

## New insights into the mechanisms of glass atmospheric alteration and application to the Cultural Heritage

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A significant part of glass objects of the Cultural Heritage (CH) preserved in a museum-like atmosphere since their manufacture show signs of chemical and physical degradation. The main known macroscopic manifestations on the glass surface are efflorescence of salts, weeping, colour modification, crizzling, flaking (Fig. 1), resulting in loss of transparency and eventually loss of material at an advanced stage. The extent of this active alteration, initially induced by moisture attack, depends on the glass composition and on the conditions of conservation (temperature, relative humidity, atmospheric pollutants) [1]. Being a serious matter of concern for conservators, it appears necessary to get a better understanding of the glass degradation processes induced in unsaturated conditions (relative humidity, RH < 100 %) in order to propose new and better efficient protective methods for museum glass objects.

To address the mechanisms of glass atmospheric alteration, we have conducted ageing experiments at 85 RH%, as a function of time and temperature (from a few hours to 3 days at 80 °C, from a few weeks to 9 months at 40°C) of three different model glass samples, in a neutral atmosphere (without any acidic pollutants). These accelerated ageings were performed either in a climatic chamber or in an hermetic box containing a saline solution of KCl in H<sub>2</sub>O. The model glasses were chosen to be representative of silicate glass compositions of the CH. Two compositions are known as “unstable”, bearing a low amount of alkaline earth oxides (CaO+MgO ≤5 wt%) and high content in alkali oxides (~22 wt% K<sub>2</sub>O or K<sub>2</sub>O+Na<sub>2</sub>O). They are representative of different glass productions that took place between the Middle-Age and the 18th century. The other composition is a “stable” soda-lime composition with a higher content in alkaline earth oxides (CaO+MgO ~10.5 wt%), a similar content in alkali oxides (~20 wt% Na<sub>2</sub>O) and a higher content in Al<sub>2</sub>O<sub>3</sub> (2.5 wt% compared with < 1wt%). This type of glass composition has spread since Antiquity.

The comparison of the phenomenology of the alteration (morphology, composition and structure of the altered layers and alteration kinetics) of these glasses was performed after the ageing experiments, following a multi-scale characterization by the mean of different analytical tools: Microscopy, SEM-EDX, ToF-SIMS, NMR (<sup>1</sup>H, <sup>29</sup>Si and <sup>23</sup>Na), FTIR, μ-Raman, TGA. In particular, the thickness of the altered layers were determined by ToF-SIMS for the smaller ones (some tens to about 200 nm) or by SEM observations on edge for high enough altered thicknesses (> 200 nm), in order to establish the kinetics of the atmospheric alteration for each glass composition. The “unstable” compositions developed thick hydrated layers and a thin top layer of alkali- and Ca-carbonate precipitates (Fig. 2 a, b, c and d). Their high hydration rate even increased in the timescale of the experiments at 40 °C or at 80 °C. The temperature dependency of their hydration kinetics was not Arrhenian, revealing a self-acceleration mechanism involving several processes [2,3]. On the contrary, the “stable” composition developed a considerably thinner hydrated layer and, relatively, a higher amount of alkali- and Ca-carbonates on its surface (Fig. 2 e and f). Remarkably, <sup>29</sup>Si and <sup>1</sup>H NMR analyses showed that the hydrated layers of the “unstable” compositions are depolymerized and retain a significant proportion of alkalis and non-bridging oxygens in a dense network of hydrogen bonds. In comparison, the hydrated layer of the “stable” composition is clearly distinguishable: it appears completely transformed in a mass of silica instead [4].

The possible origins of these very distinct chemical behaviours are discussed, in relationship to the specific properties of water in unsaturated humidity conditions.

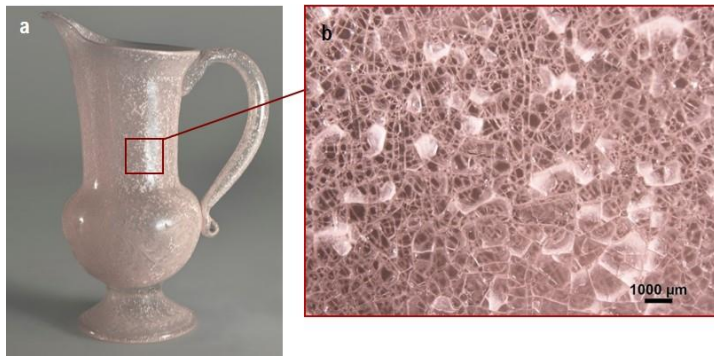


Fig. 1: Degraded glass ewer of the Musée des Arts Décoratifs, Paris (inv. 23431 - H. 19 cm) showing the advanced stage of crizzling. The optical microscopy image b) is a detail of a) showing the formation of small flakes of hydrated glass and their detachment from the surface. © C2RMF, A. Maigret and F. Alloteau. Initially colorless, the pink color is due to the atmospheric alteration through the oxidation of manganese in the hydrated layer.

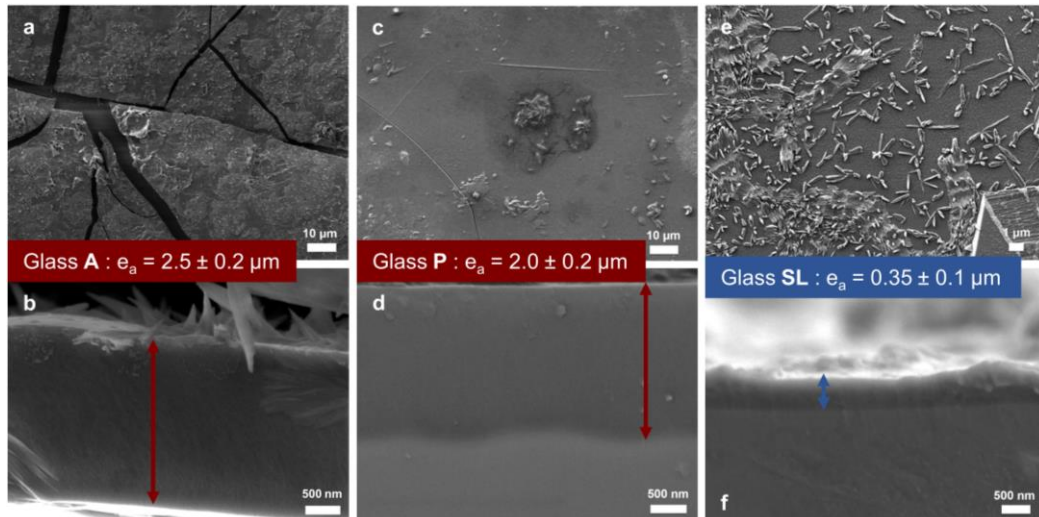


Fig. 2: Alteration layers of the three glass models (Glasses **A** and **P** are the “unstable” composition, glass **SL** the “stable” composition) after a 6-months ageing at 40°C and 85 RH% (hermetic box containing a saline solution of KCl in H<sub>2</sub>O). Secondary electrons SEM images. **a, c, e**: surfaces ; **b, d, f**: edges. In **b, d** and **f**, the double arrow corresponds to the thickness of the alteration layers ( $e_a$ ). For glass **A** in particular, the flaking phenomenon occurred very close to the interface between the alteration layer and the pristine glass.

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