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# The Influence of Environment in the Alteration of the Stained-Glass Windows in Portuguese Monuments

**Teresa Palomar [1,2,*], Pedro Redol [3], Isabel Cruz Almeida [4], Eduardo Pereira da Silva [5] and Marcia Vilarigues [1,6]**

1 Unidade de Investigação VICARTE-Vidro e Cerâmica Para as Artes, Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal; mgv@fct.unl.pt
2 Instituto de Cerámica y Vidrio (ICV), Consejo Superior de Investigaciones Científicas (CSIC), c/ Kelsen 5, Campus de Cantoblanco, 28049 Madrid, Spain
3 Mosteiro de Batalha, Largo Infante D. Henrique, 2440-109 Batalha, Portugal; predol@mbatalha.dgpc.pt
4 Mosteiro dos Jerónimos, Praça do Império, 1400-206 Lisbon, Portugal
5 Sé de Évora, Largo do Marquês de Marialva, 7000-809 Évora, Portugal
6 Departamento de Conservação e Restauro, Campus de Caparica, FCT-UNL, Quinta da Torre, 2829-516 Caparica, Portugal
* Correspondence: t.palomar@csic.es; Tel.: +34-917-355-840

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**Abstract:** This work presents the results of the exposure of soda-lime, potash-lime and mixed-alkali silicate glasses during ten and twenty months in different Portuguese monuments with historical stained-glass windows to characterize the influence of local environmental conditions. The glass samples were exposed in the Monastery of Batalha (Batalha), the Monastery of Jerónimos (Lisbon), and the Cathedral of Évora (Évora). A set of analytical techniques to assess the physicochemical effects were used, including optical microscopy and Fourier transform infrared spectroscopy. All the samples presented crystalline deposits on their surface; however, their quantity and nature depended on the atmospheric conditions during the days before the collection. Potash-lime silicate glass was the most altered glass in comparison with soda-lime and mixed-alkali silicate glasses. The samples from the Cathedral of Évora showed a high content of dust and salts on their surface but without severe chemical pathologies; however, those samples exposed in the Monastery of Jerónimos and the Monastery of Batalha presented alteration layers due to a high humidity environment.

**Keywords:** glass; degradation; stained-glass windows; Portuguese monuments

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## 1. Introduction

Portugal has an extensive collection of historical stained-glass windows from different chronologies spread around the country. The most ancient stained-glass windows in Portugal are located in the Monastery of Batalha, built between around 1388 and 1533 (for what is to be seen in-situ), in the church aisle, south transept and west windows as well as in the Founder's Chapel. Various panels of these ancient windows, preserved in the monastery, were designed by Luis Alemão (Louis the German) and present figurative and geometric motifs [1,2]. Afterward, a more realistic style of stained-glass windows was produced. An example of this movement was observed in the church choir and chapter house glazings, produced between 1514 and around 1531. They were certainly designed (and partly painted) by Francisco Henriques and financed by the King Manuel I of Portugal.

During the 16th century, stained-glass windows were frequent in Portuguese monuments; however, the majority of them have been lost. A few examples of them are still preserved either as window panels in monuments or in museums. From these examples, it is important to highlight the fragments located in the Convent of Christ in Tomar, a small heraldic panel at the National Museum Soares dos Reis in Porto, a dated piece at the Museum of Setubal, and two figurative half-panels at the Church of Viana do Alentejo. From the 17th century, some panels have been preserved in the National Palace of Pena in Sintra, along with a few more ancient ones, brought to Portugal by King Ferninand II in the 19th century.

In the 18th century, the Portuguese stained-glass windows were severely damaged, with many gaps and bad-quality restorations, due to a change in the decorative movements together with the destructive consequences of the earthquake from 1755 and the Peninsular War (1807–1814) [3]. However, in the second half of the 19th century, the stained-glass windows rose again in Portugal due to the renascence of this art as part of the architectonic context, not only in religious buildings but also in public and private constructions. They were complex works in which big uncolored pieces of glass were painted with enamels and grisailles, and the lead cames were concealed in the contours of the figures. Progressively, enamels were replaced by colored glasses in which the lead cames and the grisaille defined the contours and shadows [2]. During this period, stained-glass windows competed with the panels of ceramic tiles, very frequent in Portugal, as decorative elements [2].

Historical stained-glass windows are usually situated in buildings as part of their façade. This position permits to illuminate the inner part of the building, to serve as decoration with an instructive function, and also to protect the building from the external environmental conditions (rain, wind, extreme temperatures ... ). Nevertheless, this latter function is the most hazardous for the conservation of historical stained-glass windows.

The influence of environmental conditions has been an important field of study in recent years since many European medieval windows present a poor state of conservation [4–15]. Nevertheless, few works have been done to compare the alteration mechanism of the same glass composition in different places. In the framework of the "International Co-operative Programme on Effects on Materials including Historic and Cultural Monuments" (ICP Materials) [16,17], some glass samples with medieval and modern composition were spread around Europe in different atmospheres (industrial, urban, rural) [7,10,18]. The exposure of these samples showed that the glasses exposed in polluted environments (industrial atmosphere) present a faster alteration due to the influence of the higher concentration of the pollution gases ($CO_2$, $SO_2$, $NO_x$). With a similar procedure, the glass-sensors developed by the Fraunhofer-Institut für Silicatforschung (Germany), were used as alteration sensors in European stained-glass windows by the assessment of environmental corrosive stresses in low durability glasses. For the same time of exposure, sensors with a more advanced degradation state indicate that the stained-glass windows are in a more hazardous environment [19,20].

In spite of these works, there is not a systematic analysis of how Portuguese stained-glass windows can be affected by the environmental conditions. For this reason, the aim of this study is to determine the chemical stability of three glasses (soda-lime, potash-lime, and mixed-alkali silicate glasses) in different Portuguese monuments with historical stained-glass windows. The glass samples were exposed in the Monastery of Batalha (Batalha), the Monastery of Jerónimos (Lisbon), and the Cathedral of Évora (Évora). This research will be especially useful to evaluate the conservation strategies of Portuguese stained-glass windows.

## 2. Materials and Methods

### *2.1. Glass Samples*

Three different glasses were formulated following the composition of the most common glasses from historical stained-glass windows: soda-lime silicate (NCV), mixed-alkali silicate (MCV) and potash-lime silicate glasses (KCV) (Table 1). They were melted in the laboratory and blown into the form of a roundel using the same procedure as the historical production of crown window glass. Samples of each glass were cut into slices of $(1 \times 1 \times 0.2)\ cm^3$.

**Table 1.** Chemical composition of soda-lime silicate (NCV), mixed-alkali silicate (MCV) and potash-lime silicate (KCV) glasses analyzed by Particle Induced X-ray Spectrometry (PIXE).

| | Chemical Composition (wt. %) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Na_2O$ | MgO | $Al_2O_3$ | $SiO_2$ | $P_2O_5$ | SO3 | $Cl^-$ | $K_2O$ | CaO | $TiO_2$ | MnO | $Fe_2O_3$ | CuO | ZnO | $SnO_2$ | PbO |
| NCV | 16.91 | 1.77 | 3.15 | 66.12 | 0.02 | 0.03 | 0.01 | 2.86 | 7.30 | 0.03 | 0.09 | 0.27 | - | 1.15 | 0.28 | - |
| MCV | 11.70 | 3.43 | 6.81 | 62.97 | 0.12 | - | 0.01 | 4.72 | 8.83 | 0.12 | 0.38 | 0.55 | - | - | 0.38 | - |
| KCV | 0.10 | 1.96 | 4.16 | 57.14 | 1.76 | 0.01 | - | 17.56 | 16.64 | 0.06 | - | 0.12 | 0.01 | - | 0.45 | 0.01 |

### *2.2. Corrosion Tests*

The samples were exposed in three Portuguese monuments with historical stained-glass windows: Monastery of Jerónimos (Lisbon), Monastery of Batalha, and Cathedral of Évora (Figure 1).

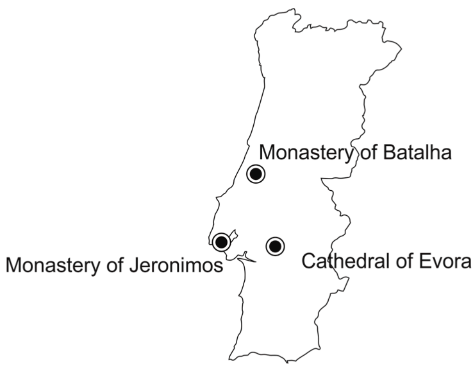


**Figure 1.** Monuments where the glass samples were exposed.

The Monastery of Jerónimos, in Lisbon, has stained-glass windows from the first half of the 20th century. The panels, designed by Abel Manta and executed in the Atelier of Ricardo Leone, showed the economic and industrial renascence of Portugal [2]. The Monastery of Batalha has stained-glass windows principally from the 15th and 16th century, but also modern windows from the 19th and 20th century with decorative or historicist style, and different restoration interventions [2]. Finally, the Cathedral of Évora had 15th-century stained-glass windows; however, they were destroyed over the centuries. Currently, two modern roses are placed face to face in the transept of the Cathedral. All these stained-glass windows are exposed as part of the building's façade, some of them with protective glazing.

To assess the environmental conditions of these stained-glass windows, replica glass samples were exposed for periods of 10 and 20 months. They were placed in a vertical position unsheltered from the rain. The meteorological conditions of the environment have been recorded by the Portuguese Information System of Water Resources and the Institute of Earth Sciences from the University of Évora (Table 2). The glasses and the support structure exposed in Batalha were stolen during the final months of the experiment.

**Table 2.** Average value of meteorological parameters in the nearest meteorological stations to the three monuments.

| | Lisbon (Caparica Station) | | Batalha (Pedrogão Station) | | Évora (Évora Station) | |
|---|---|---|---|---|---|---|
| **Meteorological Parameters** | **10 Months** | **20 Months** | **10 Months** | **20 Months** | **10 Months** | **20 Months** |
| Temperature (°C) | 16 ± 5 | 17 ± 5 | 16 ± 6 | - | 17 ± 6 | 18 ± 7 |
| $\frac{\text{Days with precipitation} > 0.1\text{ mm}}{\text{Total days of exposure}}$ (%) | 26.9 | 20.4 | 31.1 | - | 25.3 | 23.1 |
| $\frac{\text{Days with precipitation} > 1\text{ mm}}{\text{Total days of exposure}}$ (%) | 16.2 | 10.8 | 18.6 | - | 17.0 | 16.7 |
| Relative Humidity (%) | 72 ± 14 | 71 ± 15 | 69 ± 19 | - | 62 ± 15 | 60 ± 16 |

### 2.3. Characterization Techniques

Glass samples were characterized by Optical microscopy (OM) and Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance (FTIR-ATR).

OM was carried out by a Zeiss Axioplan 2 microscope equipped with the objectives ×5, ×20, ×50 and ×100 in reflective light mode with bright field. The images were taken with a Nikon digital DXM1200F camera coupled to the microscope. The particles measurements were carried out with the software Motic Images Plus 2.0 ML.

Fourier Transform Infrared spectroscopy (FTIR) was carried out with a 4300 Handheld FTIR spectrometer of Agilent Technologies. The measurements were obtained in Attenuated Total Reflection (FTIR-ATR) mode with a spectral range from 4000 to 650 $cm^{-1}$ and a spectral resolution of 4 $cm^{-1}$. Each spectrum was the product of 32 internal scans. In order to compare spectra, the horizontal baseline was corrected with the baseline subtraction in the range 3800–4000 $cm^{-1}$ and, then, spectra were normalized to the maximum peak with the software Spectragryph version 1.2.6.

## 3. Results

### 3.1. Surface Pathologies

The glasses exposed in the three locations did not have any damage or deposits before exposure (Figure 2a). However, after exposure, all glasses presented deposits on their surface. Their quantity and distribution depended on the place of exposure (Figure 2). The samples exposed in the Monastery of Jerónimos (Lisbon) presented both big (>40 µm) and medium (15–30 µm) deposits spread on the surface (Figure 2b); also, very small particles (<3 µm) were observed at high magnification. The samples from Batalha showed few big (>30 µm) and medium particles (~10 µm) distributed heterogeneously on the glass surface (Figure 2c), and the samples exposed in Évora showed very small particles (~2.5 µm) spread homogeneously on the surface (Figure 2d), together with medium and big deposits (>20 µm). The different morphology of the deposits can be related with the environmental aerosols in each place of exposure.

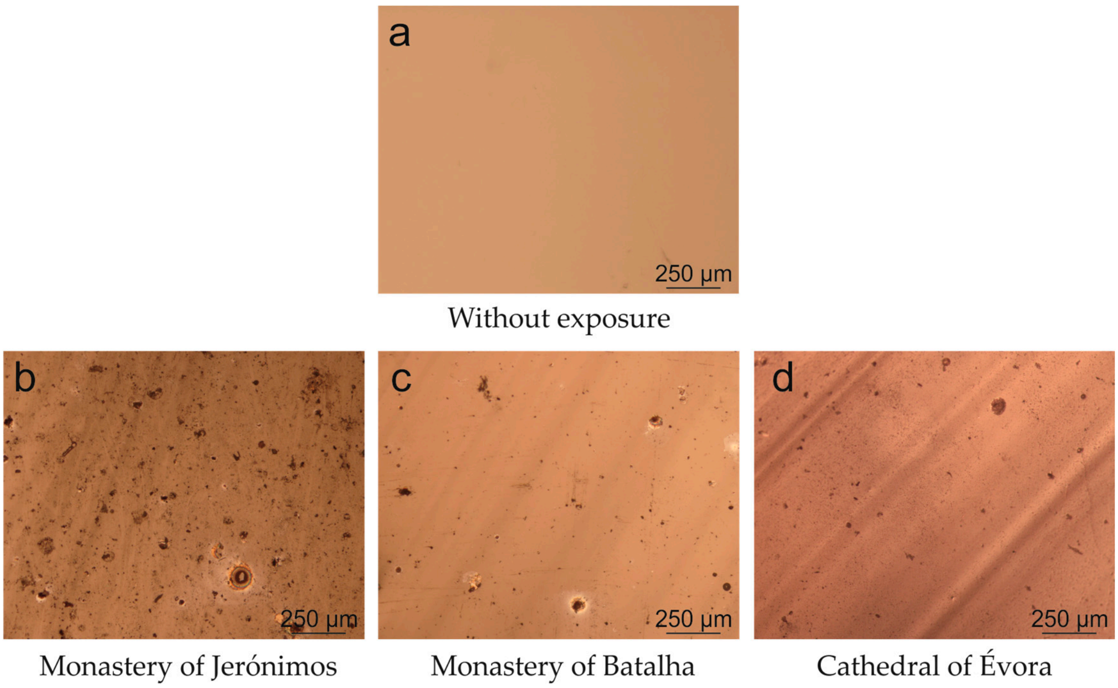


**Figure 2.** OM images of the surface of soda-lime silicate glasses (**a**) without exposure, and exposed for 10 months in the (**b**) Monastery of Jerónimos, (**c**) Monastery of Batalha, (**d**) Cathedral of Évora.

The most frequent natural aerosols in the Iberian Peninsula are small particles from European continental air masses and forest fires, and large particles from both maritime aerosols and the African desert dust plumes [21–23]. In Lisbon, marine particles contribute most to aerosols due to its proximity to the mouth of the Tagus River and the coast of the Atlantic Ocean [24,25]; nevertheless, the city also has a high content of aerosols from anthropogenic sources such as particles from road traffic activity (engine combustion, tire and brake wear, etc.) or re-suspension of road dust [26,27]. Restoration works were also carried out on the façades of the Monastery of Jerónimos, which also contributed to the large deposits located on the glasses. All contributions agree with the different diameter of the deposits observed on the glass surfaces from the Monastery of Jerónimos (Figure 2b).

The quantity of marine aerosols decreases as the distance to the coast increases [22]. For this reason, the places located inland, such as Batalha and Évora, presented a lower contribution of marine aerosols and higher contribution from European continental air aerosols [22]. These latter particles used to be smaller than those from the marine atmosphere, which agrees with the deposits observed on the glass samples (Figure 2c,d). The glasses exposed in the Monastery of Batalha presented deposits with different diameters due to the particles from road traffic activity from near main roads (IC2 and A19) (Figure 2c). The low content of deposits observed on the samples is related to the frequent rains from this place (Table 2). Regarding the samples exposed in Évora, the deposits observed on the samples showed small deposits dispersed homogeneously (Figure 2d), which could be related with the aerosols that are characteristic of continental areas [22].

Circular halos were observed around the largest deposits on the glass samples as a result of the evaporation of water drops (Figure 3a). These deposits can retain the environmental humidity on the surface, inducing the hydration and dealkalinization of the glass surface in the long-term. The static condition of this water can accelerate these alteration reactions, inducing the formation of punctual circular alteration layers (Figure 3b). These layers are very fragile and any movement (wind, physical impacts, manual manipulation . . . ) can break them, forming a hole in which the water can be retained, accelerating the alteration mechanism (Figure 3c). These marks, related to the formation of punctual pits, were observed in all the samples, but they were more abundant in the samples from the Monastery of Jerónimos, where the environmental humidity was higher (Table 2).

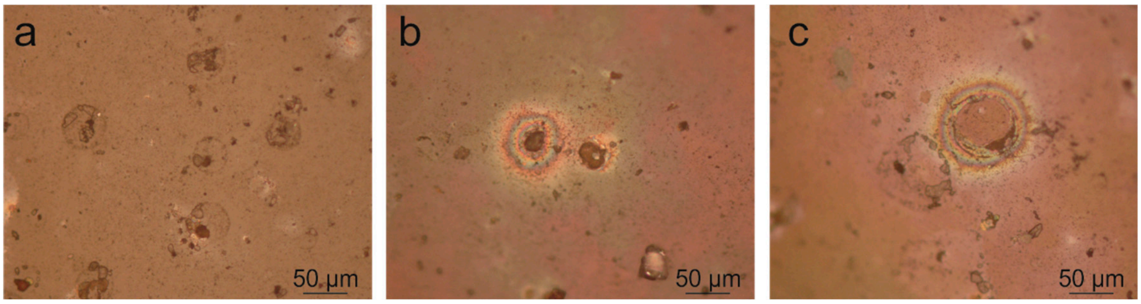


**Figure 3.** OM images of (**a**) circular halos due to the evaporation of water drops, (**b**) punctual circular alteration layer, (**c**) pit in a preliminary state, in potash-lime silicate glasses after 20 months of exposure.

In addition to the pits, potash-lime silicate glasses showed interference colors after 10 months of exposure in the Monasteries of Jerónimos and Batalha; and after 20 months in the samples from the Monastery of Jerónimos and the Cathedral of Évora. The glass samples and the metallic support exposed during 20 months in the Monastery of Batalha disappeared before their collection. These colors of interference are characteristic of the initial stage of the alteration layer. The samples exposed near the coast (Monastery of Jerónimos) showed a more intense phenomenon (Figure 4b) than the samples located far from the coast (Figure 4a). The potash-lime silicate glasses exposed in the Cathedral of Évora showed an irregular "tridimensional" morphology; however, it is an optical effect due to the formation of the hydration layer (Figure 4a) [28]. An advanced state of alteration was observed in the samples from the Monastery of Jerónimos; a homogeneous pink layer was detected on the glass samples as well as circular halos with bluish and yellowish colors and, usually, black deposits in their center (Figure 4b).

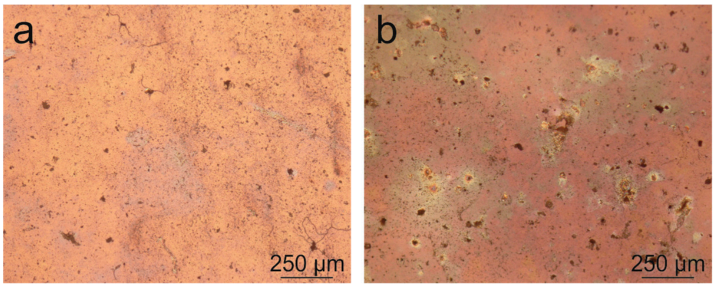


**Figure 4.** OM images of the surface of potash-lime silicate glasses exposed for 20 months in (**a**) Cathedral of Évora, (**b**) Monastery of Jerónimos (Lisbon).

## *3.2. Chemical Alteration*

The alteration of the glass surface was assessed by FTIR-ATR. Spectra of soda-lime silicate glasses after 10 and 20 months of exposure in the three monuments were similar to the original sample (Figure 5a). The modification of the infrared bands was almost negligible, in contrast to the increase on the bands of the hydroxyl groups ($\delta_{H2O}$ ~1650 $cm^{-1}$) due to the adsorption of the environmental water. Similar behavior was observed in the mixed-alkali silicate glasses (Figure 5b), in which a few increase was observed on the bands related with the water adsorption and, in the samples from the Monastery of Jerónimos, the bands of the carbonate groups ($\upsilon_{CO_3{}^{2-}}$ ~1410 $cm^{-1}$). These compounds could be environmental deposits or could be formed as a result of the reaction between the leached ions from the glass with the environmental $CO_2$. The most likely compound is $CaCO_3$, which is the most stable deposit and with less solubility according to the evolution of the crystalline phases on glass alteration [29].

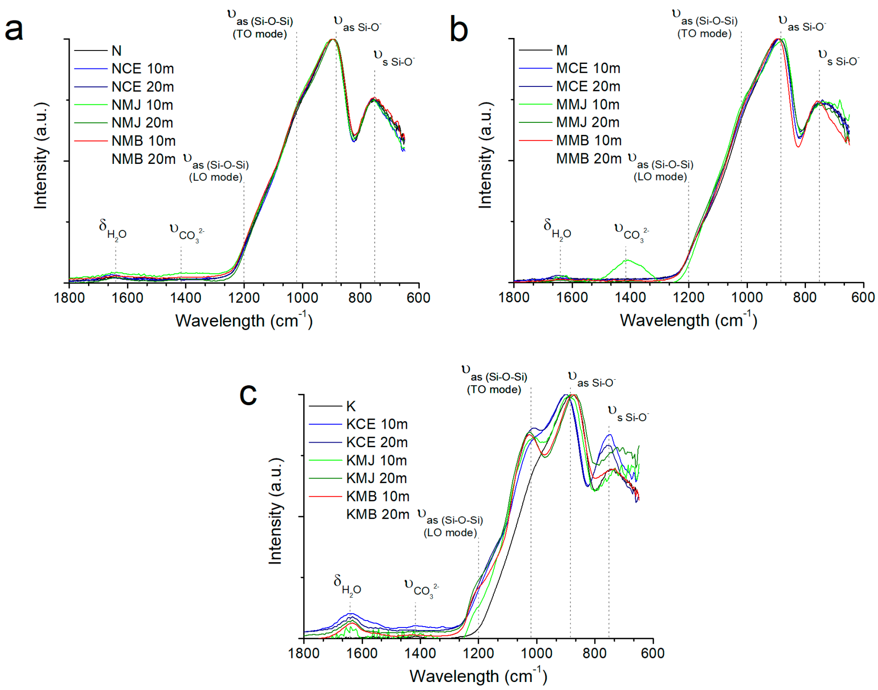


**Figure 5.** FTIR-ATR spectra of (**a**) soda-lime silicate glass, (**b**) mixed-alkali silicate glass, and (**c**) potash-lime silicate glass.

In contrast to soda-lime silicate and mixed-alkali silicate glasses, the spectra of the potash-lime silicate glasses exposed in the three environments were completely different (Figure 5c). The increase in the asymmetric stretching bands of the Si-O-Si group was observed, which can be related to the formation of the silica gel layer on the surface [30]. The band attributed to the bending of the molecular water adsorbed on the surface ($\delta_{H2O}$) also increased its intensity due to the adsorption of the environmental water (Figure 5c). It is interesting that the samples exposed in the Cathedral of Évora showed a shoulder on the silicate bands, which can be related with a very thin alteration layer; however, the samples exposed in the Monasteries of Jerónimos and Batalha presented a significant increase in the stretching band of Si-O-Si bonds due to the thick alteration layer formed on the glass surface. These alteration layers were previously observed by optical microscopy (Section 3.1).

## 4. Discussion

### *4.1. Influence of the Glass Composition*

The glasses presented different behaviors depending on their chemical composition. Soda-lime silicate and mixed-alkali silicate glasses were "almost" stable glasses, in contrast to potash-lime silicate glass which was the most altered glass.

This different behavior was related to the structural package of the glass lattice. The $K^+$-ions (0.133 nm) have a higher radius than $Na^+$-ions (0.097 nm) [31], which forms a glass network opener. This open lattice, in addition to the lower bond strength of the [Si-O-K], makes the reactions of dealkalinization (Reaction 1) and hydrolytic attack (Reaction 2) more favorable.

$$\equiv\text{Si-O-M} + H_2O \rightarrow \equiv\text{Si-O-H} + M^+ + OH^- \quad (1)$$

$$\equiv\text{Si-O-Si}\equiv + H_2O \rightleftharpoons 2 \equiv\text{Si-O-H} \quad (2)$$

The reaction between the leached ions from the glass ($K^+$, $Na^+$, $Ca^{2+}$ . . . ) with environmental $CO_2$ and $SO_2$, solubilized in the rainwater, can form crystals of carbonate and sulphates (Reactions 3 and 4).

$$2M^+ + CO_2 + \frac{1}{2}O_2 \rightarrow M_2CO_3 \text{ [M = alkaline ions]} \quad (3)$$

$$M^+ + CO_2 + \frac{1}{2}O_2 \rightarrow MCO_3 \text{ [M = alkaline-earth ions]} \quad (4)$$

The mixed-alkali silicate glass (~5% $K_2O$) showed a similar behavior to soda-lime silicate glass (Sections 3.1 and 3.2) even with the moderate content of $K_2O$. This behavior could be related to the structural package. The $Na^+$-ions can fill the empty space, creating a better structural package which protects the $K^+$-ions and avoids the hydrolytic attack.

Similar pathologies, but in an advanced alteration state, were observed on medieval potash-lime silicate glasses from the Monastery of Batalha [32–34]. The historical fragments showed fissured surfaces with detachments, interconnected holes with loss of material, iridescent layers due to the hydration of the glass surface, and the formation of a thick corrosion crust enriched in calcium carbonates.

### *4.2. Influence of the Environment*

The glass samples were exposed in three monuments with historical stained-glass windows in different regions of Portugal (Figure 1). According to the Köppen–Geiger climate classification, the monuments are placed in two different climates [35,36] (Figure 6a). The Monastery of Jerónimos (Lisbon) and the Cathedral of Évora present a warm temperate climate with dry and hot summers (Csa) (T (temperature)$_{max}$ > 22 °C, P (precipitations)$_{min\_summer}$ < $P_{min\_winter}$, $P_{max\_winter}$ > 3 $P_{min\_summer}$, and $P_{min\_summer}$ <40 mm); while the Monastery of Batalha presents a warm temperate climate with dry and temperate summers (Csb) (T (temperature)$_{max}$ < 22 °C, T$_{mean}$ > 10 °C for more than 4 months per year, P (precipitations)$_{min\_summer}$ < P$_{min_winter}$, P$_{max_winter}$ > 3 P$_{min_summer}$, and P$_{min_summer}$ < 40 mm) [37].

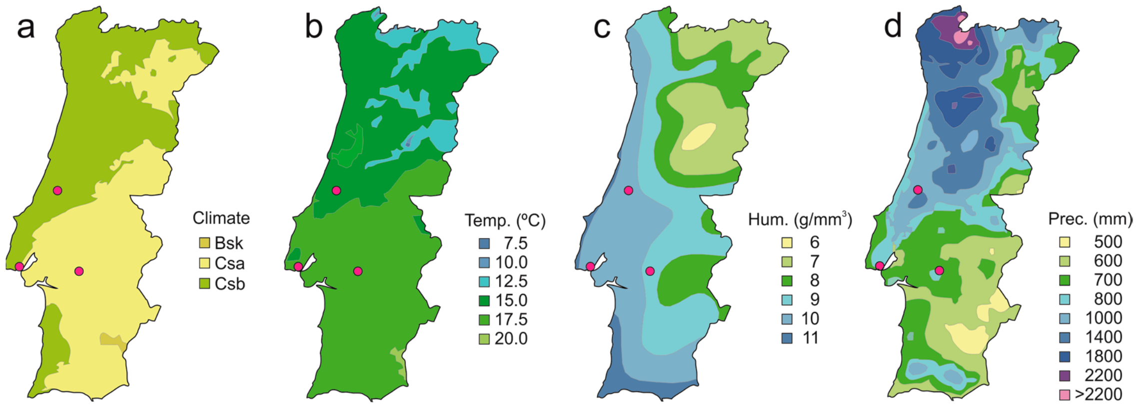


**Figure 6.** Portugal maps with (**a**) Köppen–Geiger climate classification, (**b**) mean air temperature (1971–2000), (**c**) annual average absolute humidity, (**d**) average total precipitation (1971–2000). Pink points represent the places of exposure. Maps from [36,38] modified by the authors.

During the exposure, the main air temperature in the three monuments was similar (Table 2). Nevertheless, a slightly higher value in Évora was observed, which agrees with the mean air temperature measured by the Instituto de Meteorologia de Portugal [36]. This similar value in the measured temperature will induce an equivalent alteration rate.

Évora had lowest relative humidity because it is placed in a continental area, far from the ocean (Figure 6c). On the contrary, Lisbon has the highest RH because of the influence of the Tagus River and the coast of the Atlantic Ocean (Figure 6c and Table 2). Batalha also had high relative humidity because it is located in an area with low temperature and frequent precipitations (Figure 6b,c). The high content of humidity favors the formation of few monolayers of liquid water on the glass surface [39], which can produce the dealkalization of the glass surface (Reaction 1) and the hydrolytic attack of the glass lattice (Reaction 2). The silanol bonds formed as a result of these reactions can polymerize between them to form a porous layer enriched in $SiO_2$ (Reaction 2) [40]. This silica gel layer was observed in the samples exposed in the Monastery of Jerónimos (Lisbon) and the Monastery of Batalha (Batalha) due to the high humidity in these places. However, the low humidity in Évora decreased the alteration rate, which favored the preservation of the most vulnerable glasses.

Additionally, the high content of marine aerosols in the areas near the coast, such as in the Monastery of Jerónimos, increases the alteration rate of the glasses [41]. The marine aerosols can increase the hygroscopicity of the glass surface and, also, open the glass structure, favoring the alteration of the glass surface [42–44].

Another important factor in the alteration of historical glasses is the frequency of precipitations. Rainwater can wash the leached ions (alkaline, alkaline-earth and hydroxyl ions) from the glass surface. The removal of hydroxyl ions favors the maintenance of a neutral pH in the surface glass, which prevents the basic corrosion mechanism. Precipitations in Batalha were recurrent during the exposure period (Table 2 and Figure 6c). It rained around 30% of the days of the exposure, and the precipitation was moderate (>1 mm) more than 18% of these days (Table 2). The rain washed the glass surface, and the deposits and leached ions from the glass were removed frequently [4,5]. For this reason, the samples exposed in the Monastery of Batalha showed few deposits in comparison with the samples from the other two places, and less punctual damages than the samples from the Monastery of Jerónimos (Figure 2).

The Cathedral of Évora, exposed to low humidity and occasional rainfall (Table 2), is the best environmental condition for the preservation of the exposed samples, as was observed in

Sections 3.1 and 3.2. The Monastery of Batalha is placed in an area with high humidity, which favors the alteration rate of the glass; however, the frequent rainfall in this area favored the removal of the aggressive species from the glass surface, avoiding the formation of isolated pits but forming a homogeneous alteration layer in the potash-lime silicate glass after just 10 months. Finally, the Monastery of Jerónimos, located in the mouth of the Tagus River and near the coast of the Atlantic Ocean, is exposed to high humidity and marine aerosols, but with occasional rainfall. This meteorology produces a very high risk for the preservation of historical stained-glass windows. The formation of both a homogeneous silica gel layer on the potash-lime silicate glass and isolated pits in the three glasses was observed due to the hydration and retention of environmental water on the deposits.

According to the environmental climatology of Portugal and the alteration observed on the glasses exposed, a map of the risk of alteration of historical glasses was made (Figure 7). The highest risk was observed in the coastal areas and in the south of Portugal, where higher environmental humidity was measured (Figure 6c). On the contrary, the inner part of Portugal, with drier conditions (Figure 6c,d), presented a better climatology for the preservation of historical glass windows (Figure 7).

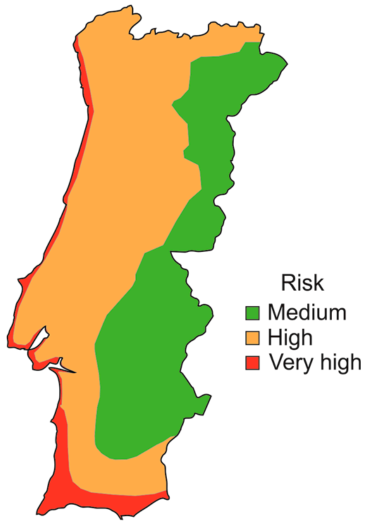


**Figure 7.** Map of Portugal with the risk of alteration of historical glasses.

## 5. Conclusions

The present study has proved that the preservation of historical stained-glass windows in Portugal depends on the type of glass used and on the meteorological conditions specific to each place. Medieval stained-glass windows, usually made with potash-lime silicate glass, are the most vulnerable because they have an open glass network which favors the hydrolytic attack of the glass. On the contrary, soda-lime silicate glass and mixed-alkali silicate glass have the highest chemical resistance to the environmental conditions because they present a better structural package.

Regarding the climatology, glasses located near the coast and in areas with high humidity were the most threatened because of the great impact of the environmental water on the glass surface. Meanwhile, those located in the inner part of the country with a drier climate, were better preserved. From the point of view of heritage conservation, it is recommended to conduct an individual study in each environment due to the specific characteristics of each place.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Hess, D. In search of Luís Alemão. Stained glass in Germany from 1400 till 1460 and the fragments in Batalha. In *O Vitral—História, Conservação e Restauro*; IPPAR: Lisboa, Portugal, 2000; pp. 44–53.
2. Ferreira Vieira, S.J. Para a História do Vitral em Portugal no Século XX—As Principais Oficinas e o Papel dos Artistas Plásticos. Master's Thesis, Faculdade de Ciências Sociais e Humanas, Universidade Nova de Lisboa, Lisboa, Portugal, 2002.
3. Lopes De Almeida, M. *História de S. Domingos by Fr. Luís de Sousa, 1623 (re-edition)*; Lello e Irmão Editores: Porto, Portugal, 1997.
4. Woisetschläger, G.; Dutz, M.; Paul, S.; Schreiner, M. Weathering phenomena on naturally weathered potash-lime-silica-glass with Medieval composition studied by Secondary Electron Microscopy and Energy Dispersive Microanalysis. *Microchim. Acta* **2000**, *135*, 121–130. [CrossRef]
5. Munier, I.; Lefèvre, R.; Geotti-Bianchini, F.; Verità, M. Influence of polluted urban atmosphere on the weathering of low durability glasses. *Glass Technol.* **2002**, *43*, 225–237.
6. Lombardo, T.; Lefèvre, R.A.; Chabas, A.; Ausset, P.; Cachier, H.; Ionescu, A. Characterisation of particulate matter deposition inducing soiling of modern glass. In *Air Pollution and Cultural Heritage*; Saiz-Jimenez, C., Ed.; CRC Press: London, UK, 2004; pp. 209–214.
7. Melcher, M.; Schreiner, M. Evaluation procedure for leaching studies on naturally weathered potash-lime-silica glasses with medieval composition by scanning electron microscopy. *J. Non-Cryst. Solids* **2005**, *351*, 1210–1225. [CrossRef]
8. Lombardo, T.; Chabas, A.; Lefèvre, R.A.; Ionescu, A. Modelling the soiling of float glass in a polluted atmosphere. *Glass Technol.* **2005**, *46*, 192–196.
9. Vilarigues, M.; Da Silva, R.C. Characterization of potash-glass corrosion in aqueous solution by ion beam and IR spectroscopy. *J. Non-Cryst. Solids* **2006**, *352*, 5368–5375. [CrossRef]
10. Melcher, M.; Schreiner, M. Leaching studies on naturally weathered potash-lime–silica glasses. *J. Non-Cryst. Solids* **2006**, *352*, 368–379. [CrossRef]
11. Favez, O.; Cachier, H.; Chabas, A.; Ausset, P.; Lefevre, R. Crossed optical and chemical evaluations of modern glass soiling in various European urban environments. *Atmos. Environ.* **2006**, *40*, 7192–7204. [CrossRef]
12. Melcher, M.; Schreiner, M.; Kreislova, K. Artificial weathering of model glasses with medieval compositions—An empirical study on the influence of particulates. *Phys. Chem. Glasses* **2008**, *49*, 346–356.
13. Gentaz, L.; Lombardo, T.; Loisel, C.; Chabas, A.; Vallotto, M. Early stage of weathering of medieval-like potash–lime model glass: Evaluation of key factors. *Environ. Sci. Pollut. Res.* **2011**, *18*, 291–300. [CrossRef] [PubMed]
14. Palomar, T. La Interacción de los Vidrios Históricos con Medios Atmosféricos, Acuáticos y Enterramientos. Ph.D. Thesis, Universidad Aunónoma de Madrid, Madrid, Spain, 2013.
15. Lombardo, T.; Chabas, A.; Verney-Carron, A.; Cachier, H.; Triquet, S.; Darchy, S. Physico-chemical characterisation of glass soiling in rural, urban and industrial environments. *Environ. Sci. Pollut. Res.* **2014**, *21*, 9251–9258. [CrossRef] [PubMed]
16. ICP Materials. International Co-Operative Programme on Effects on Materials Including Historic and Cultural Monuments. Available online: http://www.corr-institute.se/icp-materials/web/page.aspx?sid=3293 (accessed on 15 October 2018).
17. Tidblad, J.; Kreislová, K.; Faller, M.; De La Fuente, D.; Yates, T.; Verney-Carron, A.; Grøntoft, T.; Gordon, A.; Hans, U. ICP Materials trends in corrosion, soiling and air pollution (1987–2014). *Materials* **2017**, *10*, 969. [CrossRef] [PubMed]
18. Lombardo, T.; Ionescu, A.; Lefèvre, R.A.; Chabas, A.; Ausset, P.; Cachier, H. Soiling of silica-soda-lime float glass in urban environment: Measurements and modelling. *Atmos. Environ.* **2005**, *39*, 989–997. [CrossRef]

19. Fuchs, D.R.; Römich, H.; Schmidt, H. Glass-Sensors: Assessment of complex corrosive stresses in conservation research. *MRS Proc.* **2011**, *185*, 239. [CrossRef]
20. Leissner, J.; Fuchs, D.R. Investigations by glass sensors on the corrosive environmental conditions at stained glass windows with protective glazings in Europe. *MRS Proc.* **2011**, *267*, 1031. [CrossRef]
21. Basart, S.; Pérez, C.; Cuevas, E.; Baldasano, J.M.; Gobbi, G.P. Aerosol characterization in Northern Africa, Northeastern Atlantic, Mediterranean Basin and Middle East from direct-sun AERONET observations. *Atmos. Chem. Phys.* **2009**, *9*, 8265–8282. [CrossRef]
22. Obregón, M.A.; Pereira, S.; Wagner, F.; Serrano, A.; Cancillo, M.L.; Silva, A.M. Regional differences of column aerosol parameters in western Iberian Peninsula. *Atmos. Environ.* **2012**, *62*, 208–219. [CrossRef]
23. Obregón, M.A.; Serrano, A.; Cancillo, M.L.; Cachorro, V.E.; Toledano, C. Aerosol radiometric properties at Western Spain (Cáceres station). *Int. J. Climatol.* **2015**, *35*, 981–990. [CrossRef]
24. Slezakova, K.; Pereira, M.C.; Reis, M.A.; Alvim-Ferraz, M.C. Influence of traffic emissions on the composition of atmospheric particles of different sizes—Part 1: Concentrations and elemental characterization. *J. Atmos. Chem.* **2007**, *58*, 55–68. [CrossRef]
25. Almeida, S.M.; Freitas, M.C.; Repolho, C.; Dionísio, I.; Dung, H.M.; Caseiro, A.; Alves, C.; Pio, C.A.; Pacheco, A.M.G. Characterizing air particulate matter composition and sources in Lisbon, Portugal. *J. Radioanal. Nucl. Chem.* **2009**, *281*, 215–218. [CrossRef]
26. Alves, L.C.; Reis, M.A.; Freitas, M.C.; Gouveia, M.A. Elemental analysis of particulate matter and source identification in Lisbon. *X-ray Spectrom.* **1998**, *27*, 313–320. [CrossRef]
27. Almeida, S.M.; Pio, C.A.; Freitas, M.C.; Reis, M.A.; Trancoso, M.A. Source apportionment of atmospheric urban aerosol based on weekdays/weekend variability: Evaluation of road re-suspended dust contribution. *Atmos. Environ.* **2006**, *40*, 2058–2067. [CrossRef]
28. Rodrigues, A.; Fearn, S.; Palomar, T.; Vilarigues, M. Early stages of surface alteration of soda-rich-silicate glasses in the museum environment. *Corros. Sci.* **2018**, *143*, 362–375. [CrossRef]
29. Palomar, T.; Chabas, A.; Bastidas, D.M.; De La Fuente, D.; Verney-Carron, A. Effect of marine aerosols on the alteration of silicate glasses. *J. Non-Cryst. Solids* **2017**, *471*, 328–337. [CrossRef]
30. Almeida, R.M.; Pantano, C.G. Structural investigation of silica gel films by infrared spectroscopy. *J. Appl. Phys.* **1990**, *68*, 4225–4232. [CrossRef]
31. Burriel Martí, F.; Lucena Conde, F.; Arribas Jimeno, S.; Hernández Méndez, J. *Química Analítica Cualitativa*, 18th ed.; Thomson: Madrid, Spain, 2002; ISBN 9788497321402.
32. Vilarigues, M.; Da Silva, R.C. Ion beam and infrared analysis of medieval stained glass. *Appl. Phys. A* **2004**, *79*, 373–378. [CrossRef]
33. Fernandes, P.; Vilarigues, M.; Alves, L.C.; Da Silva, R.C. Stained glasses from Monastery of Batalha: Non-destructive characterisation of glasses and glass paintings. *J. Cult. Herit.* **2008**, *9*, e5–e9. [CrossRef]
34. Vilarigues, M.; Redol, P.; Machado, A.; Rodrigues, P.A.; Alves, L.C.; Da Silva, R.C. Corrosion of 15th and early 16th century stained glass from the monastery of Batalha studied with external ion beam. *Mater. Charact.* **2011**, *62*, 211–217. [CrossRef]
35. Peel, M.C.; Finlayson, B.L.; Mcmahon, T.A. Updated world map of the Köppen-Geiger climate classification. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 1633–1644. [CrossRef]
36. *Iberian Climate Atlas. Air Temperature and Precipitation (1971–2000)*; Unidad de Documentación de AEMET; Agencia Estatal de Meteorología, Instituto de Meteorologia de Portugal: Madrid, Spain, 2011.
37. Kottek, M.; Grieser, J.; Beck, C.; Rudolf, B.; Rubel, F. World Map of the Köppen-Geiger climate classification updated. *Meteorol. Z.* **2006**, *15*, 259–263. [CrossRef]
38. Tullot, I.F. *Climatología de España y Portugal*; Ediciones Universidad de Salamanca: Salamanca, Spain, 2000; ISSN 84-7800-944-2.
39. Asay, D.B.; Kim, S.H. Evolution of the adsorbed water layer structure on silicon oxide at room temperature. *J. Phys. Chem. B* **2005**, *109*, 16760–16763. [CrossRef] [PubMed]
40. Gentaz, L.; Lombardo, T.; Chabas, A.; Loisel, C.; Neff, D.; Verney-Carron, A. Role of secondary phases in the scaling of stained glass windows exposed to rain. *Corros. Sci.* **2016**, *109*, 206–216. [CrossRef]
41. Palomar, T.; De La Fuente, D.; Morcillo, M.; Álvarez De Buergo, M.; Vilarigues, M. Early stages of glass alteration in the coastal atmosphere. *Build. Environ.* **2019**, *147*, 305–313. [CrossRef]
42. Carmona, N.; García-Heras, M.; Gil, C.; Villegas, M.A. Chemical degradation of glasses under simulated marine medium. *Mater. Chem. Phys.* **2005**, *94*, 92–102. [CrossRef]

43. Dove, P.M.; Elston, S.F. Dissolution kinetics of quartz in sodium chloride solutions: Analysis of existing data and a rate model for 25 °C. *Geochim. Cosmochim. Acta* **1992**, *56*, 4147–4156. [CrossRef]
44. Palomar, T.; Llorente, I. Decay processes of silicate glasses in river and marine aquatic environments. *J. Non-Cryst. Solids* **2016**, *449*, 20–28. [CrossRef]