Glass corrosion – the cause of the white/grey precipitation on the insides of papyrus glass frames

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Historic papyrus fragments have been preserved between glass plates for more than 110 years. Yet this conservation method has often resulted in a white/grey precipitation on the inside of the plates. This paper suggests that glass corrosion is responsible for the precipitation. The glass corrosion could be caused by a particular reaction in which an exchange of ions occurs between the edges of the papyrus and the glass. During this reaction ions are released from the glass as well as from the papyrus to form a sodium dioxide coating. The process is accelerated by humidity.

The enthusiasm for collecting inscribed papyrus fragments is ever-lasting as papyri offer a window into the distant past even when these eras constitute something unimaginable and mysterious. Or perhaps that is the attraction. Ancient Egyptian problems were often similar to ours, yet we may rarely conclude anything from them. The papyrus collection of the Universitätibibliothek Leipzig not only houses the famous Papyrus Ebers, but includes a large number of documentary papyri from all periods of Pharaonic Egypt. Many of them deal with uncomplicated day to day problems of the common man. The problem discussed in this paper is also related to the past, not to text but to the papyrus structure, namely the white/grey precipitation on the insides of papyrus glass plates. In what follows, I will try to explain the appearance and cause of this phenomenon, which I have been researching for some time.

Brief history of papyrus conservation

Restored papyri are framed between sealed glass frames for convenient handling, a method that has been successfully used since the end of the 18th century. Papyrus conservator Hugo Ibscher (1874-1943) was one of the first to adopt this technique to securely store papyrus fragments in the Berlin papyrus collection. We can still find his mark in many other European collections where he restored and framed papyri. Despite the brittleness of glass, this method has been considered the most suitable as it guarantees secure storage and handling of the fragments.

The glass plates used to be hermetically sealed but more recently there is a tendency to leave the edges of the tapes open for air circulation. Regarding the type of glass employed, each collection has its own preferences and priorities. The most commonly used type is the so-called ‘float glass’, followed by acrylic safety glass with or without metal frame; and Mylar foil and glass combined with other carriers such as paper. The Leipzig papyrus collection also contains an unusual example of Greek papyri with 32 sheets pasted directly into a book (Fig. 1).²

1 The original German article was translated into English. A German abstract will be provided at the end of the article.
In this article, I will not discuss the advantages and disadvantages of these storage materials, which are a source of constant debate. Rather, I will focus on the white/grey precipitation on the insides of papyrus glass frames especially visible on papyrus kept between float glass. This precipitation usually follows the outline of the papyrus fragments (Fig. 2). Occasionally, it extends beyond the borders of the fragments, probably as a result of relatively large humidity fluctuations. Little attention has been paid to the phenomenon and papyrus restorers have tended to overlook it so long as it does not negatively affect the preservation of papyrus. Only when the legibility of the text is reduced or the fragment cannot be documented otherwise, are the glass plates opened, cleaned and sealed again.

The particular precipitation discussed in this article is visible on papyri in the Leipzig collection. The official re-opening/re-organisation of the Leipzig papyrus collection in 1997, encouraged by Reinhold Scholl (Scholl 2010, 2-5), initiated a long-term restoration and conservation plan. Priority was given to the restoration of displaced papyrus fragments in broken glass plates. During this work, a white/grey precipitation was found in 98% of the papyrus frames. Why did the remaining 2% of frames not show this deposit?

A papyrus fragment that did not show this precipitate was fixed between two sheets of acrylic glass. Even more surprising was the observation made on another frame, which was sealed between 1960 and 1970. Here, white/grey sediment could only be seen on the inside of one of the two glass plates. More detailed study revealed that two different types of glass were used, with different thickness and colour.

The white/grey precipitation

Probably the first mention of this white/grey precipitation occurs in a correspondence between W. Kolmorgen from the Staats- und Universitätsbibliothek Hamburg and H. Kühn from the Doerner Institut München. Kolmorgen expressed interest in identifying the composition of the visible coating on the glass. He assumed that the results of such investigations could predict to what extent new sediment would emerge in the newly framed papyri and whether these fragments should therefore first receive particular treatment. Kühn added that atomic emission spectroscopy and X-ray absorption fine structure analysis (XAFS) showed that the sediment consists of sodium chloride and a re-emergence would therefore be inevitable. The correspondence suggests that the papyrus fragments released sodium chloride, which then deposits on the glass. Kolmorgen described an interesting instance where only one of the inner papyrus frames showed the sodium chloride, and concluded that the papyri released it only on one of their sides.

This particular observation cannot be confirmed by the Leipzig collection where typically both insides of the papyrus frames show the white/grey sediment. The correspondence between Kolmorgen and Kühn urged me to focus further research on the presence of sodium chloride in papyri. All current observations indicate that sodium chloride is released from the papyri and subsequently attaches itself to the glass. Colleagues Banik (1985), Fakelmann (1985), Nielsen (1985, 104-150) and Böhmert (2009) addressed the issue of salt concentration on the insides of papyrus glass frames. Ingelise Nielsen investigated this problem intensively in her dissertation and sampled the glass itself (Nielsen 1985).

My first thoughts about the provenance of the salts developed along the same lines. On one papyrus fragment of the Leipzig collection (P.Lips.Inv. 109), I was able to distinguish
the salt crystals with the naked eye. The precipitation on the insides of the glass plates was very strong (Graf and Schumacher 2008, 242-248). The most straightforward conclusion was indeed that sodium chloride was released due to environmental changes and attaches itself to the glass plates (Graf and Krutzsch 2006, 23-28).

Components of papyrus as raw material

Papyrus mainly consists of hemicellulose, lignin and cellulose. More interesting for the current discussion are the minerals; sodium, potassium, silicon, and calcium (Flieder, 2001, 84-106). Susanne Böhmert also discovered phosphate, iron and nitrogen in African papyrus, which she studied for her master thesis (Böhmert 2009, 39-44). In the Leipzig papyrus fragment P.Lips.Inv. 109, the following components were detected: magnesium, nitrate, sulphate and chlorine (Graf and Schumacher 2008, 242-248). In my thesis, particular attention is given to the discovered chlorine.

The components of float glass

The terminology commonly used for soda-lime glass, lime soda silicate glass, lime soda glass or soda-lime glass is flat or float glass. This type of glass is generally used for storage and handling of papyrus fragments. Its ingredients are silica, alumina, calcium oxide, magnesium oxide, sodium oxide, potassium oxide (Schaeffer and Langfeld 2014, 15-23).

The focus of my thesis is silicone oxide as a network former and sodium oxide as a network modifier. Of further interest is the question of the structure of glass in general. To us users, glass appears to be inert, stable and un-reactive. Thermodynamics tells a different story, when it describes the behaviour of the different matter aggregate states. Each material system strives to achieve the most stable energy level, yet with glass, this is not possible. Chemists Helmut A. Schäffer and Roland Langfeld describe the speed of the movement of glass atoms and molecules as follows:

‘Glass would like to occupy an energetically stable state. It cannot be reached, however, because the cooling process increases the toughness of the glass melt (Glassschmelze) and thereby prevents a repositioning of molecules into crystals. One can also say that kinetics interrupt the thermodynamic process. In a thermodynamic sense, glass can be interpreted as a “frozen” super cooled liquid and it is, contrary to the crystalline state, not in thermodynamic equilibrium. From this it can be deduced that the glass state is not stable, since it is only temporarily, however for practical purposes sufficiently long, prevented from passing into the crystalline state.’ (Schaeffer and Langfeld 2014, 15-23).

Thesis for the white/grey sediment on the insides of papyrus glass frames

What causes a reaction between papyrus and glass? We already mentioned air fluctuation; i.e. changes in humidity levels and temperature, between the glass frames. I would explain such fluctuations by hydrolysis. The starting point for this process is an ion exchange occurring between the water ions and the glass surface. The H+ or OH- ions present in aqueous solutions, acids and alkalis, interact with the glass fabric. This reaction is known as ‘hydrolytic
attack', when easily soluble elements of the alkali group that are present in the surface, are released (I). In their place the H⁺ ions from the dissociation of water usually appear (II).

In the remaining water, OH⁻ ions can stoichiometrically be assigned to the dissolved alkali ions. Dissolved NaOH (caustic soda) forms in this way, for example. To understand this action, consider the cleaning of glasses in the dishwasher. During the cleaning process, the application of hot water which has a low pH-value and thus an acidic environment, causes enhanced dissolution of minerals from the glass surface that produces a grey veil on the glasses. In the case of the papyrus, sodium from the glass and the attested chloride ion from the papyrus collide (Graf and Schumacher 2008, 242-248). The response area is the interface between the glass surface and its direct contact point with the papyrus. The humidity of the air in and around the papyrus glass frames must be considered a factor that triggers the reaction. This can be seen clearly in frames where the edges of the papyrus fragments exhibit different expansions (Fig. 3). Here, a significant increase of the humidity in the environment of the frames can be assumed. Our investigation to identify and determine quantitatively water-soluble deposits on historical papyrus fragments through ion chromatography have revealed chloride anions (negatively charged ions). The cations (ions gaining positive charge) were not determined.

Since no sodium was identified in the Energy-Dispersive X-Ray (EDX) spectroscopy, the findings suggest that NaCl may arise in a glass composite, more specifically that the chloride ions react with the sodium ions from the glass to form NaCl. To restore the balance (i.e. electro-neutrality) the sodium ions that migrate out of the glass seem to be replaced by protons (H⁺) that emerge from the constant humidity. Consequently, NaOH emerges on the inside surface of the glass, which in turn acts in a hygroscopic manner, attracting additional water from the air or from the papyrus. In this way, chloride ions also reach the surface of the glass, where they can then react with the sodium ions into NaCl. A similar, if not identical principle accounts for the glass corrosion in medieval glasses.

Summary and perspectives

Many questions remain and research on this phenomenon is still in progress. Other components in both the frames with and without corrosion should be compared systematically. One question is whether storage in wooden shelves, which could release acetic acid, enhances the process described above. Another question is whether there is any connection between the glass’s provenance and composition. A preliminary investigation conducted with an electron microscope showed that no significant surface changes took place. It is interesting to note however, that a certain pattern is visible on new glass frames. In the next phase of study, testing will continue on borosilicate glass in order to determine whether similar white/grey corrosion can be detected. This should provide interesting results, as this type of glass is thought to have better resistance to hydrolytic attacks, acids, alkanes and reduced alkali diffusion.
Acknowledgments

Dear Bridget,
I would like to thank you for your availability for questions and advice in all possible subjects related to papyrus research. I wish you all the best, a good health and many exciting new experiences coming your way!
Thank you and many greetings from Leipzig
By Jörg Graf
Restorer/conservator VDR
Head of conservation
University Library, Leipzig

German Abstract


Bibliography


Fig. 1: cod.gr.167 (Universitätsbibliothek Leipzig).
Fig. 2: Old Glass of PLips.Inv. 211 (Universitätsbibliothek Leipzig).
Fig. 3: PLaps.Inv.87 with and without white/grey precipitation (Universitätsbibliothek Leipzig).