POSTER

# Ancient glass alteration and advancement in active conservation strategies

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Glass finds application in multiple domains, from the technological field to the artistic one. The study of its durability is central to determinig its potential as a recyclabe and sustainable material capable of replacing several dangerous and polluting constituents such as plastics, particularly in the upcoming era of circular economy.
Because of the thermodynamic properties of this material and its high variety of compositions, the evaluation of glass durability and alteration mechanisms remains a challenge.
In this work we propose a complete strategy to approach the problem of glass corrosion and stabilization. Combining the results of the macroscopic characterization of archeological glass samples and artificially aged mock-ups, we define a novel silica-based formulation for the consolidation and protection of ancient glass.

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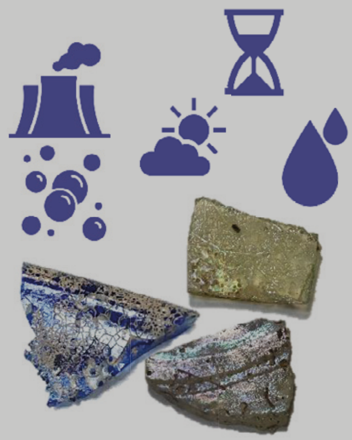

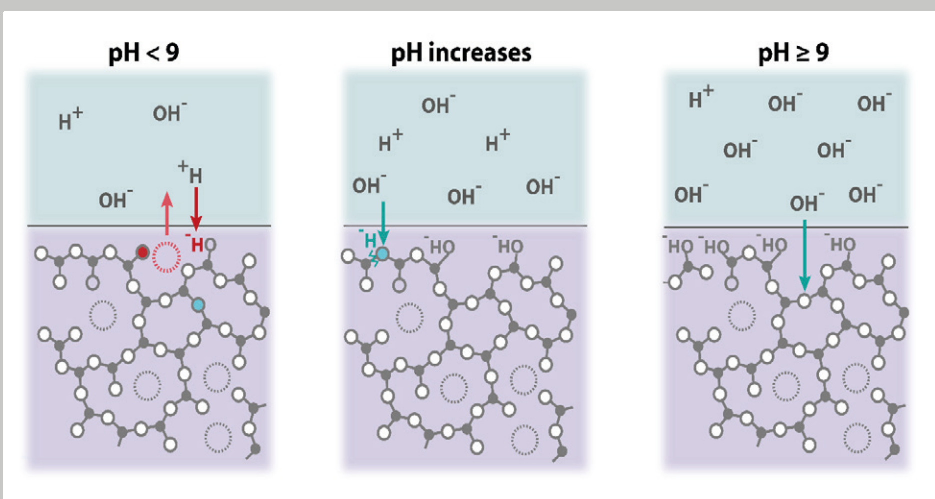


Fig. 01 Three archeological glass samples affected by different types of glass degradation (bottom), list of atmospheric agents rappresented by icons: temperature, water, pollutions, time (top).
Fig. 02 From the left to the right: protons are not strong enough to break Si-O-Si bonds, promoting the alkalys and alkaline earth ions leaching; hydroxide ions are strong enough to break Si-O-Si bonds; hydroxide ions cause the dissolution of the silica network.

# ANCIENT GLASS ALTERATION AND ADVANCEMENT IN ACTIVE CONSERVATION STRATEGIES

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GLASS - CORROSION - PROTECTION - CULTURAL HERITAGE

ITALY

**Abstract**
Glass finds application in multiple domains, from the technological field to the artistic one. The study of its durability is central to determining its potential as a recyclable and sustainable material capable of replacing several dangerous and polluting constituents such as plastics, particularly in the upcoming era of circular economy. Because of the thermodynamic properties of this material and its high variety of compositions, the evaluation of glass durability and alteration mechanisms remains a challenge. In this work we propose a complete strategy to approach the problem of glass corrosion and stabilization. Combining the results of the macroscopic characterization of archaeological glass samples and artificially aged mock-ups, we define a novel silica-based formulation for the consolidation and protection of ancient glass.

**Glass Corrosion**
The long-term perspective gained by studying ancient material culture can provide vital insights into the prediction of possibilities and consequences of future glass corrosion scenarios, opening to the possibility of developing novel and more complete theories about this process. It is generally accepted that the mechanism of glass corrosion is induced by the interaction between water and glass surface. As shown in Figure 1a, depending of the pH of the solution, two different degradation phenomena can occur. In neutral or acid conditions the leaching mechanism takes place, involving the ion-exchange between the alkalis and alkaline-earth metals of the glass network and the hydrogen ions of the aqueous solution. The leaching leads to a pH increase due to the higher concentration of alkalis and the consequent depletion of hydrogen ions in the water medium. The alkaline condition is more aggressive for the glass network since it promotes the dissolution of the Si-O-Si bonds and the formation of silanol groups (SiOH). The visible alteration of archeological samples 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. Extrinsically, different environmental parameters, such as temperature, the pH of the environment, the presence of water in liquid form (RH≥100%) or vapour (RH<100%), salts and ions concentration, relative pressure under burial or marine conditions, strongly influence the kinetic of the glass surface alteration and its chemical transformation (Figure 1b). Archaeological and ancient glass that aged under different conditions (i.e., in soil, underwater, under extreme environmental conditions) for several centuries show multiple visible symptoms of deterioration, such as pits, cracks and iridescent multi-layered patina (Figure 2). More than one of the manifestations of alteration can be found in a single glass object, thus making it sometimes difficult to individuate the most appropriate strategy of conservation and/or consolidation to be applied.

**Artificial Ageing**
Considering how complex the process of glass alteration is, in this work we performed the accelerated ageing test of *replica* samples with typical chemical composition of Roman glass in order to better understand the process of glass corrosion. The replica samples, prepared by Stazione Sperimentale del Vetro di Murano (Venice), have a composition with high content of $SiO_2$, CaO, and $Na_2O$, and low concentration of MgO and $K_2O$, as typically found in Roman glass. The artificial ageing of the glass sample was performed in a climatic chamber with constant temperature of 80°C. The cycle consists in keeping the relative humidity (RH) level at 90% for two weeks, then it was lowered down to 10% for others two weeks. Only pure water (MilliQ) was used during the artificial ageing to prevent any undesired effect of interaction between the samples and the external agents (e.g., salts present in tap water). The multi-analytical investigation of each sample collected every four weeks of ageing is ongoing.

**Glass Conservation**
The conservation of archaeological and historical glass is still a challenging aspect for the cultural heritage community because of the poor material compatibility and the toxicity of thermoplastic and thermosetting resins are widely adopted by conservators worldwide. Paraloid B-72 is one of the most widespread and known synthetic resins used in the field of glass consolidation. Even if it is appreciated in the conservators' community, it is important to highlight that it has some issues related to vapour permeability and photochemical stability. In the Center for Cultural Heritage Technology we are developing new formulations that can functionally replace or exhibit performance advantages with respect to these canonical polymeric materials. Our new formulation is 100% compatible with the glass substrate, in opposite to the existing solutions that are based on polymeric materials. This silica nanocoating was obtained by a simple sol-gel dip-coating process. Silica nanoparticles were incorporated in the coating in order to obtain hydrophobic properties thanks to the formation of a nano-level rough structure, while a silica layer obtained from tetraethoxysilane (TEOS) through sol-gel route was used as a binder to firm the nanoparticles to the glass substrate (Figure 4a). In collaboration with the Victoria & Albert museum of London, we are testing our product on a real historical degraded glass fragment (Figure 4b).

**Conclusions**
By the characterization of altered ancient glass it is possible to obtain concrete evidence of the transformation of the vitreous structure, the nature of the dissolution products, and the way a specific glass composition reacts to a particular environment. The results obtained from the characterization of ancient glass and artificial ageing are pivotal information for the development of tailor-made treatment. The innovative solution presented in this work as a great potential for the purpose of long-term conservation of artistic glass object and for the preservation of its aesthetical characteristics. In addition, it exploits the properties of nanotechnology and meets the important requirements of the green and sustainable economy.

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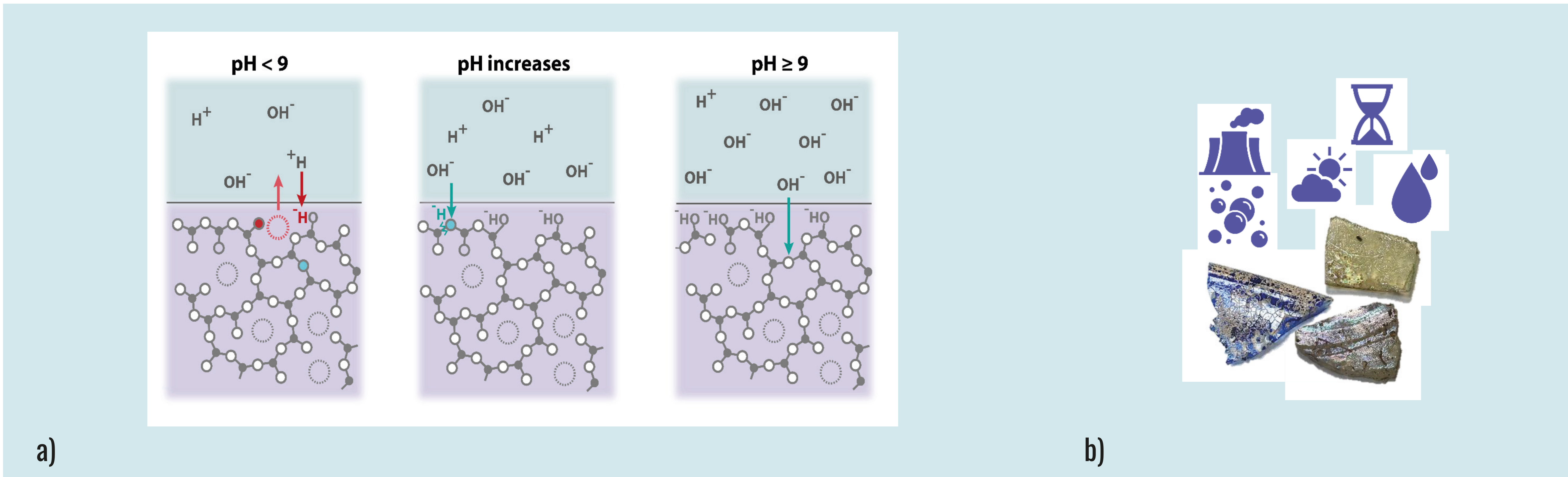


Figure 1. (a) From left to right: protons are not strong enough to break Si-O-Si bonds, promoting the alkalys and alkaline earth ions leaching; hydroxide ions are strong enough to break Si-O-Si bonds; hydroxide ions cause the dissolution of the silica network. (b) Three archaeological glass samples affected by different types of glass degradation (bottom), list of atmospheric agents rappresented by icons: temperature, water, pollutions, time (top).

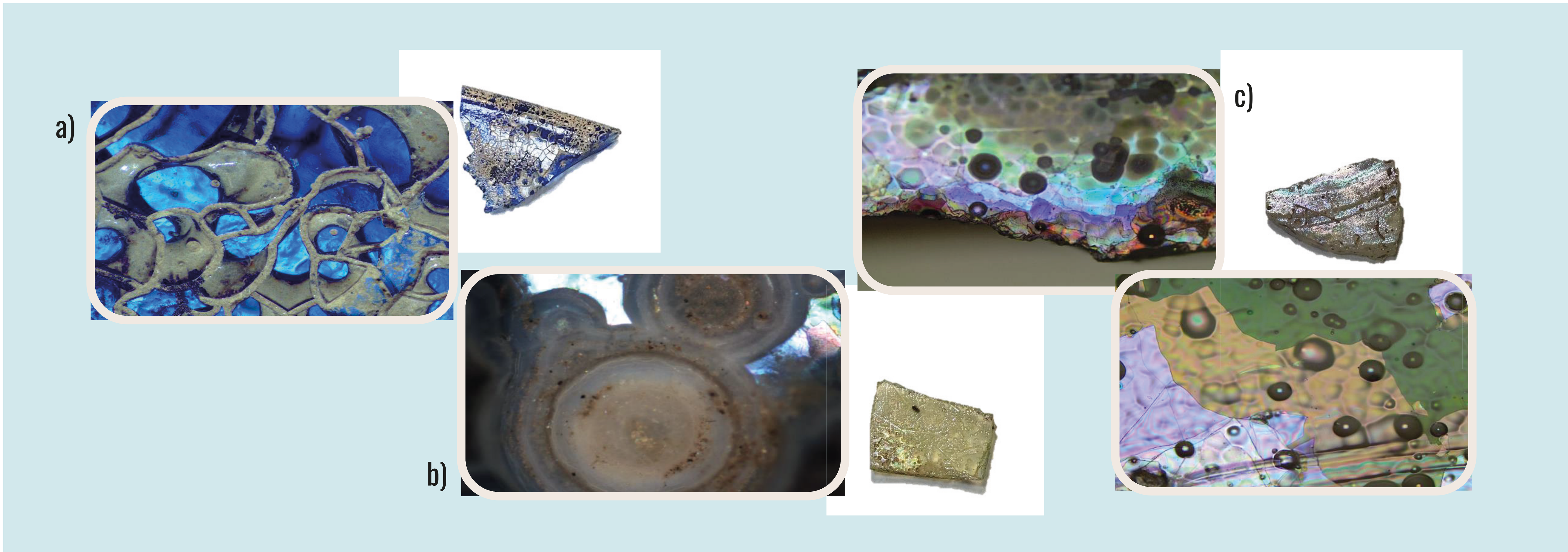


Figure 2. (a) Cracks filled with mineralised material probably coming from the soil; (b) pits resulting from the dissolution of the silica network through the rupturing of Si-O-Si bonds, that occurs in alkaline conditions; (c) iridescence appearing as a rainbow-like effect on the glass surface characterised by vivid colours like gold, pink and blue. It is a visible symptom caused by the change in the composition of weathered glass and it is often accompanied by the disintegration and flaking of the surface of early glass.

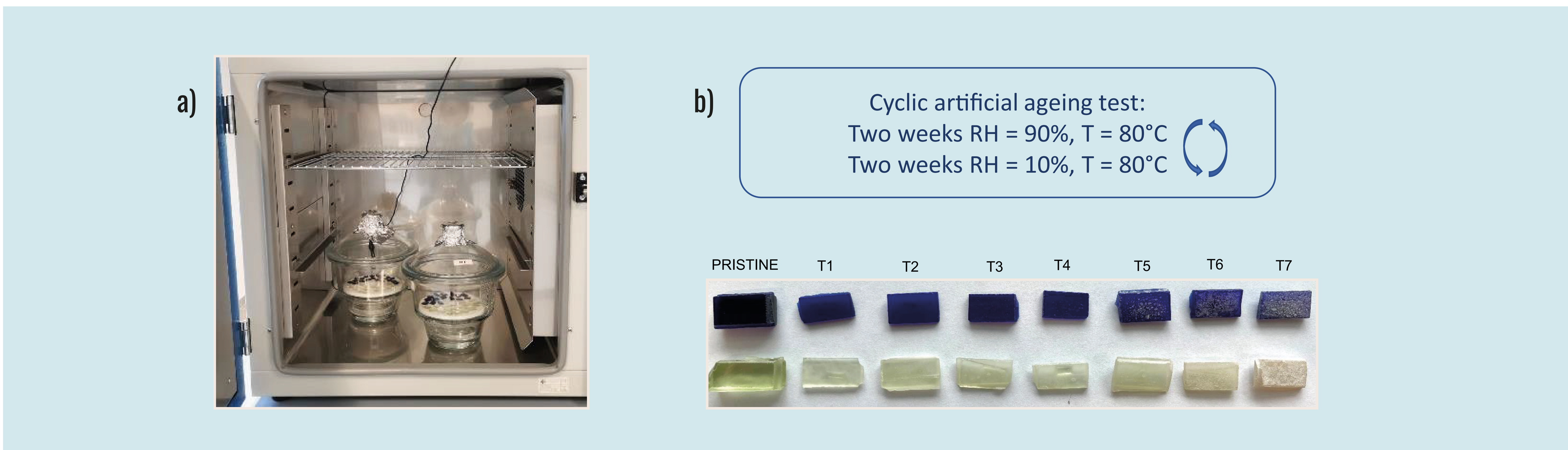


Figure 3.(a) Set-up of the artificial ageing test; (b) protocol of artificial ageing test (top), visible changes of replica surface during the artificial ageing test (bottom).

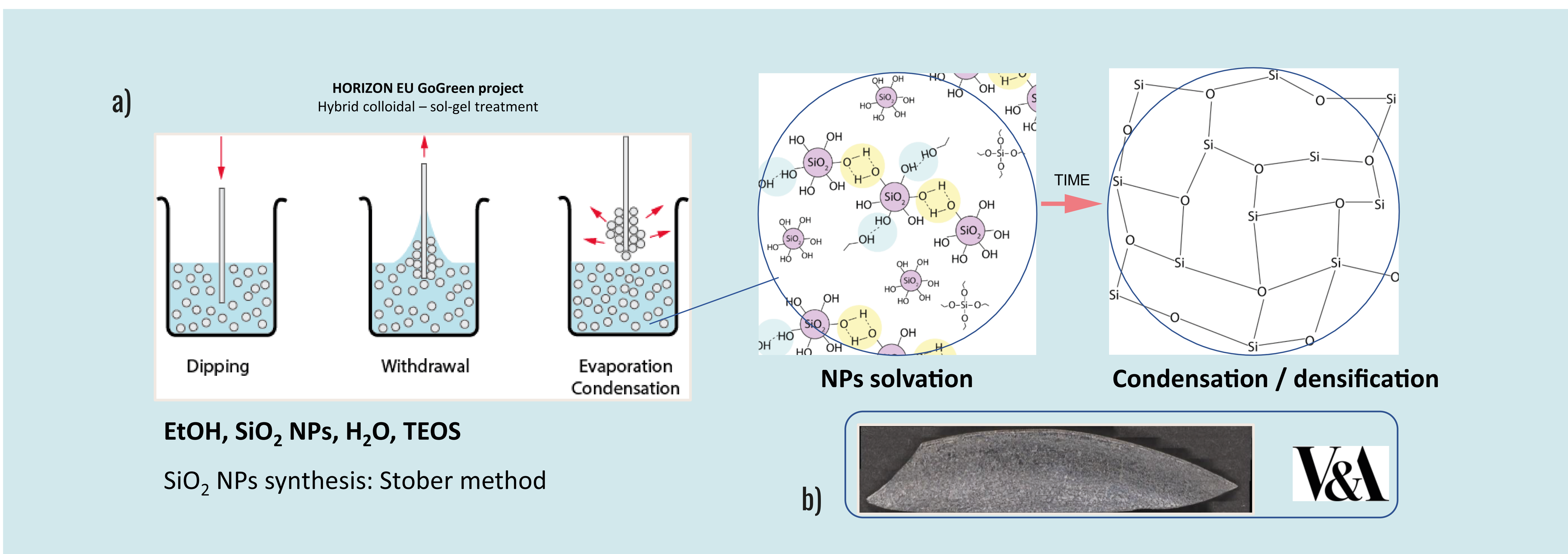


Figure 4. (a) Scheme of dip-coating deposition; (b) historical glass fragment treated with our product.

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