Sumglass, 28/09/2023

Glass alteration under atmospheric conditions

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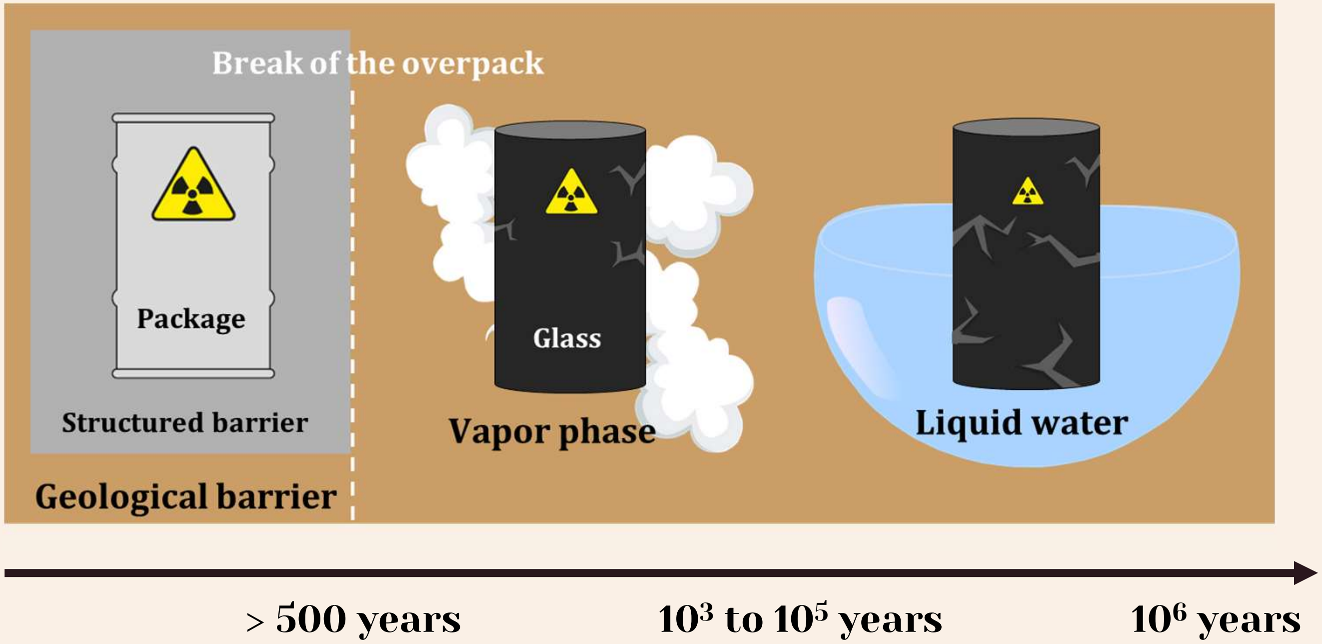
Issues

01 Safety of the nuclear wastes disposal

Andra (2016)



Yucca Mountain
--- Vapor Hydration Test (VHT)---
Abrajano et al. (1986, 1989); Bates et al. (1982a, 1982b, 1984); Ebert et al. (1991); Ebert & Bates (1989); Jiricka et al. (2001)

French disposal (ISG, SON68)
Gong et al. (1998); Neeway et al. (2012); Abdelouas et al. (2013); Ait Chaou et al. (2014, 2017); Bouakkaz et al. (2018); Jégou et al. (2021); Zhang et al. (2021, 2023)
(AVM)
Narayanasamy et al. (2019, 2020, 2022)

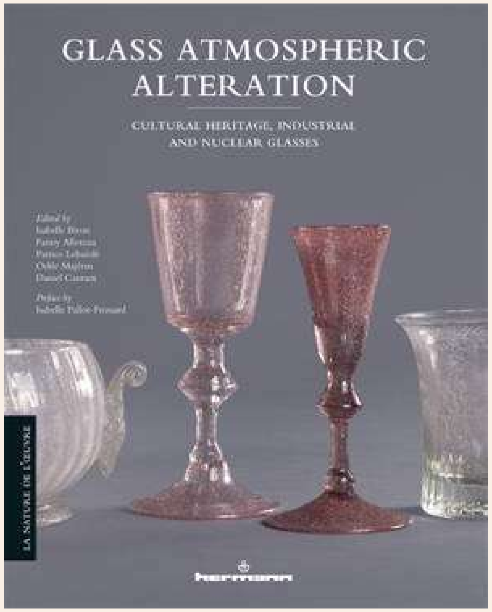
(Other glasses)
Cassingham et al. (2016); Malkovsky et al (2018)

02

Conservation of the cultural heritage

Museum collections
Robinet et al. (2007, 2009)
Rodrigues et al. (2018a,b)
Alloteau et al. (2017, 2019, 2020)
Majérus et al. (2020)

10 to 20 % of museum collections



GLASS ATMOSPHERIC ALTERATION

CULTURAL HERITAGE, INDUSTRIAL AND NUCLEAR GLASSES

LA NATURE DE L'ŒUVRE

hermann

Troyes Cathedral (© LRMH)

Stained glass windows
Verney-Carron et al. (2023) for a review

03 Guarantee of the industial glass performance

Storage of float glass panels

© V-RACKELBOOM / Saint-Gobain

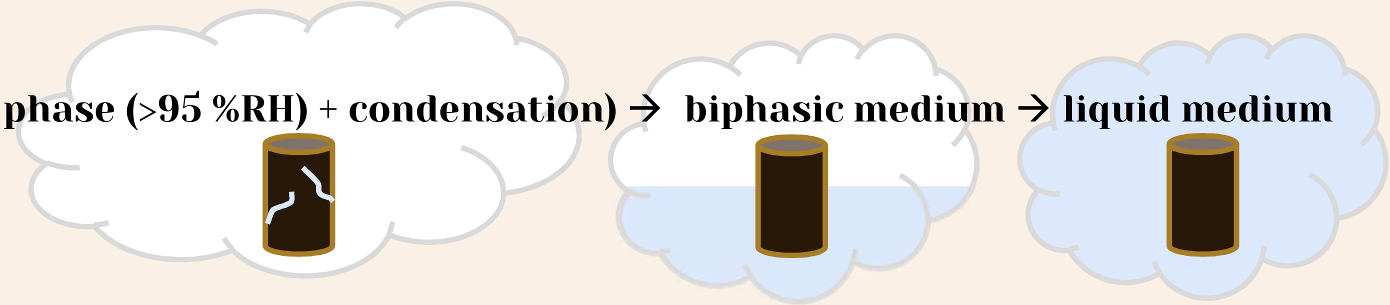
Durability of solar glass panels

© Shutterstock

Safe use of glassware

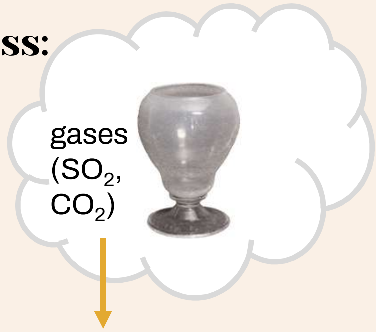
© Baccarat

Alteration media



Nuclear glass: vapor phase (>95 %RH) + condensation) → biphasic medium → liquid medium

Museum glass:



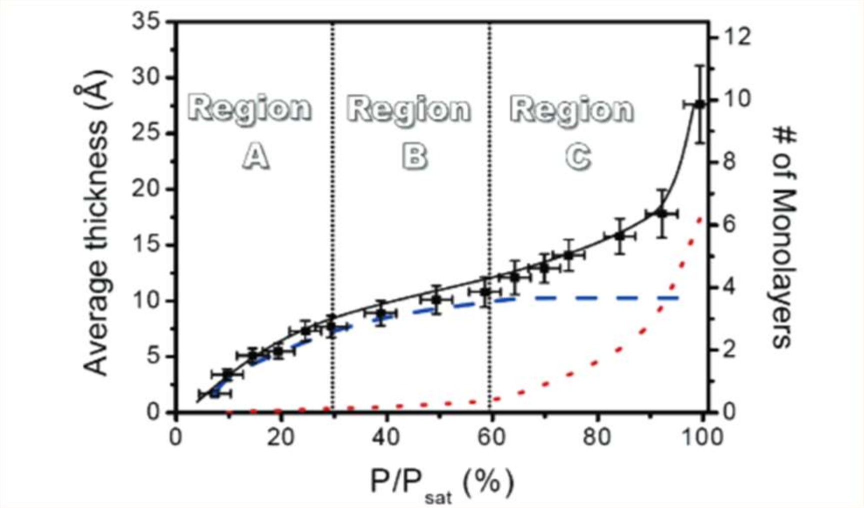
Hygroscopic salts

Stained glass window:

Alternation

⇒ Difference in terms of water phase(s) + parameters: temperature, relative humidity (RH), gases...

RH → sorption



[Asay & Kim (2005)]

A: icelike water growth
B: transitional growth
C: liquid water growth

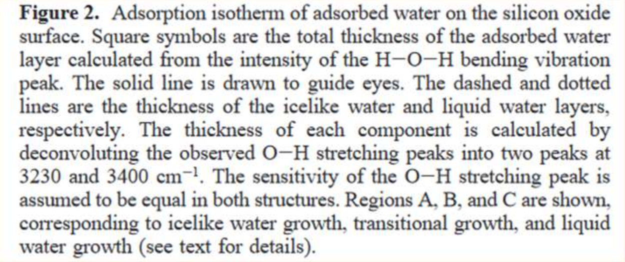


Figure 2. Adsorption isotherm of adsorbed water on the silicon oxide surface. Square symbols are the total thickness of the adsorbed water layer calculated from the intensity of the H−O−H bending vibration peak. The solid line is drawn to guide eyes. The dashed and dotted lines are the thickness of the icelike water and liquid water layers, respectively. The thickness of each component is calculated by deconvoluting the observed O−H stretching peaks into two peaks at 3230 and 3400 cm^{-1}. The sensitivity of the O−H stretching peak is assumed to be equal in both structures. Regions A, B, and C are shown, corresponding to icelike water growth, transitional growth, and liquid water growth (see text for details).

⇒ Water film whose thickness depends on RH
⇒ Dynamic system (≠ high S/V)

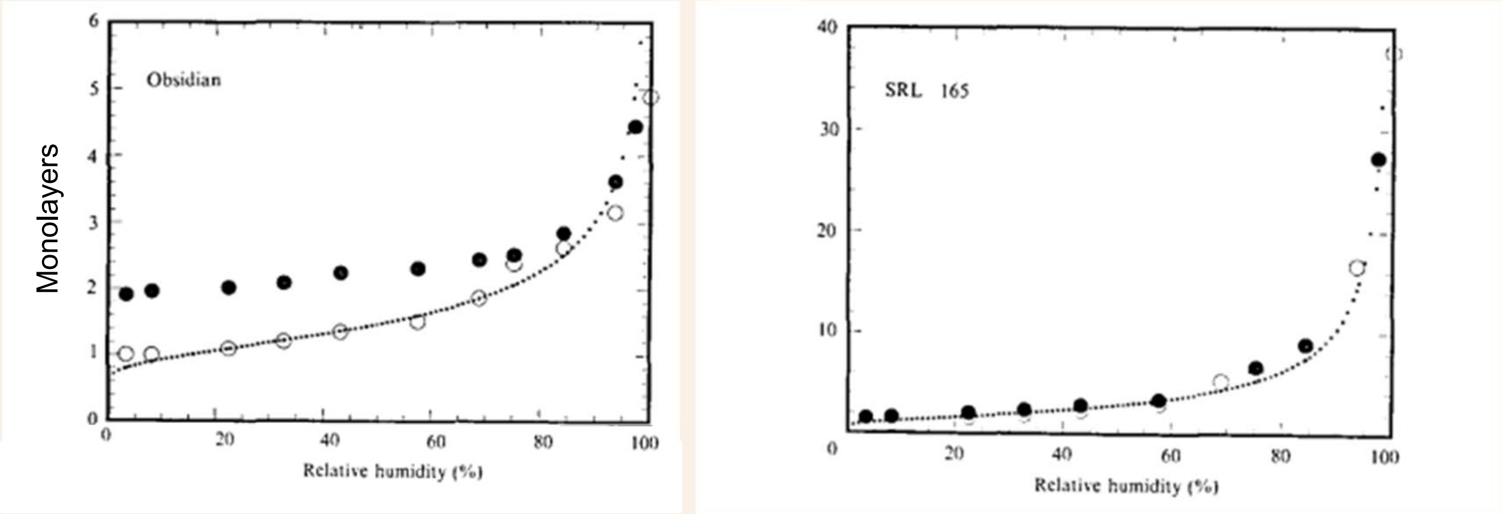


Figure 1. *Sorption isotherms for water on Coso 4–1 obsidian and SRL 165 nuclear waste glass at 23°C. The curves represent fits of the adsorption legs to Equation (2) between 1 and 99% relative humidity*

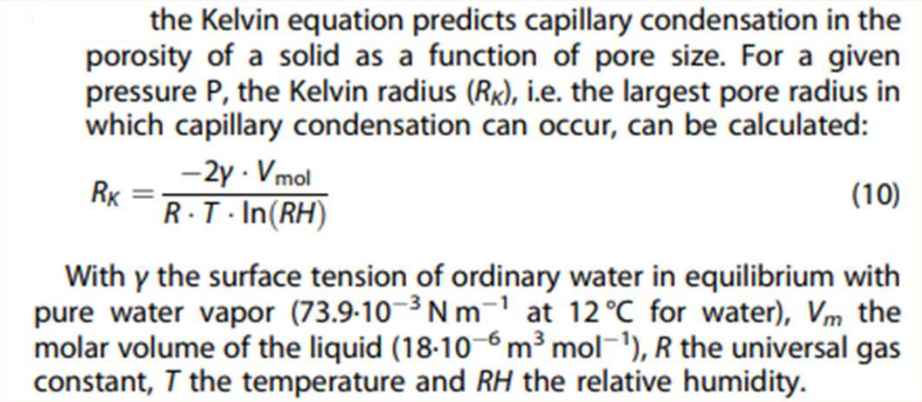
○ increasing humidity

● decreasing humidity

Ebert et al. (1991)

⇒ The number of monolayers depends on the composition of glass (silanols / NBO)

RH → condensation



the Kelvin equation predicts capillary condensation in the porosity of a solid as a function of pore size. For a given pressure P, the Kelvin radius (R_K), i.e. the largest pore radius in which capillary condensation can occur, can be calculated:

$$R_K = \frac{-2\gamma \cdot V_{\mathrm{mol}}}{R \cdot T \cdot \ln(RH)} \qquad (10)$$

With γ the surface tension of ordinary water in equilibrium with pure water vapor ($73.9 \cdot 10^{-3}\ \mathrm{N\ m^{-1}}$ at 12 °C for water), V_m the molar volume of the liquid ($18 \cdot 10^{-6}\ \mathrm{m^3\ mol^{-1}}$), R the universal gas constant, T the temperature and RH the relative humidity.

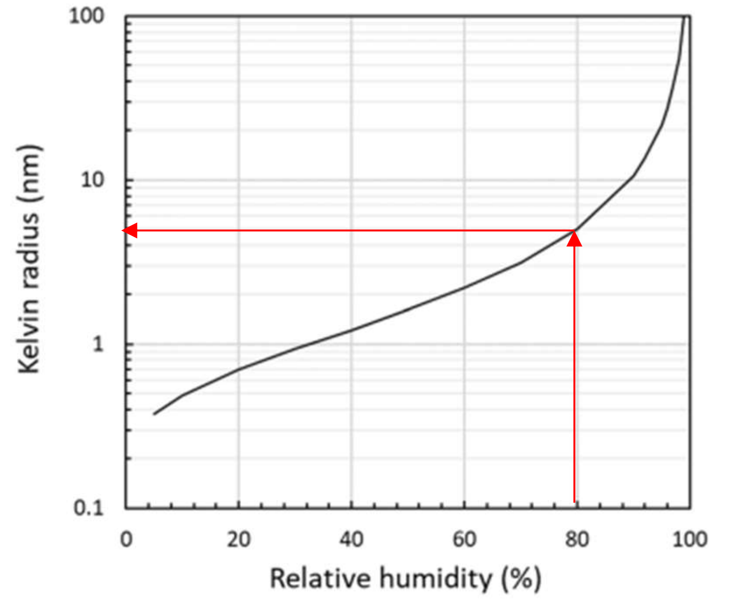


Fig. 4 Kelvin radius (in nm) as a function of relative humidity (in %). The Kelvin radius is the pore radius at which the capillary condensation would occur for a given relative humidity predicted by Kelvin equation (Eq. (10)).

Verney-Carron et al. (2023)

⇒ Condensation in small pores at high RH

Hydration

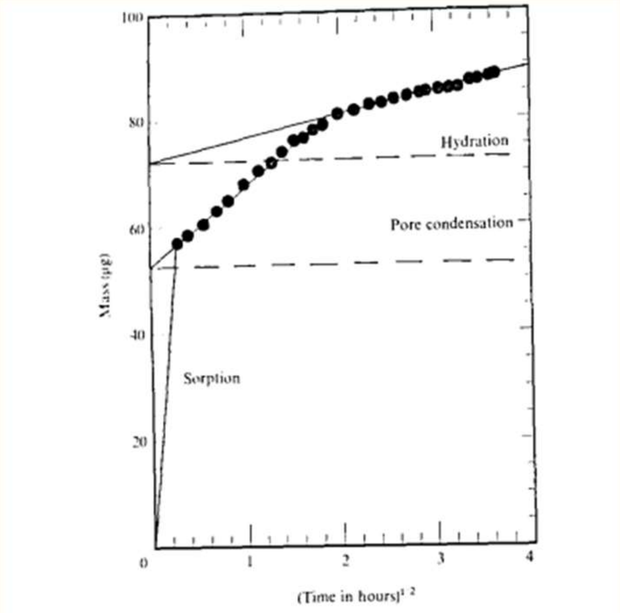
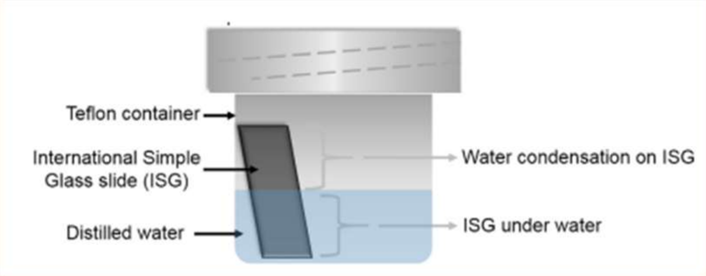


Figure 2. *Mass gain of obsidian at 84% relative humidity as a function of time at 23°C. Sample surface area = 0·14 m²*

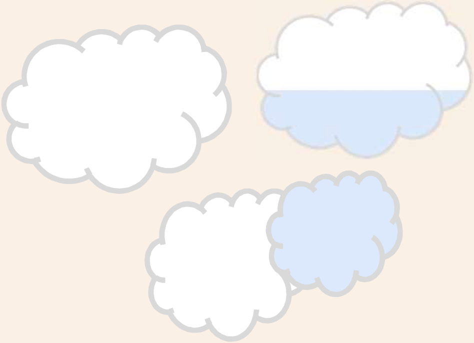
Ebert et al. (1991)

Progressive or intermittent immersion



Chinnam et al. (2018)

Questions

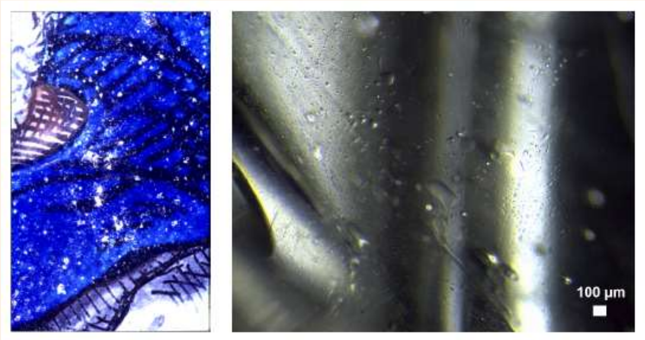


⇒ What are the specificities of alteration under atmospheric conditions ? In terms of phenomenology, mechanisms, kinetics.

⇒ How or can historic glass long-term alteration help predicting nuclear glass behavior in the geological repository?

Vapor phase – ancient samples

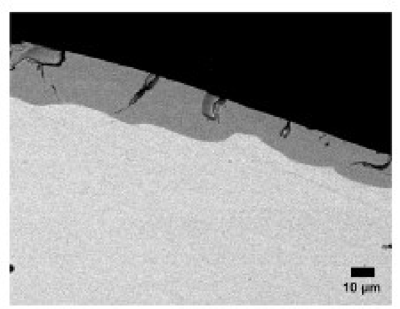
Salt deposits / weeping



White salts on the surface of weathered blue glass of a Renaissance painted enamel (©C2RMF, I. Biron)

Liquid droplets on the surface of an altered Venetian vase resulting from the deliquescence of salts (©C2RMF, F. Alloteau)

Alteration layer formation → crizzling, scaling

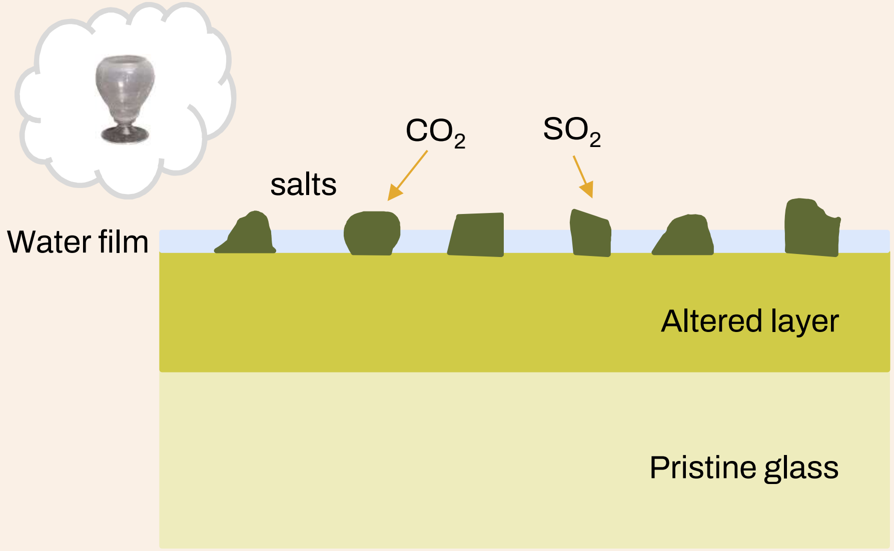


Alteration layer of a glass (enamel)
(©C2RMF, I. Biron)

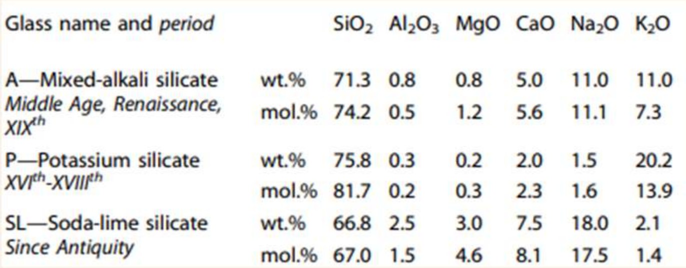
Crizzling observed on a ewer (18th c.) and scaling
(©C2RMF, A. Maigret)

⇒ AL + cracks + secondary phases = salts

Vapor phase – laboratory



Alloteau et al. (2019, 2020)



Glass name and *period*		SiO$_2$	Al$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O
A—Mixed-alkali silicate	wt.%	71.3	0.8	0.8	5.0	11.0	11.0
Middle Age, Renaissance, XIXth	mol.%	74.2	0.5	1.2	5.6	11.1	7.3
P—Potassium silicate	wt.%	75.8	0.3	0.2	2.0	1.5	20.2
XVIth-XVIIIth	mol.%	81.7	0.2	0.3	2.3	1.6	13.9
SL—Soda-lime silicate	wt.%	66.8	2.5	3.0	7.5	18.0	2.1
Since Antiquity	mol.%	67.0	1.5	4.6	8.1	17.5	1.4

For ‘unstable glasses’ (A and P)

- Thick alteration layer (2 µm after 6 months at 40°C 85 %RH)
- Few salts

For durable glass (SL)

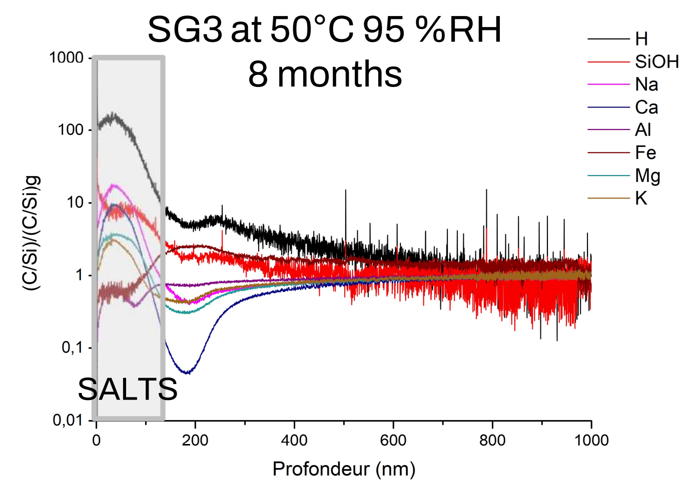
- Thin AL (0,4 µm in similar conditions)
- A lot of salts

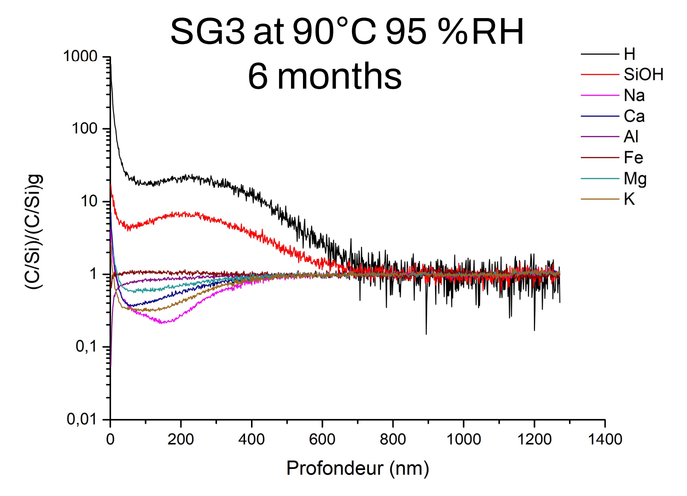
⇒ A and P: Retention of alkalis (K$^+$ hydrophobic) and alkaline-earth elements in AL → NBO and OH- in AL → increase of the alteration rate

⇒ SL: Release of modifier elements // formation of salts → hydrolysis and condensation reactions in AL → lower alteration rate

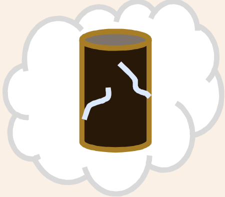
PhD Gauthier Fabre (2021-2024)

ToF-SIMS

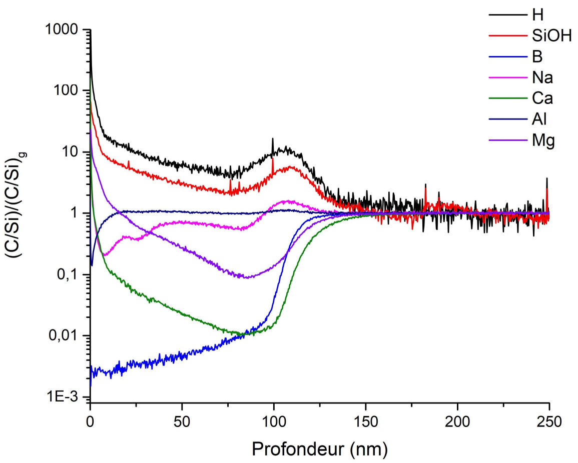

SG3 at 50°C 95 %RH
8 months


SG3 at 90°C 95 %RH
6 months

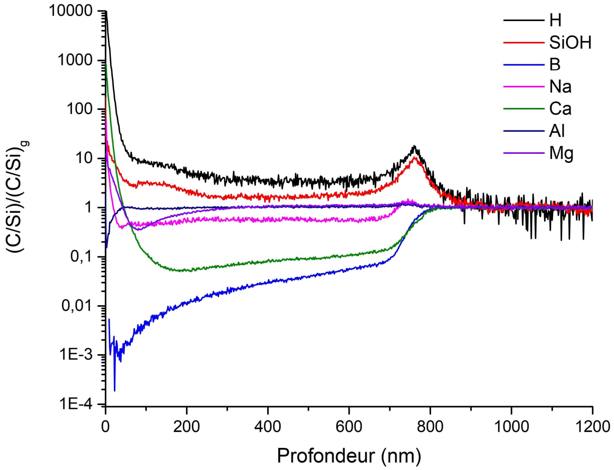
⇒ Salts at the surface
⇒ High depletion in Ca, retention of Na > K > Mg at 50°C
⇒ Retention of Mg > Ca > K > Na at 90°C



PhD Gauthier Fabre (2021-2024)



ISG2 at 50°C 95 %RH 8 months



ISG2 at 90°C 95 %RH 6 months

⇒ Salts at the surface

⇒ High depletion in B + Ca, depletion in Mg, retention of Na at 50°C (idem SG)

⇒ High depletion in Ca + B, retention of Mg, Na at 90°C

Bouakkaz et al. (2018)

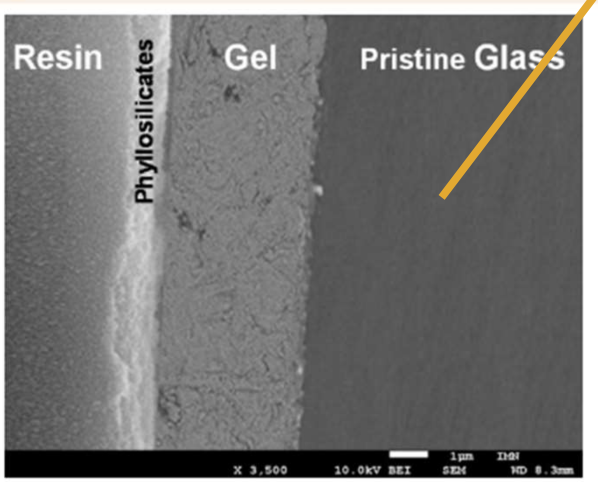
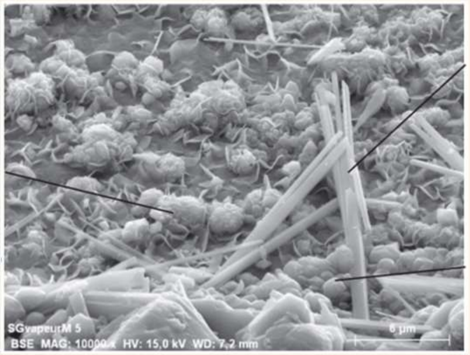


Fig. 10. Profile of the layer formed after the hydration of the sample #11 for 593 days at 125 °C and 95% RH in the presence of saline solution containing D_2O^{18} (20%). The error is about 10%.

Gel

- slightly depleted in alkalis
- more depleted in alkaline-earth elements
- depleted in boron



Neeway et al. (2012)
+ Abdelouas et al. (2013)

Secondary phases:
carbonates, phyllosilicates,
zeolites and CSH

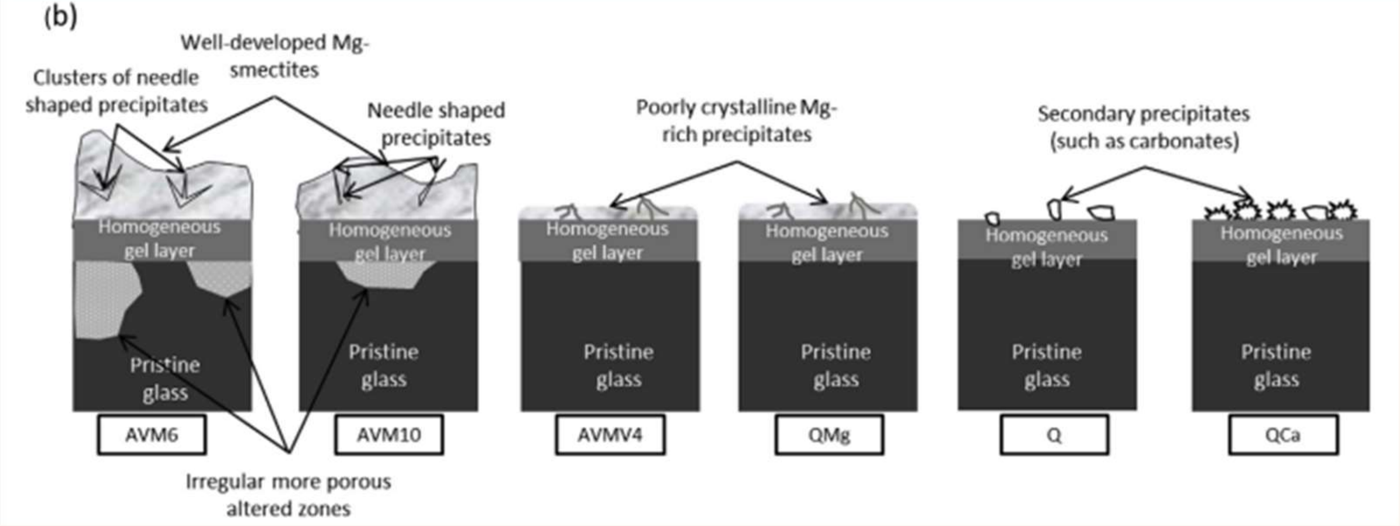
SON68 at 175°C 92 %RH 99 days

⇒ Same retention phenomenon
⇒ Phyllosilicates

Narayanasamy et al. (2019)

AVM glass
50°C, 95 %RH, 180 days

Al/Mg > 1



AL thickness (nm):	1060	630	52	53	31	52

- ⇒ Role of composition (especially Al / Mg < 1)
- ⇒ Role of secondary phases (zeolites, CSH, phyllosilicates)? Consequence of modifiers release (salts)? Driving force for the acceleration of hydrolysis?

Jégou et al. (2021)
Sessegolo et al. (2021)
Ait Chaou et al. (2017)
PhD Fabre

Kinetics

Temperature

RH

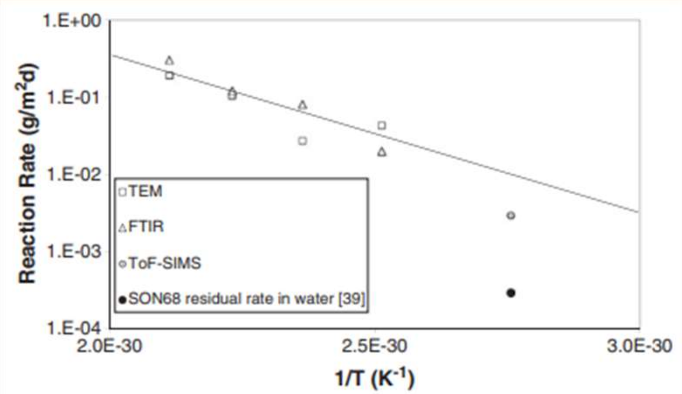
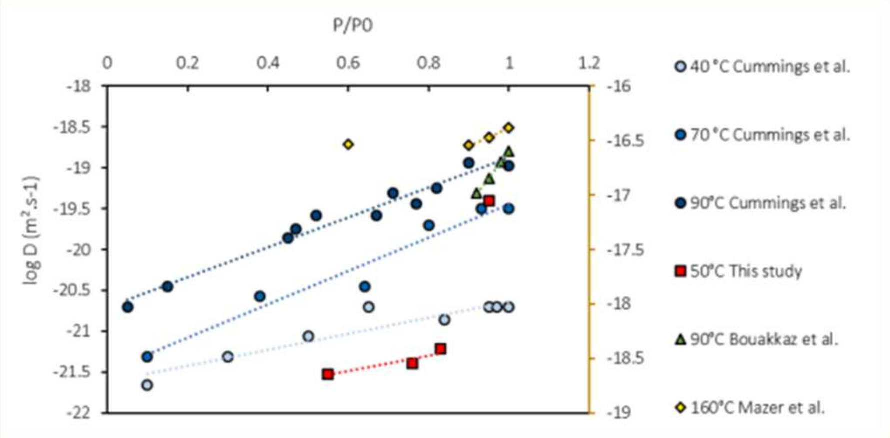


Fig. 8. An Arrhenius plot of the hydration of SON68 glass at various temperatures measured using TEM and FTIR for the thickness of the altered layer. Extrapolating this value to 90 °C shows an elevated reaction rate when compared to the residual rate measured in aqueous conditions at the same temperature and to another experiment at a high S/V ratio.



+ gas + radioactivity + roughness...

⇒ Many parameters to study...

⇒ PHENOMENOLOGY

- Hydration layer
- Secondary phases: salts + phyllosilicates (for NG)

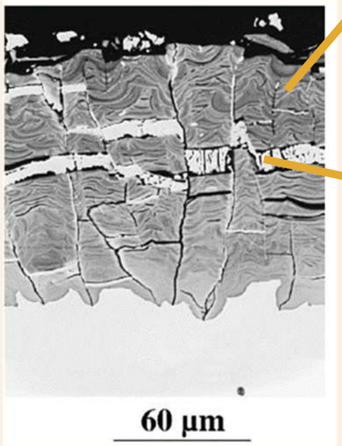
⇒ MECHANISMS

- Hydration
- Solvation of cations and migration towards surface
- Precipitation of salts (solubility) at the surface / phyllosilicates at the subsurface

⇒ KINETICS

- Influence of composition
- Influence of temperature (Ea), RH...

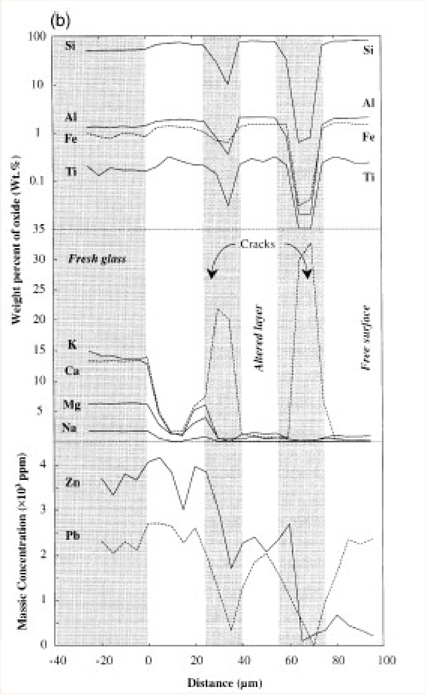
Biphasic medium – ancient samples



Alteration layer (AL) depleted in K, Na, Ca, Mg

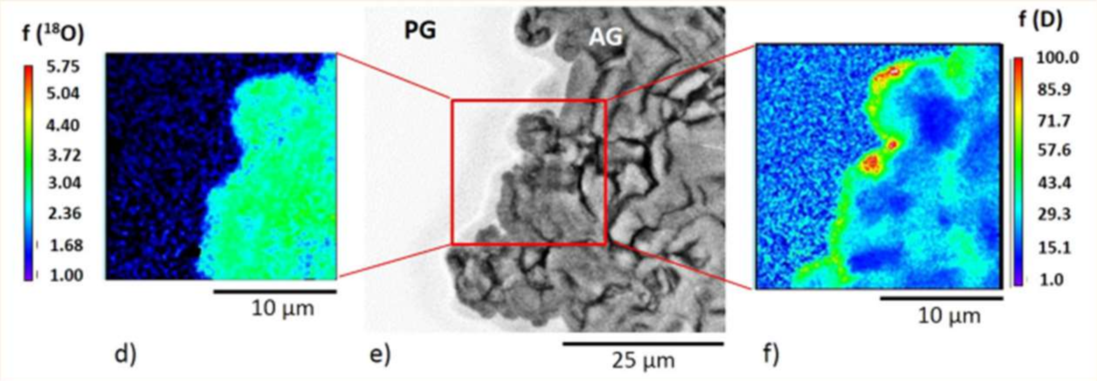
Secondary phases: gypsum ($CaSO_4.2H_2O$)

External face of stained glass windows from Tours cathedral (Sterpenich & Libourel, 2001)



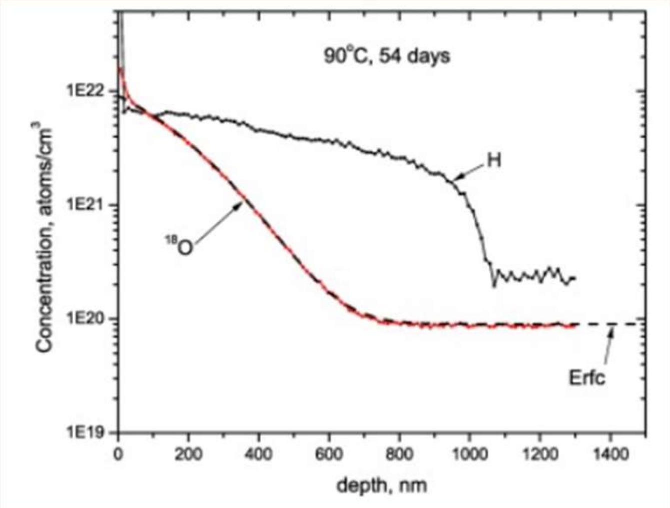
- ⇒ AL depleted in alkalis and alkaline-earth elements
- ⇒ Salts in the AL
- ⇒ Leaching of retained elements?

Ancient stained glass windows (14th c.)
9 months at 20°C and 90 %RH ($D_2{}^{18}O$)



Sessegolo et al. (2018)

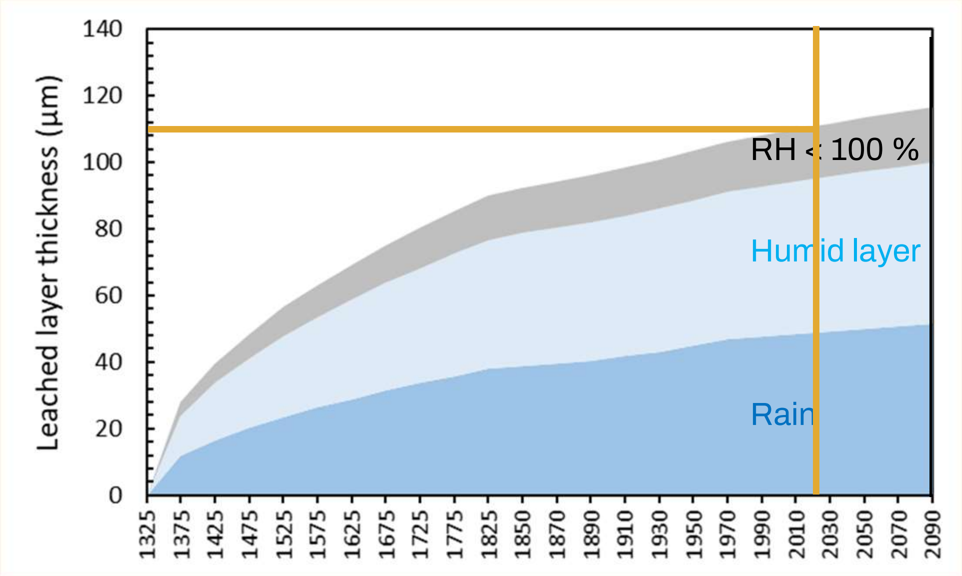
Pyrex
54 days at 90°C and 100 %RH ($H_2{}^{18}O$)

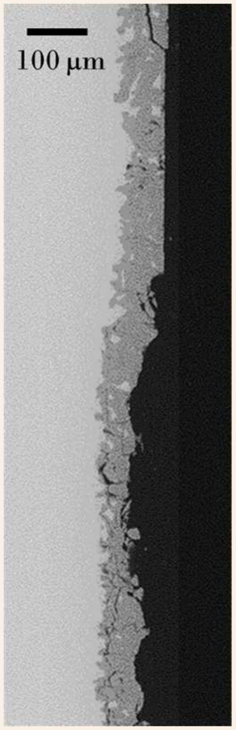


Kudriatsev et al. (2018)

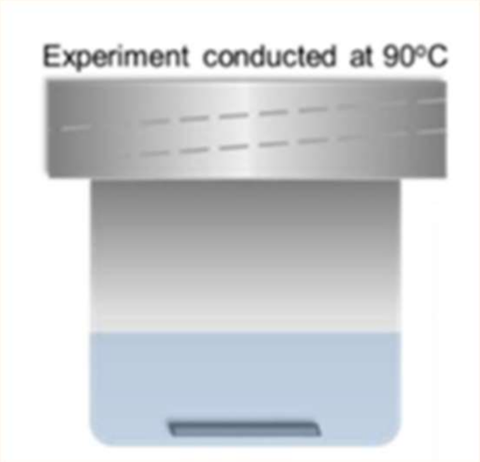
- ⇒ Sorption of H_2O + diffusion of H/D
- ⇒ Diffusion coefficient → no protective role of the AL
- ⇒ Idem with rain

Verney-Carron et al. (2023)





⇒ No passivating effect of the AL formed in unsaturated medium
⇒ Independent contributions



Bates et al. (1984, 1990)
Bouakkaz (2014 PhD)
Neeway (2010 PhD)
Narayanasamy (2019 PhD)
Zhang et al. (2023)

⇒ No passivating role of the AL formed during vapor phase
⇒ Increase of the apparent rate due to the release of retained elements and dissolution of soluble secondary phases (and probably gel)

⇒ MECHANISMS

- Leaching of retained elements
- Partial dissolution of secondary phases

⇒ KINETICS

- No protective role of the AL

⟹ Composition of glass has a key role on:

- Sorption
- Hydration rate
- Secondary phase formation

⟹ But some common results

- Retention of elements (solvation properties)
- Driving force or result: secondary phases
- Immersion → leaching / no protective role

Thank you

Questions?

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