Diffusion issues related to silicate glass corrosion

stephane.gin@cea.fr


Échantillons : Hervé Bertrand

Various types of glasses in various environments

VERRE & DIFFUSION

Ecole thématique du CNRS sur la diffusion chimique dans les phases vitreuses et liquides

3 - 8 Octobre 2021

Fréjus – Villa Clythia

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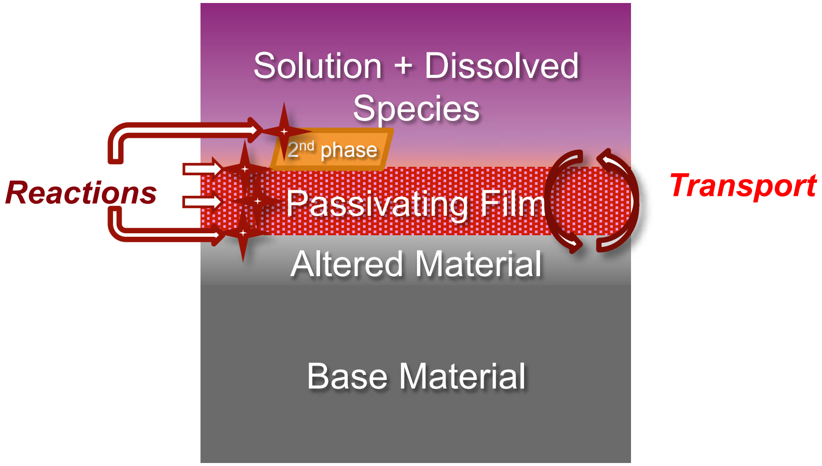
Reactions and Transport

Reactive Behaviors

- Selective dissolution of glass network
- Restructuring of glass to form gel (dissolution reprecipitation under some conditions)
- Evolution of gel structure
- Dissolution of gel
- Precipitation of 2nd phases

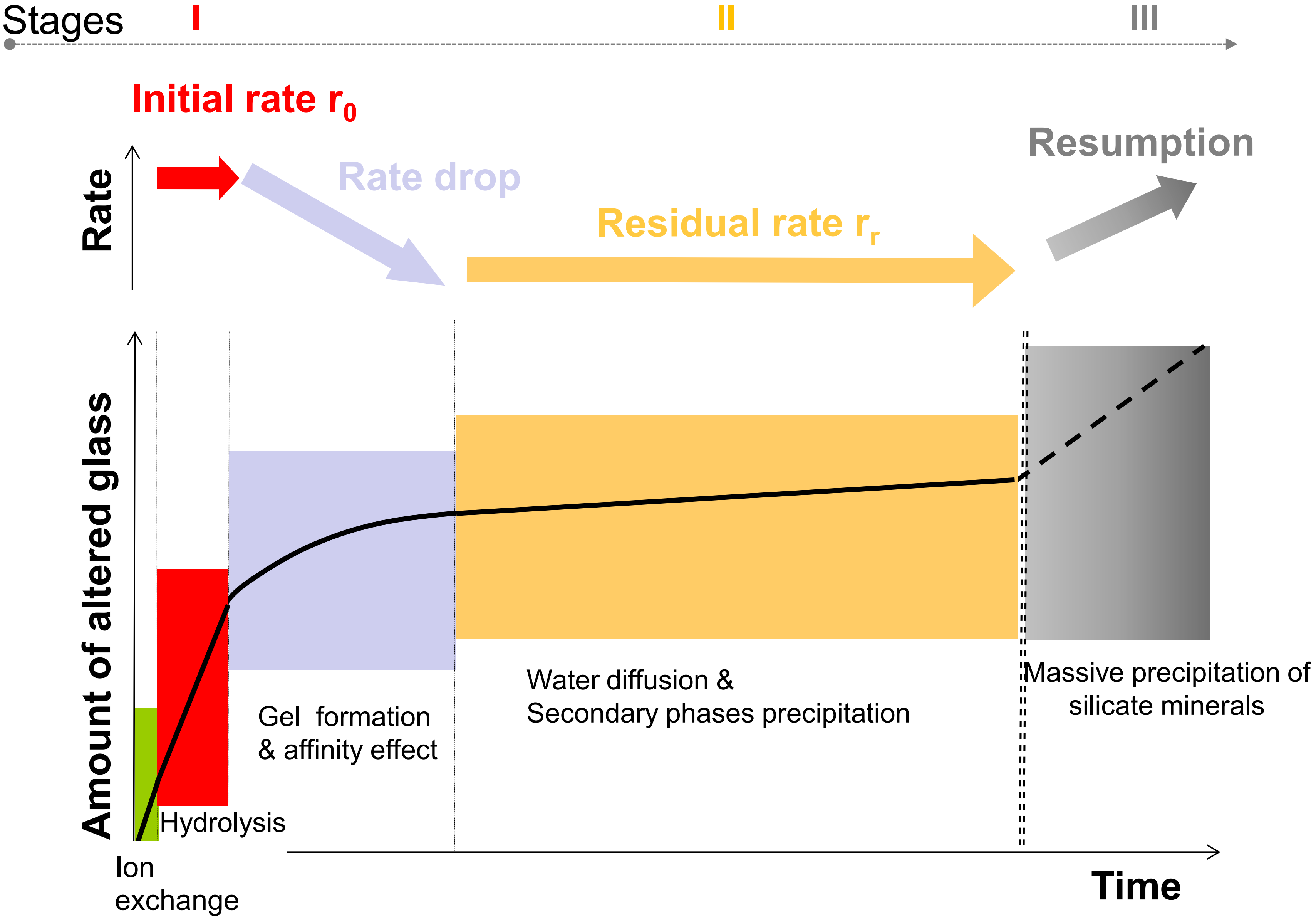


Transport Behaviors

- Reactive transport of water and dissolved species through tortuous passivating film
- Ion exchange in altered material

- These layers control both the solution chemistry and the glass dissolution kinetics
- Features and properties of alteration layers depend on many intrinsic and extrinsic parameters
- There is no predictive model available to date

KINETIC REGIMES

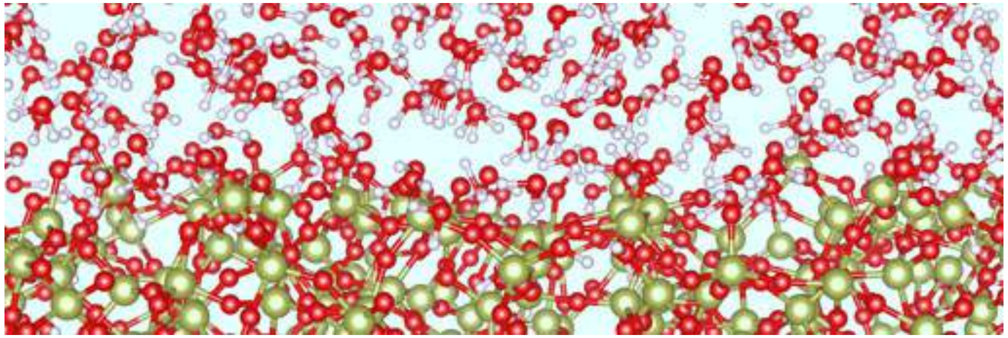


Vienna *Inter.J.Appl.Glass Sci. 4* (2013)

DIFFUSION PROCESSES

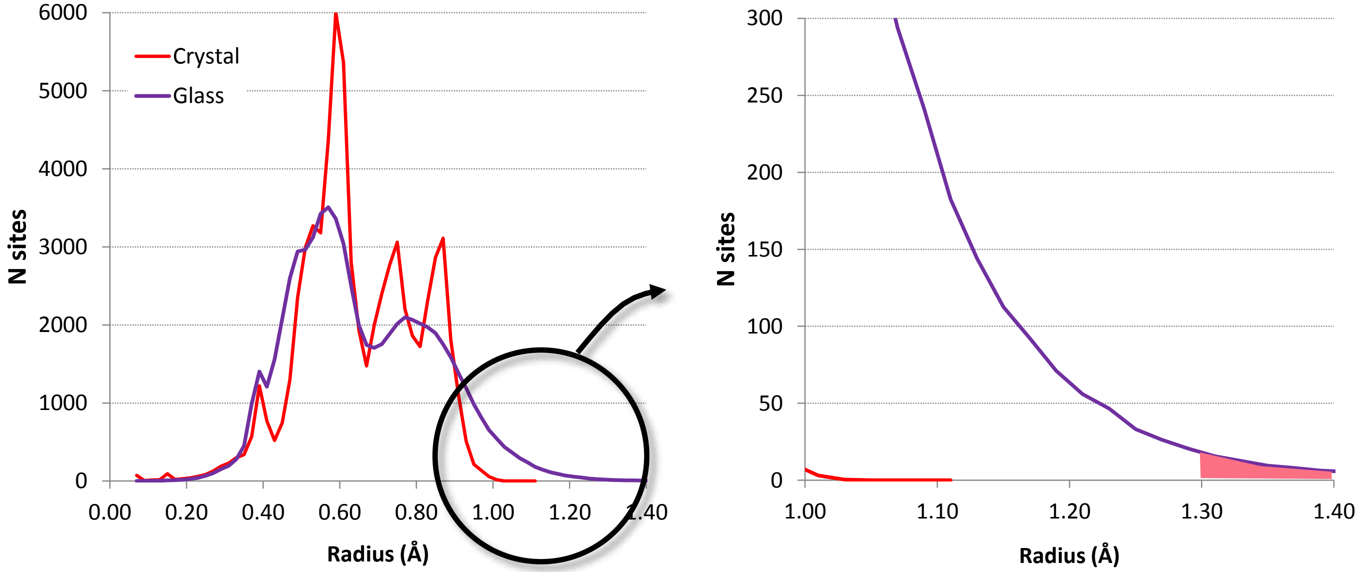
1. Diffusion in pristine glass = interdiffusion = ion exchange
2. Diffusion in gel
3. Diffusion in secondary phases

BASIC MECHANISMS OF GLASS CORROSION



Contrary to crystals, glass structure is more open, allowing small species (Li, He, H^+, H_2O…) to diffuse in the bulk material **AND** the glass surface in contact with water offers a large diversity of chemical bonds (distribution of bond lenghts and angles)

EXAMPLE OF ALBITE ($NaAlSi_3O_8$) ❶

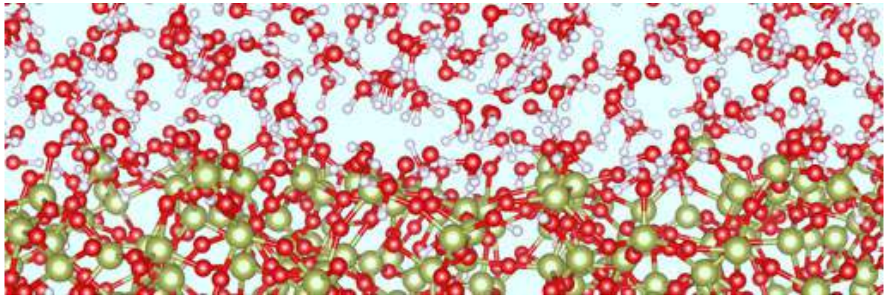


Topological analysis of interstials in crystal and equivalent glass

- Density: crystal = 2.62 g/cm^3 and glass = 2.34 g/cm^3
- Dissolution: r_{glass} ~50 $r_{crystal}$

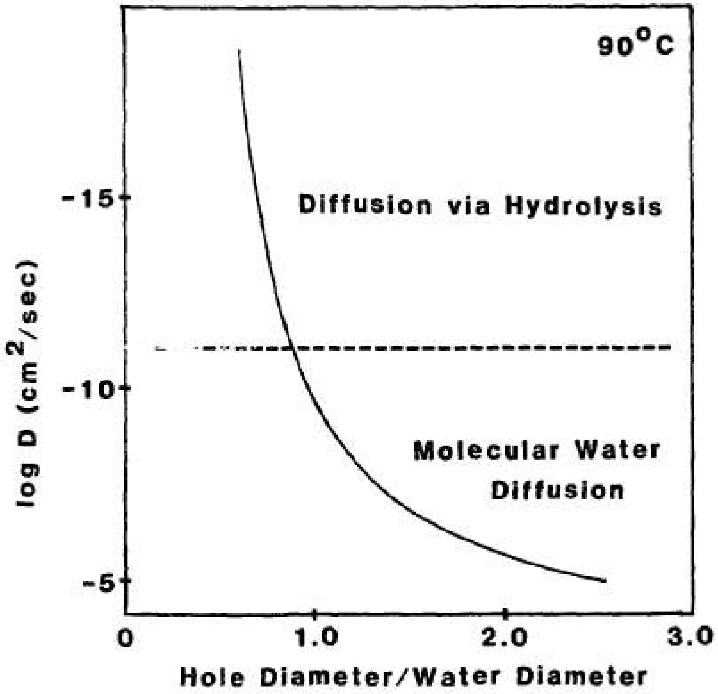
Perez et al. *Geochim. Cosmochim. Acta* **254** (2019)

Water diffusion in glass ❶

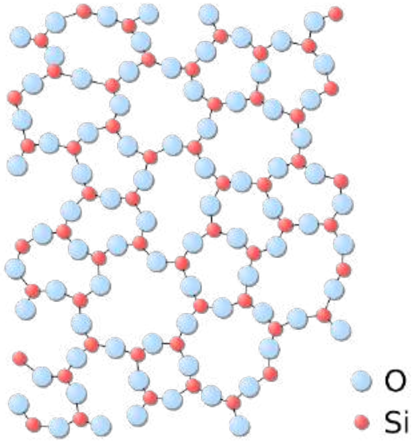


Water diffusivity in glass is strongly tied to its topology

(the degree of disorder depends on the glass composition and the fictive T)



Bunker, *J.Non-Cryst.Sol.* (1994)

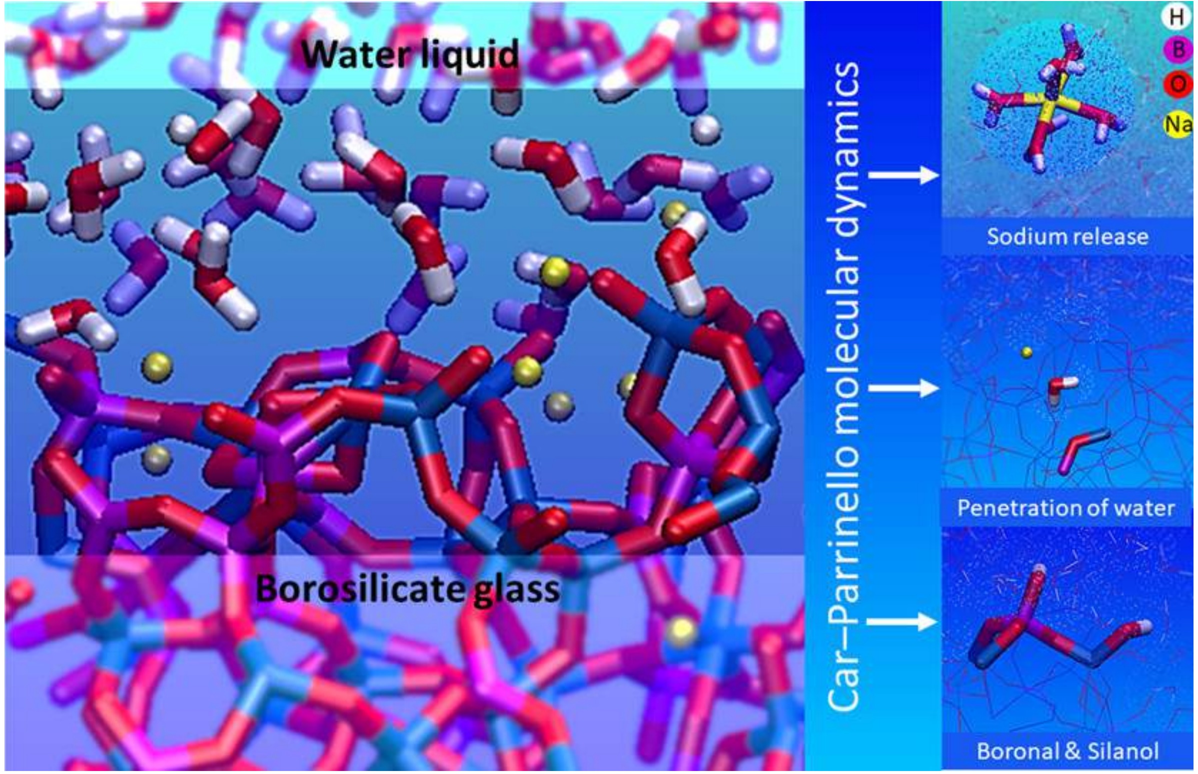


Ref	Glass	H/Na
Lanford et al. (1979)	SiO_2, Na_2O, CaO	2.9 ± 0.3
Houser et al. (1980)	SiO_2, Na_2O	1.75
Tsong et al. (1981)	SiO_2, Na_2O	2.0 ± 0.3 or 3.2 ± 0.4 depending % Na
Dran et al (1989)	SiO_2, Na_2O, CaO	~ 2 near surface, ~ 1 near diss front
Ferrand et al. (2006)	SON68	2.6 ± 0.3

Hydration/Interdiffusion ❶

Glass	D m²·s^{-1}	Temp °C	pH	Ref
Si-Na	10^{-17} - 10^{-15} 10^{-15}	60 – 100 30	Pure water 4.9	Rana et Douglas (1961b) Houser et al. (1980)
Si-Na-Ca	10^{-18} 10^{-20} - 10^{-17}	90 60-100	Pure water	Lanford et al. (1979) Rana et Douglas (1961b)
Medieval K-stained glass window	10^{-17} - 10^{-18}	T° ambiante		Sterpenich et Libourel (2006)
Medieval Na-stained glass window	10^{-20}	T° ambiante		
Si-Na-Al	10^{-18} - 10^{-19} 10^{-16}	70 25	Pure water	Smets et Lommen (1982) Boksay et al. (1975) Smit et Stein (1979)
Borosilicates	10^{-17} - 10^{-18}	90	9,5	McGrail et al. (1984)
SON68	10^{-21} - 10^{-22} 10^{-21} - 10^{-24}	90 30 – 90	7 – 10 7 – 10	Ferrand et al. (2006) Chave et al. (2007)
Obsidian	10^{-22}	22	Pure water	Friedman et al. (1966)

Ea = 30-45 kJ/mol



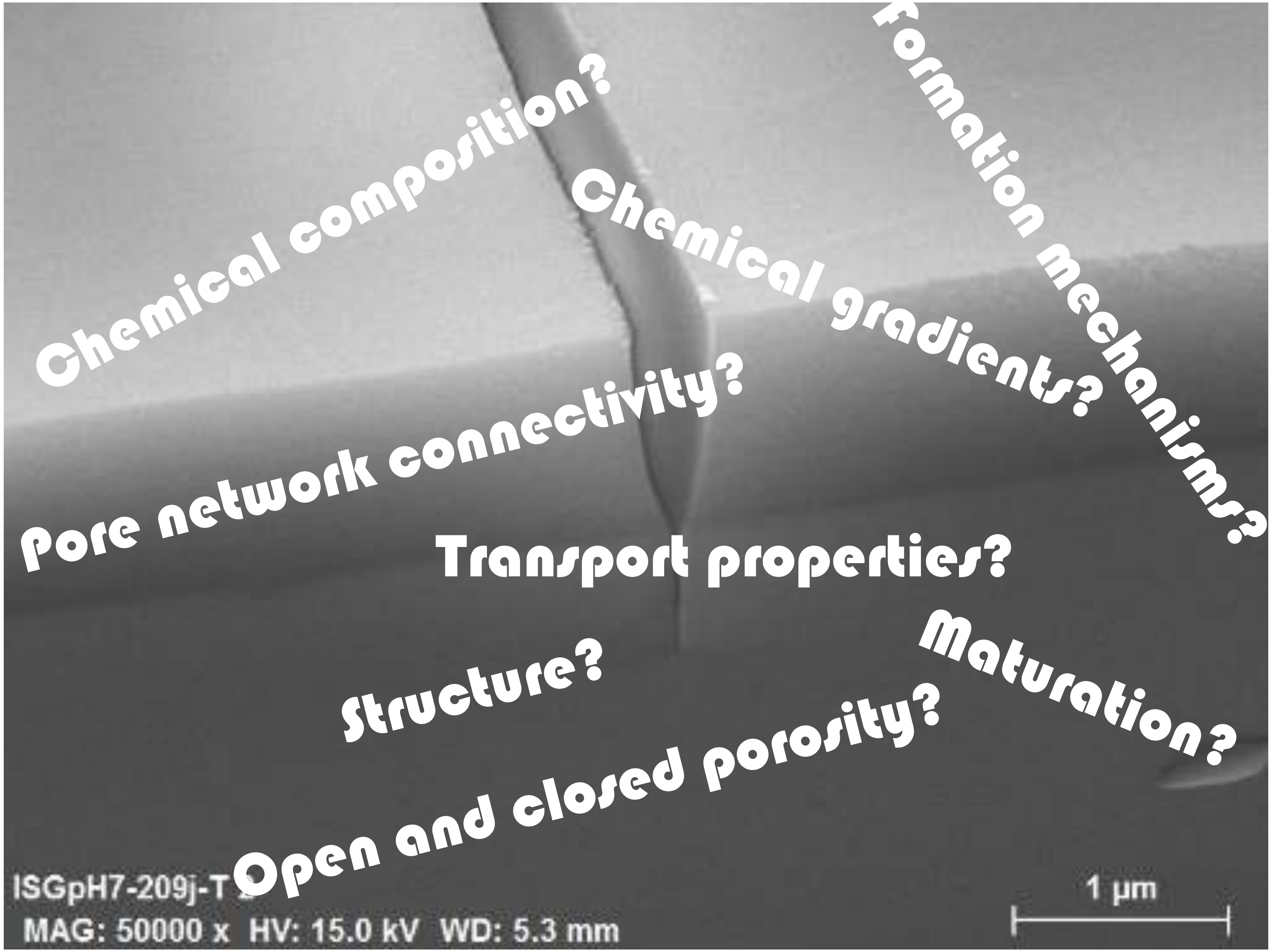
Jabraoui, *J.Phys. Chem. C*, ***125*** (2021)

- MD and ab initio calculations show that IX is a complex process that cannot be dissociated with water dissociation, SiOH, BOH formation, hydrolysis…
- The gap between the atomistic level and the macroscopic observations is not bridged.

Gin et al., *npj. Mater. Degrad.* ***5****, 42* (2021)

2 - Diffusion through the gel layer

❷



Chemical composition?

Chemical gradients?

Formation mechanisms?

Pore network connectivity?

Transport properties?

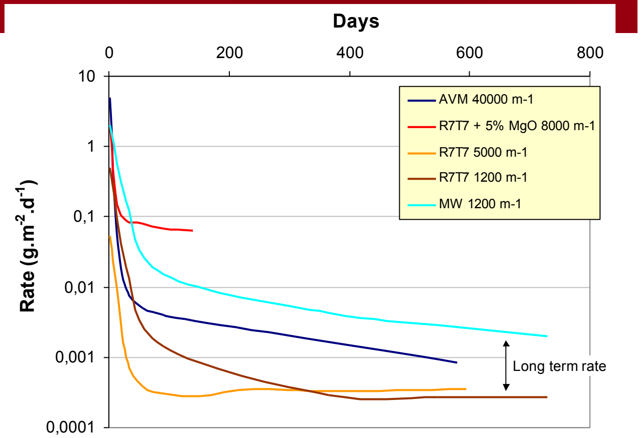
Structure?

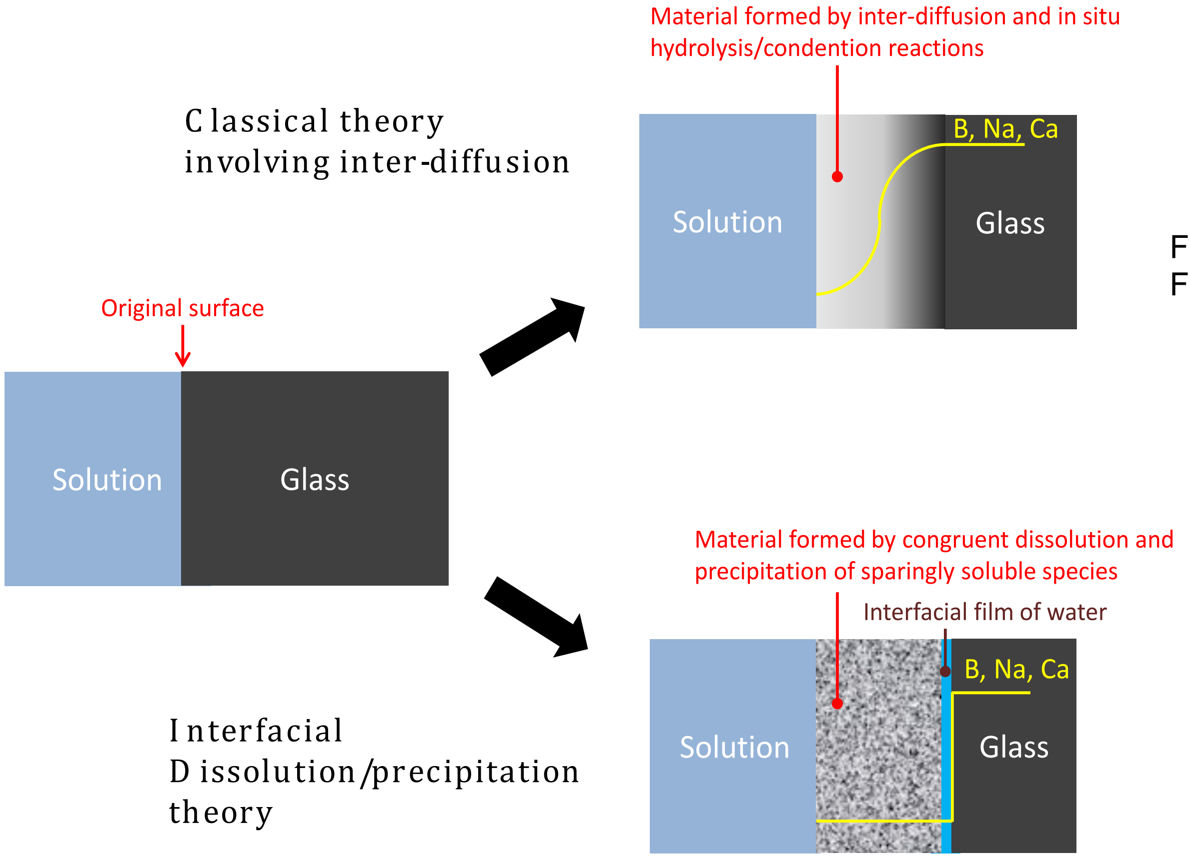
Maturation?

Open and closed porosity?

Formation of passivating layers ❷

- Passivating layers control the residual alteration of the glass, r_r, which can be 10^4 to 10^5 times lower than r_0

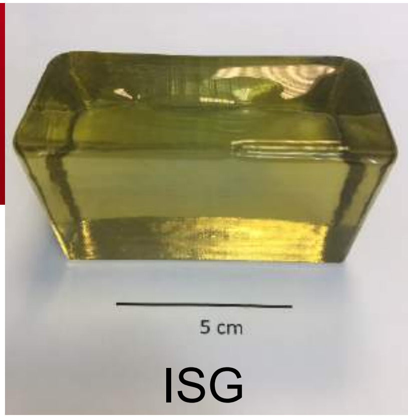




Ferrand et al., *J.Nucl.Mater.* (2006)
Frugier et al., *J. Nucl. Mater.* (2008)

Hellmann et al., *Nature Mater.* (2015)
Geisler et al., *J. Non-Cryst. Sol.* (2010)

Complementary Analytical & Numerical Techniques applied to a reference 6 oxide borosilicate glass



Chemistry

ToF-SIMS	low lateral resolution	Collin, *npj-Mat. Degrad.* 3 (2019)
SEM, TEM	qualitative, Z>6	Gin, *Geochim. Cosmochim. Acta* 202 (2017)
XPS	only 5-10 nm	Guo, *Nat. Mater* 19 (2020)
APT	time consuming	Perea, *npj-Mat. Deg.* 4 (2020)

Structure

IR, Raman		Kaya, *J. Non-cryst. Sol.*, 556 (2021)
NMR	bulk technique	Collin, *npj-Mat. Degrad.* 2 (2018)
MD	potentials dependent	Collin, *npj-Mat. Degrad.* 2 (2018)

Porosity

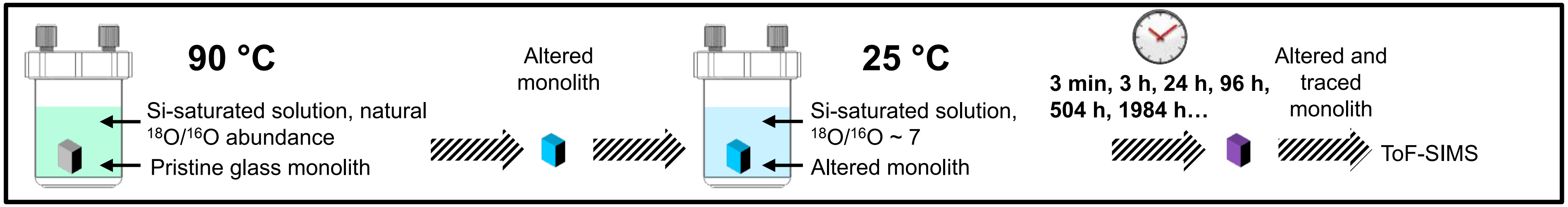
SAXS,SANS	$\Phi_{pore} > 1\text{-}2$ nm	Cailleteau, *Nat. Mater.* 7 (2015)
BET/BJH	model dependent	Ngo, *npj-Mat. Degrad.* 2 (2018)
SE		Ngo, *npj-Mat. Degrad.* 2 (2018)
Cryo-APT		Schreiber, *Ultramic.* 194 (2018)
TEM		Mir, *npj-Mat. Degrad.* 4 (2020)
MD, KMC	rules under development	Rimsza, *npj-Mat. Degrad.* 2 (2018); Kerisit, *J. Non-cryst. Sol.*, 556 (2021)

Transport

ToF-SIMS	qualitative	Gin, *Nat. Comms.* 9 (2018)
MD, KMC	for simple systems	Collin, *npj-Mat. Degrad.* 2 (2018)

WATER DYNAMICS IN THE GEL (1)

②



90 °C

Si-saturated solution, natural $^{18}O/^{16}O$ abundance

Pristine glass monolith

Altered monolith

25 °C

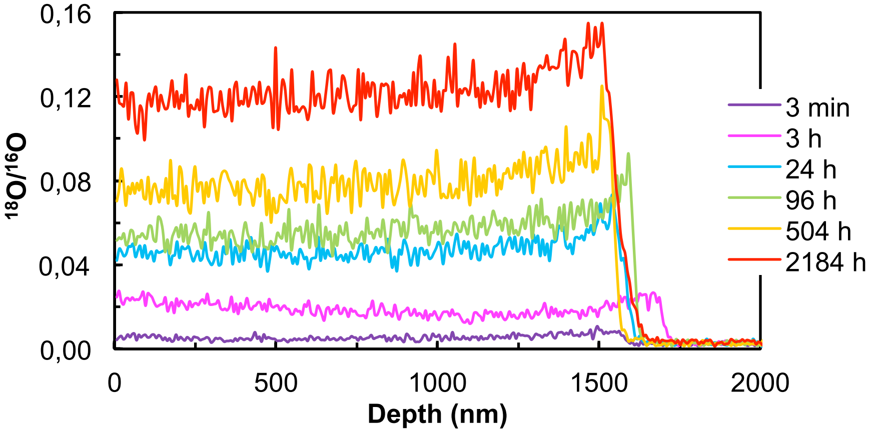
Si-saturated solution, $^{18}O/^{16}O \sim 7$

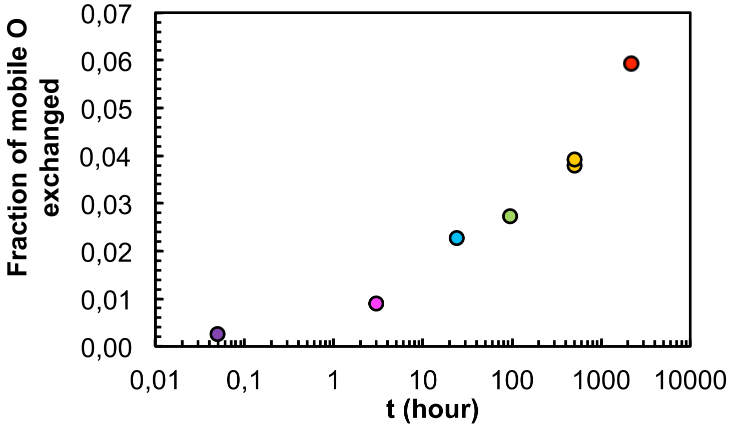
Altered monolith

3 min, 3 h, 24 h, 96 h, 504 h, 1984 h…

Altered and traced monolith

ToF-SIMS





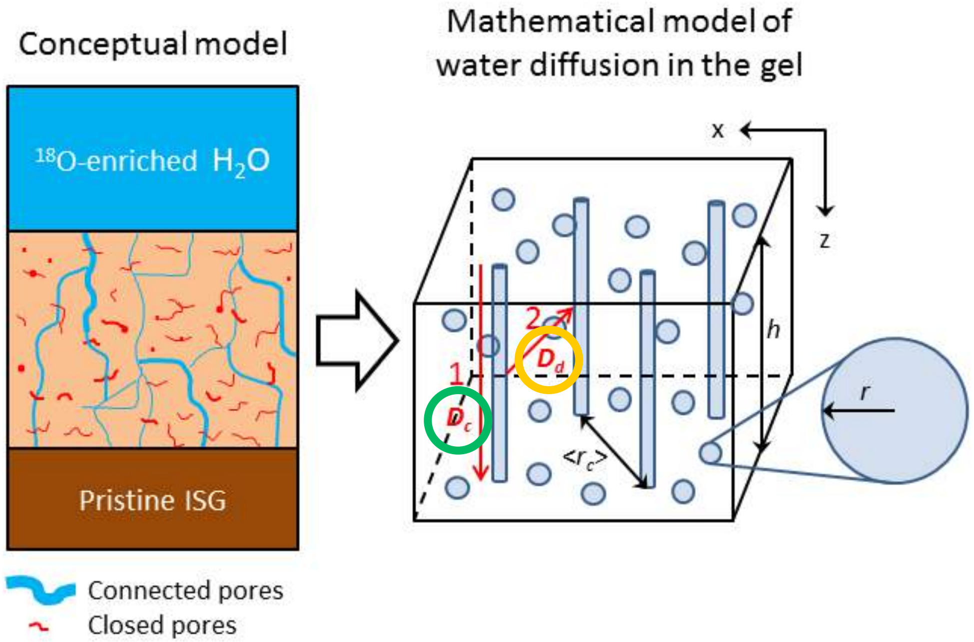
- ^{18}O· enrichment in the gel (up to the reaction front) is noticed even after 3 min of tracing
- Profiles are flat
- ^{18}O· enrichment in the gel slowly increases with time
- Quantification of isotopic exchange is possible

Gin et al., *Nat. Comms.* ***9*** (2018)

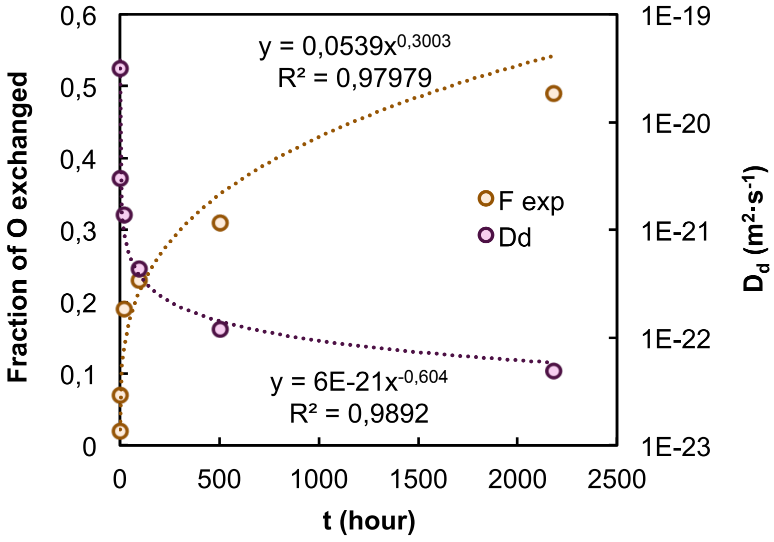
WATER DYNAMICS IN THE GEL (2)

❷

Experimental data were implemented in a mathematical model to calculate diffusion coefficients:



Schematic representation of the mathematical model considering two diffusion coefficient D_c and D_d.



D_d values calculated from experimental data (Fraction of oxygen exchanged calculated from ToF-SIMS data).

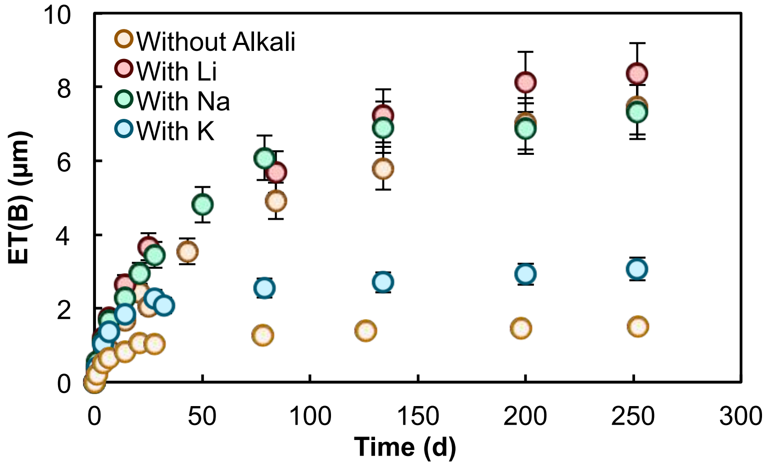
$D_c > 10^{-11}\ m^2 \cdot s^{-1}$, $D_d = 10^{-21} – 10^{-23}\ m^2 \cdot s^{-1}$

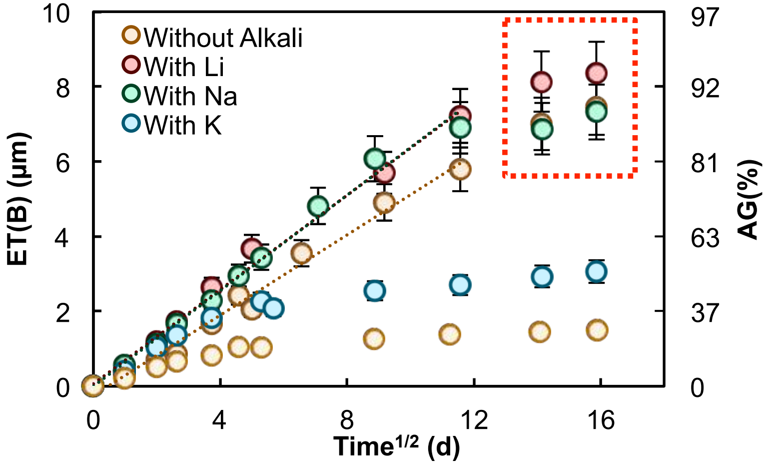
This difference cannot be explained by nanoconfinement effect only, as MD simulation yields mean diffusion coefficient of nanoconfined water ($\Phi = 1$ nm) roughly one to two orders of magnitude lower than that of bulk water → non-accessible porosity due to network reorganization.

ALKALI EFFECT ON GLASS ALTERATION

❷

Effect of alkali on glass alteration was also studied (~20 mmol·L^{-1} of *X*Cl with *X* = Li, Na, K and Cs):





ET(B) well correlated with square root of time in no-alkali, Li and Na case → diffusion coefficient can be calculated and are low (9 order of magnitude lower than that of bulk water).

Sample	D (10^{-18} m^2.s^{-1})
ISG – PW	3
ISG – Li	4
ISG – Na	4

Huge effect of exogenous species on glass alteration and passivation.

Collin et al., *npj-Mater. Degrad.* **2** (2018)

GEL MATURATION (1)

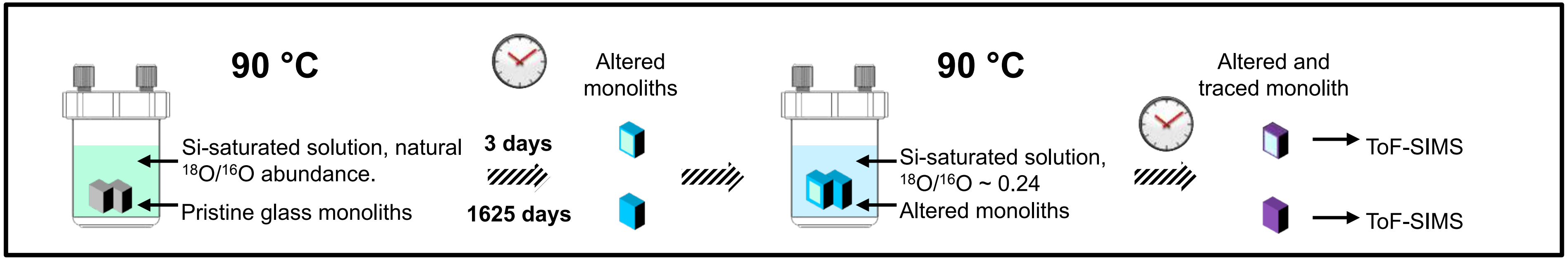
❷

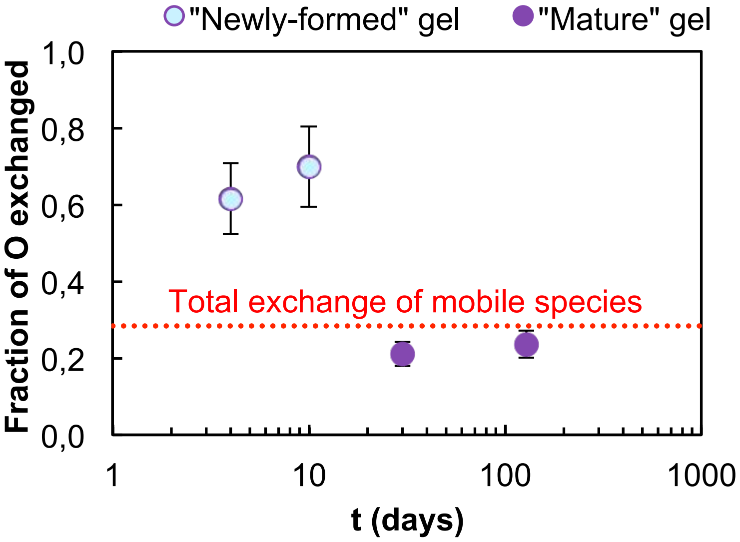
Knowing **O repartition** (%):

O_{BO}	O_{NBO}	O of H_2O mol
71.6	15.5	12.9

In the following mass balance calculations
Mobile species in red

Let us play again with O isotopes





>60% of O exchanged after 4 or 10 days of tracing for baby gel (3 days of pre-alteration), <24% of O exchanged after 4 month of tracing for adult gel (1625 days of pre-alteration).

- **Gel reactivity decreases with aging**

GEL MATURATION (2)

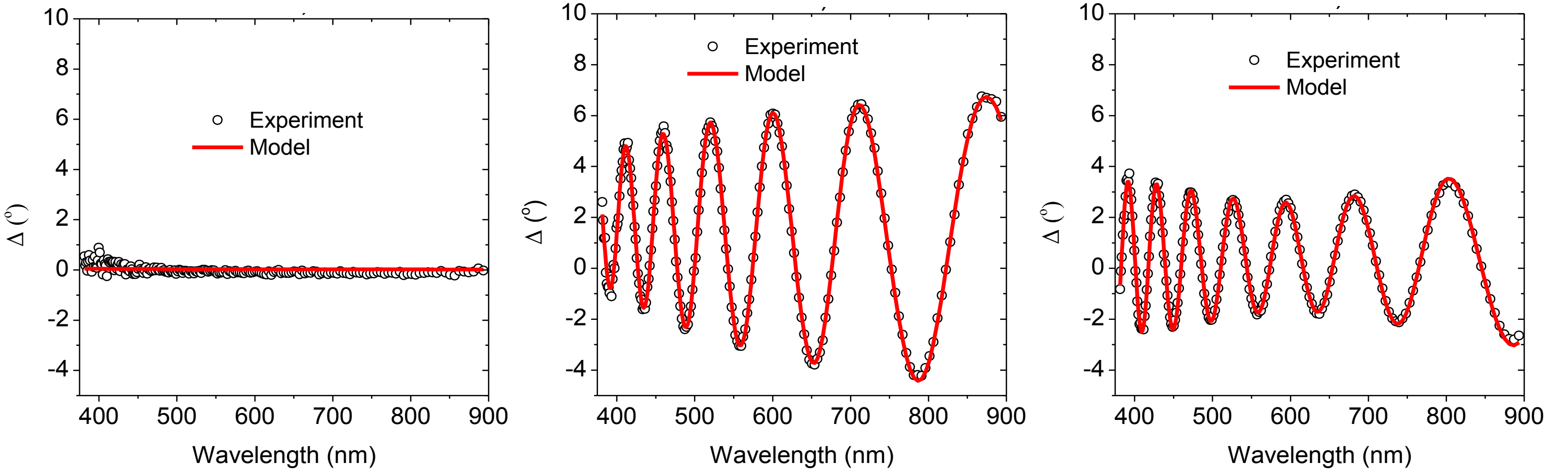
❷

Spectroscopic Ellipsometry experimental data were collected on pristine glass, newly-formed gel and mature gel:

Pristine glass ······▶ **Neoformed gel** ······▶ **Mature gel**

(7 days)

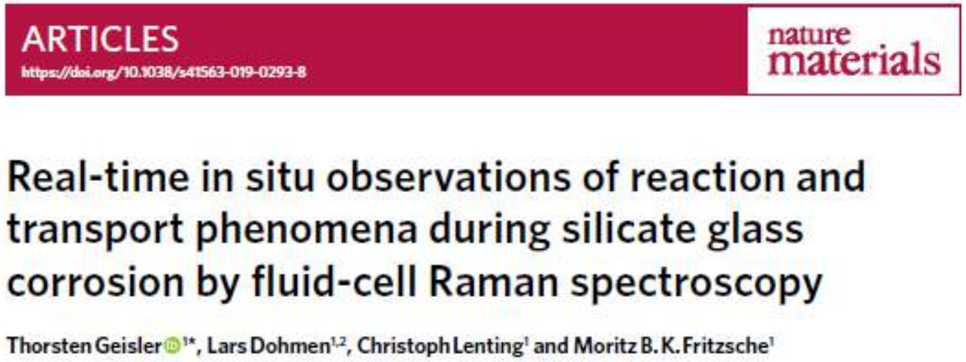
(1625 days)



No porosity ······▶ **~1 nm Φ pores** ······▶ **~2 nm Φ pores**

Maturation of gel lead to a bigger-sized porosity, but less accessible → **network reorganization leads to a rate drop.**

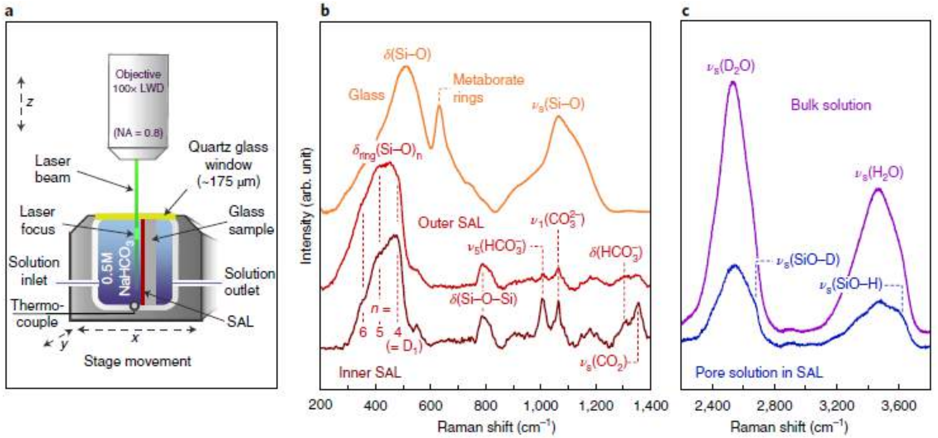
Ngo et al., *npj-Mater. Degrad.* ***2*** (2018)



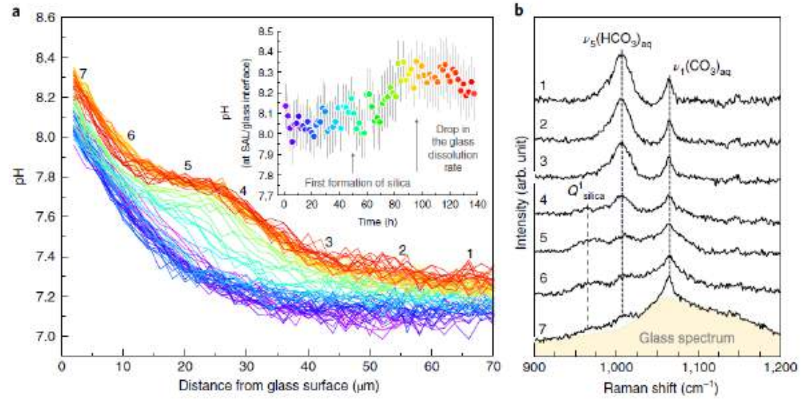
ARTICLES
https://doi.org/10.1038/s41563-019-0293-8
nature materials

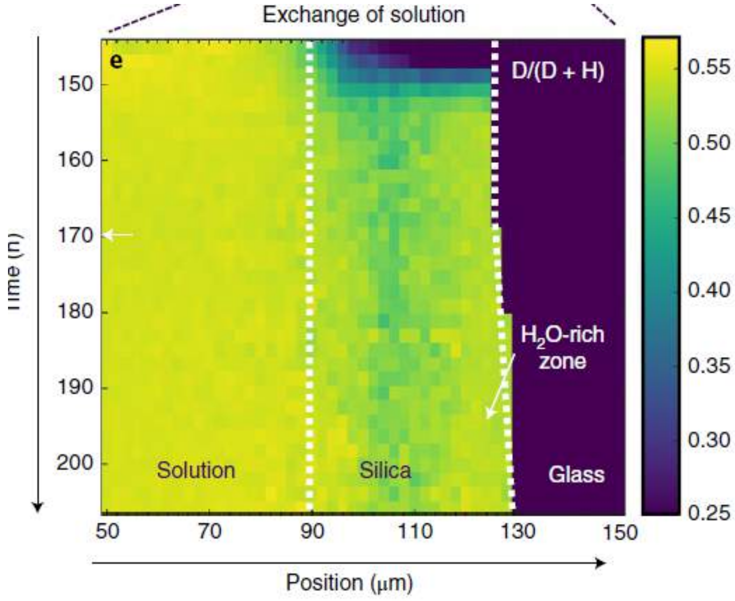
Real-time in situ observations of reaction and transport phenomena during silicate glass corrosion by fluid-cell Raman spectroscopy

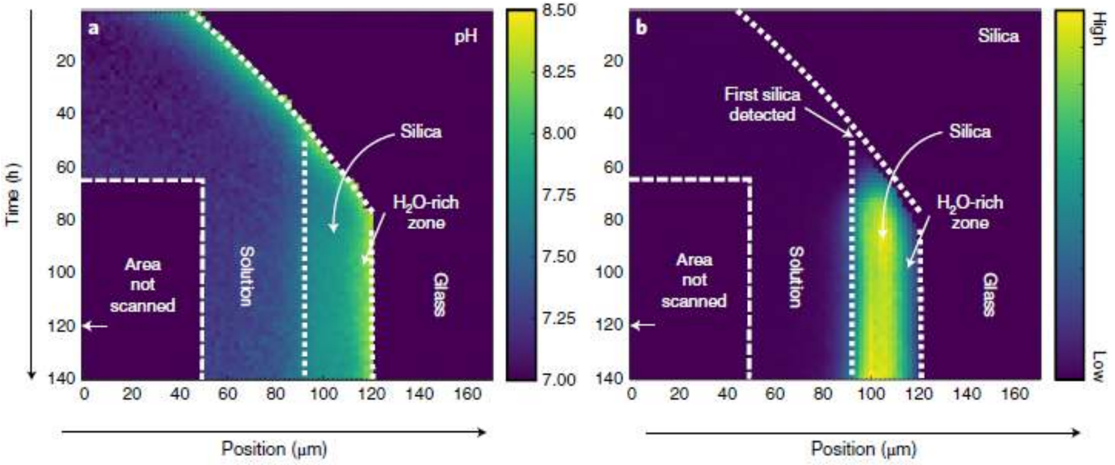
Thorsten Geisler[1*], Lars Dohmen[1,2], Christoph Lenting[1] and Moritz B. K. Fritzsche[1]



Glass 60 SiO_2, 20 Na_2O 20 B_2O_3
Altered at 85°C in $NaHCO_3$ and D_2O







$$D_{water} = 2 \times 10^{-14}\ m^2 \cdot s^{-1}$$

❷

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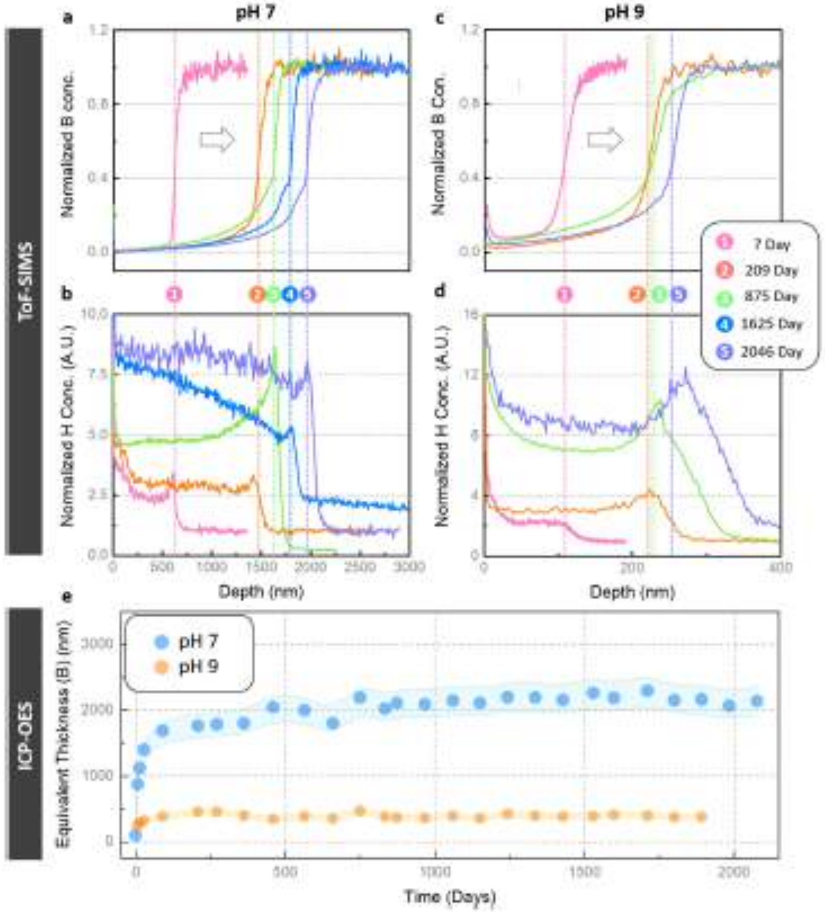
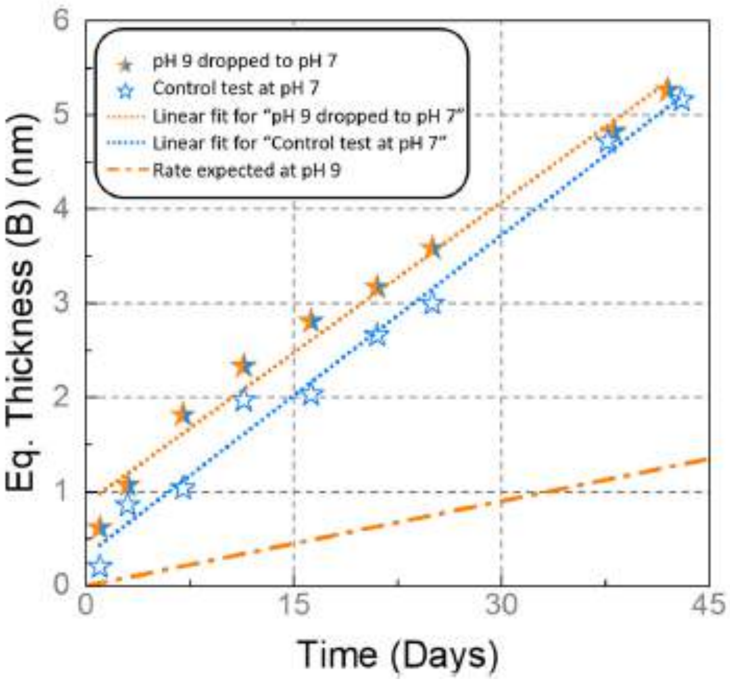
ARTICLE OPEN

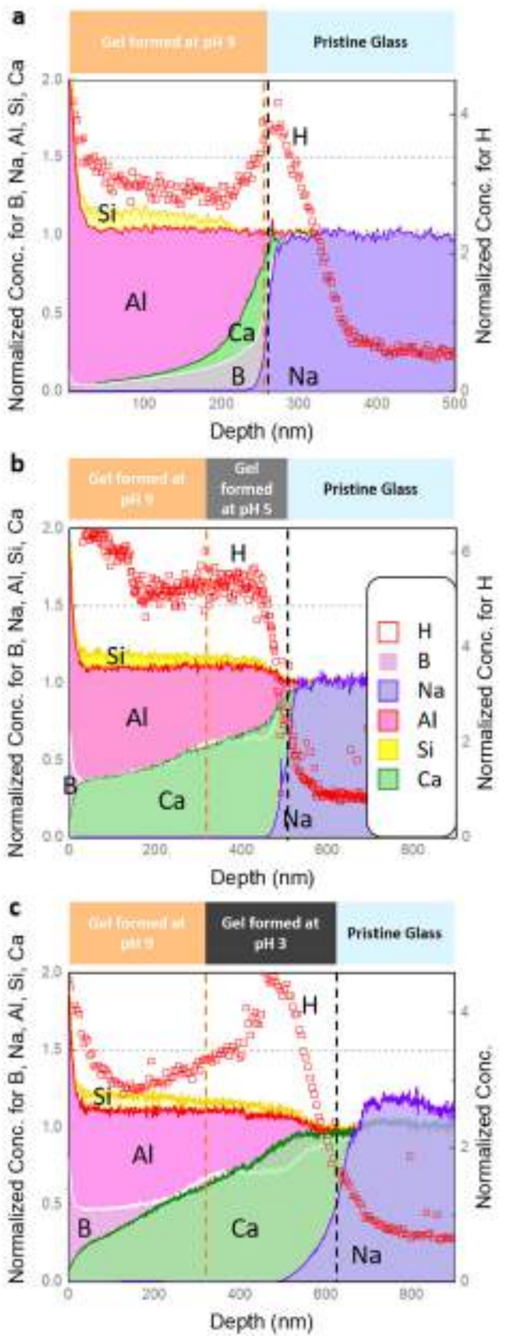
Check for updates

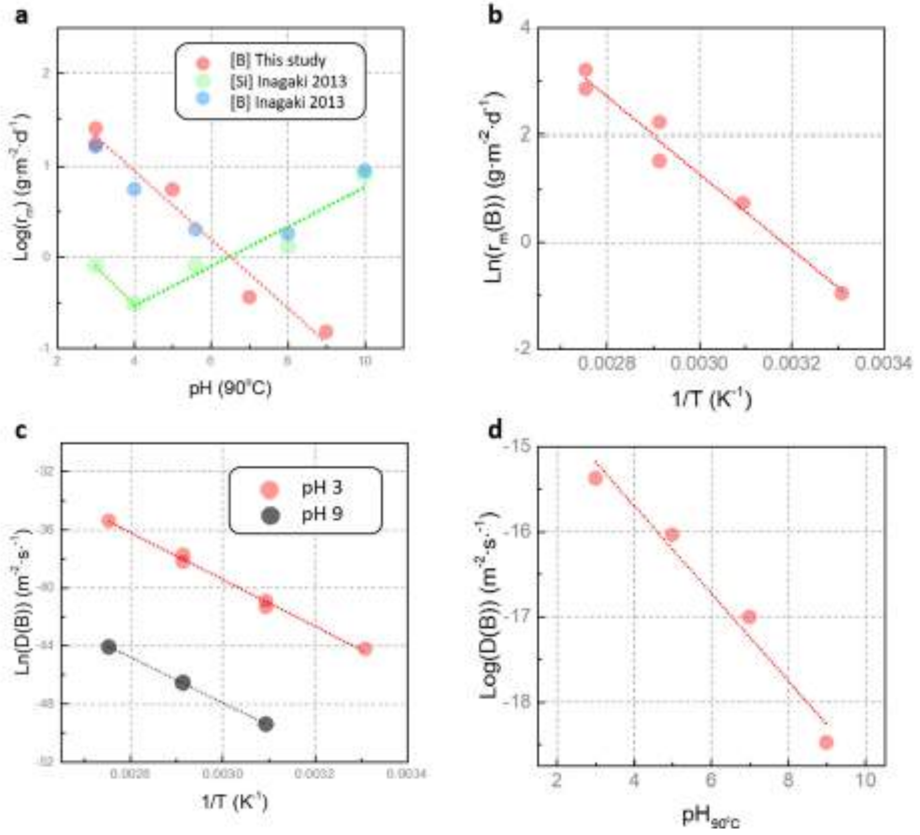
Insights into the mechanisms controlling the residual corrosion rate of borosilicate glasses

Stephane Gin[1✉], Xiaolei Guo[2], Jean-Marc Delaye[1], Frédéric Angeli[1], Kamalesh Damodaran[1], Véronique Testud[3], Jincheng Du[4], Sebastien Kerisit[5] and Seong H. Kim[6]









Interestingly, the continuous and monotonic trend displayed by r_m(B) over a broad pH range may suggest that the same reaction could control B dissolution between pH 3 and 9. According to first principles simulations, this reaction implies the nucleophilic attack of H^+ on B and the hydrolysis of B–O–Si by H_2O[47]. The apparent activation energy for B release at pH 3 is 59 ± 5 kJ mol^{-1} (Fig. 5b), a value close but slightly lower than that for Si dissolution (64 ± 3 kJ mol^{-1} from pH 3 to 5.6)[35]. From the parabolic trend following the initial release of B, an apparent diffusion coefficient of B was calculated at 90 °C (Fig. 5d):

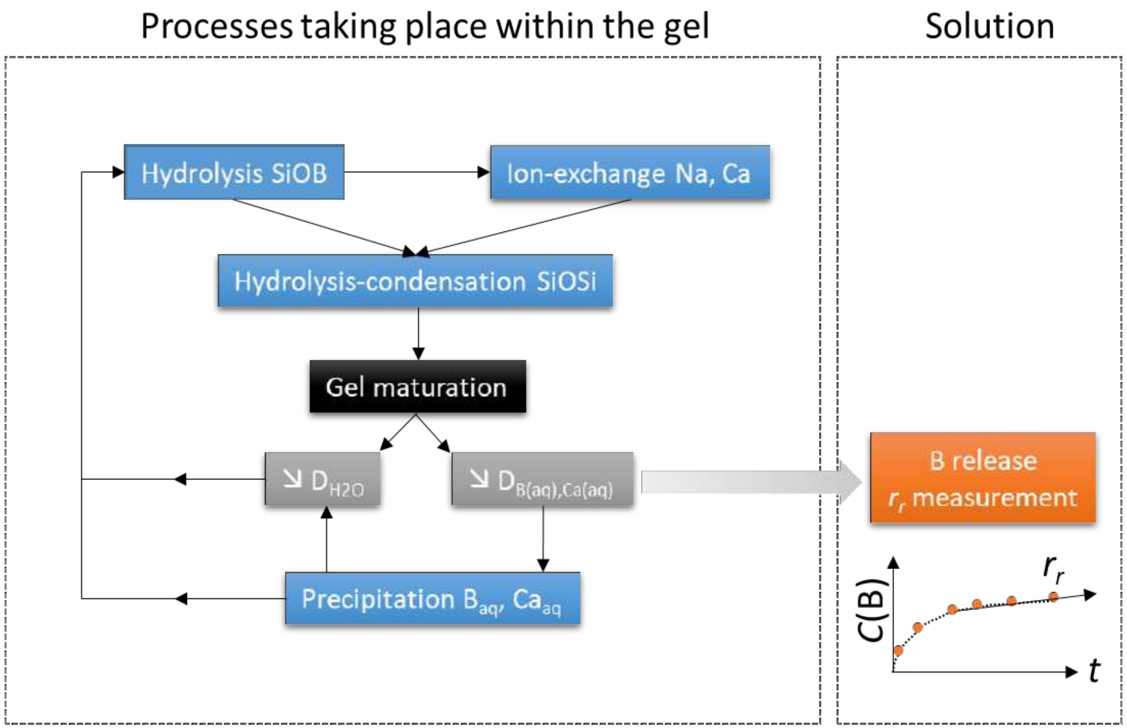
$$D_B(m^2s^{-1}) = 10^{-13.65-0.51pH} \qquad (2)$$

❷

Etudes récentes sur le verre ISG à 90°C pH 7, 9, 5, 3

1. Les liaisons Si-O-B s'hydrolysent d'autant plus vite que le pH est bas. L'Ea associée est légèrement plus faible que celle associée à la dissolution des Si-O-Si. Il est proposé qu'une seule réaction impliquant les protons contrôle l'hydrolyse des liaisons Si-O-B.
2. Na et Ca ne sont dissous que si les laisons Si-O-B sont hydrolysées.
3. Certaines liaisons Si-O-Si sont hydrolysées mais le Si ne passe pas en solution.
4. Le départ du B permet la recondensation des Si-OH, étape clé de la restructuration du gel
5. Le départ du B est responsible de plus de 90% de la porosité du gel
6. Le B hydrolysé diffusent lentement dans le gel. Si l'hydrolyse est plus rapide que la diffusion, il s'accumule dans le gel et ralentit la poursuite de l'hydrolyse.

Modèle de formation du gel par réorganisation in situ sans précipitation de phases secondaires



QUESTIONS OUVERTES À INSTRUIRE

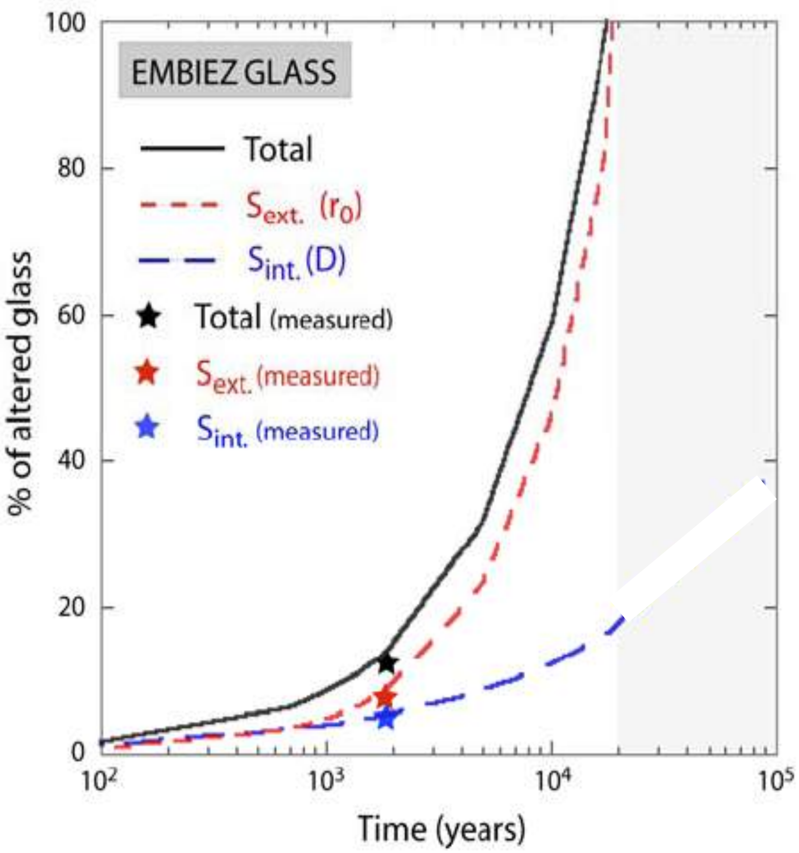
Questions préalables à l’établissement d’un modèle pour la Vr

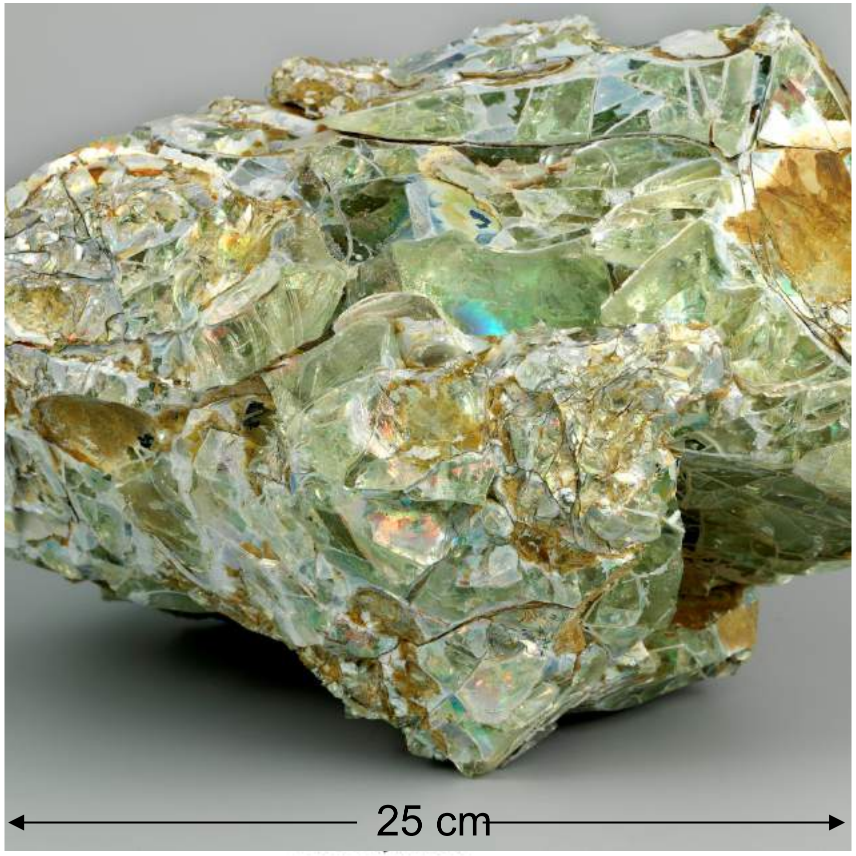
1. Où se fait le blocage dans le gel (H_2O et B_{aq})?
2. Le B dissous et piégé dans le gel a-t-il un rôle sur la diffusion de l’eau?
3. Quelle est la spéciation et la diffusivité du B dissous dans le gel ?
4. Quelle est l’activité de l’eau et des ions en milieu confiné ?
5. Comment est répartie la porosité dans le gel (ouverte vs fermée) en lien avec la taille des espèces diffusantes ?

3. Diffusion in alteration products

❸

Verney-Carron et al., *Geochim. Cosmochim. Acta* 2008 ; 2010
Verney-Carron et al., *J. Nucl. Mat.*, 2010





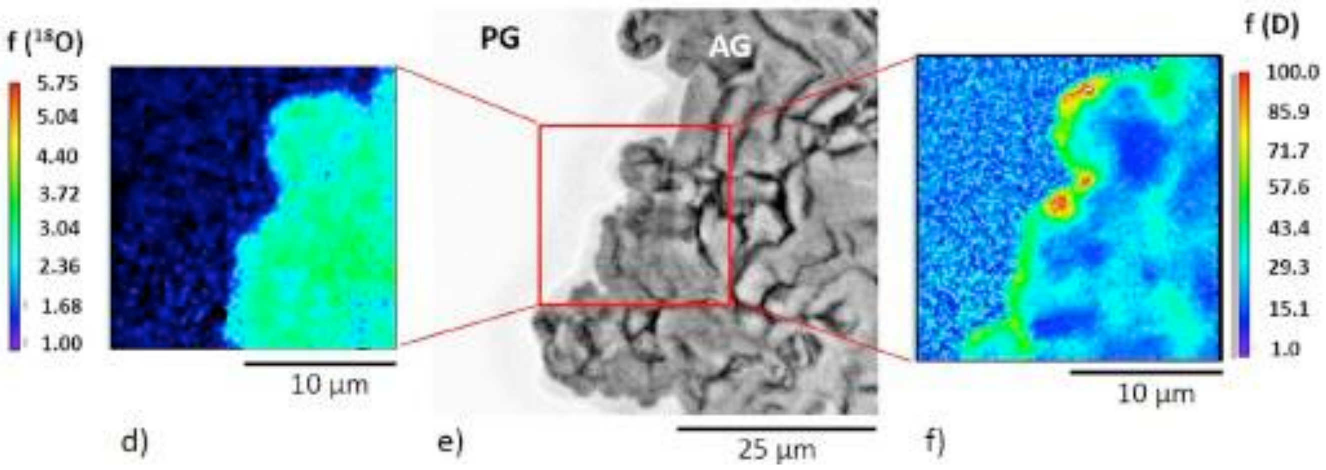
Quantitative validation of a mechanistic model over 1800 years – Applicable to other glasses by the analogy of the mechanisms involved

NANO-SIMS FOR PROBING ATMOSPHERIC CORROSION OF STAINED GLASS WINDOW

❸

Altered stained-glass window (14th century), re-corroded in laboratory under 90% RH of $D_2{}^{18}O$

Sessegolo et al., *npj-Mater. Degrad.* **2** (2018)



❑ Alteration resumed – Interdiffusion is the dominant mechanism
❑ The alteration layer is not protective
❑ An interdiffusion coefficient of 5×10^{-20} m^2/s is derived

ACKNOWLEDGEMENTS

Collaborators:

Patrick Jollivet, Pierre Frugier, Frédéric Angeli, Jean-Marc Delaye, Christophe Jégou, Magaly Tribet (CEA)

John Vienna, Joe Ryan, Sebastien Kerisit (PNNL)
Jincheng Du's group (North Texas University)
Seong Kim's group (Penn State)
Gerald Frankel's group (OSU)
Damien Daval (Univ. Grenoble)

Ph.D. Students:

Marie Collin, Kamalesh Damdaran, Mélanie Taron, Hicham Jabraoui

Funding support from:

DOE EFRC, CEA, Orano, Andra

Martiane Cabié, Université de Marseille
Emmanuel Cadel, Université de Normandie
Laurent Dupuy, Tescan Analytics
WastePD collaboration

Thank you for your attention

French Alternative Energies and Atomic Energy Commission

Alternative Energies and Atomic Energy Commission
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 64 50 10 00| F. +33 (0)1 64 50 11 86

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