample was only moderately hard so that a pressure of at most 0.6 bar was sufficient with all the jets tested to remove the layer. A different abrasive was used for each of the cleaning zones (2-6) and compared to the results achieved using a scalpel (zone 1). The size of the jet nozzle is chosen to match the grain size of the abrasive used (Figure 6). The abrasives used were: sodium hydrogen carbonate (2) and plastic granules (3), both delivered through a nozzle with a diameter of 0.6 mm; English granulated walnut husk (4) and cereal flour (6) using a nozzle diameter of up to 1.2 mm; and German granulated walnut husk (5) delivered via a 1.4 mm nozzle. Guided by results achieved in pre-

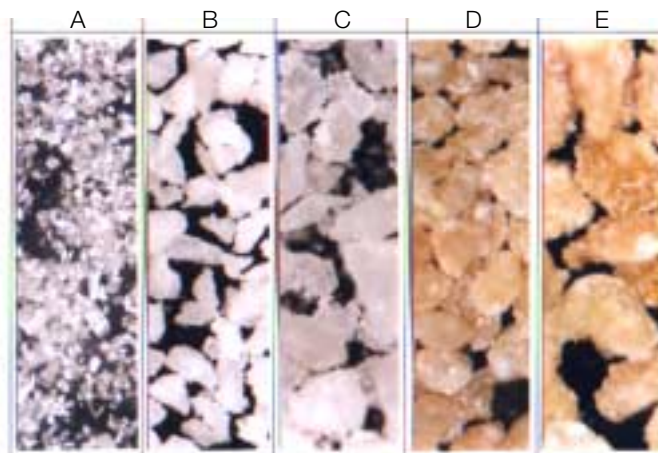
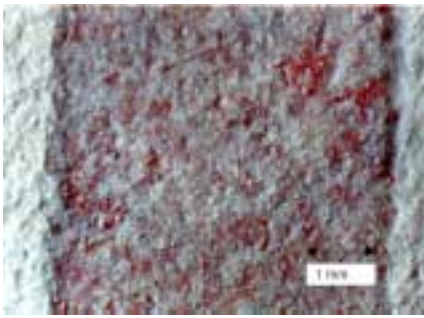


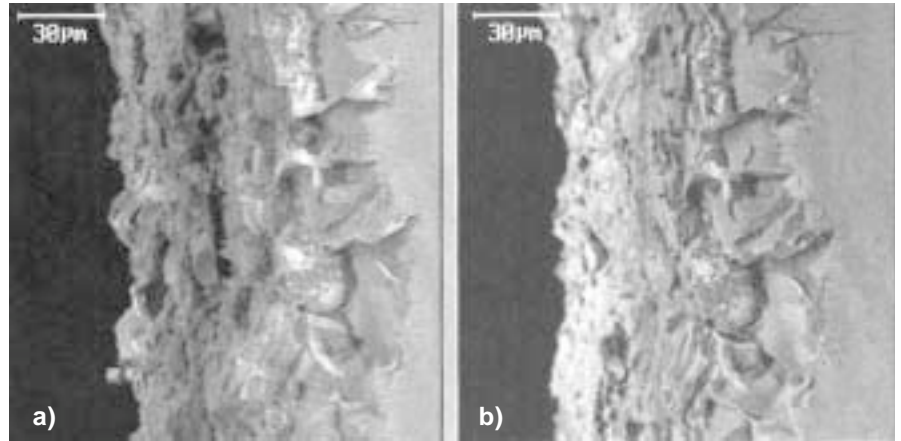
Fig. 6. Texture and grain size of the abrasives used:
 A: sodium hydrogen carbonate, ~50 µm (2);
 B: plastic granules, 60-80 µm (3);
 C: instantized flour, ~80 µm (6);
 D: walnut husk granules from Canterbury, ~80 µm (4);
 E: walnut husk granules 125-400 µm (5)
 (Figures in brackets refer to the cleaning zone in which the respective abrasive was used, see Fig. 5)

² Historische Glasmalereien ; Schutzverglasung-Bestandssicherung-Weiterbildung [Historical Stained Glass Windows; Protective Glazing – Conservation – Further Training. In German] Project sponsored by the Deutsche Bundesstiftung Umwelt [German Federal Environmental Foundation] Berlin-Brandenburgische Akademie der Wissenschaften [Berlin-Brandenburg Academy of Sciences] Verlag Edition Leipzig, 1999 ISBN 3-361-00500-0



◀ Fig. 7. Glass sample from Cologne Cathedral; cleaning zone: 2; abrasive: sodium hydrogen carbonate

Fig. 8a/b. Glass sample from Cologne Cathedral. Electron micrograph of cross-section through cleaning zone 4 before (a: left) and after microblast jet cleaning with walnut husk granules (b: right)



liminary investigations, other parameters varied were: the distance between the nozzle and the target, the jet angle, the duration of abrasion and the vibration setting which controls the flow of abrasive to the nozzle opening. Figure 7 shows the sharply delineated cleaning zones on the edge of the sample. The areas cleaned with the fine abrasive jet are clearly visible. The surface profile in zone 2 indicates that the thickness of the corrosion-induced crust has been reduced by 80–100 µm. Compared to the uncleaned area, the transparency of the glass in zone 2 has increased significantly. The electron micrographs of the edge of the glass segment before and after the cleaning procedure show that the gel layer is still present even after the partial removal of the crust and that damage to the unweathered core of original material can therefore be ruled out (see Figures 8a/b). By comparing the cleaned surfaces with the cross-sectional electron micrographs, one can determine the best means of cleaning a particular corrosion layer. Abrasive removal with a jet of flour or plastic granules proved to be quite coarse and irregular. Better results were achieved using granulated walnut husk, with the more finely ground variant being more effective. The best results were obtained with sodium hydrogen carbonate. However, these results only apply to this specific corrosion layer. For other layers having a different chemical composition, preliminary tests will be required to determine the optimum method of cleaning the surface. Corrosion-induced crusting that is very inhomogeneous and strongly bonded to the glass often cannot be removed mechanically without damaging the unweathered core

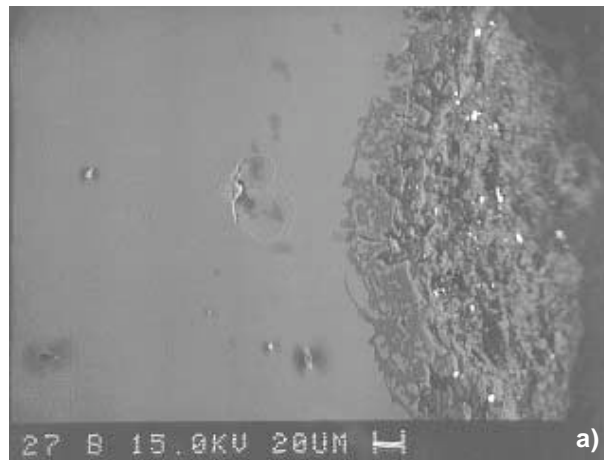


Fig. 9a/b. Cross-sectional electron micrograph recorded in 1993 (at the location marked) of a sample of medieval glass from Erfurt Cathedral before (a: left) and after removal of the corrosion-induced crust with cleaning compresses (b: right). Images recorded 1993

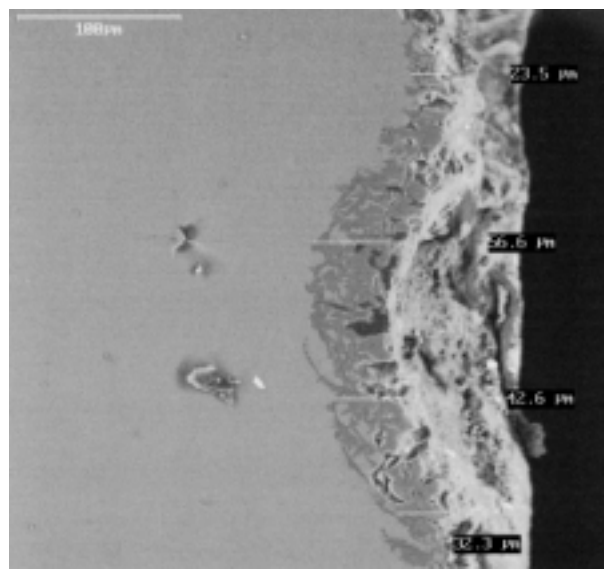
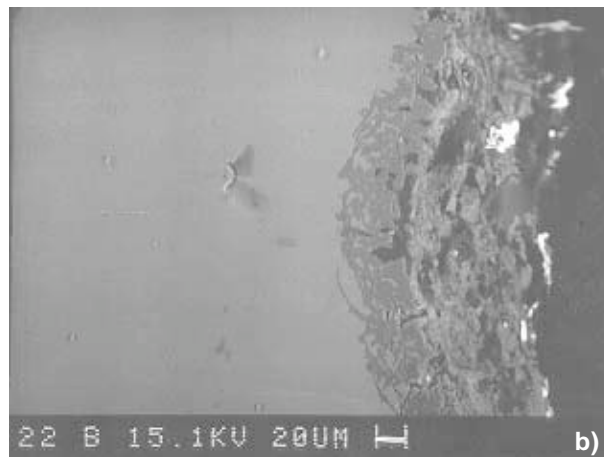


Fig. 10. Cross-sectional electron micrograph recorded in 2000 (at the location marked) of the same sample of medieval glass from Erfurt Cathedral

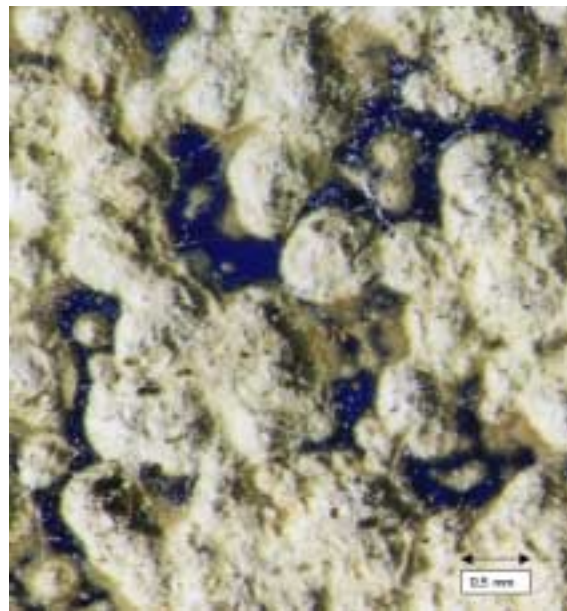


Fig. 11.
Microscopic image of the cleaned exterior surface showing pitting craters and exposed unweathered glass

glass. As part of a joint project, a chemical cleaning method was developed, tested and then used to restore an original segment of stained glass from a window in Erfurt Cathedral, Germany³. By using special compresses soaked in an ammonium carbonate solution, the transparency of the stained glass could be improved significantly. A crucial factor in the decision to use this method was that no immediate or long-term damage to the original window material was to be expected. The cleaning compresses can be used to partially remove corrosion products. Using this technique, unweathered glass elements below the weathered outer crust could be revealed (Figure 11) Electron micrographs of the ground and polished cross-section, recorded at the same point on the sample, before cleaning (Figure 9a) and after cleaning (Figure 9b) show that the structure

of the gel layer remains unchanged. The Vickers indentation on the edge of the glass enables the point of examination to be identified years later. Figure 10 shows the examination area seven years after removal of the corrosion products with the chemical compresses. The morphology of the gel layer is unchanged (c.f. Figures 9a/b) so that subsequent corrosion of the glass can be ruled out.

Today, historical stained glass windows are preserved behind an external glass screen. This 'isothermal' protective glazing with its ventilated air space has been in

use for decades in a large number of countries, and has established itself as the most important means of protecting and preserving stained glass windows⁴.

³ Römich, H.; Jägers E.; Torge, M.; Müller W.; Adam K.; Reinigung - eine Gratwanderung [Walking the tightrope - cleaning historical stained glass. In German] In: Restaurierung und Konservierung historischer Glasmalereien ['Cleaning and Conserving Historical Stained Glass'. In German] Verlag Philipp von Zabern Mainz, 2000 ISBN 3-8053-2648-3 S. 101-127

⁴ Historische Glasmalereien ; Schutzverglasung-Bestandssicherung-Weiterbildung [Historical Stained Glass Windows; Protective Glazing - Conservation - Further Training. In German] Project sponsored by the Deutsche Bundesstiftung Umwelt [German Federal Environmental Foundation] Berlin-Brandenburgische Akademie der Wissenschaften [Berlin-Brandenburg Academy of Sciences] Verlag Edition Leipzig, 1999 ISBN 3-361-00500-0

Fig. 12a/b. Photograph taken with transmitted light of a segment of medieval stained glass from Erfurt Cathedral (1405) before (a: left) and after removal of the corrosion-induced crust with cleaning compresses (b: right)

