Archaeological glasses: a closer look

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Résumé **Verres archéologiques : une vision rapprochée**
Les verres modernes sont appréciés pour leur transparence et leur stabilité. Les verres historiques sont plus sensibles en raison de leur composition chimique et de leur dégradation qui s'est produite au cours des siècles dans des environnements variables. Les fragments de verre, ainsi que les vestiges de production de verre, sont très importants en archéologie et ceci tout particulièrement depuis qu'ils s'avèrent être un véritable indicateur du développement technologique de l'humanité. De plus, les objets archéologiques en verre sont importants pour l'histoire de l'art, reflétant ainsi le potentiel créatif et l'expression artistique de l'artisan dans les différentes sociétés. Les études des phénomènes de dégradation et des processus chimiques conduisant à l'altération sont essentielles pour adapter les stratégies de conservation et préserver ainsi les verres archéologiques qui représentent une part importante de notre héritage culturel.
Mots-clés **Archéologie, verre, dégradation, histoire, conservation.**

Abstract Modern glass is appreciated for its transparency and its stability. Historic glasses are more fragile due to their chemical composition and because of their degradation in various environments over the centuries. Glass fragments and traces of glass production are considered important for archaeology, since they represent indicators for the technological development of mankind. Furthermore, archaeological glass objects are important for art history, reflecting the creative potential and the artistic expression of craftsmen in different societies. Studies of the degradation phenomena and the chemical processes leading to degradation are essential for tailoring a conservation strategy, aiming at the preservation of archaeological glass as an important part of our cultural heritage.
Keywords **Archaeology, glass, degradation, history, conservation.**

History of glass-making

The cradle of glass-making is difficult to define, both concerning the date and the place of birth for this new technology. Northern Mesopotamia at a time prior to 2500BC is an estimation shared by many experts. At first, decorative objects and glass beads were hand-formed or cast using simple tools and finished by abrading. Later, glass was moulded or pressed to form vessels. Around 50BC the technique of glass-blowing was invented, which is considered a technological milestone for the production of glass [1-3].

Throughout the Roman Empire, new centres for the manufacturing of vessel glass were established. Glass was no longer considered an item of luxury, but was also used to produce containers for storage of goods. After the decline of the Roman Empire, glass-making experienced a decline both in quality and quantity. Natron, as a source for soda, an important raw material for the production of glass formerly supplied through Roman trade routes, became difficult to obtain. By the end of the first millennium, potash, derived from the ashes of burnt trees, replaced soda as fluxing agent in northern Europe. This change in raw materials defines an important shift in chemical composition, from soda-lime silicate glasses to potash-lime silicate glasses. The difference in durability of the two types of glasses has significant consequences for their degradation and conservation [1, 3]. *Figure 1* gives an example of a potash-lime silicate glass from an archaeological context.

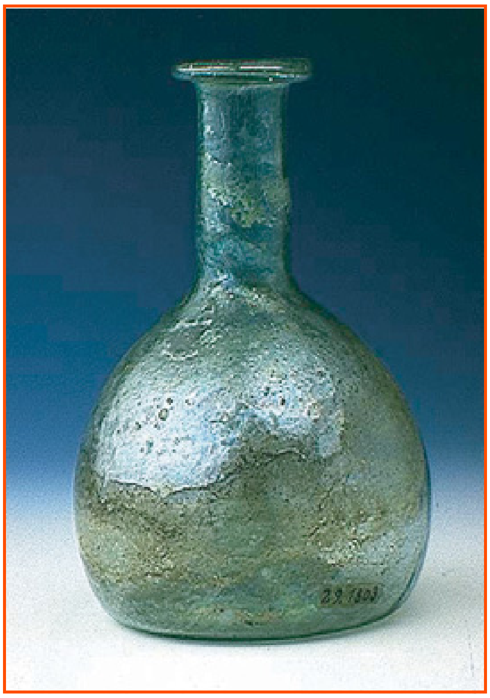

Figure 1 - Glass bottle, dated to 1st century AD, excavated in Cologne, Germany (Jacobstrasse, Augustinerkloster).
The slightly green transparent glass has developed iridescent surface layers during exposure in the soil (picture provided by Roemisch-Germanisches Museum/Rheinisches Bildarchiv Koeln).

Structure and composition

The structure of glass is closely connected to its chemical composition and thus to the raw materials used for its production [4-5]. Sand (SiO_2) was the main component for the production of ancient glass. Lime ($CaCO_3$) or magnesium carbonate ($MgCO_3$), soda (Na_2CO_3) or potash (K_2CO_3) was added to reduce the melting temperature and to facilitate the production process. For soda-lime or potash-lime silicate glasses, these elements represent already more than 90 weight-% of the complex composition. Nevertheless, most historic glasses contain up to 30 different components, which are present only in minor quantities or as trace elements. Some of them were not added deliberately, but are present as impurities contained in the main components. Others have been chosen as colouring agents. It should be stressed that not only the amount of a specific transition metal oxide determines the colour of a glass, but also its oxidation state, which can be regulated during the production process by controlling the atmosphere in the furnace [1, 3].

Degradation reactions of glass in the soil

The term "corrosion", originally referring to the oxidation of metals, is frequently used as a synonym for the degradation of glass [4]. The chemical degradation of glass is initiated by the attack of water and clearly dependent on the pH-value of the liquid. Two dominant mechanisms, the ion-exchange and the network dissolution, are competing with each other, leading to surface changes in the range of nanometers up to several micrometers. Degradation layers on glass have a different composition as compared to the bulk glass: network modifiers such as sodium, potassium and calcium have been depleted and replaced by water and hydronium. In addition, soil components might migrate into the glass. Due to a sequence of dissolution and precipitation reactions, a layered structure with variation in chemical composition can be formed.

The rate of degradation strongly depends on the glass composition. As a general rule, the higher the percentage of silica, the more stable the glass. Since sodium ions have stronger bonds within the network than potassium ions, the durability of sodium silicate glasses is mostly greater than that of potassium-rich glasses. However, all glass components interact with each other, a fact which complicates any prediction. Furthermore, apart from the chemical composition, the surface roughness, the thermal history and the production process, as well as the presence of inhomogeneities have an influence on the chemical durability. However, the interacting medium plays a dominant role during any kind of corrosion process. The reaction of glass in contact with soil is influenced not only by the moisture content and the pH value but also by the presence of salts, oxygen, complexing agents, organisms and organic compounds.

Archaeological glass and its burial environment is a topic where the key parameters are defined but their interaction still needs to be explored [6-9]. A simplified model is given in *figure 2*.

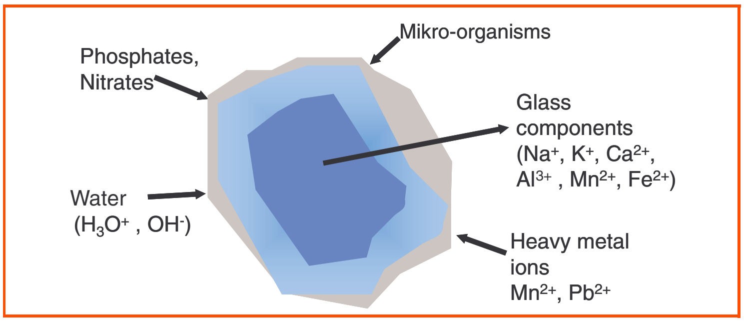

Figure 2 - Simplified presentation of reactions occurring during exposure of glass in the soil.

Figure 3 - Selection of archaeological glass fragments with various phenomena of decay.

Degradation phenomena

Historic glasses – especially those originating from antiquity and the Middle Ages – are mostly retrieved from archaeological excavations. It can be only briefly mentioned in the context of this article that window glasses, such as the prominent masterpieces of the Gothic period, are subject to environmental weathering and thus develop different characteristics of decay [2].

Archaeological glasses comprise mostly vessel glass and glass jewels, rarely found as entire pieces but more commonly as fragments (*figure 3*). Their degree of degradation is highly variable, ranging from slightly altered to completely corroded, all dependent on the parameters discussed above [7-8].

In general, Roman glass (sodium-rich) is quite stable. The only sign of alteration after hundreds of years in the soil is often the formation of a thin altered surface layer (*figure 4*). For less durable glasses this layer can reach several hundreds of micrometers, exhibiting "iridescence" (rainbow-like coloration), if several thin layers of altered glass are superimposed (*figure 5*).

Surfaces of archaeological glasses may appear dull and pitted, with brown spots or dark stains. Enamel-like surface layers may render the glass into a completely opaque material. In these cases the surface appears smooth, with no crystal deposits, although the degradation layer is thick (leaving only a minor core of bulk glass uncorroded) and exhibits a laminated structure due to precipitation processes. The fluctuations in chemical composition within this surface layer can be visualised in a cross section (*figure 6*). One feature is the depletion of calcium from the degradation layer, which is however enriched in some parts, correlated with the presence of phosphorus.

Considering the broad variety of decay phenomena on archaeological glasses, it is difficult to estimate whether the archaeological record stored in our museums is representative of what was produced and used in antiquity. The finds have gone through various selection processes by archaeologists, conservators and curators. Highly sensitive glasses, especially those in waterlogged environments, may have been degraded completely and so were not identified as glass during the excavation. A large quantity of glass

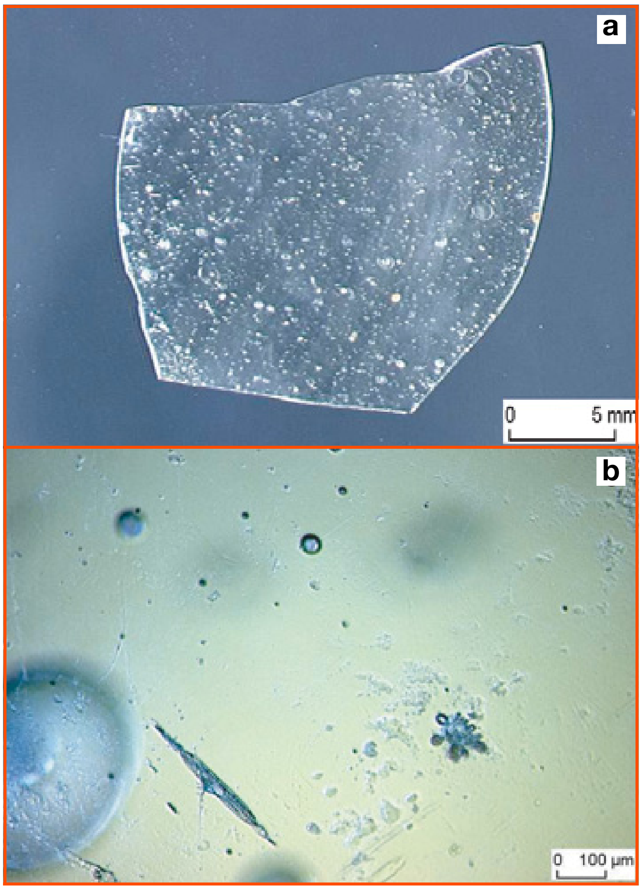

Figure 4 - Late Roman glass (4th Century AD, Germany). a) The overview picture shows that the glass has survived well the burial in the soil; b) the optical microscope confirms that the surface is smooth, featuring only some bubbles (originating from the manufacturing process).

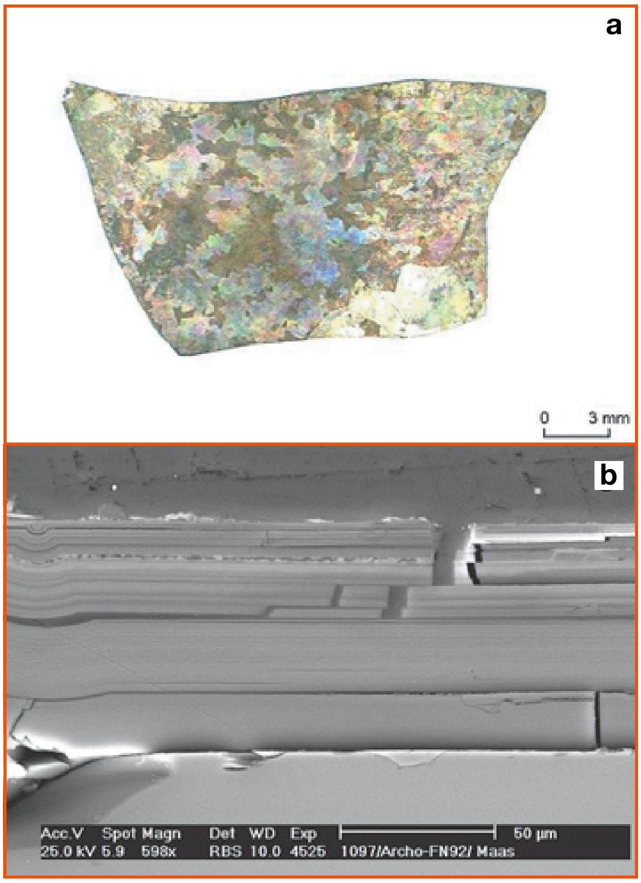

Figure 5 - Glass fragment from 15/16th century (Germany). a) The entire fragment is covered with iridescent layers; b) a polished cross section investigated in the scanning electron microscope (SEM) shows the reason for iridescence – thin parallel layers of degraded glass form a package of about 50 micrometers and cause the scattering of light.

fragments, which can not be re-assembled into representative whole objects, are still in the storage rooms of museums, awaiting re-discovery.

Detecting the damage

Most analytical techniques used for modern glass have also been applied for the analysis of archaeological glass [2, 4]. Some techniques, such as Rutherford backscattering spectroscopy (RBS) or infrared spectroscopy (IR), are too sensitive or require smooth surfaces. Light microscopy and SEM are still the most popular and effective methods to characterise the surface. However, the surface condition can be misleading and to gain a more complete sense of the condition of the object, it becomes desirable to examine the interior. In these cases a polished cross section has to be prepared, requiring the removal of a sample of the glass, with the associated risk of loss or even destruction of the object. The strong need for non-destructive analytical techniques has led to some progress, such as the application of desktop microfocus X-ray computed tomography (mCT) [10].

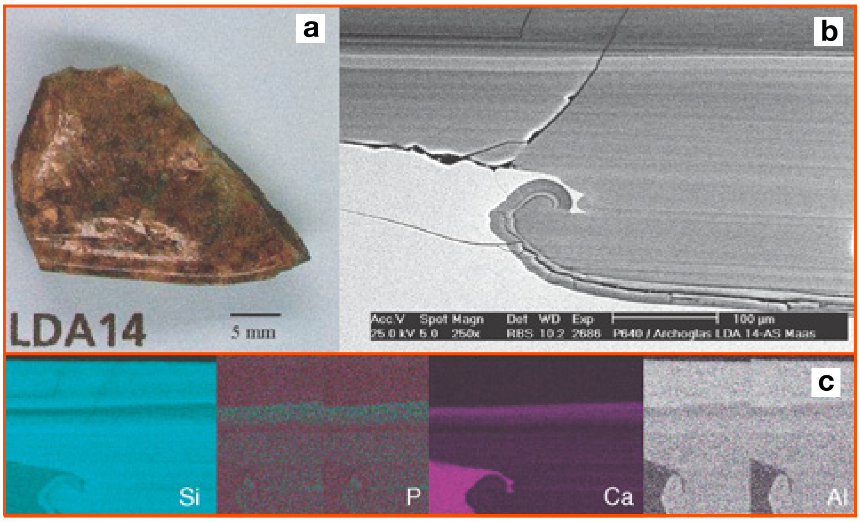

Figure 6 - a) Medieval glass fragment from Germany: the original green colour is not visible through the brown degradation layer. b) Same glass investigated as polished cross section in the SEM; the laminated structure of the degradation layer is not homogeneous in thickness. c) The investigation in the SEM coupled with element mapping by EDX (energy dispersive x-ray) analysis shows the variation in chemical composition of the layered structure as compared to the bulk glass.

Further research in this section is encouraged, since it is necessary to distinguish glasses which need special care from those that are rather stable and not in need of targeted protection.

Challenges in conservation

Glass conservators have a variety of organic natural and synthetic polymers at their disposal to repair broken pieces, for edge bonding and filling of gaps. Their challenge is to match the refractive index of the glass so that the join becomes less visible, and to create as perfect a bond as possible. Polymers have also been used as coatings to protect the surface, although the risk of the treatment, due to incompatibility of glass and polymer or the change of properties during aging of the coating (such as yellowing and shrinkage), has limited this type of conservation strategy. The consolidation of highly fragile and flaking glass surfaces is another crucial issue in research and conservation practice, since the right method for detecting the polymer in the cracks still has to be found [1-2, 5].

Additional research into optimal storage and display environments is also necessary. Recent studies have shown that highly degraded glasses react with great sensitivity to fluctuations in relative humidity, thus reflecting the need of a glass from a waterlogged environment to transition slowly to the drier museum climate. For very precious objects, the optimum level of relative humidity in the show case is still a question discussed frequently amongst experts [1, 5].

Archaeological glasses are still a neglected source of history. A closer look at their degradation and need for special conservation may open new perspectives for their discovery.

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