

## Motivation

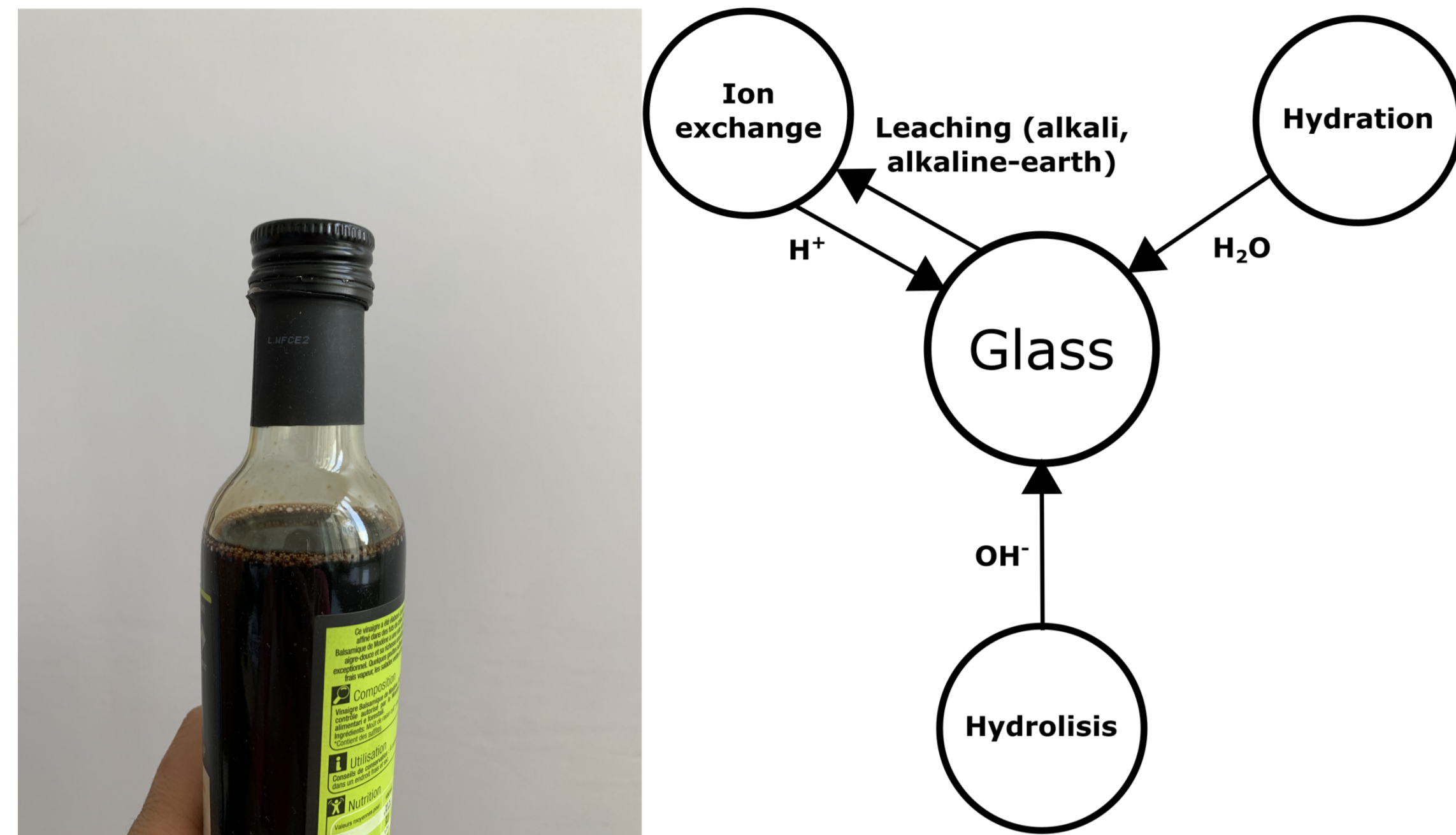


Figure 1. Glass used as a container an acidic substance (vinegar, containing acetic acid). Summary of the processes that occur during glass corrosion. Modified from [1].

Glass is commonly considered a durable material. One of its main applications is as a container for liquids to either hold (tableware, bottles) or cook (kitchenware) food (figure 1). In both cases, it is often exposed to both relatively high temperatures and corrosive media. Glasses often contain potentially toxic elements (PTE) such as Co, Cr, Cu, Pb, Sb, Zn, and Zr, either those naturally present in rocks or to improve their aesthetics (coloring, increasing the refractive index). Industrial producers are increasingly responsible for the safety of their products (i.e. European REACH and Food Contact Materials regulations). The relationship between the role of the elements inside the glass and the leaching processes is not fully understood.

## Material and Methods

This study has focused on K-bearing lead silicate glass. Using a combination of monolithic and powder samples (figure 2) altered in the same containers enables us to analyze both the chemical changes in the liquid (acetic acid, pH = 2.4) and the block of glass. The block of glass can be mapped to obtain a spatially resolved image of glass alteration.

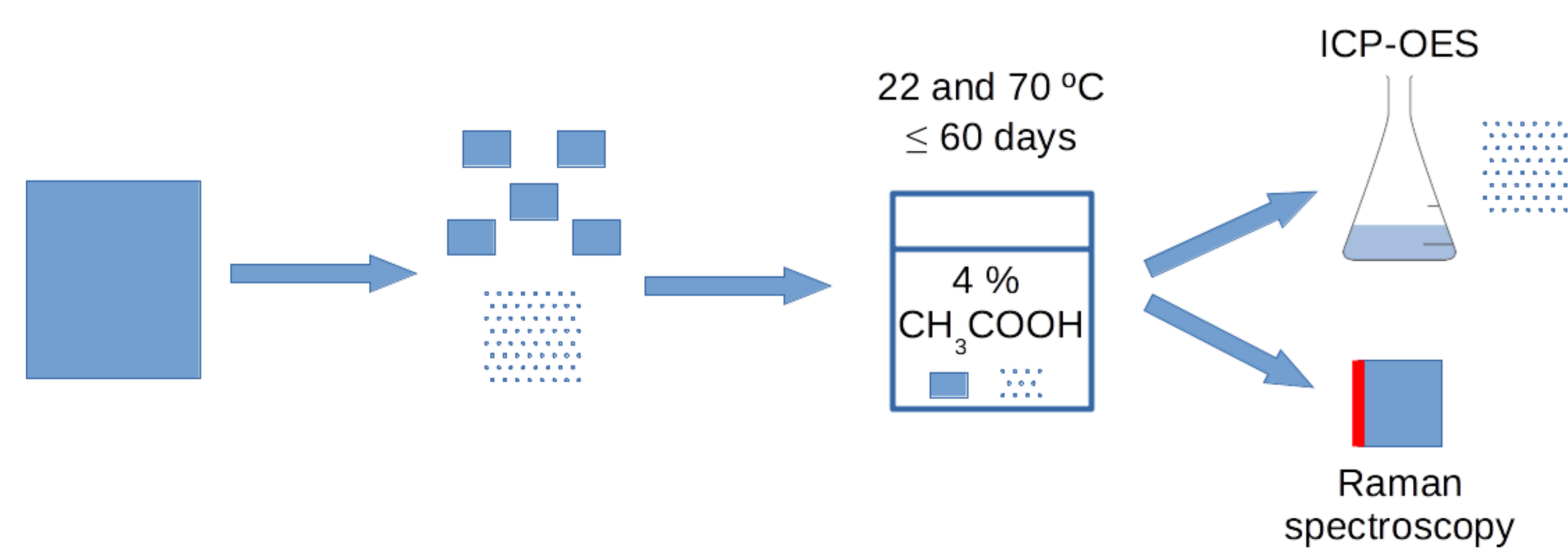


Figure 2. Scheme of the alteration process in acetic acid. Two types of samples were prepared: glass monoliths and glass powder (grain size between 40 and 100 μm). The red line shows the zone at the edge of the monolith analyzed using Raman spectroscopy.

## Mapping glass alteration using Raman spectroscopy

A set of spatially resolved Raman spectra (spatial resolution about 1 μm) measured on a single monolith altered at 70°C during 231 days show changes in both the silicate network between 860 and 1350 cm<sup>-1</sup> and water speciation between 3000 and 3900 cm<sup>-1</sup> from the edge towards the interior of the glass (figure 3).

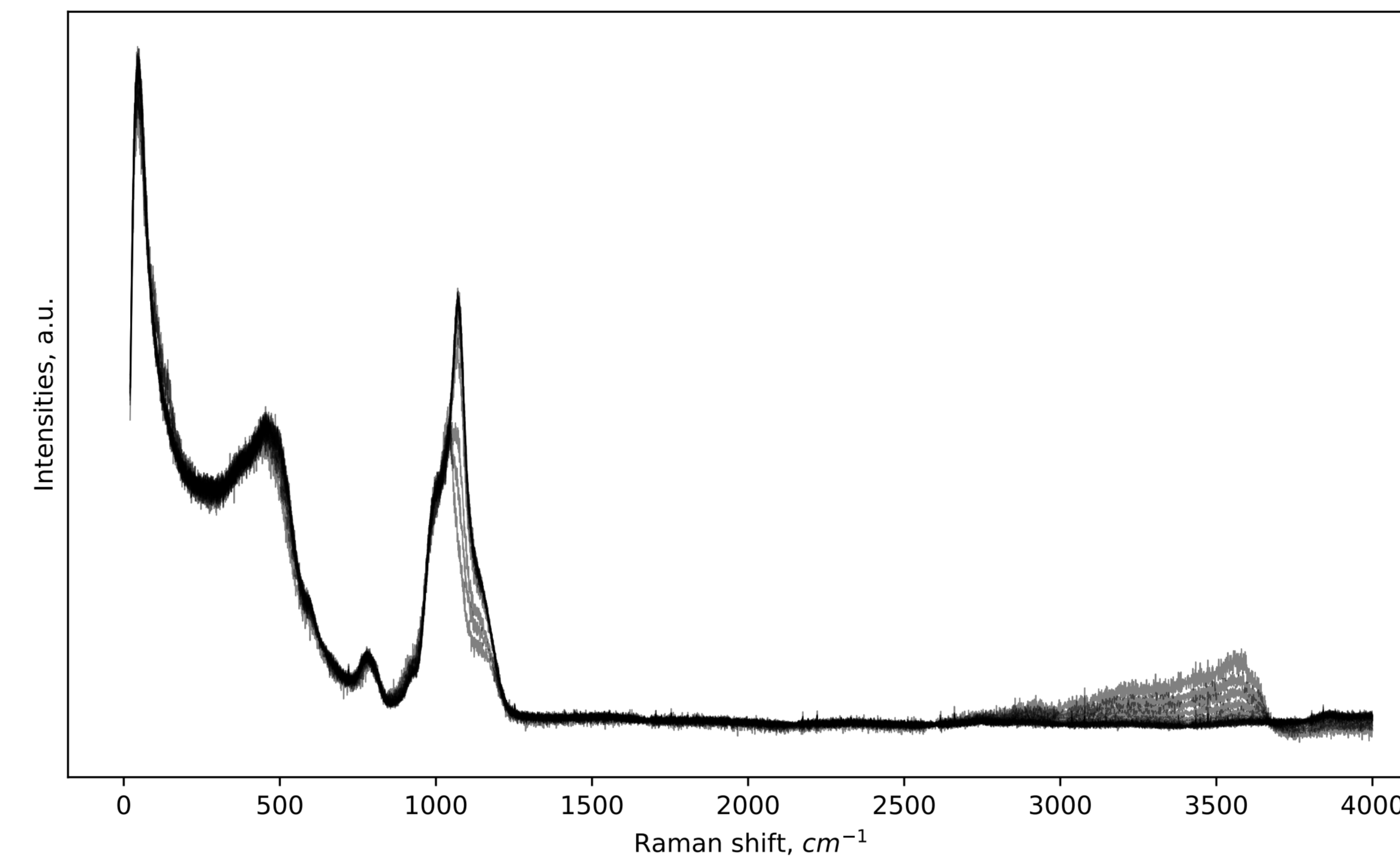


Figure 3. Raman spectra on a line from the edge towards the interior of the glass (from most altered (grey) to pristine (black)). The alteration of the glass appears in two different regions of the spectra: the bands related to the silicate network (large envelope around 1000 cm<sup>-1</sup>) and the water bands (between 3000 and 3900 cm<sup>-1</sup>).

## Progress of the alteration

The maps of the changes in the silicate network and the water region (figure 4) show that glass alteration is concentrated at the edge of the monoliths. The water front has progressed further than the silicate network.

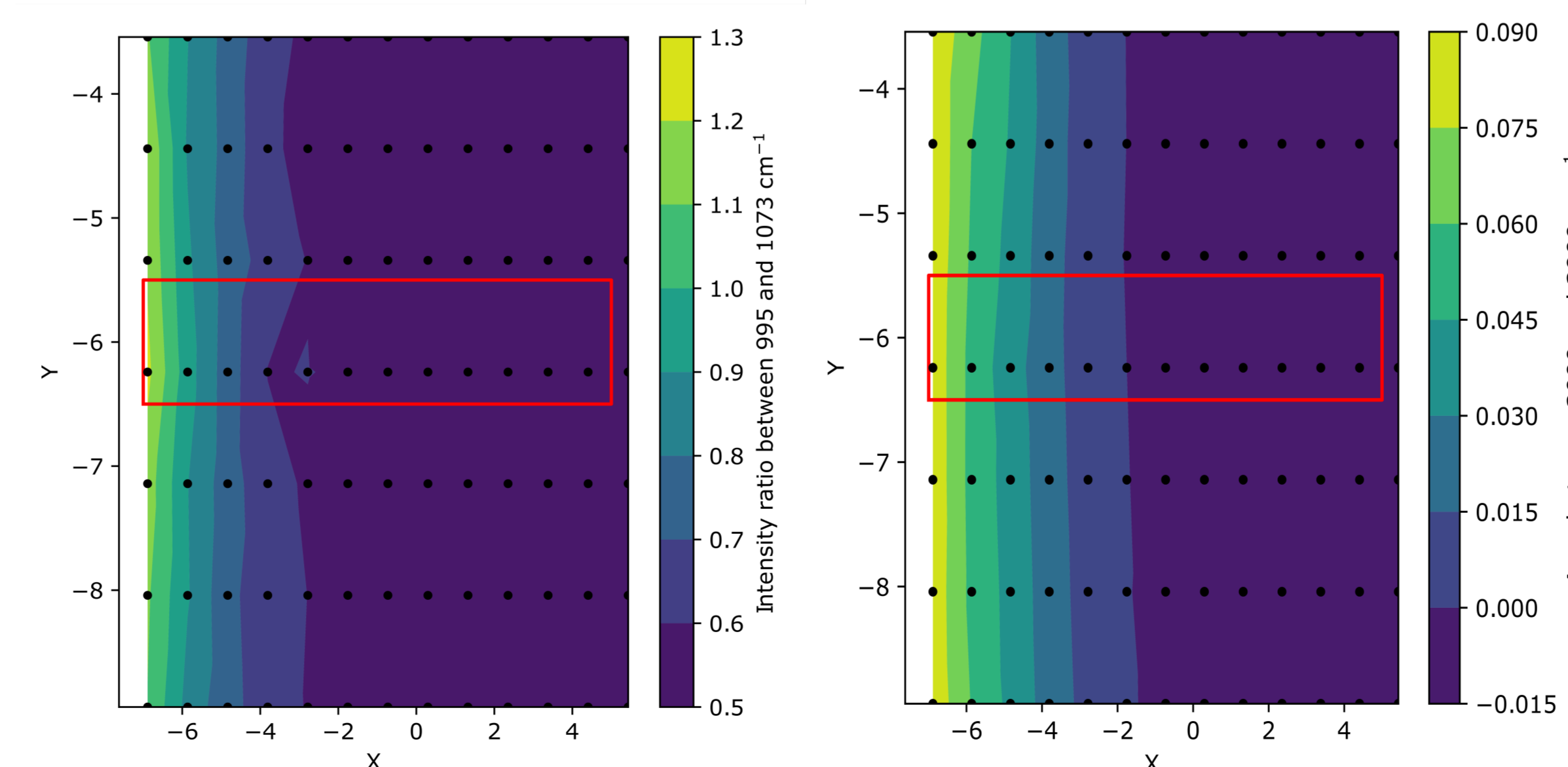


Figure 4. Left: map of the intensity ratio measured on the Raman spectra between 995 and 1073 cm<sup>-1</sup>. Right: map of the area below the Raman spectra between 3000 and 3900 cm<sup>-1</sup>.

## Diffusion coefficient

Understanding the alteration process requires an approximation of its speed. We have used 1D Fick's 1st law to assign a diffusion coefficient (D) for water inside the glass and an analogous parameter for the changes in the silicate network which enables us to represent the progression of the alteration front.

$$J = -D \frac{d\phi}{dx}$$

where J is the diffusion flux, φ is the concentration (assuming an ideal mixture) and x is the position.

The water front has progressed further towards the inside of the glass monolith, preceding the changes of the silicate network (figure 5).

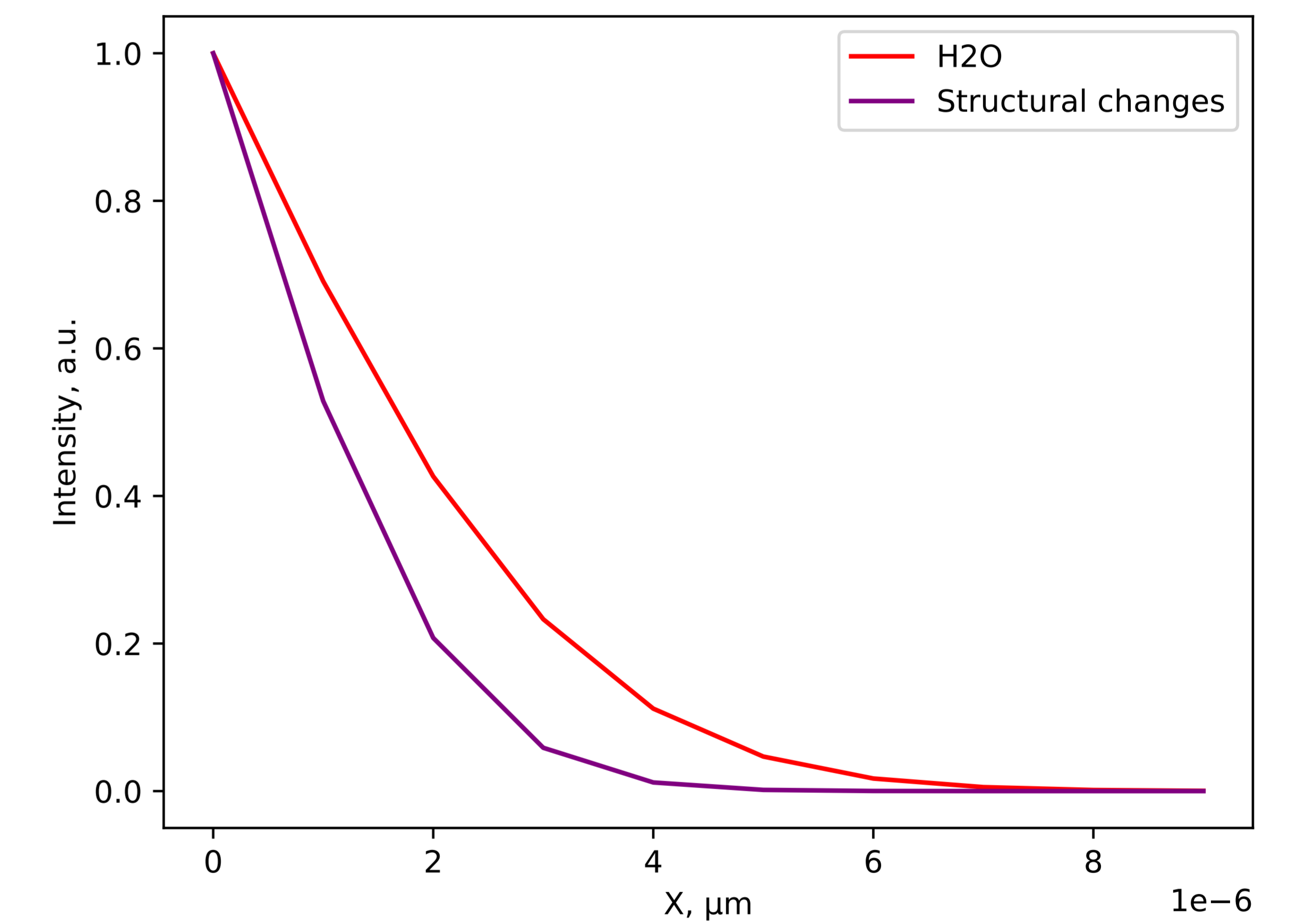


Figure 5. Diffusion coefficient of water in the glass and progression of the alteration front assimilated to the modifications of the silicate network.

## Take-home message

- Diffusion processes in glass at temperatures relevant to domestic use are slow.
- Glass alteration causes changes both the concentration of water and the silicate network.
- The diffusion front of water within the glass precedes the modifications of the silicate network.

## References

[1] Willemien Anaf. Study on the formation of heterogeneous structures in leached layers during the corrosion process of glass. CeROArt, (EGG 1), November 2010.