

REVIEW ARTICLE OPEN



A review of glass corrosion: the unique contribution of studying ancient glass to validate glass alteration models

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Glass has been used in widespread applications within several sectors since ancient times and it has been systematically studied under different perspectives. However, its thermodynamic properties and the variety of its compositions, several aspects related to its durability and its alteration mechanisms remain still open to debate. This literature review presents an overview of the most relevant studies on glass corrosion and the interaction between glass and the environment. The review aims to achieve two objectives. On one hand, it aims to highlight how far research on glass corrosion has come by studying model systems created in the laboratory to simulate different alteration conditions and glass compositions. On the other, it seeks to point out what are the critical aspects that still need to be investigated and how the study of ancient, altered glass can add to the results obtained in laboratory models. The review intends also to demonstrate how advanced analytical techniques commonly used to study modern and technical glass can be applied to investigate corrosion marks on ancient samples.

npj Materials Degradation (2023)7:38; <https://doi.org/10.1038/s41529-023-00355-4>

INTRODUCTION

Throughout history, glass has played a central role in the production of goods for widespread use, making it a material that has been extensively studied from various perspectives. However, due to its thermodynamic properties and the vast range of existing compositions, there are still several aspects of its nature that are not fully understood. For instance, evaluating glass durability and alteration mechanisms remains a challenge, as it requires taking into account numerous factors, some of which are difficult to replicate in laboratory experiments. One of the most prominent challenges is the time required for the transformation of the glass structure, which is directly responsible for the kinetics and dynamics of the processes involved.

Technological innovation has recently introduced new tools for studying the durability of glass and shedding light on the deep connections in extremely complex materials between compositions, structure, and the surrounding environment. As an example, a recent review¹ reported about the possibility of employing mechanistic models to study aqueous glass alteration. Thanks to the availability of such novel techniques, glass alteration mechanisms and kinetics can be hypothesised using non-conventional experimental methods (simulations) and without direct experimental validations. In parallel, the long-term perspective provided by studying ancient vitreous objects can inform and underpin the predictions obtained through simulation and laboratory methods^{2–6}.

Most of the studies performed to understand glass corrosion are based on artificial ageing experiments that are designed to monitor, step by step, the process of glass alteration and the physicochemical evolution of the glass structure^{7–10}. Because of the great variability of the experimental conditions involved in these studies, however, results are not yet conclusive, and the glass transformation process is still only partially described in literature.

Standard approaches to the study of glass corrosion are limited in that they are valid in some specific experimental conditions, but not in others. Indeed, most of the available research focuses on the corrosion mechanisms of glass with specific compositions (lead-rich or borosilicate families), or under conditions of saturated humidity (relative humidity, RH \geq 100%)^{11–13}. In both cases, the atomic diffusion occurring in the material alteration processes is assisted by two key parameters, which are the presence of ionic species with high mobility and the presence of liquid water on the surface, respectively. Only a handful of published works^{2,7,8} –focused on ageing under conditions of RH < 100% and on a wider variety of glass compositions, like those of the silica-soda-lime (SSL) glass family– are available nowadays in literature: they represent valuable experimental approaches to determine and separate the relative influence of different parameters on the chemical and environmental durability of glass.

In view of the above, this review focuses on the literature available on glass alteration and related structural investigations that have contributed to the comprehension of the modifications occurring in the glass network when glass degrades. In addition, an examination of the existing –but limited– literature on the analysis of ancient glass will bring to the attention of the chemistry community a vast amount of unexplored information that is relevant also for the study of contemporary glass types, to validate the prediction of glass behaviour obtained through laboratory experiments. The most advanced techniques to study alteration on heritage glass will be described with the aim of highlighting how deepening the understanding of altered ancient glass properties is key for a full understanding of the phenomenon of natural ageing of both modern and ancient glass objects.

For better clarity, the term *archaeological* glass will be used to refer to glass specimens that have aged in soil or marine environments for centuries, whereas the term *historical* glass will be used when speaking about glass aged under the effect of environmental moisture fluctuations (in museums or private

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collections). The term *ancient* glass is more generally used to refer to both the above mentioned categories.

By using a combination of comprehensive characterization of ancient samples and laboratory-based ageing experiments, researchers can obtain valuable information about glass alterations that have occurred over hundreds of years while also monitoring the alteration process step-by-step. This integrated approach offers a unique opportunity to consolidate and supplement current theories of glass corrosion and validate predictive models using real-world examples of long-term alteration. Overall, this approach provides a more complete understanding of the complex process of glass corrosion and can help guide the development of more durable glass materials.

GLASS STRUCTURE AND ITS DISSOLUTION PREDICTION: KEY HIGHLIGHTS

Glass is an amorphous material that shares structural features at the atomic level with a supercooled liquid, while exhibiting mechanical properties typical of solids.

Zachariasen¹⁴ was the first to describe the amorphous structure of glass in 1932. His studies led him to conclude that there is no long-range atomic periodicity in glass structure. He also defined the requirements for a particular oxide to exist in the vitreous state. Silicon dioxide, also known as silica, is the primary network former in both ancient as well as in modern glass.

In silica-based glass, the bonding forces involved in the formation of the glass network are those of crystalline SiO_2 , which has a tetrahedral structure with 4 oxygen atoms located at the corners of a tetrahedron and a Si atom placed in the middle of the structure¹⁵ (Fig. 1). The glass network can be figured as a built-up of such tetrahedral elements, which share each corner with neighbouring tetrahedra, one per corner. The remaining corners are available to form other chemical bonds. SiO_2 is considered a primary network former, but other oxide types exist with these same properties, such as B_2O_3 or P_2O_5 . The addition of alkali oxides, such as Na_2O , K_2O , Li_2O , to the glass network former is responsible for breaking some of the Si-O-Si bonds bridging silicon atoms and for including the alkaline cations into the glass structure. These network modifiers generate the formation of non-bridging oxygens (NBOs) in addition to the bridging oxygens (BOs) of the silica network. NBOs hold a negative charge that is locally compensated by one highly mobile alkali cation with a positive charge (i.e., Na^+). The main effect of such network modifiers is to decrease the viscosity of the glass melt, thus facilitating its workability at lower temperatures. Alkaline earth oxides like CaO are added to the glass batch as network stabilisers¹⁶. They connect to two NBOs and are commonly considered as lower mobility ions (i.e., Ca^{2+}) that are possibly

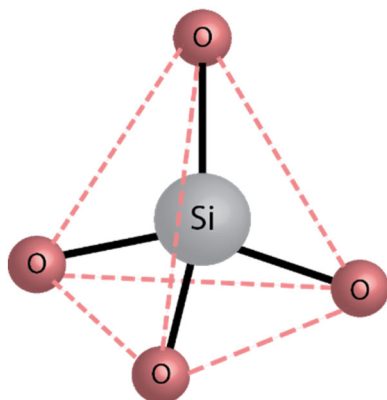


Fig. 1 Tetrahedral silica unit. Schematic representation of a tetrahedral silica unit (not to scale).

effective in inhibiting the diffusion of other cations across the silica network, hence improving the chemical resistance of the glass (Fig. 2). It is now clear why 90% of commercial glass is made of a mixture of silica (as network former), sodium and calcium oxide (as network modifiers). Nevertheless, the positive influence of alkaline earths in increasing glass stability against alteration has not been fully demonstrated yet, and several works indicated that Ca^{2+} and Mg^{2+} ions are at least as mobile as alkalis within the hydrated layer in atmospheric conditions^{17,18}.

The structure of glass is not in thermodynamic equilibrium. The durability of glass depends on both the kinetic and thermodynamic stability of its oxide components. In a state of thermodynamic equilibrium, the chemical potential of the species on the glass surface and those in solution are equal, and as a result, no net mass transfer occurs. However, glass does not exist in a state of thermodynamic equilibrium and is therefore prone to undergo chemical reactions that can result in degradation over time. The understanding of the kinetic and thermodynamic stability of glass components is crucial for developing more durable and long-lasting glass materials.

An essential factor to be taken into consideration to predict glass dissolution is the knowledge of the relative concentration of bridging and non-bridging oxygen atoms¹⁹. The latter are bonded to only one silicon atom and their quantity within the glass network is proportional to the concentration of modifier ions.

Considering the two possible configurations for an oxygen atom (BO and NBO), the silicon atom may be found in five different tetrahedral arrangements: Q_0 , Q_1 , Q_2 , Q_3 , and Q_4 , where the subscript indicates the number of bridging oxygens (Fig. 2). The structure of the glass network is the result of the distribution of the rings and voids regulated by the interconnection between these different silicate tetrahedra. The size of the voids in the network controls the rate of water diffusion, which is kinetically favoured when the dimension of the voids is comparable to the diameter of the water molecule (0.28 nm). In complex glass (mixed alkali glass), modifier cations can totally or partially fill the voids, but when the material is exposed to high relative humidity conditions, these alkali ions are leached from the glass surface and replaced by hydrogen ions as part of molecular water. The ion-exchange reaction drives the hydrolysis of the glass network with kinetics depending on both the distribution of local structural units (Q_n) and the modifier content. In addition, the exchange of high-radius cations as K^+ from the bulk is considered to leave a bigger void in the glass network compared to the exchange of smaller cation as Na^+ , thus facilitating the entrance of water molecules into the deeper areas. In general, it can be said that the higher the concentration of NBO, the higher the number of ion exchange sites available and the rate of ion-exchange and network hydrolysis, following the reaction trend: $Q_1 > Q_2 > Q_3 > Q_4$ ^{19,20}. For this reason, in the discussion about the kinetics of the processes of ionic exchange and hydrolysis reactions it is essential to take into consideration the chemical composition of glass.

Taking into account what has been said above, knowing the chemical composition of complex glass and its Q_n concentration and distribution is fundamental for the appreciation of its chemical stability and leaching resistance, so as to adopt an adequate preventive conservation strategy. Nevertheless, the glass reactivity does not depend on Q_n species only. Understanding the correlation between local structural features of the glass and the activation energies of individual bonds is also crucial to predict the dissolution mechanism of the glass network. Potential Mean Force (PMF) calculations estimated the activation barrier for Si dissolution in presence of aluminium (Al). They revealed that Al is easily dissociated from glass network, but Si dissociation is hindered when Al is present as a second neighbour²¹. As a result, Al causes opposing effects on glass durability if added at low and high concentrations: the addition of Al in small concentration increases the durability by reinforcing

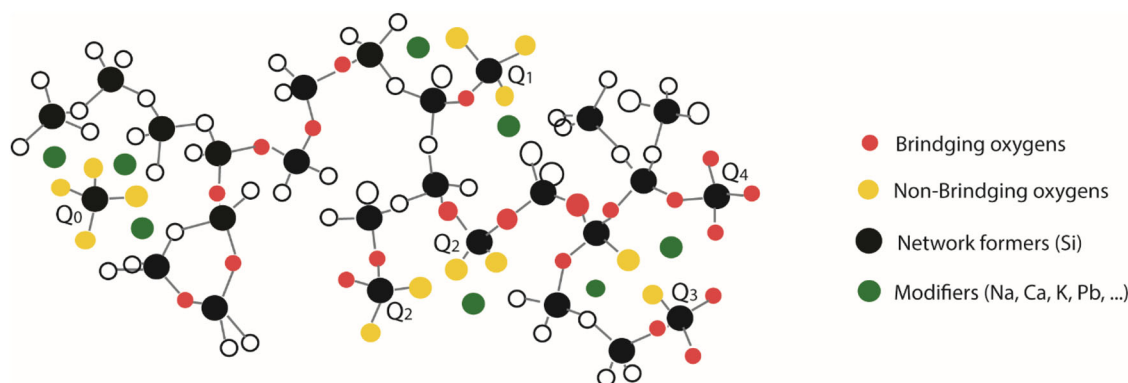


Fig. 2 Scheme of the SSL network based on Zachariasen representation. For clarity's sake, only the BOs and NBOs helping to identify the Q_n configuration in the silica network are coloured in red for BO and in yellow for NBO.

the strength of Si and increasing the polymerisation of the glass network, while at high Al concentration, the preferential release of Al results in the weakening of the silicate network. This predicting method can be extended to understand the role of Na, Mg, or B in more complex glass compositions.

Since the prediction of dissolution of glass network is a complicated topic of research, many recent works^{22–24} reported the use of machine learning based approaches to account for the percentage of bridging oxygen species, network connectivity, average ring size, as well as the composition modification due to the preferential release of modifier cations during the incongruent dissolution.

Several glass studies demonstrated the usefulness of Raman spectroscopy as an analytical technique to discriminate the characteristic vibrational modes of each Q_n configuration^{25–28}. Through the deconvolution of the Raman bands typically associated to the glass network it is possible to determine the single Q_n distribution and associate the variation of the area of the related Q_n band with the chemical composition of the sample analysed^{29,30}. When using this analytical approach, Raman spectroscopy can be adopted as a technique to distinguish a stable glass from an unstable one by means of the rigorous deconvolution of the vibrational bands of the glass network^{29,31,32}.

Nowadays, an analytical protocol that combines the potentialities of Raman spectroscopy described above with the advantages of using portable instrumentation to evaluate the chemical stability of glass, to predict the glass network dissolution for preventive conservation purposes, or even to establish the suitability of glass as storage material for nuclear waste is not available. Moreover, the in-depth spatial resolution of Raman spectroscopy is inadequate if one wants to determine the layered structures on an altered surface, whose features, in fact, sometimes vary on the nanometre scale. The association of other complementary analytical techniques would be ideal to optimise the reliability of Raman spectroscopy results.

X-ray absorption near edge structure (XANES) spectroscopy at the Si K-edge is another interesting technique that has been used to study the polymerisation degree of SiO_4 tetrahedra silica glass. In XANES spectra, position and structure of the absorption edge are largely determined by the charge of the absorber atom and by geometry of the first coordination shell, which depends on the coordination of the nearest neighbour atoms, the degree of polymerisation, and the presence of network modifiers and network substitutes³³. A study conducted on silicate glass reported that, with the increase in the polymerisation degree of the silica tetrahedra, the Si K-edge shifts towards higher energy, while it shifts towards lower energy when Si is substituted for another network former (Al)³⁴.

The chemical changes occurring at the surface of a corroding glass often cause an alteration of the local environment of metal

atoms, especially of the metal-oxygen pair distribution. These characteristics have been measured using conventional and glancing angle extended X-ray absorption fine structure (EXAFS) techniques, able to give information about number and distance of the atoms surrounding the absorber one. Examining the modifiers distribution in the vicinity of the surface gives important hints on how the surface is modified as corrosion advances³⁵.

As transition metal cations are generally of interest for the application of X-ray absorption techniques, their study can be easily exploited to monitor the decay of ancient glass. The modifications of the chemical environment of chromophore species (i.e., transition metal cations) can be recorded using both XANES and EXAFS techniques by monitoring the spectra of a selected metal species in an altered glass sample. By means of this method, it was possible to establish a relationship between the oxidation state of Fe and Cu cations during glass decay. Whereas, the Mn oxidation state was not directly correlated with the glass decay of the samples studied³⁶.

XANES and EXAFS analysis are not common and straightforward techniques, since they require the preparation of tailored samples from analysed objects (which is not always possible when dealing with cultural items) and the access to a synchrotron facility. However, this type of analysis provides important information to help the identification of structural and chemical changes in altered glass samples when investigating the molecular changes around cations with high field strength and well-defined short-range order.

In the following section, the main models of glass corrosion will be explored: they are based on the observation of the interactions between glass structure and external environment and on the different mechanisms in place during the process of glass alteration.

EXPLORING THE MECHANISMS OF GLASS ALTERATION THROUGH THE DIFFERENT EXISTING MODELS

The terminology used in the published works is imprecise. The terms *corrosion*, *alteration*, *degradation*, and *deterioration* are often found to be frequently used interchangeably as synonyms, despite having different shades of meaning. For the sake of clarity, all these terms will be used here as synonyms when talking about the phenomena that induce a change in glass physicochemical properties, regardless of the intrinsic or environmental factors that have determined such change. The term *dissolution* will be, instead, used to refer only to the rupture of the Si-O covalent bonds and the breakup of the structural silica network, and the term *leaching* will be used to identify the step of degradation that consists in the loss of alkali and alkaline earth metals ionically bonded to the silica network that precedes the network dissolution³⁷. Even if leaching is often associated with the initial

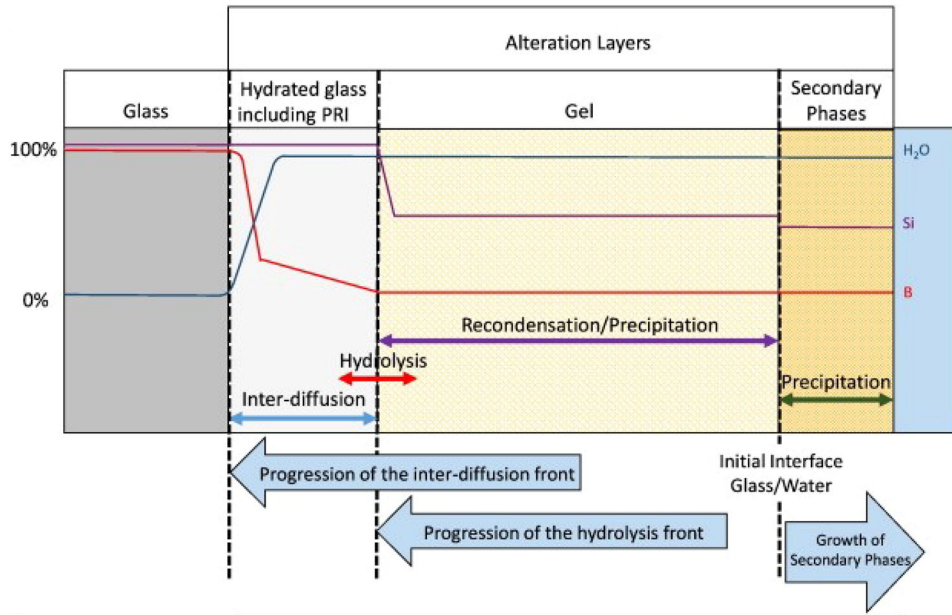


Fig. 3 Schematic representation of the alteration layers resulting from the inter-diffusion controlled glass corrosion mechanism (CID) and composed by an inner diffusion zone between the pristine glass and a depleted highly porous layer (gel layer) and an altered outer zone. The latter consists of a hydrated, cation-depleted layer resulting from a selective cation release. Courtesy of Gin et al.⁴⁸.

steps of glass degradation, the loss of alkalis can be a secondary phenomenon in specific conditions of high temperature (RH < 100%) and unstable glass compositions¹⁶. In other particular conditions, the degradation process occurs without any loss of alkalis, because the water penetrated into the glass network is unable to solvate them^{8,9,18}.

The interaction between water and glass can activate two different degradation phenomena, i.e., leaching and network breakage, mainly depending on the pH of the solution in contact with the surface. During leaching, the aqueous solution in contact with the surface typically has pH < 9^{38,39}. In this condition (pH < 9), ion exchange that involves alkalis (Na, K) and alkaline earth metals (Ca, Mg) occurs, forming ionic bonds with the oxygen of the glass network and the H⁺ ion from the aqueous solution¹⁶. This is a diffusive phenomenon and the thickness of the glass region involved in the reaction (indicatively a few microns) depends on the glass composition and on the time and temperature of exposition. The altered layers that form on the surface can act as a diffusion barrier to further extraction, even if hazardous cracks that allow the penetration of water molecules into the pristine glass may form. The alteration due to leaching does not affect the Si atoms: the network distribution does not change, only the Si-O-M bonds do.

On the other hand, the ions interdiffusion during leaching leads to a pH increase (eventually above 9) due to the formation of Na⁺ OH⁻ species in solution and Si-OH acid from the reaction between Si-O-Na and H₂O. An alkaline environment results in more aggressive attacks to the glass network, since it promotes the dissolution of the Si-O bonds⁴⁰. The reaction with the hydroxyl ions (OH⁻) breaks the Si-O-Si bonds and silanol groups Si-OH are formed.

The sites left free by the leaching of cations from the glass surface can be easily filled by hydrogen ions, which have small ionic radius. The hydrolysis process induces the introduction of H₂O molecules and OH⁻ ions into the opened silica structure, thus increasing the rate of the hydration process and the ion exchange.

The interactions and reactions that occur between aqueous solution and glass have been over the years the subject matter of extensive research focusing on the mechanism involved in this process at different scales of observation, research that has been

key to support the formulation of the classic theory of alteration and Interfacial Dissolution Precipitation model for dissolution of vitreous materials.

The Classic Inter-Diffusion (CID) model of glass corrosion is based on diffusion-controlled hydrolysis and ion exchange reactions⁴¹, which lead to the formation of structurally and chemically distinct zones (Fig. 3).

The classic theory of glass corrosion is underpinned by different formulated models of ion-exchange that take into consideration the effects of the preferential dissolution of more soluble cations during the initial part of the leaching process^{42,43}.

Many experimental and theoretical results obtained from observation in liquid conditions (and not in unsaturated humidity ones) have reported that the leaching mechanism involves the preferential release of alkali and alkali-earth ions rather than that of network formers, such as Si or Al ions, with a consequent formation of alumina/silicate-rich layer on the glass surface^{38,43}.

In general, the concept of preferential leaching is based on the thermodynamic and kinetic stability of the different glass modifiers. At lower temperatures and for ions with the same charge, the diffusion of larger ions (for example Ba²⁺ or Ca²⁺) becomes energetically unfavoured, while the smaller ions (for example Mg²⁺) can move more easily through the glass network⁴⁴. In any case, double-charged ions usually show less diffusivity in SSL glass than single-charged ones, mainly because of the marked effect of the very intense local electric fields acting on them. If the leaching mechanism proceeds, the solution becomes richer and richer in OH⁻ and its pH increases favouring the dissolution of silica through the break of O-Si-O network. Preferential leaching supports the selective removal of specific cations (non-stoichiometric release) and designs a theory about incongruent dissolution of glass that explains the formation of altered surface layer.

The technological developments of the last decades have made it possible to reveal increasingly more detailed evidence on the process that controls glass corrosion¹¹. The chemical reactions proposed in the general mechanism of glass corrosion (hydration, hydrolysis, and interdiffusion) are still considered valid in the most recent studies. However, over the last years the attention of the scientific community has been focusing more on understanding

how these reactions evolve kinetically and thermodynamically during the alteration process, and how they influence the structural and microstructural properties of the alteration layer at the atomic scale^{1,45}.

In 2015, a nanometre-scale study⁴⁶ of glass corrosion was performed using a combination of high mass and spatial resolution techniques, proposing a revised theory of glass corrosion called the Interfacial Dissolution-Reprecipitation (IDP) model. The IDP model is based on the congruent dissolution of silicate glass coupled in space and time with the reprecipitation of amorphous spherical silica aggregates of variable size. In opposition to the traditional glass alteration model, this recent theory supports the stoichiometric dissolution of glass without interdiffusion-controlled ion-exchange mechanisms at the glass reaction front⁴⁶.

Hellmann et al. validated this model through the study of artificially aged borosilicate glass altered at 50 °C in deionised water, using a unique combination of techniques with high spatial and mass resolution⁴⁶. By following the mobility of the major constituent elements of complex borosilicate glass, an identical release behaviour was noticed for modifier and former ions, regardless of their charge. These results validate two processes at the basis of this novel corrosion mechanism, i.e., the stoichiometric release of all the glass elements and the precipitation of amorphous silica with the formation of an altered surface layer. Furthermore, the interface between pristine glass and altered zone was demonstrated to be chemically and structurally well defined, with elemental gradients in the nano- to sub-nanometric range.

A schematic representation of the IDP model is presented in Fig. 4 according to the results of oxygen and silicon isotope tracer experiments in ternary borosilicate glass⁴⁷.

As described above, the IDP model entails the formation of alteration layer through the precipitation of hydrated species from the thin film of water to the hydrolysis front, with high degree of liberty to reorganise (Fig. 5). This leads to a sharp concentration profile of highly soluble cations and an interstitial water layer that would allow an easy separation of the altered layer from the pristine glass⁴⁸.

The rate of the reactions involved in the glass corrosion (ion-exchange, hydration, and dissolution) depends on factors such as glass composition, temperature, and pH. All of them may occur simultaneously during process of alteration in contact with liquid water and can be rate-limiting in function of the experimental conditions. In conditions of unsaturated humidity, studies demonstrating the existence of a rate drop followed by a residual regime are lacking. For these reasons, both the two models presented in literature (CID and IDP) are not able to describe universally the distribution of mobile ions and hydrous species inside the alteration layer.

A work published in 2017⁴⁹ reported the in-depth characterisation using atom probe tomography (APT), transmission electron microscopy (TEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) of the alteration layer formed under close-to-saturation conditions. The results revealed the presence of an alteration layer with a more complex structure, made of three different sub-layers (Fig. 6): (i) close to the pristine glass, a thin hydrated layer containing all the glass components, (ii) moving towards the surface, a passivating layer with constant concentration of glass formers (Si, Al) and decreasing concentration of modifiers (Na, Ca) which is delimited by a rough interface where alkaline and alkaline earths are preferentially leached out, and (iii) an external nanometric layer where Si undergoes hydrolysis and condensation reactions⁴⁹. These results contradict the IDP model of glass corrosion recently designed, which highlights that many gaps are still present in the explanation of the mechanism of glass alteration.

The authors of this review would like to emphasize that the universal application of the IDP model and other intermediate models to all silicate glass types is still an open question. This is because most recent research has focused solely on the artificial alteration of borosilicate glass, and the applicability of these models to other types of silicate glass remains uncertain. The characterisation of synthetic and geological glass altered over long time periods can be key to understand both the complex mechanisms responsible of the long-term transformation of glass network and the physicochemical features of the material transformed by the alteration. Multi analytical and high spatial and mass resolution investigation performed on surface of ancient glass provide clues about the characteristics of the altered layers and about how they reorganised their internal structure during long time periods. Instead, looking at the interface between the alteration layer and the pristine glass provides information about the mechanisms of glass alteration². In this way, this approach promises to be efficient in validating the above mentioned debated kinetic models. The knowledge of the long-term behaviour of glass structure is also pivotal to predict the network dissolution in burial conditions in nuclear waste management studies^{4,50}.

EVIDENCE OF DEGRADATION ON ANCIENT GLASS

Archaeological glass shows multiple and clearly visible symptoms of deterioration that can help identify well-distinguished classes of glass alteration⁵¹ depending on the conditions it aged in (i.e., in soil, underwater, under extreme environmental conditions) for several centuries. Dulling, iridescence, weeping, pitting, discolouration and cracking of the surface affecting the specimens are common phenomena that can be observed on glass that has been recovered from archaeological excavation⁵². The formation of one or the other of them depends both on the physicochemical properties of the glass and on the environmental factors it has been exposed to. More than one of the manifestations of alteration can be found in a single glass object, thus making it sometimes difficult to identify the most appropriate strategy for conservation and/or stabilisation.

The atmospheric deterioration of glass appears markedly different from the degradation that occurs when glass objects have been buried for centuries, for example under soil, and it is rarely observed on this type of glass that has remained interred up to discovery and recovery. *Crizzling*, also known as glass sickness or glass disease, has been identified as the major alteration symptom for glass objects stored in museums and in private collections.

Alteration of ancient glass in archaeological stratigraphic contexts

The term *dulling* is used to refer to the loss of clarity and transparency typically observed in ancient glass and caused by the formation of layers of alteration products on the glass surface⁵².

As discussed above in the section dedicated to the general mechanism of glass corrosion (Section "Exploring the mechanisms of glass alteration through the different existing models"), in presence of neutral or acidic conditions, elements like alkalis are typically leached out from the first glass layers onto the surface. These leached species, reacting with humidity and moisture of the environment, tend to form corrosion products (like salts) that build up on the object's surface and determine at first the loss of the original clarity⁵³. In addition, at advanced stage of alteration, also hydrated silica (silica-gel) particles can also reprecipitate on the glass surface, leading to the formation of thicker alteration layers and causing an additional loss of glass transparency and the appearance of translucency⁵⁴. This phenomenon is due to a combination of effects occurring between the local presence of

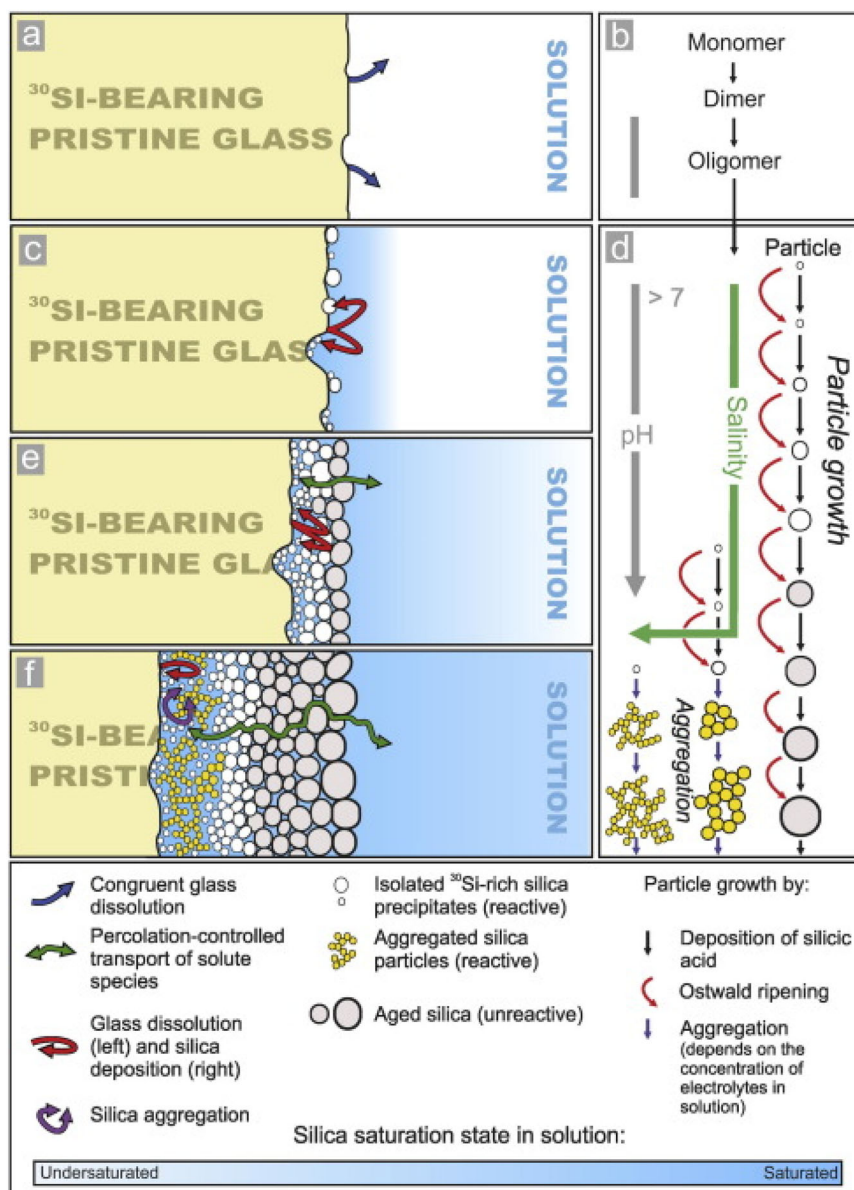


Fig. 4 Schematic outline of the phases that describe the interfacial dissolution-precipitation model of glass corrosion Courtesy of Geisler et al. **a** Initial congruent dissolution of glass is the first step occurring at the glass-water interface. This stage continues until the amorphous silica solution is supersaturated and etching pits are formed on the surface; **(b)** Si-rich interfacial solution layer is formed depending on the ratio of silica in solution to silica released during glass dissolution. Under this condition, the localised saturation of silica in solution promotes condensation and nucleation reactions that lead to the polymerisation of monomeric silica to form dimers and oligomers; **(c)** Precipitation of silica in the form of spheres on the dissolving glass surface occurs after silica supersaturation and nucleation in the solution; **(d)** Formation of SAL (Surface Alteration Layer) composed of altered amorphous silica proceeds along with congruent glass dissolution and further diffusion of dissolved species through the developing SAL; **(e)** Diffusive transport of water and dissolved species through the corrosion rim continues depending on the porosity of the SAL, i.e., higher porosity values correspond to higher diffusion rates; **(f)** Precipitation of secondary minerals like zeolites and clays sometimes occurs within and at the silica surface.

water and the composition of glass, which determines the diffusion of ionic species from the first atomic layers under the surface to the environment and the consequent reprecipitation of hydrated silica and other alkali-derived compounds. The extent of the visual effect is much more considerable as the ion exchange proceeds and the thickness of the deposited layers on surface increases.

In more advanced stages, dulling can lead to the formation of *iridescence* patinas (Fig. 7) that may eventually detach in the form of crusts from the original glass substrate. In 1863 Brewster⁵⁵ demonstrated that this iridescent effect is due to the diffraction of incident light from layers of weathering products containing metal

oxides formed after ion leaching. The rays of light are reflected from thin alternating layers of air and weathered glass crusts. These densely overlapping layers gradually penetrate deeper into the glass and they eventually change in colour towards darker hues⁵⁶. The cationic species leached from the glass are often prone to reacting with the anionic species derived from reaction between OH^- (especially in basic conditions) and atmospheric acid gases, thus forming salts with hygroscopic properties on the surface. This generates a phenomenon called *weeping*, which was first described by Organ in 1956. Weeping can lead to the formation of crystals or solutions of salts, depending on their deliquescence relative humidity⁵⁷.

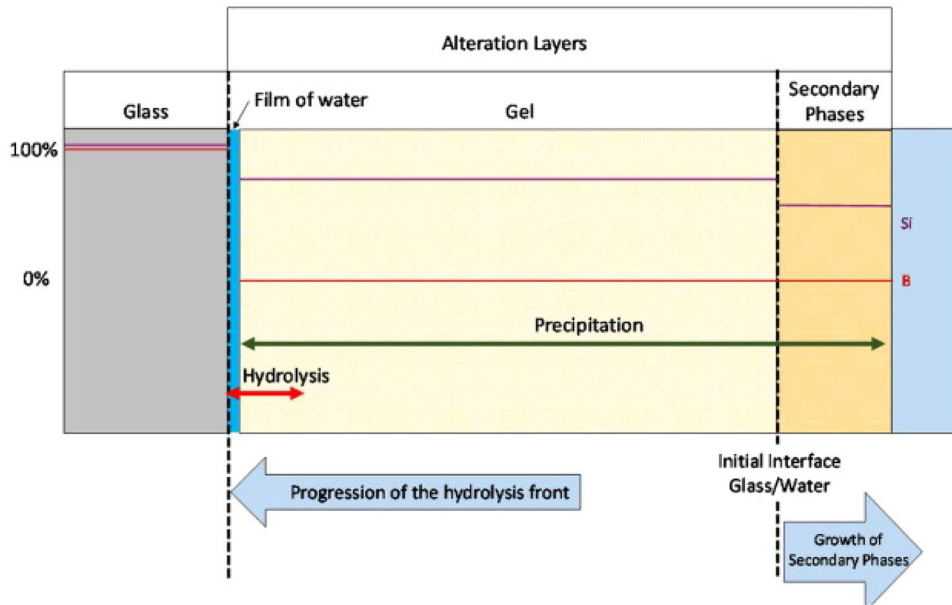


Fig. 5 Schematic representation of the formation of the alteration layer resulting from the interfacial dissolution-precipitation model (IDP) of glass corrosion. Courtesy of Gin et al.⁴⁸.

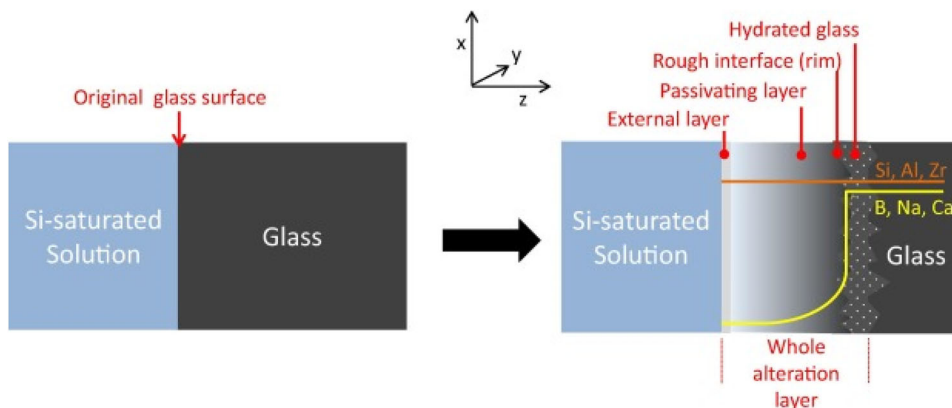


Fig. 6 Schematic representation of the formation of the alteration layer resulting from the in-depth characterisation of borosilicate glass altered in silica saturated conditions. Courtesy of Gin et al.⁴⁹.

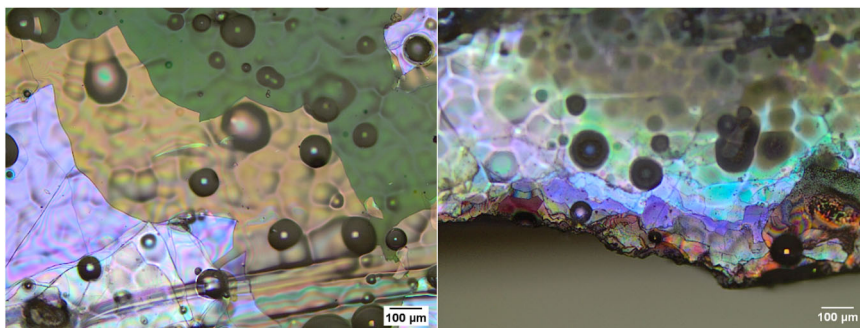


Fig. 7 Bright field optical microscopy images of an iridescent multilayer patina on a SSL archaeological glass sample. Images collected with Olympus BX43F optical microscope, x10 magnification. A detail of the indented rim where the overlapping of thin layers of altered patina is clearly visible (right panel).

The alteration phenomenon called *pitting*, is described as micro, small or large based on pit size, and it can occur simultaneously at different individual sites that later merge into interconnected complex structures producing an altered top layer, which causes the loss of glass transparency⁵².

Contrary to dulling, pitting is a visible mark of the weathering process, which occurs in alkaline solution⁵⁸ and commonly found on excavated glass. As described in Section “Exploring the mechanisms of glass alteration through the different existing models”, during the alteration process in alkaline solution, the prevailing deterioration

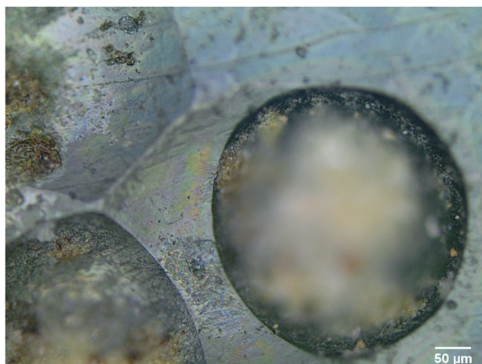


Fig. 8 Bright field optical microscopy image of one pit on the surface of a SSL archaeological glass sample. Image collected with Olympus BX43F optical microscope, x10 magnification.

mechanism is the dissolution of the silica network through the breaking of Si-O-Si bonds. Subsequently, the prolonged presence of a layer of moisture on the surface of glass causes an increase in the pH of the attacking solution, and ultimately pits are formed as a result of local dissolution of the silica network⁵².

A model that explains the formation of altered pits was recently developed by observing the decay process of different silicate glasses in river and marine aquatic environments⁵⁹. The experimental results showed that the alteration of SSL glass is characterised by a two-step mechanism. The first step, called “hydration period”, is short and causes the formation of isolate fissures, while the second step, called “pit development period”, involves the creation of basic species (OH⁻) during the dealcalinisation process that progressively break the silica network, thus widening the fissures to form pits. According to the results of this work⁵⁹, the formation of pits is correlated to a dynamic loss of mass, i.e., the slow rate of the first step of hydration allows the diffusion of solution and the consequent basic attack inside the fissures, causing local network dissolution.

Figure 8 shows the surface of a Roman archaeological sample affected by pitting.

Discolouration can be often seen on archaeological glass surface in combination with other types of weathering phenomena described above. It is closely related to darkening, which occurs when the oxidation of specific leached ions, such as iron, manganese, and copper, changes the colour of the weathering crusts, or to the production of hydrogen sulphide by sulphur-reducing bacteria in anaerobic environment and the formation of lead sulphide⁵³. The latter case occurs only when the glass contains a high concentration of Pb oxide, and it is buried under anaerobic condition. In other cases, the presence of manganese and iron causes the darkening of glass with the formation of brownish pits⁶⁰, as those visible in Fig. 9. Ancient glass contains these elements in the form of impurities present in raw materials (sand and wood ash) or as a result of their deliberate addition as chromophores or/and decolourant agents in the form of minerals (i.e., pyrolusite)⁶¹.

In the case of archaeological glass that has been interred for centuries, cracks may be present on the surface of the glass fragments: these are caused by the shrinkage of the alkali-deficient layer due to temperature and humidity changes. Typically, these cracks are filled with mineralised material, likely originating from the soil in which it was buried. The mechanism of their formation is currently being studied since it has not yet been fully understood.

Alteration of glass in atmospheric conditions

Crizzling has been identified as the appearance of minute cracks on the surface of glass (Fig. 10) developing over time. These cracks

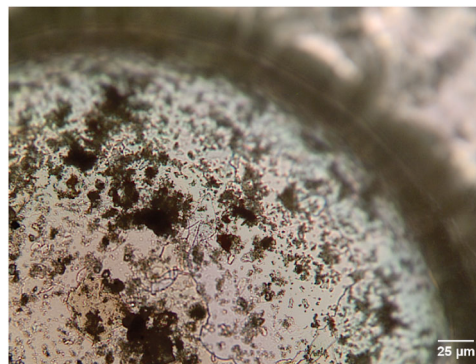


Fig. 9 Bright field optical microscopy image of brownish deposition formed on the surface of a colourless SSL archaeological glass sample. Image collected with Olympus BX43F optical microscope, x10 magnification.

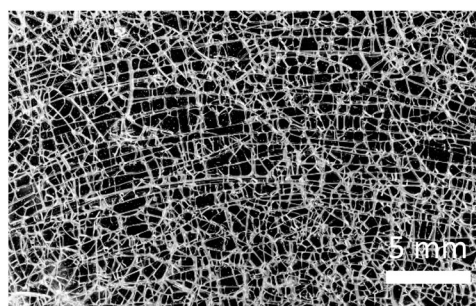


Fig. 10 Macroscopical evidence of crizzling in historical Venetian glass. Object exposed at the Museo Civico di Modena (Italy). Picture by Renaud Bernadet.

penetrate deeper in the body of the object, ultimately resulting in its physical collapse. This phenomenon is due to two main factors: the unstable composition and the storage in fluctuating humidity environments⁶². Better storage conditions can slow down, but not stop the deterioration, because the role of glass composition remains a key factor in the evolution of the crizzling alteration⁶³.

Early publications reported the chemical effects causing crizzling through experiments that reproduced the condition of glass alteration in the laboratory. The results showed that crizzling is mostly associated with glass compositions characterised by high alkali and low CaO contents, and/or a high K/Ca ratio⁶⁴.

In 1975 Brill⁶³ first used the term crizzled to describe glass with a decrease in its transparency due to the formation of fine cracks on the surface. He noted that certain glass objects that were in contact with water for centuries do not exhibit a high degree of degradation; however, once they are exposed to museum storage conditions (light, low RH and temperature), they display the formation of crizzling. This alteration mechanism is due to the dehydration of the glass surface, i.e., the low RH in museum display cases (15–20 %) causes a loss (up to twenty percent in weight) of the water that penetrated the gel layer of altered glass, bringing on a significant loss of volume in the gel layer itself which ultimately results in the cracking of the glass surface^{62,63}. In general, the cracking of the hydrated gel layer formed on the surface of unstable glass can be attributed to several factors, including the dehydration of the gel layer itself - as mentioned above - the leaching process, which can lead to network contraction after the replacement of larger alkali ions (Na⁺) by smaller hydrogen ions (H⁺), and the different coefficient of expansion of the bulk glass and the gel layer¹⁶.

The guidelines of the Corning Museum of Glass⁵² describes the process of crizzling indicating five stages. In the first stage (Initial

stage) the glass has a blurred appearance due to the presence of leached alkali on the surface. During this phase, it is still possible to wash the surface and the glass can return to its original appearance. Conversely, in the second stage (Incipient crizzling) the haziness remains also after washing and the glass surface exhibits fine cracks like tiny silvery lines. Cracking progresses in stages three (Full-blow crizzling) and four (Advanced crizzling) until it gets to the deepest regions, leading to the loss of small fragments. Eventually, crizzling is so deep that the glass loses its structural integrity, even without any external contribution (Fragmentation stage).

Often crizzled glass has a pinkish hue. When alkaline leaching occurs and the glass structure is open, the manganese ions present in the surface cracks oxidise, yielding a pink colour⁶². This phenomenon is more evident in ancient glass which contains manganese as a decolourant.

To limit the evolution of the crizzling process, preventive conservation is an essential strategy for the safety of museum glass objects. The Corning guidelines set the optimal RH range for glass conservation between 35 to 65%, however crizzled glass or glass with a particularly fragile composition require specific individually controlled cases with a stable RH condition in the range of 40–50% inside⁶⁵.

In addition to preventive conservation, the development of an innovative and compatible consolidation treatment for the protection or repair of cracked glass is an open challenge for the scientific community of cultural heritage conservation.

INTRINSIC AND EXTRINSIC PARAMETERS INFLUENCING GLASS DETERIORATION

As already mentioned, atmospheric conditions, such as temperature, the pH of the environment, salts and ions concentration, relative pressure under burial or marine conditions, and the presence of water in liquid form ($RH \geq 100\%$) or vapour ($RH < 100\%$), strongly influence the kinetic of the glass surface alteration and its chemical transformation.

Many published papers of archaeological interest use the term *weathering* to refer to the typical degradation process that affects archaeological glass that has been exposed to particularly unfavourable environmental conditions (especially in burial and underwater contexts)⁵². Weathering is a degradation process occurring through contact with water in the environment, both in the vapour and in the liquid state, whereas the term *atmospheric deterioration* is used to describe glass that aged under the effect of water in the form of moisture (especially in protected environments like museum display cases), which means in the form of vapour state interaction.

The study of extrinsic factors, that are closely linked to the environmental conditions acting during the alteration process over centuries requires the development of appropriate artificial ageing protocols, which allow the modelling of the phenomenon as a function of these parameters. Real cases of glass degradation are the result of the combined actions of the intrinsic and extrinsic factors mentioned above, which generate entangled mechanisms of ionic interdiffusion from the glass network to the environment and vice versa. From an experimental point of view, studying this interconnected process of ionic interdiffusion and the formation and growth of novel phases implies the need of relying on simplified model systems to investigate the effect of specific variables to the detriment of others, which are kept constant.

The study of the effect of the various factors on glass degradation has attracted the curiosity of researchers since the beginning of the XX century. Already in 1925, G. W. Morey⁶⁶ stated that the subject was still in an empirical state, despite the considerable number of works carried out. At that time, to understand the effect of water on the alteration process many

experiments were conducted by varying temperature, the pH of the environment and glass composition.

The following paragraphs describe the effect of various parameters that have a primary influence on the process of glass alteration. The studies there cited use ancient glass samples as evidence of the long-term effect of these parameters.

Effect of glass composition

Many ancient finds of SSL glass are macroscopically preserved intact in their shape, despite the physicochemical alterations caused by the burial environment over the centuries. Currently, 90% of globally manufactured glass is still based on the SSL composition, which has been kept largely consistent over the centuries except for a few modifications introduced at the beginning of the 20th century to enhance chemical durability and resistance to devitrification⁶⁷. Besides SSL glass, many other types of ancient glass exist, such as potash lime glass ($K_2O - CaO - SiO_2$), lead silicate glass ($PbO - SiO_2$), or potash lead silica glass ($K_2O - PbO - SiO_2$)⁶⁸. The optimal preservation of certain ancient samples and the complete collapse of others is the result of a complex interplay between their intrinsic material properties and the extrinsic factors acting on them.

Intrinsically, glass physicochemical properties play a significant role in determining its degradation behaviour. Such properties typically correspond to the chemical composition of glass, the nature of its surface, the presence of impurities, inclusions, inhomogeneity, and phase separations. In particular, the concentration of silica, alkali (soda, potash), stabiliser (lime, lead), as well as the inclusions of trace elements and additives like metal oxides, added into glass as chromophores, opacifiers and decolourants all strongly affect material durability⁵³. Small variations in the concentration of these components determine strong variations in glass durability. Diffusion through the leached layer is more likely to occur for smaller ions, such as Na, Mg, Li, rather than for larger ones, i.e., Ca or Ba. Although all types of alkaline silicate glass are susceptible to weathering degradation, from a thermodynamic point of view stability increases as in the following: $K_2SiO_3 < Na_2SiO_3 < Li_2SiO_3$ ³⁸.

Silica rich glass, such as Roman SSL glass, is more durable than poor silica glass, like medieval glass⁶⁹. In addition, K^+ , which is contained in medieval glass as a monovalent cation modifier, is more susceptible to leaching out from the deeper region of the glass network during weathering alteration than bivalent cations such as Ca^{2+} , which are present in Roman glass^{70,71}. This behaviour is due to the bivalent cations forming stronger bonds with non-bridging oxygen, as previously mentioned. The preferential leaching of K^+ over Ca^{2+} during the weathering process was also confirmed by an experimental study that investigated the weathering phenomena on naturally weathered potash-lime-silica-glass⁷². This behaviour of K^+ cations was also observed during leaching experiments in aqueous acidic solution.

The study of the varieties of composition of ancient glass and their resistance in $RH > 100\%$ have made it possible to identify the presence of compositions that are more chemically stable than others and to define general conditions to discriminate between *stable* and *unstable* glass⁷³.

In 1978⁷⁴, Hench systematically studied the surface of glass exposed to pure water and distinguished between 6 main types of surfaces with increasing inclination to deterioration in relation to their composition. The surface layers of the different glass types may have protective or non-protective properties for the glass substrate, depending on the capacity of reducing ion leaching and glass dissolution. In this work Hench distinguished *stable* and *unstable* glass based on the different compositions of the alteration products that form the first surface layers when glass is altered in liquid conditions. However, the protective character of hydrated layer has not been demonstrated in unsaturated humidity conditions yet; and,

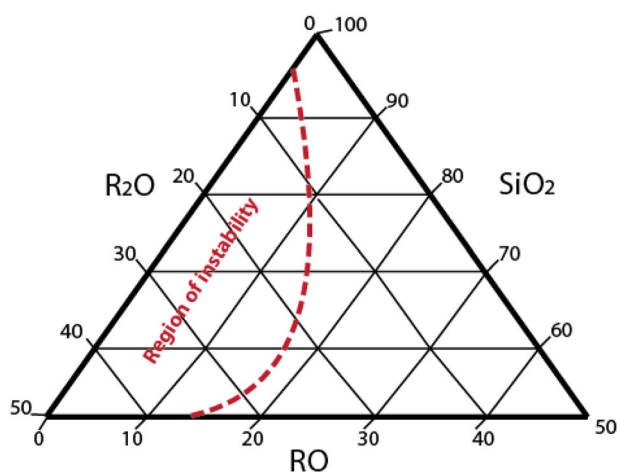


Fig. 11 Triangular representation of the stability of glass composition. R_2O represent the content of network stabilisers (monovalent oxides), RO the content of network modifiers (divalent oxides), and SiO_2 the content of silica.

moreover, a work of Sessegolo *et al.*⁷⁵ studied medieval stained-glass windows in unsaturated conditions with isotopic water experiment and demonstrated that the alteration layer is not protective against vapour transport and interdiffusion.

A further way to discriminate a stable glass from an unstable one could be to use the ternary diagram of Fig. 11, which was formulated in 1975 by Newton *et al.*⁷⁶ with a view to help predict the weathering behaviour of different types of glass. Plotting the concentration (mol. %) of network stabilisers (RO), network modifiers (R_2O), and silica (SiO_2) determines the chemical stability of a given glass composition, i.e., highly durable glasses are placed near the centre. This diagnostic model may work well when binary or ternary glass is considered, however complications may occur when classifying ancient glass, which has a more complex composition, because it may be necessary to consider the combination of multiple formers (SiO_2 and Al_2O_3), monovalent oxides (R_2O) and divalent oxides (RO).

By using electron microprobe analysis (EMPA) and hydration-dehydration experiments on ancient glass Brill observed that a deficit of stabiliser (CaO content less than 4 wt%) combined with an excess of alkali (over 20 wt%) in SSL glass easily leads to an extensive surface deterioration known as crizzling⁶³. He defined as unstable glass the one with total alkali oxide concentration over 20%; this composition range determines silica network configurations that are open enough to facilitate the migration of monovalent cations. In line with these findings, other studies reported that an increase in the CaO to SiO_2 ratio increases glass stability, while a concentration of calcium oxide over 15 wt% entails rapid glass instability³⁸. Recently, a comparison in terms of glass chemical stability was made using artificial mock-ups with different glass compositions which were exposed to high humidity environment and different levels of formic acid⁷⁷. The results showed that glass with a higher content of stabilisers exhibits greater stability, especially glass with calcium.

The presence of potash as a modifier and the low silica content in the composition make glass particularly fragile and susceptible to chemical alteration. Numerous works reported the considerable damage that affects medieval glass windows with Si-K-Ca-based composition, which is considered one of the most unstable^{78–80}. Typical alteration marks are mainly pitting⁸¹ or the formation of a corrosion crust⁷¹ on the surface due to the combined attack of water and increased pollution in the air. The weathering crust is often very heterogeneous and fractured because of the wetting-drying cycle conditions and generally consists of calcite, gypsum and/or syngenite formed by the reaction between the alkaline and

alkaline-earth elements released during ion-exchange and sulphur dioxide in the atmosphere⁶.

Effect of minor components in glass composition

In addition to the major elements discussed above, other minor elements may be present in the composition of ancient glass as decolorising, coloring or impurities of the raw materials used for their production. These minor elements can in turn contribute to the alteration process of the glass itself by giving rise to distinctive corrosion marks.

Several authors have remarked that manganese that accumulated between the altered layers may have originated from the burial environment^{82,83}. Dark deposits have been detected inside the dealcalinisation layer on the surface of Roman glass samples⁸⁴. Secondary electron images have uncovered that these deposits are formed from the interconnection of spherical particles of about 2 μm in size, with iron and manganese oxides as their major components. These studies clarify that during the leaching process Fe (II) and Mn (II) ions are hydrated and oxidised, giving rise to the formation of dark amorphous products that precipitate into the pores of the leached silica film.

It is well-known that glass technologists used to add Mn, as well as Sb, to the glass melt as a decolorising agent, but it is also known that, in this type of glass, the appearance of brownish areas on the altered surface is due to an oxidation process of Mn(II) to higher oxidation states. It is generally observed that in the dark areas Mn is present in +IV oxidation state^{85,86}. Nevertheless, a recent work performed using synchrotron radiation X-ray absorption spectroscopy (XAS) analysis on historical stained-glass windows demonstrated that the most extended brown altered areas mainly contain Mn mainly under a +III oxidation state⁸⁷.

Through the analysis of 14th–17th century window glass, Schalm *et al.*⁸² concluded that the formation of Mn-rich inclusions takes place simultaneously with the growing of leached layers settling along their interfaces and their concentration is mainly caused by the environment (soil) in which the glass was buried for several centuries.

Although brown/black staining has mostly been attributed to manganese compounds, iron (and titanium) compounds were often reported in association with the manganese⁵³. Other elements which are often present in historical glass network as impurities can improve the chemical stability of glass. For example, low amounts of ZrO_2 (2 %wt) increase the acid and alkaline durability of glass⁸⁸, and a hydrated ZrO_2 surface can act as a barrier to further dissolution of other ionic species. More recently, it was demonstrated that the substituting an insoluble oxides like zirconia to a fraction of silica slows the glass dissolution kinetics, but prevents the alteration gel reorganisation inhibiting the pore closure mechanisms and leading to greater degree of corrosion⁸⁹.

These results show that it is essential to know the exact composition of an ancient object to determine a range of the aging behaviour that it is prone to. To do that, it is important to also consider the presence of elements in lower or trace concentrations to fully describe the corrosion phenomenon and formulate models that are closer to real cases of ancient glass alteration.

Effect of liquid vs atmospheric water

Water was observed to be the primary environmental ageing factor that causes glass deterioration by Lavoisier already in the early 1770s. Lavoisier also indicated two different mechanisms of water penetration into the glass network, i.e., through network voids between oxygen atoms in molecular form, and by hydrolysis and condensation reactions with the metal-oxygen bonds¹⁹.

The alteration of silicate glass differs when it occurs in liquid-phase or in vapour-phase regime. In contact with water the glass

Table 1. The six types of glass surface described by Hench and Clark (1978).

Type I	Formation of a thin hydrated surface layer with no significant difference with the bulk glass. Stable glass.
Type II	Formation of a silica rich protective film due to the exchange of selective alkali ions, with no further damage to the silica network.
Type III a	Formation of two layers of protective surface film of aluminium silica or calcium phosphate on top of a silica rich layer.
Type III b	Formation of multiple layers of hydroxides or oxides on the glass surface when exposed to water, especially on alkali borosilicate glass.
Type IV	Formation of a silica rich non-protective film when the silica concentration in the glass composition is not high enough to prevent loss of alkali or destruction of the silica network. Unstable glass.
Type V	Formation of soluble glass with silica dissolution and equal loss of alkalis.

surface undergoes chemical attack through ion-interdiffusion and hydrolysis of metal-oxygen bonds⁶. In vapour conditions (RH < 100%) the hydration process does not release elements into the fluid, but it involves a redistribution of elements in the alteration layer (expect for volatilised elements)⁹⁰. The formed hydrated layer has chemical composition and porosity that are different from those obtained in liquid conditions, thus resulting in the glass durability properties specific for liquid or vapour-phase regimes. Even if the molecular process is the same, the interplay between the intrinsic and extrinsic variable changes affecting the macroscopic transformation of the material⁴⁵.

During the phenomenon of water diffusion, no matter in which RH condition, the glass surface is covered by different monolayers of water, depending on the water partial pressure in the atmosphere. As soon as the silica network of a freshly made glass encounters moisture from the environment the chemisorption of water molecules starts from the first layers of the surface, which is consequentially more subjected to physical and chemical transformation. Water is chemisorbed on the glass surface and a thin film of water of few molecular layers builds up onto the chemisorbed layer, depending on RH condition.

One of the first characterisations of altered glass surface was conducted by Hench in 1975⁵⁶, using a combination of analytical techniques that enables to obtain physicochemical information from different depths of the altered glass surface. He systematically studied the glass surface altered in liquid water, using techniques like Auger electron spectroscopy (AES), infrared reflection spectroscopy (IRRS), and electron microprobe (EMP), and distinguished 6 main types of surfaces with increasing inclination to deterioration (Table 1). Of these, only Type I is stable and shows no main differences with bulk glass. The other types are considered unstable and prone to deterioration over time. Type II and type IV are of interest for historical deterioration. Type II is formed when the glass contains a high level of network formers, and it involves the formation of a silica-rich layer on the surface that acts as a protective film, preventing the leaching of alkali ions and the rupture of the glass network (Si-O-Si). On the other hand, no protective film is formed for Type IV and so the leaching of alkali can proceed. This latter situation is typical of unstable glass.

According to Hench's classification, ancient glass has a surface that corresponds to Type II and Type IV surfaces, which are characterised respectively by the presence of silica-rich surface protective layers (when the concentration of network formers is high enough) and the presence of non-protective surface layers that allow the alkali leaching to proceed (when the soda to silica ratio is high enough)⁵⁶.

In the case of discontinuous contact with aqueous media, which is typical of the atmospheric alteration, the formation of laminated structure on the altered glass surface has been explained by the intermittent water supply⁶. Through the observation of ancient glass surface by TEM, a sequence of bands of different thickness has been recently distinguished⁹¹, i.e., thinner bands called lamellae (20-50 nm) and thicker ones called laminations (0.1-4 µm), which consist in groups of laminae with the same orientation. The amorphous laminae, which are depleted of

alkaline ions, are formed from the local rearrangement of glass elements resulting from the repetition of several cycles of interdiffusion and glass dissolution processes. Moreover, cracks are developed perpendicularly and parallelly to the laminae and laminations. Based on this study, two main processes take place within the cracks, i.e., the migration of atmospheric solutions deeper into the bulk glass, thus moving the alteration front further, and the precipitation of secondary mineral phases which favours the mechanic separation and the loss of glass fragments.

In 2016, a study of the altered layers observed in ancient glass proposed a model to explain the formation process of this laminated degradation⁹². Thanks to optical microscope, field emission-scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX) analyses, it was possible to describe surface lamellae as an alternation of random amorphous silica nanoparticles with different packing densities and with thickness between 0.1 and 10 µm. Moreover, the growth of nanosized silica particles on the surface of the altered glass was observed to be one of the by-products of the leaching process of glass components that occurs under alkaline conditions.

While glass alteration in contact with water in a liquid state was widely studied during the 1900s, testing approaches in unsaturated atmosphere have been seldom explored until more recently⁹³. In 2020, Majerus et al.⁷ published an overview of the experimental protocols for glass alteration tests in unsaturated atmosphere. All the tests reported were conducted under RH < 100% condition and, when a saline solution was present, their configuration ensured that the samples were never in contact with it. These results obtained under RH < 100% suggested that the glass alteration mechanism was different from the one obtained in contact with liquid water (RH > 100%). In contrast to saturated humidity conditions, in unsaturated environments, the hierarchical order of glass alteration processes involves network hydrolysis first and interdiffusion second, particularly for glass with compositions classified as unstable.

Alloteau et al. recently demonstrated that in water vapour conditions, the process of glass hydration is independent from dealcalinisation: at higher temperature (80 °C) hydrolysis predominates over diffusion processes and solvation, whilst at lower temperature the two processes proceed together in parallel. To state that, they performed ageing test in static conditions (no T and RH cycling) at controlled temperature and humidity (RH 85%) on three different types of unstable historical glass (soda-lime silicate from antiquity, mixed alkali silicate from middle-age/renaissance and potassium silicate from XVI-XVIII century). The conditions were set to avoid any liquid water flow on the samples during tests.

Sessegolo et al.⁷⁵ evaluated the respective contribution of rain, wet periods and unsaturated humidity on the kinetics of formation of the alteration layer of potash-lime-silica glass. The results demonstrated that the fluctuation of dry and wet periods (non-static condition) leads to the formation of an altered layer rich of cracks, pits, and scales, which constitute a network of pores and fractures behaving as a major vector for interdiffusion of liquid and vapour water. The characterisation of this fracture network is particularly important in case of prolonged alteration in

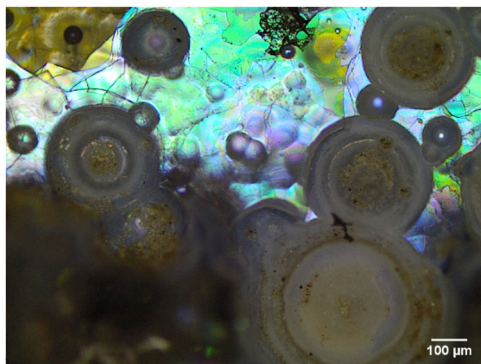


Fig. 12 Bright field optical microscopy image of alteration rings on the surface of a SSL archaeological glass sample aged in burial lagoon environment. Image collected with an Olympus BX43F optical microscope, x10 magnification. Interconnection between adjacent rings can be observed.

atmospheric conditions, where liquid and vapour water phases are systematically combined in the associated diffusion processes. In another subsequent work⁹⁴ the authors proposed a model to estimate the thickness of alteration of stained glass windows subjected to liquid water (such as rain), comparing the expected value of alteration thickness extrapolated linearly over 650 year with those observed on ancient stained glass. The values predicted by the developed model match well with the alteration layer thickness observed on real ancient medieval samples^{6,95,96}.

Effect of saline and burial environments

In the last two decades, several works have been done to explore the effect of ageing in burial or marine environments on the alteration mechanisms of glass and on the formation of new alteration phenomena. A considerable number of works focused on the prediction of the durability of high-level nuclear waste glass and the migration of radioactive and non-radioactive elements into the burial soil^{9,97,98}.

Verney-Carron et al.⁵ studied ancient Roman glass blocks naturally aged in seawater obtaining the kinetic parameters to develop a geochemical model to simulate the alteration of archaeological glass. Comparing the results obtained from the characterisation of ancient glass with those from the computer simulation, this work demonstrated the importance of archaeological glass for validating the predictive capacity of geochemical long-term model, thus bridging the gap between the results obtained from short-term experiments and long-term alteration of complex systems.

Palomar devoted many studies to weathering and to the comprehension of the environmental effect on the stages of glass alteration^{59,99,100}. In particular, she reported the effect of coastal atmosphere on glass degradation¹⁰¹, which is a scarcely investigated subject. The alteration of glass surface exposed to coastal environment is mainly caused by the high presence of liquid water that covers the glass surface, thus inducing a hydrolytic attack and the dealkalisation process, and by the high wind speed, which favours the transportation and deposition of sodium and chlorine ions on the glass surface. Marine aerosol in elevated concentrations represents a hazardous agent for the chemical stability of glass, since its action could increase the hygroscopicity of the glass surface and open the glass structure, allowing the alteration to proceed deeper into the glass.

Another visible mark of degradation observed on the surface of glass altered in saline environment is the formation of peculiar chemical ring-like patterns that have been explained according to the Liesegang theory (Fig. 12). Diffusion, reaction, nucleation and crystal growth are all phenomena that have been used to

formulate models that explain the Liesegang rings formation^{102,103}. Dal Bianco et al. observed these weathering rings present on glass fragments from the Roman ship *Julia Felix* found on the Grado lagoon, in North-East Italy, and dated back to the 2nd century AD^{104,105}. Their characterisation study showed a maximum diameter of the rings of about 1 mm and the interconnection of interface lines during the simultaneous growth of adjacent rings. This study did not report an exhaustive theory about the formation process of rings, but the authors observed that the structure was similar to the descriptions of Liesegang kinetic evolution of precipitates in gel found in other research works^{106,107}. This assumption is acceptable since hardly corroded glass structure can be assumed as a gel where weakly soluble salts periodically precipitate due to the reaction between two soluble substances, one of which is dissolved in the gel medium. The final appearance of the precipitates depends on their solubility and on the initial concentration ratio of the reagents, but generally their aspect is concentric around the centre in which precipitation starts¹⁰⁸.

Nowadays, the formation of this type of rings on archaeological glass has been observed on the surface of samples recovered in submarine environment^{104,109}. The authors of this review suggest that a saline-rich environment, whether seawater or wet soil, play a role in the formation of the rings. The soluble substances present in these environments may react with soluble substances from the aged glass forming salt precipitates on the surface of glass that act as centre of nucleation for the growth of the concentric structure.

The mechanisms that generate the formation of rings on altered glass surface have not been analytically confirmed, and the study of the evolution of the kinetics that controls ring growth on archaeological glass remains incomplete, despite the availability of modern techniques. Although the layers observed and experimentally described by Schalm¹¹⁰ can be compared to the bands structure obtained from Liesegang kinetics, there is a lack of systematic experimental work in the literature to confirm whether this theory can be applied to the dissolution-precipitation mechanisms of glass.

Chemical studies on the composition of the soil where archaeological glass aged for centuries might validate the hypothesis of ionic exchange between the elements of the soil and the elements of the glass network, providing the opportunity to understand how the interaction with the external environment can drive the process of alteration in different types of glass.

Many published research studies mention that also for glass samples that altered buried in soil the most common pathology observed is the formation of dealkalisation layers^{111–113}. One of these performed a stratigraphical analysis using a non-invasive technique (laser induced breakdown spectroscopy, LIBS) to observe the progressive dealkalisation of glass bulk composition, reporting an increase in the calcium and sodium intensity signals on the glass surface⁸⁴.

In the field of ancient glass, experimental studies simulating ageing in soil are less common^{114–116}. In a recent work, Palomar et al. tried to replicate ageing in soil in a natural burial environment to understand the corrosion mechanisms acting on different ancient glass types (Roman, medieval, lead crystal glass, common window glass)¹¹⁷. The burial tests were set up to last 300 days and were carried out at 60 °C, to accelerate the alteration processes. The pH of the burial soil and the glass composition showed to have a key role in controlling the reactions between the constituent glass elements and those from the environment.

When considering burial artificial alteration of mixed alkali glass compositions with low silica concentration, acidic or neutral conditions (pH 6.5 – 7.5) lead to the formation of micro pits and cracks; an iridescent and translucent layer is formed, instead, on the surface of glass under alkaline soil condition (8.0 – 9.0)¹¹⁸. Silica-soda-lime glass shows a different behaviour. In fact, in acidic soil the formation of both isolated and interconnected fissures

may be observed. However, under neutral and alkaline soil conditions an increase in the number and depth of pits, whose rate of accretion depends on the content of alkaline oxides in the glass, can be detected, with a considerable increase in the diffusion of surface degradation under the alkaline condition¹¹⁷. This experimental evidence is a clear example of the necessity to consider glass composition and environmental factors simultaneously when approaching the understanding of the glass corrosion mechanism.

Effect of the environmental pH

A pivotal factor in determining the rate of glass corrosion is the pH of the attacking solution both in case of vapour and liquid conditions¹⁰. Under conditions of low pH (acidic solution), the deterioration mechanism predominantly involves the ion-exchange process due to the abundance of hydronium ions in solution and the formation of silanol groups [Si-OH], generating a hydrated gel on the surface which slows down degradation¹¹⁷. Differently, at high pH, the interaction between the glass surface and the alkaline solution leads to the dissolution of the silica network through the rupture of the Si-O-Si bonds, which implicates a more aggressive condition.

In works performed in 2016⁹² and 2021¹¹⁰, Schalm et al. observed that glass surface is transformed in both acid and alkaline condition, but different morphologies can be developed depending on the pH of the solution. At pH<7 the transformed glass has a homogeneous morphology determined by the dissolution of leached silicate network and precipitation of dissolved compounds as amorphous silica forming linear and randomly branched chains of alteration product that can be described as a silica gel. At pH between 7 and 10 of the local solution the transformation process leads to the formation of silica nanoparticles packed into alternating density lamellae. The authors successfully reproduced the lamination in laboratory experiment performed around pH 10, where silica solubility is highly variable and induces the cyclical dissolution-precipitation of silica. The mechanism of formation of consecutive lamellae with alternating packing density is proposed to be dependent on the pH oscillation in the local solution during the alteration process. In extreme alkaline condition (pH>10) the fast dissolution of silica network occurs without any material precipitation.

A recent work⁹⁴ highlighted how the pH-dependency is linked to the specific composition of glass and consequently to the solubility of different glass constituents. The results show that the pH-dependency of Ca-Mg-silicates highly differs from the behaviour of aluminosilicates, and that Si-K-Ca medieval glasses have a very low pH dependency at alkaline conditions.

Effect of pollutants

Air pollution was identified as a particularly dangerous agent that enables to speed up and enhance alteration processes. In the museum context, the presence of carboxylate acids pollutants is generally the main cause of glass corrosion and of the formation on the glass surface of efflorescence salts as deterioration products¹¹⁹. With regards to historical stained glass, an experimental work carried out over a six-year period to quantify the influence of various air pollutants from different local environments (Europe and North America) on the degradation of potash-lime-silica glass, which has a similar composition to that of medieval stained glass, showed the formation, after exposure to rain and solar radiation, of crystalline carbon-rich products unlike those of samples aged under sheltered conditions¹²⁰.

Melcher and Steiner¹²⁰ performed a 6-year experiment to evaluate the effect of acid gas and pollutant on replicas of stained glass, comparing the leaching depth formed on potash-lime-silica glass replicas to former leaching studies performed on medieval stained glass. This work demonstrated that the hypothetical

leaching depth cannot be directly related to pollution data because, while the leaching depth increases with time, the leaching rate decreases. Even a paper of Robinet *et al.*³⁰ highlighted the role of the organic pollutants formic acid, acetic acid and formaldehyde in the alteration of unstable soda silicate glass. He confirmed that museum wooden cabinets emitting organic pollutants must be avoided since they foster the progressive alteration with an estimated rate of ~2 nm/day.

ADVANCEMENTS IN MONITORING ANCIENT GLASS CONSERVATION STATE

The kinetics of glass corrosion, as well as the sequence of events involved and the prevalence of one interconnected mechanism over another, are dependent on both the chemical composition and structure of the glassy material and the environmental conditions to which it is exposed. These conditions include the amount of water that reacts, the chemistry and pH of the solution, and the duration of exposure. Given the complexity of these factors, the alteration of glass is a complex phenomenon that requires careful study. Therefore, particular attention should be paid to the analysis of ancient glass samples that have undergone modifications over time scales that cannot be replicated in the laboratory. These samples provide valuable insights into the long-term alteration mechanisms of glass and can aid in the development of more accurate predictive models for understanding the complex behaviour of glass materials in various environmental conditions.

The characterisation of altered ancient glass provides concrete evidence of the transformation of the vitreous structure, the nature of the dissolution products, and the way in which a specific glass composition reacts to a particular environment^{3,4,7,70,121,122}. Over the course of history, the evolution of glass manufacturing has led to the production of various types of glass, such as Roman SSL glass, medieval stained glass, or Venetian crystal glass (*Cristallo*). Artefacts (and their fragments) made from all of these types of glass inherited from the past represent an exceptional opportunity to better understand the processes involved in glass corrosion on a long-term scale. This is due to their specific chemical stability, resulting from their unique chemical composition, and their aging in soil, underwater, or confined spaces with specific microclimates for centuries.

The analysis of glass surfaces is currently considered the most effective scientific approach for studying chemical and physical variations that occur at the interface between the atmosphere and the glass surface. Advanced surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS) and ToF and/or dynamic SIMS, provide high-resolution data that enable the investigation of the chemical composition of the glass surface's first nanometres and facilitate monitoring of its modification during the alteration process^{67,123}. SIMS is widely considered one of the most suitable techniques for studying corroded glass¹²⁴, due to its ability to detect hydrogen and investigate the glass surface up to a depth of a few microns. Another technique commonly reported in the literature for studying the weathered surface of ancient glass is laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which allows for the acquisition of 2D and 3D elemental distribution with spatial resolution as high as the spot size used for the analysis. Only one work, published in 2013¹²⁵, presents the procedure to obtain elemental maps to investigate surface layer phenomena on pitted ancient glass. The results of this application showed that the dealkalinisation of glass sample occurred on surface, as the direct or indirect consequence of the hydration process, resulting in the final formation of pits and of the so-called Liesegang rings on the surface of the sample. Despite the novelty of this research, the spot size of the laser beam used in this work (diameter of 80 µm) is higher than the average size of the corrosion marks present on ancient samples. The spatial resolution

on the reconstructed maps can be improved by using smaller spot size of the laser beam (down to 10 μm) making it possible to obtain a resolution suitable for appreciating the chemical variability of extremely heterogeneous samples. This can potentially increase the understanding of the mechanisms of formation of these altered phases.

Critically speaking, the extensive study of glass surface composition using these advanced analytical techniques is still seldom considered when investigating the corrosion mechanism of glass both on ancient samples and through an artificial ageing approach in the laboratory^{30,126,127}. Each surface technique has its own peculiar applications and limitations¹²⁸, but a combination of different techniques allows a complementary and more comprehensive characterisation of corroded glass.

Collecting morphological, structural, and chemical information through a multi-scale analytical approach is necessary to gain a comprehensive understanding of the evolution and kinetics of glass alteration, including the modification of glass composition. Well-designed experiments are crucial due to the co-operation and mutual influence of different mechanisms involved in glass corrosion. This approach allows for investigation from a macroscopic to a nanometre scale observation. The information gathered can help determine how and when to intervene for conservation and preservation of glass objects, whether they are of industrial or historical significance.

The evaluation of storage parameters such as relative humidity, temperature, and light, as well as the condition of the glass, are crucial for preventing degradation of glass objects in museum collections or other sites of cultural interest. This approach is particularly important for understanding the influence of intrinsic and extrinsic factors in the processes of alteration and finding the best conditions for conservation. Surveys^{129–131} conducted in various museums in Europe have shown that a significant number of glass objects are in critical condition due to extensive degradation, highlighting the need for preventive actions. For example, at the Victoria and Albert Museum, out of 6,500 glass vessels optically investigated, more than 400 showed clear signs of glass deterioration⁵⁴. Similarly, the glass storage conditions of the Royal Palace of Madrid and the Technological Museum of Glass (Segovia) were evaluated during the period from September 2019 to November 2020, detecting a high concentration of formic acid in the display cabinets and wardrobes, mainly due to the presence of wood, which results in a higher glass surface hygroscopicity (pH=8)¹³².

Several methods have been used to categorise unstable glass from museum collections based on its appearance⁶⁵ or by analytical techniques –like X-ray fluorescence (XRF)¹³³, ion beam techniques (particle-induced X-ray emission, PIXE, and particle-induced gamma ray emission, PIGE)¹³⁴ or spectroscopic techniques (Raman and Fourier-transform infrared, FTIR)^{135,136} – in order to determine glass composition. Using these techniques to analyse cultural heritage objects can be complex due to many operative limitations, as for instance the need of carrying out micro-sampling (which is often not possible) or moving the objects to the specialised laboratories where the instruments are hosted. With the aim to distinguish stable from unstable glass in museum collection, the ideal analytical technique should provide the chemical composition of the sample, be highly sensitive, and have a very fast time of analysis to characterise as many samples as possible in a short period of time, while operating in a non-invasive way. Consequently, it can be safely stated that no scientific and straightforward approach for understanding the chemical nature and composition of unstable glass in a non-invasive way and for large museum collections of glass objects has been developed yet.

CONCLUSION

In the light of the above, it is evident that the most effective approach to study glass degradation involves the integration of two main distinct but interconnected methods:

- the evaluation of the surface of ancient glass artefacts;
- the evaluation of intrinsic and extrinsic causes for glass alteration.

Advanced analytical techniques can be used to characterize ancient glass surfaces and observe the products of the long-term transformation of the glass structure resulting from the alteration process. In parallel, laboratory-based aging experiments can be used to evaluate intrinsic and extrinsic causes of glass alteration, distinguishing the effects of different parameters and identifying the most relevant factors that influence glass alteration kinetics. Parameters such as the content of alkalis and stabilizers in the glass composition, as well as temperature and humidity, strongly impact the chemical durability of glass by affecting the concentration of alkalis and hydroxyl or non-bridging oxygens in the hydrated layer. It is difficult to determine which factor has the most significant influence on the process of glass alteration because the final degradation symptoms are the result of a mutual effect between all the aforementioned.

As evidenced, over the years many experiments aimed at understanding the phenomenon have been reported in literature and almost as many methods have been proposed. This abundance of results represents an outstanding opportunity for future research studies in this field, which will be able to rely on advanced analytical approaches and more accessible high-resolution techniques even for the domain of cultural heritage science. The results obtained from the study of ancient materials are pivotal to validate the long-term capacity of kinetic models –which are based on experimental data only – and to strengthen current theories of glass corrosion.

Moreover, comparing the characteristics of artificial replicas with those of ancient glass enables a better understanding of the glass corrosion phenomena, that in turn can underpin both the formulation of new protective solutions to preserve and protect glass artefacts in the long-term and the design of technologies exploiting glass properties in a variety of applications.

Received: 13 June 2022; Accepted: 25 April 2023;

Published online: 20 May 2023

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ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the anonymous reviewers: their insightful comments and critiques helped to significantly improve the quality and clarity of this paper. The authors are deeply grateful for their time, effort, and dedication.

AUTHOR CONTRIBUTIONS

Both G.F. and R.Z. contributed equally to the concept, drafting and revision of this review. E.C. and A.T. revised and critically reviewed this work.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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