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Use of hydrogen isotopes to understand stained glass weathering

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Abstract

In order to assess the kinetic role of the alteration layers formed on stained glass windows weathered for several centuries, a specific experiment was designed. An ancient stained glass sample was subjected to an artificial simulated fog doped in deuterium for 13 weeks. The aim was to trace the circulation of water through the alteration layer and to locate reactive zones. Results demonstrate that the solution rapidly circulates in the alteration layer via pores and cracks, so that transport (especially the supply of protons at the interface between pristine and altered glass) is not rate-limiting in the alteration process. The alteration is rather controlled by the release of glass alkalis from ion exchange with protons at an estimated diffusion rate, consistent with the long-term apparent kinetics measured on medieval stained glasses.

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1. Introduction

In atmospheric medium, stained glass degradation induces irreversible chemical modifications corresponding to the formation of a gel layer, losses of matter by dissolution (pits) and deposits (secondary phases or soiling) at the glass surface. In order to preserve this inestimable heritage and to have suitable restoration strategies, it is necessary to understand alteration mechanisms and to determine the corresponding kinetics in this specific environment.

Mechanisms of glass alteration are common to all silicate glasses in contact with aqueous solution. Three

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mechanisms can be distinguished: (1) interdiffusion or ion exchange between glass alkali elements and hydrogenated species in solution (H^+ , H_3O^+ , H_2O) that leads to a selective leaching and to an increase of pH of the solution¹, (2) dissolution of the glassy network by hydrolysis of ion-covalent bonds (Si-O-Si, Si-O-Al)², and (3) secondary phase precipitation. Interdiffusion and/or local reactions of hydrolysis/condensation cause the formation of a hydrated glass or a gel³. Secondary phases (mainly salts such as sulfates, nitrates, carbonates, and phosphates in atmospheric medium^{4,5}) can also precipitate and particles (such as soot, dust or metallic debris) can be deposited.

The gel formed on silicate glasses is often assumed to be protective as it imposes a diffusive transport of solution through the altered layer⁶. The solution diffuses in the nano-porosity (a few nanometers) of the hydrated glass (solid diffusion) at very low diffusion rates ($< 10^{-17} m^2/s$, see ⁷ for a review). However, in the case of stained glass, this layer is fractured because of the variation of hygroscopic conditions, so that this must hinder its passivating effect. The solution could diffuse in the macro-porosity (liquid diffusion) at diffusion rates close to free water diffusion or diffusion in porous media (10^{-9} to $10^{-11} m^2/s$). If the gel layer is too fractured and not dense enough to impose a low diffusive transport, then the alteration process would not be limited by the transport of solution, but rather by the glass itself.

The kinetic role of the gel layer needs to be addressed because restorers wonder if they have to remove or maintain this layer. From a fundamental point of view, this could help to understand the role of the gel on long-term kinetics in order to model the alteration of these artefacts. To this purpose, a specific experiment was designed by using deuterium (2H or D) to trace the circulation of water through ancient weathered stained glass subjected to artificial rainfall events.

2. Materials and methods

A medieval stained glass sample was chosen: Ev1 coming from the Cathedral Notre Dame d'Evreux (Fig 1.a) dated from the XIVth century. A previous characterization study⁵ has shown that this uncolored medieval glass displays an opaque external face with a continuous alteration layer of about 110 μm thickness.

The sample was placed in a chamber (at a temperature varying between 22 and 32°C) and wetted using a nebulizer to simulate fog events. After 1 day of fog, the sample was dried for 6 days to ambient atmosphere (with a relative humidity of 75%). Thirteen cycles were carried out. The solution consisted in a synthetic rainwater with a composition (major elements) close to rainwater collected in Paris and doped in D_2O . The D/H ratio was 0.27 (for a natural ratio of 0.000156).

Five zones of the sample were then analyzed by nanoSIMS (Secondary Ion Mass Spectrometry) for D/H mapping by using the Cameca NanoSIMS 50 at MNHN (Paris). The sample surface area was rastered by a primary Cs^+ beam over areas of $20 \times 20 \mu m^2$ or $30 \times 30 \mu m^2$ divided in 256×256 pixels, at a raster speed of 1 ms/pixel. The beam current was set to 50 pA. Prior to each analysis, a 650 pA primary beam was rastered during 300 s to remove gold coating and surface contamination.

3. Results and discussion

The H maps (not shown) allowed the different zones corresponding to altered glass and pristine glass to be readily discriminated. The D/H maps (Fig. 1.b to f) allowed the enrichment in D (and so the path of water) to be observed. For comparison, a reference sample that was not in contact with deuterium was also imaged. The D/H ratio is around 0.00015, close to the natural ratio. All analyzed zones in the gel of Ev1 exhibit a D/H ratio higher than the natural ratio (by a factor 3 to 10, see Fig. 2). This indicates that the whole surface has been soaked by water. Solution evaporates during drying periods and at the end of the experiment, but part of the deuterium remains adsorbed. Cracks are not preferentially enriched in D, which indicates that solution circulates through the cracks as well as through the porosity of the gel.

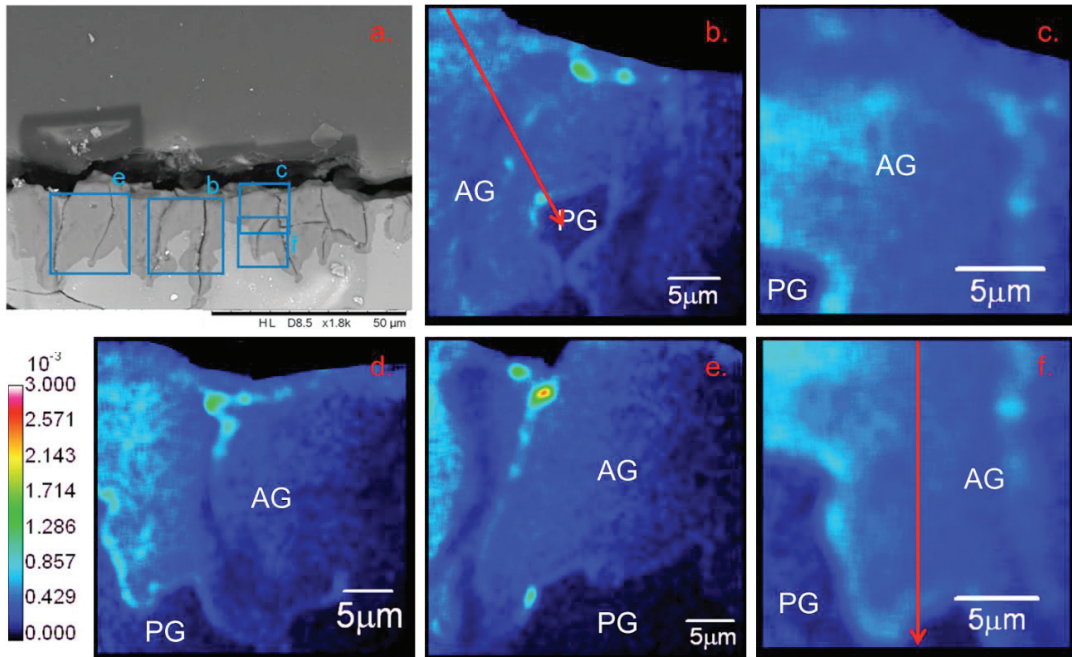


Fig. 1. (a) SEM microphotography of a cross-section of sample Ev1 and location of analyzed zones (except (d)) (red squares); (b), (c), (d), (e), (f) D/H repartition mappings acquired by nanoSIMS. Red arrows correspond to profiles presented in Fig. 2. AG = altered glass and PG = pristine glass.

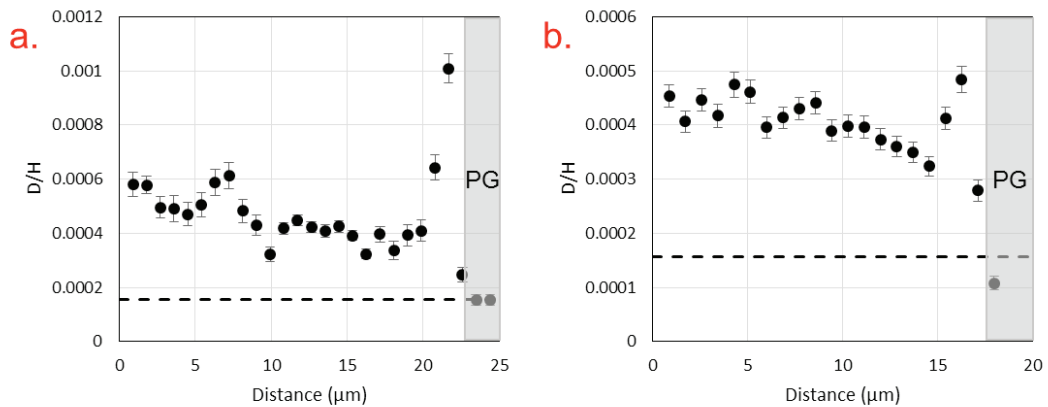


Fig. 2. D/H profiles as a function of distance: (a) and (b) profiles correspond to images (b) and (f) on Fig. 1, respectively. The horizontal dashed line indicates the natural D/H ratio (0.000156). PG = pristine glass.

For each analyzed zone, a slight or clear enrichment in D is observed at the interface between the pristine and the altered glass, which thickness is around 2 μm . This enrichment inside the altered layer could be caused by the pursuit of the alteration in the bulk glass. By knowing the thickness (e) and the cumulative time (t) of the rainfall event (13 days), it was possible to calculate a diffusion coefficient (D) corresponding to the ion exchange between protons and the alkalis released in solution by using the second Fick's law:

$$e = \sqrt{\frac{D \cdot t}{\pi}} \quad (1)$$

The calculated diffusion coefficient is $2.8 \cdot 10^{-18}$ m²/s for an altered thickness of 2 μm. Despite large uncertainties, this value is one order of magnitude lower than the results of Sterpenich and Libourel (2006)⁸ based on SIMS measurements of H in potash stained glass buried in soil. The later authors provided a value of $1 \cdot 10^{-17}$ m²/s at lower temperatures than those measured in the experimental chamber (22-32°C). This could be explained by the difference of media. Even if alteration conditions of buried samples are not precisely known, humid acids can impose a low pH and increase the alteration rate. Furthermore, this value can also be compared to measured alteration thicknesses on ancient medieval samples (between 40 and 180 μm⁵). By multiplying the diffusion coefficient by 650 years, it gives an alteration thickness of 270 μm. Based on environmental data, time with rainfall events or high relative humidity (> 90%) is considered to be half the time or less. Consequently, calculated alteration thicknesses are consistent with observations on historic glasses. This demonstrates that the alteration kinetics of stained glass in atmospheric environment is controlled by the diffusion rate (corresponding to the release of alkalis).

4. Conclusions

Experimental weathering of an ancient stained glass by a solution doped in deuterium permitted to trace the circulation of water during the alteration process. The results show that the alteration layer does not seem to limit the transport of water. The gel is sufficiently porous and cracked, that the solution can reach the interface between fresh and altered glass faster than the release of alkalis by ion diffusion. The alteration is thus primarily controlled by the rate of ion exchange between protons and alkalis in the glass with an associated diffusion coefficient of around 10^{-18} m²/s. This is consistent with long-term apparent kinetics measured on ancient stained glasses.

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