Early stages of surface alteration of soda-rich-silicate glasses in the museum environment

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ABSTRACT

This paper studied the alteration of three soda-rich-silicate glass types (*Cristallo*, *façon-de-Venise* and soda-lime silicate). Replica samples were exposed to different environments simulating museum-like conditions – room temperature and different relative humidities (RH). Results were analysed by SIMS, μ-FTIR, Optical Microscopy and Optical 3D profilometry. *Cristallo* appears as the most vulnerable, whilst the soda-lime glass appears as the most resistant to the environmental deterioration. The thickness of the altered layer is proportional to the time of exposure and to the RH of the surrounding atmosphere. From the results obtained, the glass composition and the water available and adsorbed to the surface strongly influence the kinetics of the surface alteration.

1. Introduction

Damage to cultural property within the museum occurs mainly due to environmental conditions (*e.g.* humidity, among other factors) which have long been the concern of conservators [1]. Although it is correctly seen as chemically stable, glass artefacts exposed to the environment undergo surface transformations and deterioration [2,3]. Glass alteration by atmospheric water is a well known problem, and it expressly takes place in the museum environment. Depending on its chemical composition and on the environmental weathering conditions, the time required for this slow process to produce damage can range from hours to years. Therefore, different alteration behaviours have been reported [4,2,5].

The use of combined surface analysis methods to thoroughly characterise the glass durability and corrosion through a systematic approach to a series of compositions and environments has long been demonstrated [6] and has until now proved its importance [7,8]. Surface characterization techniques are applied in this case to investigate the thin corroded layers formed as consequence of glass weathering processes [9].

Several studies have been published concerning corrosion models and mechanisms on soda- and soda-lime-silicate glasses (recent publications are, for instance [10,11]). Many of the studies of this type of glass and corrosion are, nevertheless, directed at the commercial glasses

and industrial production improvements (*e.g.* [12]) and to waste glass, whose properties and corrosion behaviour are strongly dependent on the environment at which they are exposed to (aqueous, acidic and alkaline solutions, with the contribution of several other corrosive materials, such as toxic waste) (*e.g.* [13–15]).

Studies on aqueous solutions (*e.g.* [12]) and accelerated ageing at high temperatures (*e.g.* [1,4]) have also been carried out in the past. Important corrosion models have arisen from these works (*e.g.* [16]). It is a fact that some may apply or are related with historical glassworks, namely for objects in waterlogged or ground-water environment [17–23], window glass [13,24,9,25], or museums environment accelerated tests [11]. Nevertheless, only a few recent studies concern the problems directly related to museum glass objects and their real environment (and can be found mainly in [26,7,27–32]).

Museum objects have varying compositions and origins and the wide variety of alteration behaviours still lacks understanding, as part of the implementation of a preventive conservation strategy.

The main point of this paper is to characterise the surface alteration of a selected set of historical compositions. The *Cristallo* glass [33–35], which was a well defined exquisite and broad glass formulation produced during the Renaissance period; a selected *façon-de-Venise* glass composition and a selected soda-lime composition that differ from the former in specific compounds. The authors intend to investigate the influence of these compounds in particular. The replica formulations

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were based on the analysis of composition carried out to some objects from the collection of King Ferdinand II of Portugal, currently located in the storage rooms of Museu Nacional de Arte Antiga (Lisbon), as well as on the literature compositional data from the same period. This collection, being at an international level, has a wide range of glass objects from different European production centres within a wide chronology, and for this reason it becomes a good case study.

1.1. Historic soda-rich glass

In the Renaissance period, Venetian glasses became precious by the extraordinary technical skill and artistry attained by the glassmakers and by the quality of the glass artefacts themselves. The most renowned glass produced with those properties was called *Cristallo*, since a similar crystal-clear glass with such fine quality could not be obtained in any other contemporary glassmaking centre [2,33,36,37]. By the 16th and 17th centuries, commissioners wanted this type of glass at their hand, and produced in their own country [38,39]. Venetian glass began to be imitated by the second half of the 16th century, when glassmakers escaped from Murano to many other European centres [38,39,34,40–42], and it was called *à la façon de Venise*. From the technological point of view, in both Venetian and *façon de Venise* compositions coastal plants were used as flux agents, which particularly combined high amounts of two major glass components: soda and lime [33,36,40,43,35]. The soda-lime compositions were also used for the production of less luxurious glass objects, being used since the Roman times [37]. These are mainly the types of glass here under study.

1.2. The role of structure and composition of soda-rich glasses in the deterioration process

The structure of a soda-rich and soda-lime silicate glasses suffers from partial breakdown of the silica network continuity. Whilst the alkali transforms a Si–O–Si group into two Si–O$^-$ units [44], the presence of the Ca^{2+} ion is known to stabilise the lattice, since it presents a stronger bond to the oxygens non-bridged to silicon (NBOs). In the disrupted and irregular structure bond angles differ within a certain range and their strength varies from one point of the structure to another due to variability of the atoms in this region [2,45].The composition of glass is a determinant of the glass structure, which in turn determines the distribution of exchangeable sites [46]. For instance, the addition of bivalent cations can be responsible for reducing the alkali mobility by (i) double-bonding with NBOs, (ii) or possibly by the Na–Ca pairing [7,6].

It is well known that the composition of a newly formed glass surface is usually far different from that of the bulk glass composition. The chemistry of the alteration of a glass surface is (at least to a certain extent) determined by the structure of the upper layer derived from a certain composition, and the proneness of that layer to react [12,47]. The surface structure of silicate glasses has unsatisfied Si–O– and Si– bonds, as a consequence of a surface formation. These bonds react rapidly with atmospheric water to form Si–OH groups. Such a layer is dependent on the glass composition, its heating and cooling regimes, the surface finishing, and the RH of the surrounding environment. The nature of physical and chemical adsorption on glass depends on the surface structure, and the hydroxyl sites act as adsorption and reaction points. The thermal history of glass is therefore an important factor to its adsorption behaviour. Physically adsorbed molecules are apparently bonded to the hydrogen atom on a Si–OH group. In particular, water molecules tend to adsorb to either isolated or adjacent hydrogen-bonded pairs of hydroxyl groups [48].

During glass alteration, the properties of the layer formed on the surface will thus depend on the glass composition, on the chemistry of the wet film adsorbed, on the reactions time and on temperature. The latter will not be taken into account as only room temperature is what is of interest in this case study. After being formed, the surface layers can

act as a physical barrier to the transport of reactants and corrosion products depending on their inherent characteristics, and can also influence the chemical affinity of the glass to further reactions [49].

1.3. Deterioration and the environment's influence

When glass is in contact with the atmosphere, water molecules from different origins are available to interact with its surface. The amount of water molecules is affected by several factors, among them the relative humidity (RH) [2], which proved to be a factor of paramount importance in a museum environment. Under certain conditions it can prove to have a more dramatic effect on the hydration rate than some levels of pollutants [5].

The deterioration model proposed for glasses in aqueous solutions can be applied also for atmospheric alteration, the same way as some authors state that the fundamental decay mechanisms are the same for all alkali-silicate glasses [3,48], although it can only go so far. This is true for the following steps of the process: (i) water adsorption at the surface, (ii) three competing simultaneous reactions, all resulting in the hydration of glass surface [11] (hydration, ion exchange, and hydrolysis), and (iii) occasionally, the formation of alkali salts which may react with the silicate structure [11,4,46,3,48]. However, corrosion of glass surfaces in wet gases is different [48,50]. In the case of atmospheric alteration the period of time that a water film (liquid water) forms on the glass surface [44], the surface-area-to-volume ratio (SA:V) [12], and the mobility and reactions of the water inside the glass network [51] need to be taken into consideration in the weathering mechanism.

The different corrosion behaviours of different chemical compositions for most glasses may be explained by the rate-controlling step being the entrance of water molecules in the glass lattice [46]. Assuming that hydrolysis is likely the way of penetration, its kinetics depend on two factors: the distribution of the local structural units and the chemistry of the solution (where pH can locally depend on the SA:V ratio [12]). Hence, the glass structure influences the kinetics since it determines local deformations which can influence the reactivity of silica, as well as the ionic-exchange process. The initial leaching seems to be a transport process rather than a reaction-limited process [46]. According to Hench and Clark [12], the ion-exchange step seems to be kinetically controlled with a $t^{\frac{1}{2}}$ dependence, while the hydrolysis process seems to be controlled by an interface reaction with linear t^1 dependence [12]. The network hydrolysis shows, in general, a higher rate when NBOs are present, and follows the trend $Q_1 > Q_2 > Q_3 > Q_4$. However, the rate of hydrolysis depends also upon the content in the different modifier cations [46].

As already presented in the literature, by V. Jain, glass alteration in water vapour-containing atmospheres differs from corrosion in solution in that [49]:

1. '*the glass surface contains functional surface groups in their acidic form, e.g. Si–OH, or in combination with alkali ions of the glass*,'
2. '*alkali ions leaving the glass after interdiffusion [can] form compounds, which accumulate at the surface*,'
3. '*and the glass network, even if attacked chemically, does not dissolve, so that protons and alkali ions interdiffuse without formation of a steady state*.'

All three items will be further discussed together with the results presented in this paper. These results are based on a glass deterioration process using model glass (with historic compositions and technique), with no accelerated ageing, but rather actual museum-like conditions. The authors believe that the rinse of surfaces, or the use of high temperatures in former cases can promote different equilibria at which unlikely occurring phenomena can take place concurrently to the real-time weathering ones.

Table 1
Replica glass samples compositions in wt% and mol%. Major oxides sums and ratios.

Oxides	Target composition						Replica composition (PIXE analysis)						Oxides	Sums and ratios (mol%)		
	wt%			mol%			wt%			mol%						
	$Crist_A$	fdV_B	SL_C	$Crist_A$	fdV_B	SL_C	$Crist_A$	fdV_B	SL_C	$Crist_A$	fdV_B	SL_C	Target/Replica	$Crist_A$	fdV_B	SL_C
Na_2O	17.2	14.8	14.2	16.7	14.2	13.9	17.07	15.89	14.90	17.68	15.50	14.85	$Na_2O + K_2O$	18.6	16.2	16.4
MgO	2.00	3.10	2.00	2.99	4.69	3.07	1.67	2.77	1.90	2.52	4.15	2.91	$CaO + MgO + Al_2O_3$	8.8	10.9	14.7
Al_2O_3	0.70	1.00	2.50	0.41	0.62	1.49	1.30	1.65	3.20	0.77	0.98	1.94	Na_2O / SiO_2	0.24	0.20	0.20
SiO_2	70.5	70.5	67.8	70.5	70.5	68.8	70.5	70.8	66.0	71.90	71.27	67.86	$\frac{Na_2O + K_2O}{CaO + MgO + Al_2O_3}$	2.11	1.49	1.12
P_2O_5	0.15	0.16		0.06	0.07		0.08	0.11		0.04	0.05					
Cl	1.00	1.00		1.70	1.78		0.49	0.49		0.85	0.84		$Na_2O + K_2O$	19.4	17.2	17.3
K_2O	3.00	3.15	3.80	1.92	2.01	2.46	2.63	3.16	3.70	1.71	1.71	2.43	$CaO + MgO + Al_2O_3$	7.8	9.4	14.9
CaO	5.00	5.25	9.35	5.36	5.62	10.15	4.45	4.59	8.90	4.87	4.95	9.80	Na_2O / SiO_2	0.25	0.22	0.22
MnO	0.30	0.53	0.10	0.25	0.44	0.10	0.36	0.53	0.10	0.31	0.45	0.09	$\frac{Na_2O + K_2O}{CaO + MgO + Al_2O_3}$	2.47	1.84	1.16
Fe_2O_3	0.20	0.21	0.25	0.08	0.08	0.10	0.26	0.27	0.30	0.12	0.10	0.12				

A – *Cristallo*; B – *façon de Venise*; C – Soda-Lime.

2. Material and methods

2.1. Sample preparation and exposure

As aforementioned, soda-rich compositions were chosen based on their lime and alkali content and on the idea that these components influence the corrosion processes. Besides, some of the objects in the museum collection were already evidencing alteration symptoms, especially the *Cristallo* type, which possess a higher alkali content (see $Na_2O + K_2O$ in Table 1).

Glasses for repeatable experiments were chosen and produced based on the chemical composition analysis of original and ancient glassworks in the collection of Ferdinand II of Portugal. Replica glass samples were produced with the compositions summarised in Table 1. Compositional data obtained by analysis the original glass objects, together with literature information on chemical composition of historical glass of the same types and typologies were used as guidelines. The compositions reproduced intended to be representative of well-known international productions [52].

The model glasses were melted in an electric furnace, using refractory ceramic crucibles, at 1400 °C. The temperature increased 6.5 °C per minute, and reached 1400 °C, dwelling for about 4 hours. Afterwards, the glass melt was free-blown into a rondel shape (disc). In this way, not only the compositions were being replicated, but also the historical technological process of glass blowing. In this way, the surface of the replica samples would become as similar as possible to an historic glass vessel. Finally, the glass rondel was annealed at ca. 515 °C until it cooled to ambient temperature (around 20 °C). The glass discs were cut into pieces of $(1 \times 1 \times 0.2)$ cm$_3$.

Replica samples were exposed in an ambient of unfiltered laboratory air at room temperatures (21–24 °C), for various lengths of time (2, 4, 6, 8 weeks and 1 year). All samples were exposed in four RH chambers which kept the RH fixed within 5% (45%, 55%, 65% and about 75%). The ageing conditions were chosen based on the assessment of the condition of the current storage-room – the higher values can actually be observed in the museum environment, whilst the RH values (around 45% RH, or 42% RH) are recommended for storage of historic glass objects (*e.g.* [53,54]).

2.2. SIMS analysis

Surface analytical investigations were carried out by means of secondary ion mass spectrometry (SIMS). The technique was used to observe the concentration of elements as a function of depth in aged glasses over the nanometre scale. It can provide a very wide dynamic range of elements and can measure elemental concentrations with high resolution and sensitivity (parts per hundred to parts per billion).

SIMS depth profiling analyses were carried out on the altered glass using an IONTOF TOF-SIMS V instrument. Samples were sputter depth-profiled using an O_2^+ primary beam of 150 nA to 300 nA, depending on the surface ageing and accelerated on to the sample surface with a net impact energy of 1 or 2 keV. The analytical primary ion beam was a 25 keV Bi^+ LMIG. Secondary ions of H, Na, Al, Si, K, Ca, Mg, Mn, Fe and some molecular species were collected. Charge compensation was performed using a low energy electron gun.

The concentration of each ion was considered to be 100% on the plateau of the profiles curves, and it was considered that the bulk composition was this way represented. Therefore, the concentration of the ions was normalised to the concentration of the bulk, and were transferred to [0, 1] for comparison between more than one ion species. Moreover, the profiles obtained were processed to obtain the value of the alteration depth and ion concentration of certain ions (namely Na^+, Ca^+, $SiOH^+$). The alteration depth was considered at 95% of the slope of the profile curve, admitting 5% error margin in every case. In a similar way, the area under the curve was used to estimate the concentration of the same ion at a certain depth.

2.3. 3D optical profiles

An optical microscope ZYGO was used to obtain 3D profiles of the glass surface alteration over time, using a white light interferometer system, which offers a non-contact, high-precision and fast 3D optical profiling of surface features.

The optical interferometer was also used to measure the depth of the crater, from which the sputtering rate was calculated and used to plot the SIMS obtained profiles.

2.4. μ-FTIR

Micro Fourier Transformed Infrared (μ-FTIR) spectroscopy was used to study the chemical alteration of the glass surfaces. The μ-FTIR analysis was performed using an Agilent 4300 Handheld FTIR Spectrometer in ATR mode. Spectra were obtained covering the 4000–650 cm^{-1} range, with spectral resolution of 4 cm^{-1}. The collected spectra were obtained with 64 scans before Fourier transform. Data was acquired by MicroLab® software.

All spectra were normalised to the peak around 900 cm^{-1}, since it represents the highest absorbance value of all the spectra.

2.5. Optical microscopy
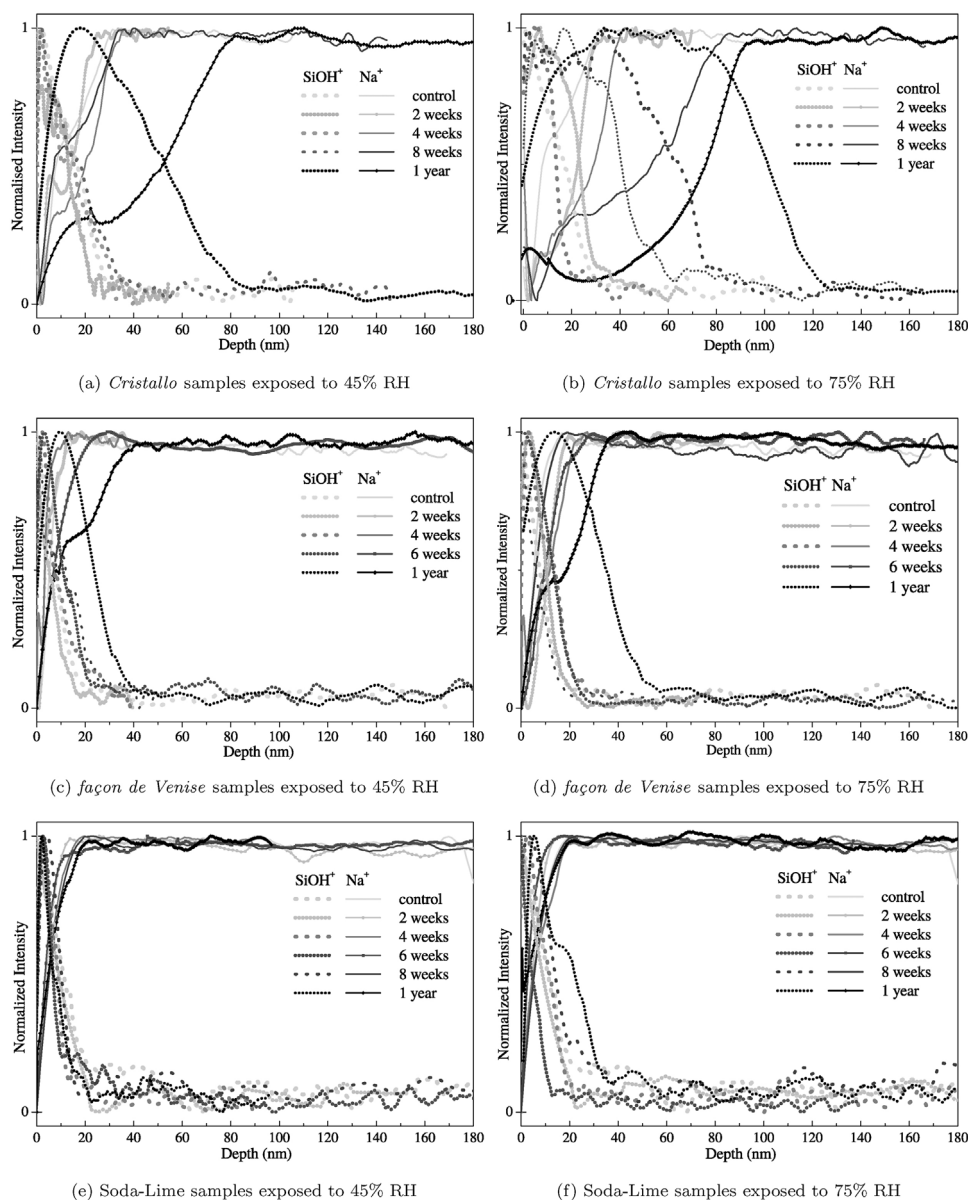
The microscopic documentation was carried out using a light

(a) *Cristallo* samples exposed to 45% RH

(b) *Cristallo* samples exposed to 75% RH

(c) *façon de Venise* samples exposed to 45% RH

(d) *façon de Venise* samples exposed to 75% RH

(e) Soda-Lime samples exposed to 45% RH

(f) Soda-Lime samples exposed to 75% RH

Fig. 1. SIMS profiling data of the ions Na$^+$ and SiOH$^+$ collected for both 45% RH and 75% RH environments for all glass samples, where visible differences between the pristine and the aged surfaces can be seen. *Cristallo, façon de Venise* and Soda Lime glass samples were aged up to 1 year.

microscope (Axioplan 2, Zeiss) with digital camera (Nikon DMX) on all the samples (from $t_{0 \text{ days}}$ to $t_{1 \text{ year}}$). The whole surface area was observed in order to identify surface features.

3. Results

The SIMS profiling data of the ions Na$^+$ and SiOH$^+$ collected for both 45% RH and 75% RH environments are shown in Fig. 1 for all glass samples. In these profiling results, it is possible to observe visible differences between the pristine surfaces and the same type of surfaces aged over time concerning the chemical changes caused by RH attack of glass. The changes presented based on the concentration profiles of the constituents of the surface layers provide information on the hydration of the surface (through the concentration of the silanol groups), on the mobilization/diffusion of the main network modifier by ion-exchange (Na$^+$ ions). In the typical depth profile of the soda-rich glasses, the normalised intensity for sodium is decreased whilst the intensity of the silanol species is increased compared to the bulk (Fig. 1a to f) – which is reached at the plateau of the curves.

The pristine glass surface is consistent with the first item referred by V. Jain "*the glass surface contains functional surface groups in their acidic form, e.g. Si–OH, or in combination with alkali ions of the glass*". It can easily be verified by looking at the profiles in Fig. 1 that there are silanol groups at the surface, in particular by looking at the control surfaces which already contain Si–OH groups in the first few nanometres depth. But it becomes even more evident from Fig. 1 that, concerning the alteration promoted by atmospheric water attack, the alkali diffusion is slower than the hydration of the surface layer – which is very clear for all of the 75% exposed samples. After 1 year exposure the Si–OH group – representative of the water content of the surface – is observed at greater depths within the glass, compared to the depletion depth of the alkali ions.

3.1. The effect of RH on glass alteration process

When looking at the results obtained in Fig. 1, it is possible to observe an alkali leaching behaviour similar to what Walters and Adams (1975) have reported: alkali releases do not always increase with

humidity [4]. The authors registered that at 30% RH some glass compositions have a weathering quantitative effect almost as great as other at 90% RH [4]. On the other hand, the water binding to the network indeed increases with RH for all cases in Fig. 1. This has been mentioned by Cummings et al. (1998), who presented evidence for a linear increase of the rate decay with RH [3]. It is stated that increasing RH leads to an increase of the hydration rate of glass, for water adsorption increases with time and RH [4,44].

In *Cristallo* glass surfaces exposed to 45% (Fig. 1a) and 75% RH (Fig. 1b), the depletion in Na^+ ions (depth of the ion-exchange layer, represented by the slope before the *plateau*) reaches a quite similar value in both RH's after one year of exposure, although the Si–OH groups are observed at a greater depth on the sample for the glass aged in the 75% RH environment. This fact suggests that the hydration reaction or hydrolysis reaction is correlated to the amount of water available, while the diffusion of the alkali seems not. A similar behaviour can be found in glass surfaces exposed to 45% and 75% RH both for *façon de Venise* and Soda-Lime types, although less evidently (Fig. 1c–f).

On the other hand, changes on the surface chemistry related to surface hydration were also obtained by FTIR and are summarized in Fig. 2, for all glass samples. As it can be seen from Fig. 2, the amount of water of hydration at the surface is detected by FTIR in every case. It is

less evident for the Soda-Lime type (Fig. 2c), which suggests that the composition of this surface might be less hygroscopic. Although there is no evident change in the Si–O–Si stretching bands (between 1250-850 cm^{-1} [55–57]) of all types of glass up to 1 year, the water of hydration at the surface differs when comparing the 45% and 75% RH environments, as well as among the different compositions, as mentioned for Soda-Lime.

3.2. Surface reactions and products

The release of Na^+ onto the surface was analysed by SIMS surface scanning technique and is shown in Fig. 3 for *Cristallo* (Fig. 3a), *façon-de-Venise* (Fig. 3b) and Soda-Lime (Fig. 3c) glass types.

Cristallo glass type shows the formation of surface Na-rich aggregates (areas/regions) becoming very evident after 8 weeks exposure to both 45% and 75% RH atmospheres. The second item above cited from V. Jain [49] ('*alkali ions leaving the glass after interdiffusion [can] form compounds, which accumulate at the surface,*') refers to corrosion products, and can be correlated with the observations made. In fact, in some cases of this static deterioration, condensation and evaporation without any washing away phenomena occurs [44,46]. This is naturally common for museum glass objects, and these surface regions enriched in Na^+ are possibly part of this process of the formation of those
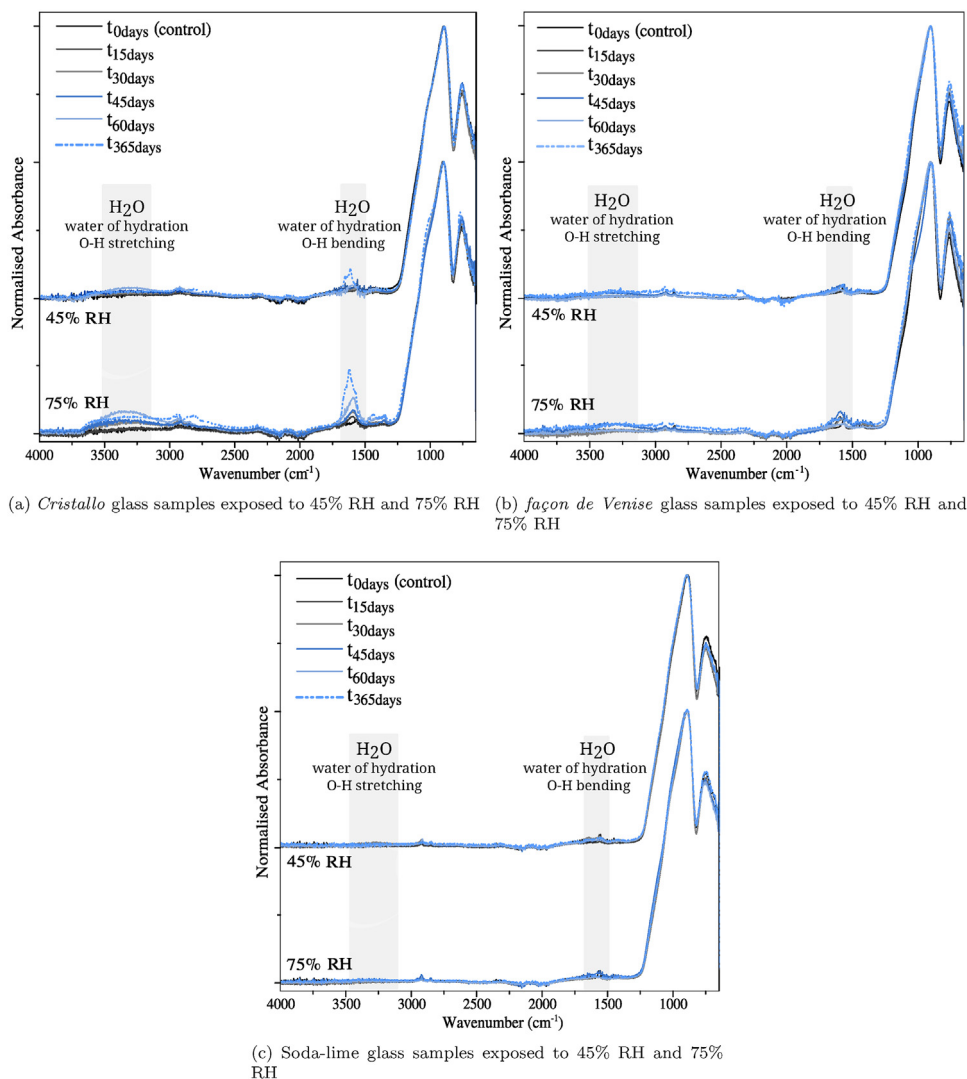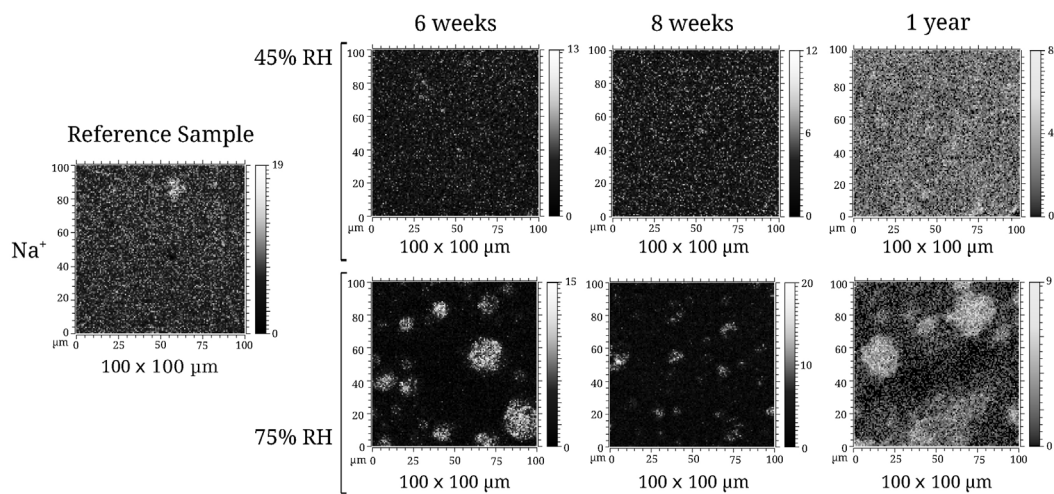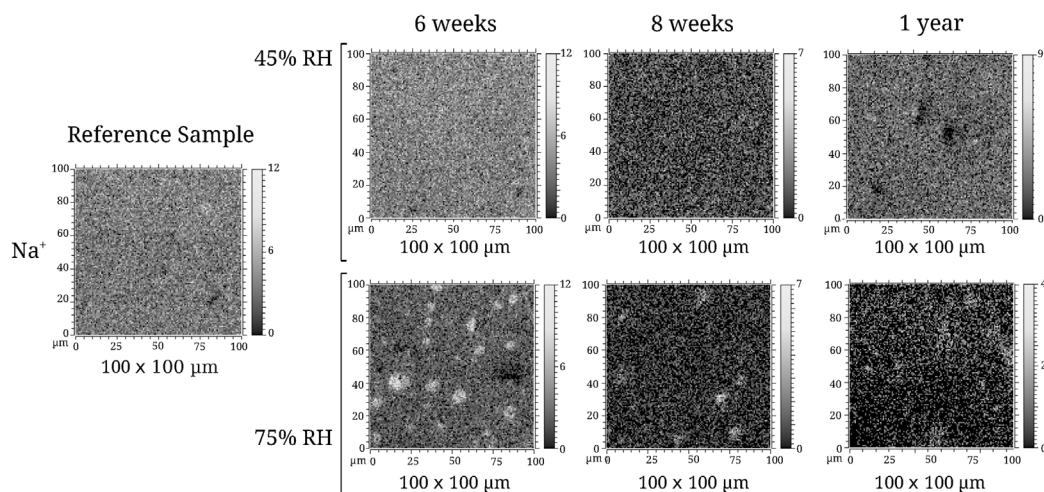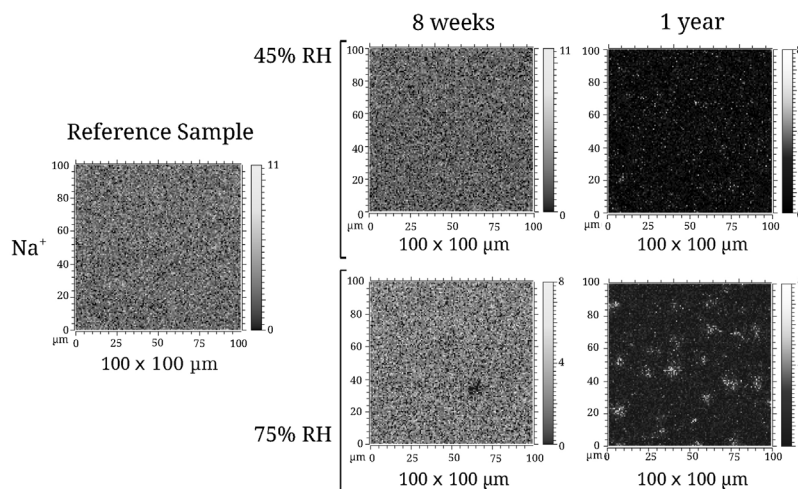

(a) *Cristallo* glass samples exposed to 45% RH and 75% RH

(b) *façon de Venise* glass samples exposed to 45% RH and 75% RH

(c) Soda-lime glass samples exposed to 45% RH and 75% RH

Fig. 2. μ-FTIR spectra of the *Cristallo* (a), *façon de Venise* (b) and Soda Lime (c) glass samples aged up to 1 year. $t_{0\,days}$ = pristine or control samples, up to $t_{365days}$ = 1 year exposure), at the 45% RH and the 75% RH environments. The H_2O stretching and bending bands are highlighted since the main alterations occur in terms of the surfaces hydration.

(a) Surface scanning of the release of Na$^+$ ions for the *Cristallo* surfaces exposed to 45% and 75% RH

(b) Surface scanning of the release of Na$^+$ ions for the *façon de Venise* surfaces exposed to 45% and 75% RH

(c) Surface scanning of the release of Na$^+$ ions for the Soda-Lime surfaces exposed to 45% and 75% RH

Fig. 3. SIMS surface scanning results for the release of Na$^+$ onto the surface for *Cristallo* (a), *façon-de-Venise* (b) and Soda-Lime (c) glass surfaces aged up to 1 year.

compounds.

In Fig. 3b it is possible to verify that the behaviour for the *façon de Venise* glass is slightly different, since the surface features have a more uneven evolution in terms of their size increase with time.

The case of the Soda-Lime type is the farther away from the *Cristallo* glass behaviour. The former does not show any surface feature evidence until one year exposure to both environments (45% and 75% RH), when the formation of Na-rich aggregates can be first observed (Fig. 3c).

As it is shown for the three glass types in Fig. 3, the reaction products enriched in sodium remain in contact with the glass surface. Hence, they are available to react with ambient gaseous species and to ultimately form corrosion crystalline products [44,46].

With respect to the influence of the moisture in the environment, it is evident the effect of the higher amount of water available to the formation of the alkali aggregates at the surface level (Fig. 3a is the most representative case) due to the accumulation of the alkali ions at the surface after interdiffusion. The availability of water is playing a role in the formation and the size of the Na-rich aggregates. Large areas enriched in Na^+ ions can be observed after a short time of exposure of the samples to the 75% RH environment, whilst small ones are observed after the same period or after longer exposure to the 45% RH environment. The size of the aggregates increases with time in most cases. This was observed by the increase in roughness of the surfaces (measured by optical profilometry), by optical microscopy, as well as by the SIMS surface scanning where it is possible to observe the increase of the Na^+-enriched regions in size. Fig. 4 presents these observations for the *Cristallo* glass case, which is the most altered and well representative of the alteration of the surfaces and formation of these features. It can be observed that there is a small signal from Na_2OH^+ species, but Na_2COOH^+ and $Na_2CO_3^+$ (already identified in other studies by this technique, and related to formates and carbonates on the glass surface [30]) are absent (or are too low signals to be seen within the SIMS scanning resolution).

The composition of glass appears to be playing its role as well, and it seems to be associated with the alkali leaching rate. Calcium ions could possibly be involved in the leaching process. It is known that when aqueous attack occurs, a ternary CaO-containing glass loses Na^+ ions from the lattice more slowly compared to a binary Na-rich glass [7,6]. Besides, Ca^{2+} seems to be able to promote clustering of NBO by reactions similar to $2Q_3 \rightarrow Q_2 + Q_4$, the latter being much more resistant to attack [5]. Nonetheless, in the present study the role of Ca ions is not clear from any of the SIMS profiling, nor does it appear as a leached ion in any surface scanning.

3.3. The influence of glass composition

In Fig. 5, the alteration depth at 95% of the slope of curve of the profiles is plotted *versus* the time of exposure of samples to each of the four RH environments. The alteration depth is relative to each ion, thus it is considered to be the depletion depth of Na^+ ions (Fig. 5a) and the depth at which $SiOH^+$ can be observed inside the glass surface (Fig. 5b). Fig. 5 shows that the altered layer at the surface increases in a non-linear way. Considering the third item mentioned above from V. Jain [49] ('*the glass network, even if attacked chemically, does not dissolve, so that protons and alkali ions interdiffuse without formation of a steady state.*'), altered layers are formed on the surface as the reactions progress, which occurs since the corrosion processes are being affected by non steady state conditions [49,58]. Since the products resulting from the interdiffusion accumulate on the surface and the network is not dissolved, the ion-exchanged layer tends to grow in thickness with time [48,50].

The trend presented in the profiles in Fig. 1 is better shown in Fig. 5a, where it can be clearly observed that the Na^+ ions are decreasing in concentration with increasing depth. As Tournie et al. mention, the composition of the corrosion layers (*i.e.* the altered surfaces) has been seen as a film almost totally depleted in alkali oxides

(Na_2O, K_2O) and MgO, and depleted in CaO and P_2O_5 to lesser extents; Al_2O_3 and Fe_2O_3 could remain constant or be enriched, and enrichment is usually strong on the silica content [9]. Nonetheless, the film formed on the glass surfaces under study was not yet depleted in either K_2O, MgO nor CaO, although the enrichment in silica was observed as described in the literature.

In the present scenario – on which the environmental conditions are similar for the three different soda-rich glass types – the evidences of the influence of the glass composition are visible. By looking at Figs. 5 and 6, and correlating this information with the profiles in Fig. 1, it is possible to verify that the three glass types exposed to both environments differ from one another very evidently. While *Cristallo* glass samples show an initial surface depleted in Na^+ ions, the *façon de Venise* type shows a less depleted surface from the start, and the Soda-Lime type an even less alkali-depleted surface. The hydration depth follows this trend as well, as it can be seen by the $SiOH^+$ species information (Fig. 5b). The water bands detected by FTIR around $3500–3200$ cm^{-1} and $1700–1500$ cm^{-1} are also evidence of the different hydration behaviour. These bands are less visible in the Soda-Lime glass type, which suggests that the composition of this surface might be less hygroscopic. If on one hand, the latter characteristic already promotes some protection to the surface, delaying the environmental effect, the fact that the Soda-Lime glass has a higher (double) $CaO/(Na_2O + K_2O)$ ratio than the other two glass types (see Table 1) seems to have a strong influence on the alteration of the surface (as explained in Section 1.2), at least at its initial phase CaO has a very effective role in stabilising silica-rich layers and retarding glass dealkalinisation, namely as it has early been reported by Hench and Clark [12], among other. This seems to be very well attributed to the fact that there are fewer unsatisfied bonds and therefore it provides an effective chemical barrier to further Na^+ diffusion [12]. Nevertheless, the amount of CaO or the ratio between CaO and other alkali oxides is a crucial factor, as it has been confirmed that common soda-lime silicate glass submits a strong interaction with water [5].

The summary of profiling information in terms of variation of concentration of two ions species is presented in Fig. 6 – Na^+ ions in Fig. 6a and Ca^+ ion in Fig. 6b. The concentration information was calculated based on the normalisation to the theoretical bulk concentration, by admitting that amount was reached at the plateau of the curves. It can be seen in Fig. 6a that the release of glass components from its surface is a complex non-linear mechanism as a function of time. This behaviour shows the combined effect of parameters such as composition, formation of secondary phases, and the environment [49]. It is incontestable that the higher content in alkali and alkaline-earth ions in the glass, the higher the number of sites which are available for ion-exchange reactions. Also, the migration of the alkali ions towards the surface results in a silica-enriched porous layer, and apparently in a group of aggregates probably distributed in its pores – as presented in Section 3.2. Considering the three types of glasses under study, this behaviour is definitely dependent upon the composition and ion ratios. The glass with the highest content in lime – the Soda-Lime glass type – shows indeed the higher stability, but it is closely followed by the *façon de Venise* glass type (Figs. 5 and 6). Knowing that usually a low-durability glass produces a thicker film than a high-durability glass under identical conditions [59], *Cristallo* glass can be relatively classified as the less durable, followed by the *façon de Venise*, and finally Soda-Lime will be the more stable among these three types.

The most interesting fact upon the comparison of these glass compositions is that the *façon de Venise* glass has a content in lime similar to the *Cristallo* glass, which evidences a much more altered surface after 1 year exposure to all environments. By looking at the ratios between alkali modifiers and network stabilisers ($Na_2O + K_2O / CaO + MgO + Al_2O_3$), it seems that these ratios being lower for both Soda-Lime and *façon de Venise* glass types than the *Cristallo* one (Table 1) has a stronger influence than the content in lime alone. It is not solely the amount of CaO that is slowing the rate of the *façon de Venise* surfaces alteration
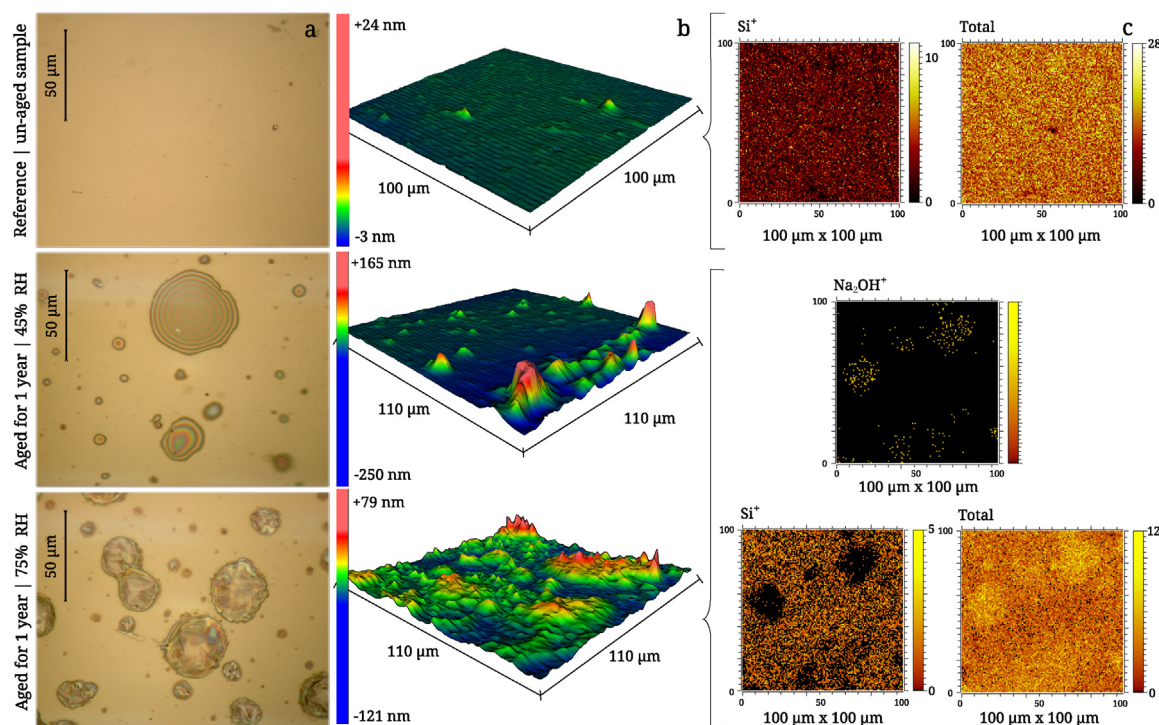
Fig. 4. Detailed observations of the *Cristallo* surfaces through (a) optical microscopy (unaged samples and samples aged over 1 year), (b) 3D profiles of the same surfaces and (c) SIMS surface scanning of the unaged samples (Si^+ ions and total concentration) compared to the samples aged over 1 year at 75% RH (Si^+, Na_2OH^+ species, and total concentration) which evidences the over surface enrichment in Na^+ ions.

with time and with RH, for it is almost the same. The difference in the remaining oxides between the two glass compositions is enough to contribute to a different surface alteration behaviour. Finally, the results obtained do not show any evidence for the leaching of Ca ions in the altered layer formed on *Cristallo* glass surface (Fig. 6b and Fig. 7[1]), which suggests that if this ions are mobilised, this phenomenon occurs later in time. It is broadly reported that *Cristallo* glass is of rather low durability [60,28,30,61,62]. A layer depleted in sodium, calcium and magnesium oxides has been observed in aged Renaissance glassworks [60]. The results from the early stages of corrosion of this composition under the selected exposure conditions do not present evidence for the leaching of either species from the surface layer (the same way as the Ca^+ SIMS profile presented in Fig. 7a, the Mg^+ profiles show a similar behaviour).

4. Discussion

This paper addresses the atmospheric alteration behaviour of three different soda-rich historic glass compositions that typically could be found in similar conditions in a museum. This study has allowed to reveal early-stage features formation under mild conditions such as the ones existing in actual museum environments. Moreover, the kinetics of the process and the most relevant factors to its progression were able to be analysed in detail.

4.1. Atmospheric deterioration kinetics

The progression of the surface alteration for the *Cristallo*, *fdV* and Soda-Lime glasses has a clear dependence on the water availability and

penetration on the surface, as it can be drawn from the results of the silanol species in the SIMS profiling previously presented. Water penetration was found to be independent of alkali diffusion (a kinetically controlled phenomenon with a $t^{\frac{1}{2}}$ dependence) [12], since it progresses further deep into the glass surface. The $t^{\frac{1}{2}}$-dependence of the growth of the alteration layer is related to a transport-controlled process [63]. The more complex rate of the present scenario differs from a $t^{\frac{1}{2}}$-dependence, but it does not seem to be linear either. Thus, the hydrolysis and re-precipitation of insoluble phases of the glass surface in the case of a humid atmosphere, where the amount of water molecules on the surface available and able to react or solvate other species is limited, affects the rate of the reaction [63,64]. Moreover, as far as the initial stages of the surfaces alteration observations have evidenced, the alteration behaviour of the surface is not homogeneous and this seems to be the case for all three glass types studied.

The absence of an alteration depth linear with the increase of the RH of the exposure environment can also be verified (Fig. 8). It would be likely that the intermediate RH environments (55% and 65%) would represent intermediate levels of alteration in all glasses compared to the extreme environments used (45% and 75%). These results would be in accordance with an hydrolysis controlled process, with a linear time dependence [12]. However, the results for all RH environments do not fit well into a linear tendency, which should be rightly interpreted due to both a non-homogeneous surface-process occurring, as well as to the lack of other RH environments experimental data. Considering the error deviation of each measurement, and this combined with the observed formation of features distributed over the surface on specific regions (probably dictated by porosity, hygroscopicity, the surface roughness resulting from production technology, among other factors), the non-linearity of the relation was not unexpected.

In order to understand elementary steps of reactions on this multi-component system, it is important to have knowledge of the physico-chemical parameters of the dominant reactions in the process [65]. In most cases, the adsorption from the surroundings gaseous or liquid phases is the first step of the sequence of a reaction [65]. The present

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[1] The surface enrichment in Ca^+ ions in *Cristallo* is apparently relative to the leaching of Na^+ ions, rather than the mobilisation of the former ion (Fig. 7a) In Fig. 7b it occurs to a much lesser extent to the *façon-de-Venise* glass type, and a very similar behaviour occurs in the Soda-Lime SIMS depth profiles that were collected for the same ion.
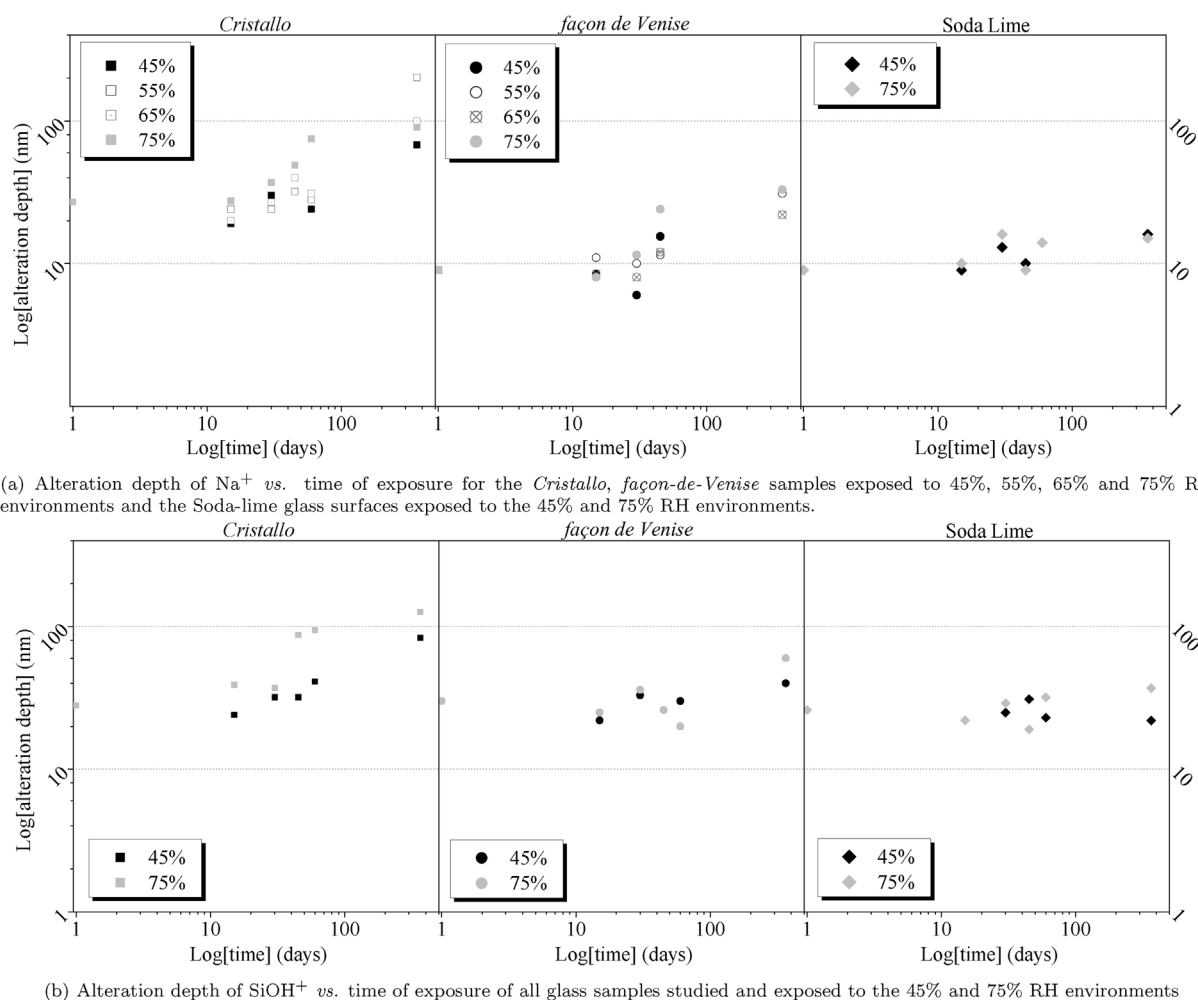
(a) Alteration depth of Na$^+$ *vs.* time of exposure for the *Cristallo*, *façon-de-Venise* samples exposed to 45%, 55%, 65% and 75% RH environments and the Soda-lime glass surfaces exposed to the 45% and 75% RH environments.

(b) Alteration depth of SiOH$^+$ *vs.* time of exposure of all glass samples studied and exposed to the 45% and 75% RH environments

Fig. 5. Alteration depth of a specific ion species (Na$^+$ or SiOH$^+$) measured and plotted against the time of exposure for the three types of glass studied (*Cristallo*, *façon-de-Venise* and Soda-Lime glass surfaces aged up to 1 year).

study revealed that the *Cristallo*, *fdV* and Soda-Lime glasses surface alteration under a museum-like atmosphere develops quite accordingly to an hydrolytic first occurring and/or controlling step, since it should be the first step of the sequence of reactions. All surface reactions lead to a lowering of the surface free energy of the glass, from the thermodynamic point of view. More stable compounds are formed, impurities are segregated and interfaces are favoured since this lowers the surface energy [65]. Surface energy is in fact an important property and factor in terms of the reactivity of the glass surface with the surrounding environment, namely ambient water [48]. The accumulation of water molecules on the glass surface has been already reported as contributing to the diffusion of alkali ions through the glass (bulk → surface) driven by a chemical potential [66]. According to the results presented, it appears that the localised adsorption of water molecules, and the amount of these molecules (determined by RH) available to form more or less layers over the glass [67] are factors that are strongly affecting the kinetics of the process.

On the other hand, since water can penetrate the surface either via diffusing into void space, or by hydrolysis and condensation reactions [3], and that from the reverse hydration reaction it is clearly possible that a rearrangement of the structure of the network can occur, both the amount of water molecules available and the space in the lattice can be a determining factor for the progression of the alteration. In other words, both the RH in the environment and the glass composition, which determines the structure of the network and the size of the voids and spaces in the lattice or the ones than can be formed by the
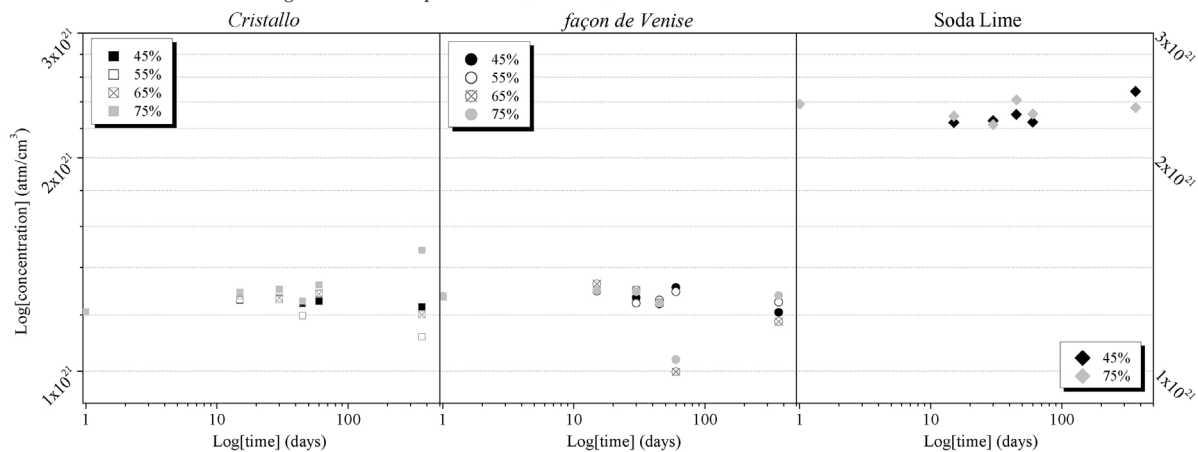
movement of alkali ions, are determining the surface alteration phenomena. The amount of water molecules that enters the glass depends on the space available in the lattice. The rate of the water penetration (molecular diffusion pathway) is dictated primarily by the size of the voids in the lattice. If the tetrahedra rings present in the structure promote small voids, or if these are blocked or filled by modifier cations (as Na$^+$, Ca^{2+}, Mg^{2+}), the only way for the water molecules to enter the network is via hydrolysis. This seems to be the case of most glasses [46], and the current results have proven that the interdiffusion is a second phenomenon in time (see Fig. 8, where the Na$^+$ ions alteration depth is always below the SiOH$^+$ species alteration depth). Hence, it is reasonable to consider that the chemical durability will be higher the more compact is the glass structure (*i.e.* the fewer the water molecules can enter the matrix [51]), and that consequently it would be likely that the kinetics of the alteration (*Cristallo* > > *façon de Venise* > Soda-Lime) would be an indicator of the difference of these matrices voids size and of their proneness to grow under moisture attack.

4.2. Glass surfaces alteration behaviour

It was verified in this study that the depletion of Na$^+$ in depth (Fig. 1a and b), together with the formation of Na$^+$ enriched regions on the upper level of the surface, is associated with Si and K enrichment according to the profiles of these two ions – which would be expected at least for the case of silica [9]. However, the regions enriched in the alkali ions (Na$^+$) present a lower signal of Si$^+$, K$^+$, and a smaller
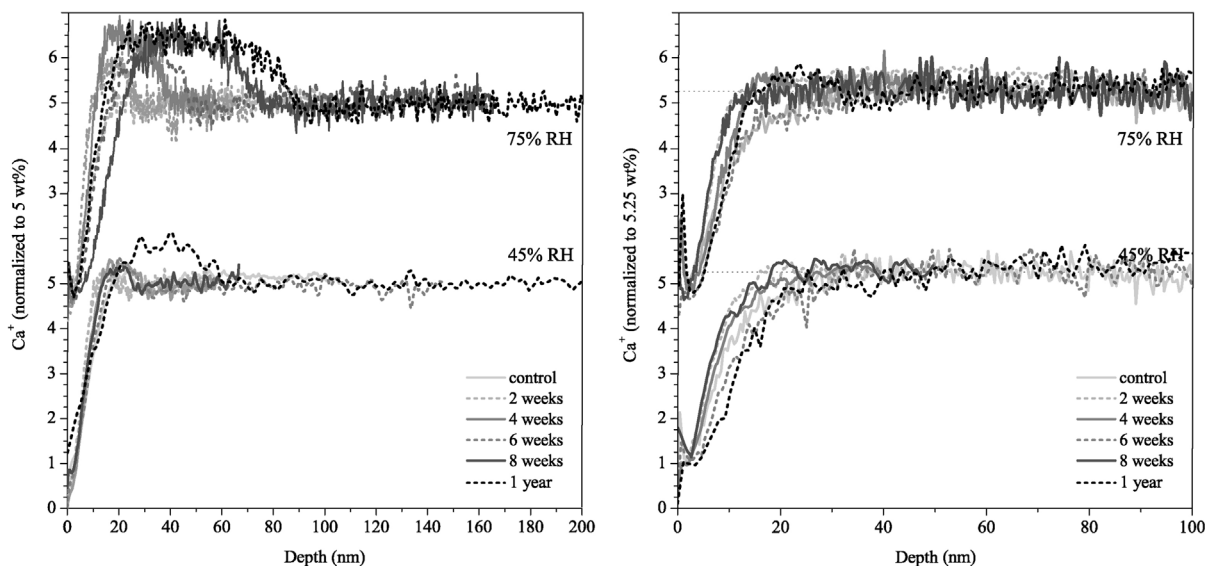
(a) Na$^+$ surface composition *vs.* time of exposure for the *Cristallo*, *façon-de-Venise* samples exposed to 45%, 55%, 65% and 75% RH environments and the Soda-lime glass surfaces exposed to 45% and 75% RH environments.

(b) Ca$^+$ surface composition *vs.* time of exposure for the *Cristallo*, *façon-de-Venise* samples exposed to 45%, 55%, 65% and 75% RH environments and the Soda-lime glass surfaces exposed to 45% and 75% RH environments.

Fig. 6. Composition of a specific ionic species (Na$^+$ or Ca$^+$) calculated and plotted against the time of exposure for the three types of glass studied (*Cristallo*, *façon-de-Venise* and Soda-Lime glass surfaces aged up to 1 year).

(a) Ca$^+$ depth profiles collected from the *Cristallo* samples exposed to 45% RH and 75% RH

(b) Ca$^+$ depth profiles collected from the *façon-de-Venise* samples exposed to 45% RH and 75% RH

Fig. 7. SIMS profiling data of the ions Ca$^+$ collected for both 45% RH and 75% RH environments for *Cristallo* and *façon de Venise* glass samples aged up to 1 year.
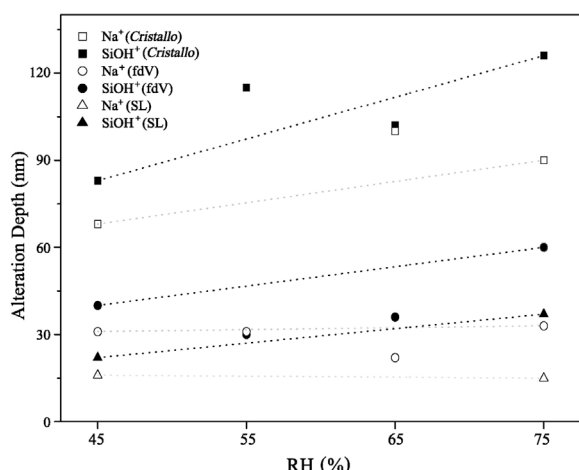
Fig. 8. Alteration depth of the SIMS collected Na^+ and $SiOH^+$ species after 1 year exposure of the samples (*Cristallo*, *façon de Venise* or *fdV*, and Soda-Lime or SL), against the RH of the environment. Lines were added as a guide to the eyes.

enrichment in Na_2OH^+ species collected – see Fig. 4. The roughness of the surfaces increases, and the diameter of the regions observed both by optical microscopy and SIMS surface scanning increases as well. Nonetheless, the height of these regions cannot be precisely determined. It is proposed that they occur at a nanometre scale, more pronounced in the outer surface than inside the glass itself. The low signal obtained for the Na_2OH^+ species can be interpreted as the OH^- ions balancing the charge of some of the Na^+ leached ions, or it can be representative of water molecules solvating the alkali ions. The absence (or too low signals) of Na_2COOH^+, Na_2CO3^+ and $Na_3SO_4^2$ (which this technique was able to identify if present [30]) suggests that crystalline products may have not yet been formed at this stage. Despite the fact that it has been reported and verified that sodium formate is the main crystalline species on the surface of unstable glass (as in [68–71]), the absence of the formation of crystalline phases of this compound is not surprising due to its low deliquescence point at room temperature (50.2–52.1% according to [71]). If on one hand there would be a higher probability of formation of that compound with the increase of the 'solution' volume (RH, and hence water availability), on the other hand the salts would not be precipitating in the higher RH environments. On the contrary, both sodium carbonates and sulfates have high deliquescence points [71,72] and would be expected that these species could be forming already some crystalline compounds even at 75% RH. Nonetheless, as it was observed by Alloteau et al., only when samples are removed from the climatic chamber and are left to dry for a few months under ambient atmosphere (about 40% at 25 °C in the case of [64]) and the water from the hydrated surface regions evaporates, it will be possible for evaporite salts to form (such as Na_2CO_3) [64]. Moreover, two other factors are mentioned by these authors: (i) the temperature of the liquid-vapour transition is higher in confined medium, and (ii) the number of Na^+ and OH^- ions actually solvated inside pores and available in reality to react with the atmospheric CO_2 molecules can be rather limited [64]. In addition, Bourg and Steefel also found that only in silica nanopores ≥ 2 nm can be found water molecules with bulk-liquid water behaviour at the centre of the pore [73]. This suggests that if smaller pores exist, the solvation properties should be rather limited.

A possible explanation for the observations made on all the glass surfaces – although to a different extent with relation to the glass type, the RH environment and the time of exposure – is schematically presented in Fig. 9. The process is explained as follows.

(1) It is known that if only few molecules are available, some can adsorb on the surface and form a few layers [67]. The water molecules will be acting at a local level, for they may not be covering all the

surface. Besides, the ability of this 'film' to solvate the leached Na^+ ions will be quite limited. This is consistent with the observed results for the samples exposed to the 45% RH environment: (i) much lower hydration bands detected by FTIR in all glass types (2), (ii) less mobilised alkali ions as can be seen by the SIMS profiles (Fig. 1) or the concentration plots (Fig. 6), and (iii) very small regions enriched in Na^+ ions at 45% RH for all three glass types, observed by SIMS surface scanning imaging (Fig. 3).

(2) If enough water molecules are available from the air moisture, they would be able form agglomerates or droplets. With more water molecules adsorbed on the surface, the process will be enhanced: the hydrolysis and hydration of the surface can progress deeper and faster into the glass surface, and the chemical potential of the adsorbed 'solution' will be higher, thus increasing the leaching of the Na^+. However, this occurs probably also at a local level. The formation of the observed large regions enriched in Na^+ at 75% RH is consistent with the possible localised role of water droplets. Moreover, the cumulative effect of leaching (increasing the hygroscopicity) and adsorption over time will probably be the reason for the increase of these regions.

Due to the fact that no washing away phenomena is likely to occur in this static deterioration conditions [44,46], the condensation and evaporation should not remove the leached Na^+ ions. One hypothesis is that these alkalis can be solvated in the water droplets adsorbed on the surface, and it was these regions that the SIMS surface scanning analysed. There is yet another possibility, although the results from the present work do not provide evidence for it. A significant part of the alkali ions can also be still strongly embedded in the layer structure, rather than completely free from the hydrated silicate network (Fig. 9), since this has been observed by dissolution tests performed by Alloteau et al. [64].

When comparing the above mentioned results for the three glass compositions studied, the hygroscopicity and porosity of the pristine surfaces may be two determining factors for the different alteration behaviours. The proposed sketch seems to also be in accordance with progression of the degree of alteration of the surfaces in the order (*Cristallo* > > *façon de Venise* > Soda-Lime), considering that the hygroscopicity and porosity of the three surfaces will cyclically promote:

(i) adsorption of water molecules on the surface and in the pores;
(ii) from (i), the hydrolysis reaction will create more or larger pores (voids in the matrix), and silanol groups (which increases hygroscopicity);
(iii) promoted by (i) and also influenced by (ii), the leaching of the alkali to the surface, which in turn increases the hygroscopicity;
(iv) both (ii) and (iii) should contribute to more water adsorption.

5. Conclusions

The adsorbed water and the composition (or the structure) of the glass surface both contribute to the kinetics of the surface reactions with the environment. Hence, one of the new insights of this paper is the study of the deterioration process using model glass (with historic compositions and technique), with no accelerated ageing, but rather actual museum-like conditions. The composition of the glass surface is considered, as well as the chemistry of surface layers formed during the glass samples production. Therefore, the surfaces prepared are as close as possible to the real historic surfaces and this revealed to be an important factor for the understanding of the alteration of these surfaces in the initial state.

For all three glass types, the thickness of the surface altered layer is proportional to the time of exposure and to the relative humidity of the surrounding atmosphere, which is directly related to the environmental water molecules availability. The depth at which alkali ions are leached is always below the hydration depth for the same exposure conditions,
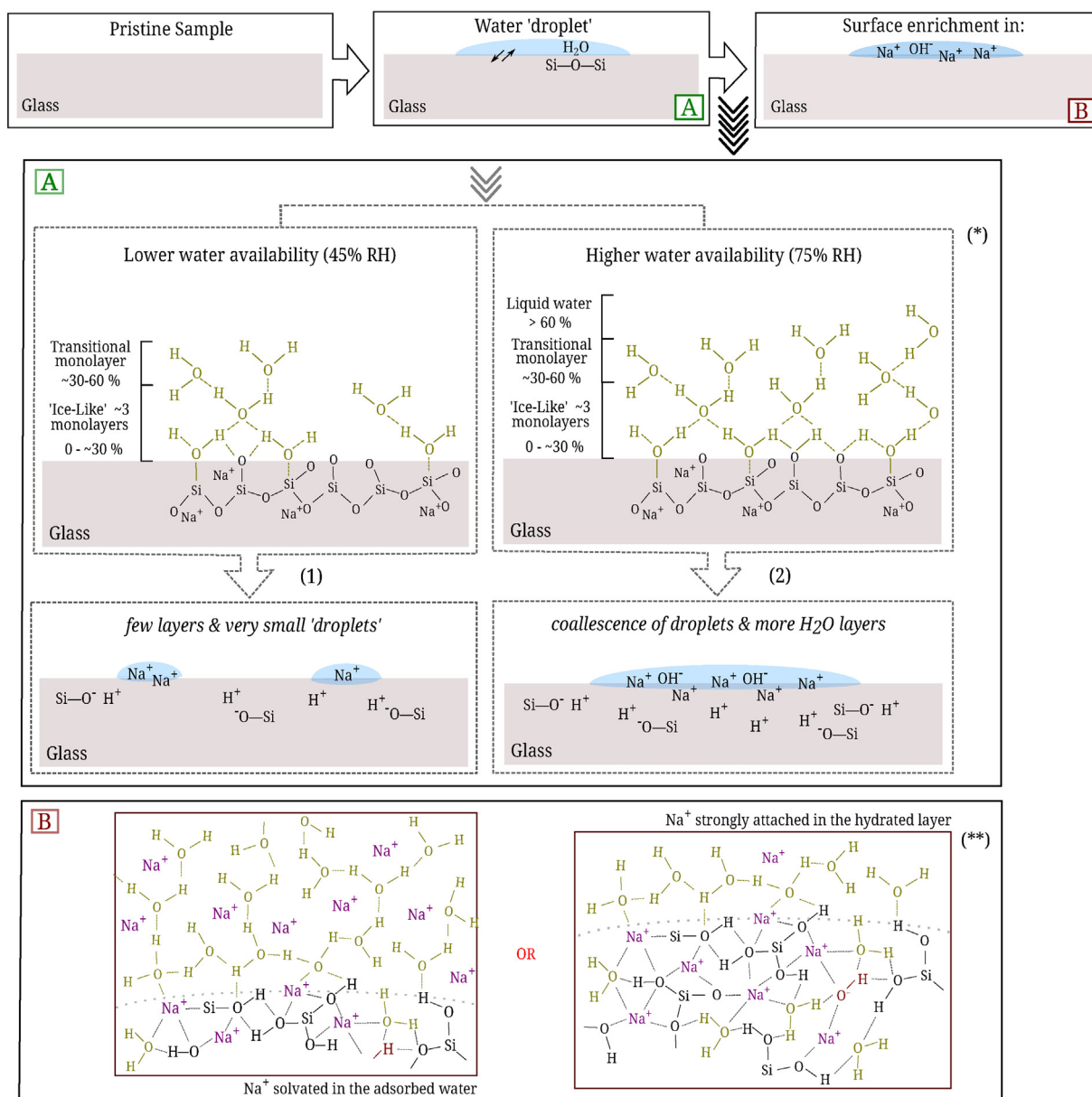
Fig. 9. Schematic illustration of the evolution the process of surface alteration with the formation of upper-surface regions enriched in the leached Na^+ (- - - hydrogen bonds, | covalent bonds). The 2D illustrations are not to scale. | (A) The proposal includes the differences in the processes occurring at high and low RH. (1) and (2) are processes discussed in section 4.2. (*) The formation of the monolayers in the surface or in pores is in accordance with [67,73]. | (B) Two hypotheses exist for the Na^+ enrichment: the top scheme represents that Na^+ leached ions can be solvated in water adsorbed on the glass, and the bottom scheme represents that the main part of the Na^+ ions could alternatively be still strongly attached to the hydrated layer. (**) The structure presented in the bottom image is in accordance with [64]gr9

which suggests that hydrolysis may be the controlling reaction. The kinetics of the reactions seems to be indeed slower in the presence of low RH, which is evident for all three glass types at 45% RH. Moreover, the higher RH environment promotes the formation of large regions on the surface enriched in Na^+ ions, at a faster rate then lower RH environments. These Na^+-rich aggregates may represent an initial state of surface alteration, likely associated to the atmospheric moisture adsorption in localised areas. This local enrichment of the surface has not been observed in any other studies, where the presence of sodium is usually observed associated with crystalline products (for instance: Na_2CO_3).

The information obtained with the in-depth and the surface-scanning profiles by SIMS showed that when comparing the alteration of *Cristallo*, *façon de Venise* and Soda-Lime glass surfaces, the latter seems to be the type of glass less prone to corrode even under high RH

conditions. For the same environmental conditions, there are rather different states of surface alteration. Soda-Lime glass is more stable both in terms of alteration depth and depletion of Na^+ ions at the surface level. The *façon de Venise* glass shows an increase in the alteration depth between the *Cristallo* and Soda-Lime types, and a Na^+ depletion behaviour closer to the Soda-Lime type (more stable, less depleted). *Cristallo* glass is the more vulnerable to alteration both in terms of surface depletion in Na^+, hydration of the surface and increase of the altered layer. The composition of the glass seems to have influence on the structure of the surface (including the porosity, and the lattice voids size and number) and on its hygroscopicity (which has impact in its reactivity). From this point of view, it is clear that the composition of the glass has a strong influence on kinetics of the glass surfaces alteration under the same conditions, which is a very important factor for conservators and curators to be aware of when trying

to prevent this type of glassworks degradation.

These three compositions are representative of large productions of luxury glass objects along the centuries, being *Cristallo* glass the one of most relevance. It is broadly reported that this material is of rather low durability [60,28,30,61,62], although it is a glass with a high silica content. The present study allowed to better understand the early-stages of the process of deterioration of this glass type. Further research is necessary to verify in which conditions or at which stage of the process will the layer depleted in sodium, calcium and magnesium oxides (observed in aged Renaissance glassworks [60]) starts to form.

6. Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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