



## New insight into atmospheric alteration of alkali-lime silicate glasses



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### ABSTRACT

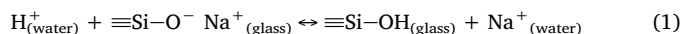
A mixed alkali lime silicate glass altered in atmospheric conditions (80 °C/85%RH, Relative Humidity) for various lengths of time was characterized at all scales. The altered glass forms a hydrated solid phase bearing about 10 wt% of H<sub>2</sub>O in the form of Si-OH groups and molecular water. No alkali depletion was observed after ageing tests. Structural results from <sup>1</sup>H, <sup>23</sup>Na and <sup>29</sup>Si MAS NMR point out the close proximity of Si-OH, H<sub>2</sub>O and Na<sup>+</sup> species. This study gives new insight into the mechanisms of the atmospheric alteration, essential to conservation strategies in industry and cultural heritage.

### 1. Introduction

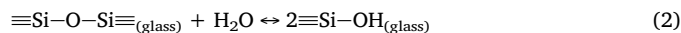
Alteration of multicomponent silicate glasses under atmosphere (referred to as atmospheric alteration) has been reported for several decades, in particular stained glasses and ancient glass objects represent very long-term examples [1–3]. Industrials as well as cultural heritage curators also have to deal with short-term atmospheric alteration [4–8]. For instance, active deterioration is observed on the surface of numerous glass objects stored in museum collections, through macroscopic manifestations mainly like white salt deposit, weeping, crizzling, resulting on a loss of transparency and material disintegration [2,3,9–11]. It is now well known that moisture is the main contacting medium responsible for atmospheric alteration. At first water molecules physisorb on glass surface adsorption sites which highly depend on the surface state [12]. Physisorbed water molecules then break surface chemical bonds to form a hydroxylated surface on which water molecules can be adsorbed on some layers. The number of water molecule layers on surface rises with the relative humidity [13]. Then the penetration of water molecules into the silicate network is responsible for the glass degradation, but the underlying mechanisms are not well understood yet probably because of the diversity of the parameters involved. These parameters can be intrinsic to the glass: silicate glass composition (principally the nature and content of alkali ions known as network modifiers, of alkaline earth ions known as network stabilizers, and of minor oxides such as alumina), process of fabrication, surface state and strains. Extrinsic parameters such as temperature and relative humidity (RH) [3,14,15], atmosphere gas and

pollutants [15,16] also play an important role.

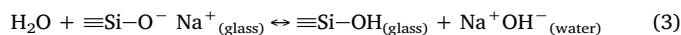
Although our concern is the alteration of glasses in atmospheric conditions, in literature the most studied phenomenon is the alteration of glasses in immersion conditions in water, or aqueous alteration (notably in the field of nuclear waste containment glasses [17]). During aqueous alteration, the elementary steps of water penetration into the silicate network are [18–20]: (i) the diffusion of water molecules as intact species through the voids of the glass network, (ii) an ion-exchange process between alkali ions of the glass and hydrogen bearing species from the solution (H<sup>+</sup> or H<sub>3</sub>O<sup>+</sup>) which occurs preferentially in acidic conditions:



(iii) the hydrolysis of the silicate network, that is strongly catalyzed at basic pH (> 9):



Another mechanism (iv) referred to as diffusion of water molecules followed by immobilization at the non-bridging oxygen atoms has also been proposed [21] and involves the dissociation of molecular water on the non-bridging oxygen sites by acid-base reaction:



The predominance of one or the other among these reaction steps is highly dependent on the glass composition and on the pH and temperature of the aqueous media in contact [20,22].

With respect to aqueous alteration, glass atmospheric alteration

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involves different parameters and exhibits different macroscopic manifestations. Of great importance, surface defects (dust, scratch, cracks, alteration products) can greatly modify the attack conditions under atmosphere: liquid water can locally collect by capillarity and its pH then increases due to Reactions (1) or (3), that promotes heterogeneous alteration and pits [3,23–25]. Symptomatic manifestations are the appearance of alkali salts, reported as the first macroscopic manifestation, and crizzling of the glass surface [2,9]. Visible crizzling, known as ‘developed crizzling’, occurs after a period of invisible crizzling, called ‘incipient crizzling’. Incipient crizzling refers to hydration of the glass surface and sub-surface accompanied with the formation of unopened cracks that appear as very fine threads to the unaided eyes. Developed crizzling happens as a second step, probably when the glass hydration has reached a certain level [9,11]. Very few studies deal with the structure of the hydrated glass layer, the dependency of the alteration kinetics on compositional, temperature and humidity parameters, and more generally the mechanisms of atmospheric alteration.

In this paper, we focus on atmospheric alteration under indoor atmosphere when the climatic conditions prevent any water runoff on glass surface and in a neutral atmosphere (without any acidic pollutants). This situation corresponds to the simplest conditions to study the mechanisms and represents as well the best monitored museum conditions. The study of this atmospheric alteration process is made difficult because of its relatively low kinetics under ambient temperature. Moreover few ancient glasses preserved in air with known period of fabrication are available, and their storage conditions over time are never known. Therefore, ageing tests at high temperature and relative humidity (80 °C, 85% RH) in climatic chamber have been performed on glass replicas representative of chemically unstable ancient glass objects (high alkali and low lime content). With the objective to get a better understanding of the atmospheric alteration mechanisms, attention was focused on the chemical composition, morphological and structural evolution of the altered surface layer, during as well as after the ageing tests. The variety of the analysis tools and the particular attention paid on the preparation of altered samples before the analysis allowed us to precisely describe the composition and the structure of the hydrated layer. These results provide new insight into atmospheric alteration phenomena.

## 2. Experimental methods

### 2.1. Sample preparation

One replica A, a mixed alkali (Na, K) lime silicate glass representative of one sort of chemically unstable ancient glass was studied (enamels on metal from the late Middle-Age and Renaissance period, and glass objects from 19th century) [26]. Glass A was fabricated by Saint-Gobain Recherche (France) by melting the mixture of reagent grade powders at 1450 °C for 2 h, annealing the casted block at 560 °C and then cooling down slowly for 1 h to relieve stresses and enable cutting. The composition was checked by Particle-induced X-ray emission analysis (PIXE) and is very close to the as-batched composition: (wt%) SiO<sub>2</sub> 71%, Na<sub>2</sub>O 11%, K<sub>2</sub>O 11%, CaO 5%, MgO 1%, Al<sub>2</sub>O<sub>3</sub> 1%.

Samples were cut into plates (1 × 1 × 0.3 cm<sup>3</sup>) and polished on one face up to 1 μm by means of cerium oxide powder in aqueous solution. In this study the repeatable polishing procedure was chosen to minimize glass surface heterogeneities prior to the ageing tests and to perform surface analysis techniques that require as much as possible flat and smooth surfaces. Shortly before the ageing tests, glass plates were carefully cleaned with sodium dodecyl sulfate (SDS) 1 M to remove organic dirt, rinsed with milliQ water and then ultrasonically cleaned in ethanol during 10 min. Samples were then dried during 5 s with an air flux (T ≤ 40 °C). SIMS analysis conducted on glass plates after these preparation steps and before atmospheric alteration tests showed an outermost surface layer of about 30 nm that is partially

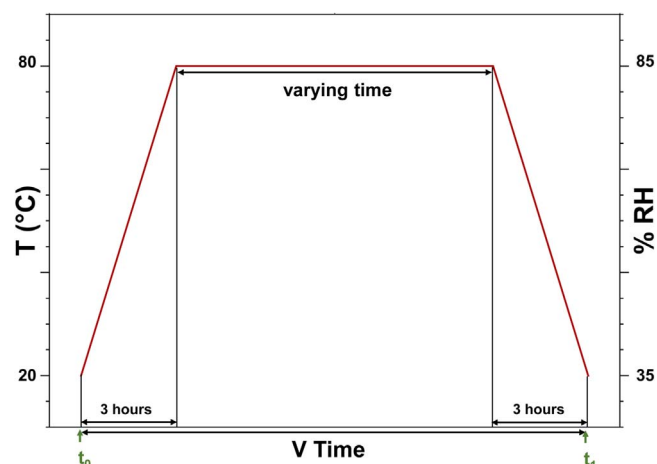


Fig. 1. Accelerated ageing program in climatic chamber (V test). Time noted  $t_0$  refers to the beginning of the V test, time noted  $t_1$  to its end.

alkali depleted.

Glass powders A were also prepared for structural studies: glass was crushed and sieved to recover the 32–50 μm, 80–125 μm and 125–180 μm size fractions. Powders were rinsed several times in ethanol then acetone under ultrasonic agitation in order to remove small particles stuck on the grain surface. Afterwards, the size homogeneity was checked under a binocular magnifier. The specific surface area was measured by the BET method, using a Belsorp Max analyser with krypton as adsorbing gas (280 ± 2 cm<sup>2</sup>/g, 410 ± 5 cm<sup>2</sup>/g and 1200 ± 100 cm<sup>2</sup>/g for the powder fractions of 125–180, 80–125 and 32–50 μm respectively).

### 2.2. Ageing tests

Glass plates and glass powders were submitted to an accelerated ageing test in climatic chamber at 80 °C and 85% RH for various time periods from 6 h to 144 h. These tests are noted V or V × h tests with × the total duration in hours, including the ramps (Fig. 1). Glass plates were put horizontally with the polished face upwards, and powder was scattered on Teflon dishes. The operation of the climatic chamber was chosen to prevent from any liquid water flow on the samples during the heating ramp, the temperature and humidity dwell, and the cooling ramp. At every time of the test program, the relative humidity was kept below or equal to 85% RH, by adjusting the vapor pressure in the chamber according to the temperature and % RH set value, thanks to a water bath maintained at the dew point temperature, and a psychrometric measurement of the vapor content in the chamber. We have checked that temperature and relative humidity were close to the set values at samples position by using external sensors (MadgeTech data logger). The sealing of the climatic chamber prevented any air exchange with the outdoor. The quantity of CO<sub>2</sub> in the chamber (not renewed during a V test) was estimated at about 10<sup>-3</sup> mol. In this paper, time noted  $t_0$  refers to the beginning of the V test, while time noted  $t_1$  refers to its end (Fig. 1). At  $t_1$ , altered glass plates were left in laboratory atmosphere at room temperature and a special attention was paid to protect glass plates from dusts. Temperature and RH variations in laboratory were checked with a MadgeTech data logger (average temperature: 21.7 °C; average RH: 36.2%). Altered glass powders were not put in the atmosphere of the laboratory but they were kept in Eppendorf tubes stored in desiccators until their characterization, to limit interaction with the atmosphere.

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