DE LA RECHERCHE À L'INDUSTRIE

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Passivation, phénomène clé gouvernant le comportement à long terme des verres nucléaires

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Main issues in waste conditioning in glass

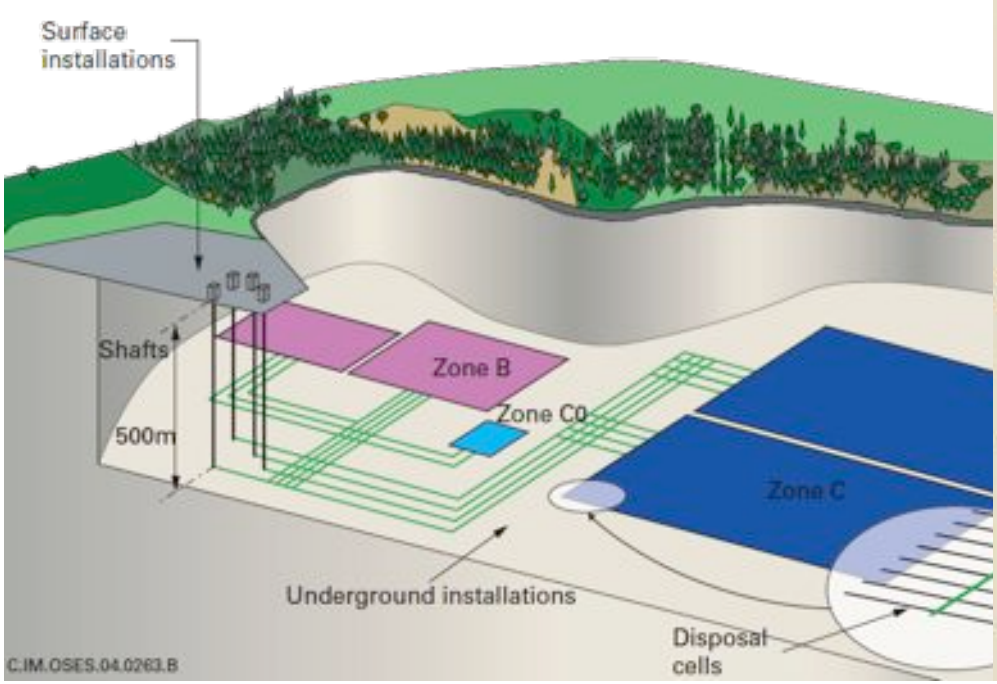
HLW & ILW
95% of all RN
~ 5000 m^3
~ 40-60 y of interim storage prior to their final disposition

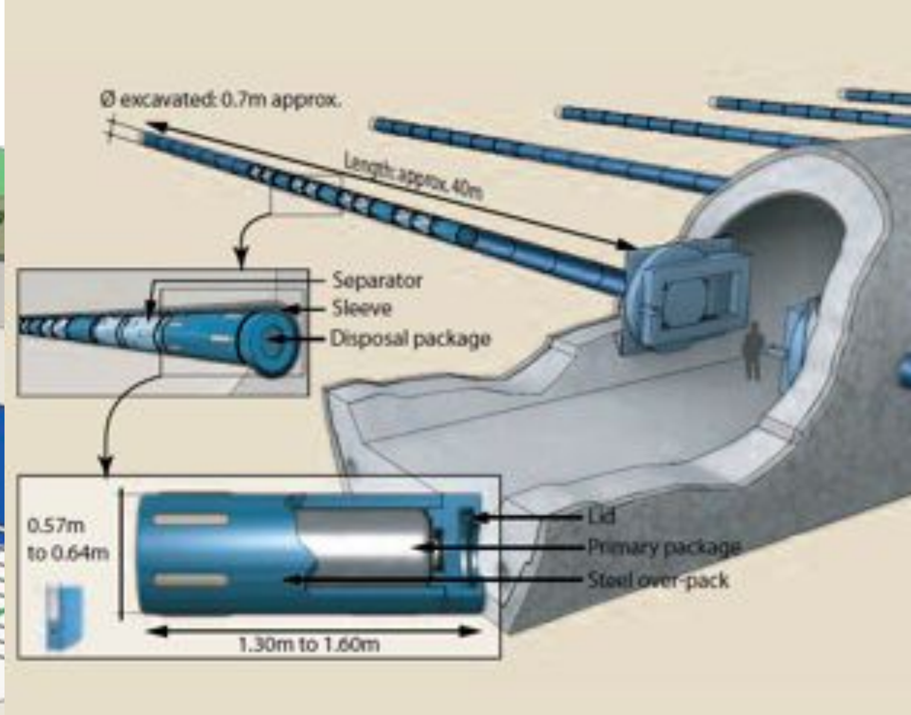
Why Glass Aging Must Be Studied?

- **Study the long-term behavior of existing glasses (→ safety assessment of the geological disposal)**
- Support R7T7 vitrification operations
- Design new vitrification processes and new glasses for other types of wastes (including ILW)

Context

- Minor actinides and fission products arising from spent fuel reprocessing in France are confined in **borosilicate glasses, made of >30 oxides**
- Deep geological disposal—currently the most consensual solution for these wasteforms—requires a study of their **long-term behavior** to assess their environmental impact.

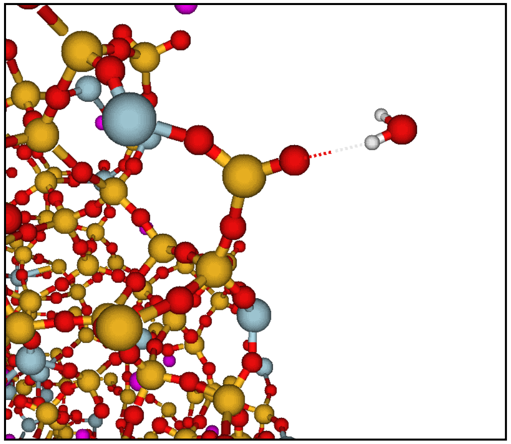


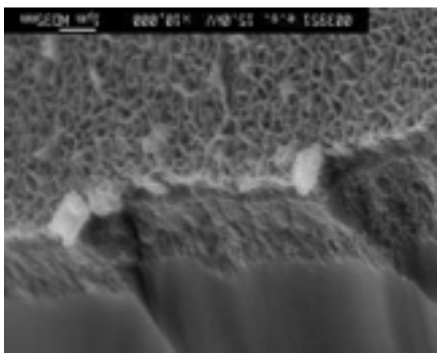


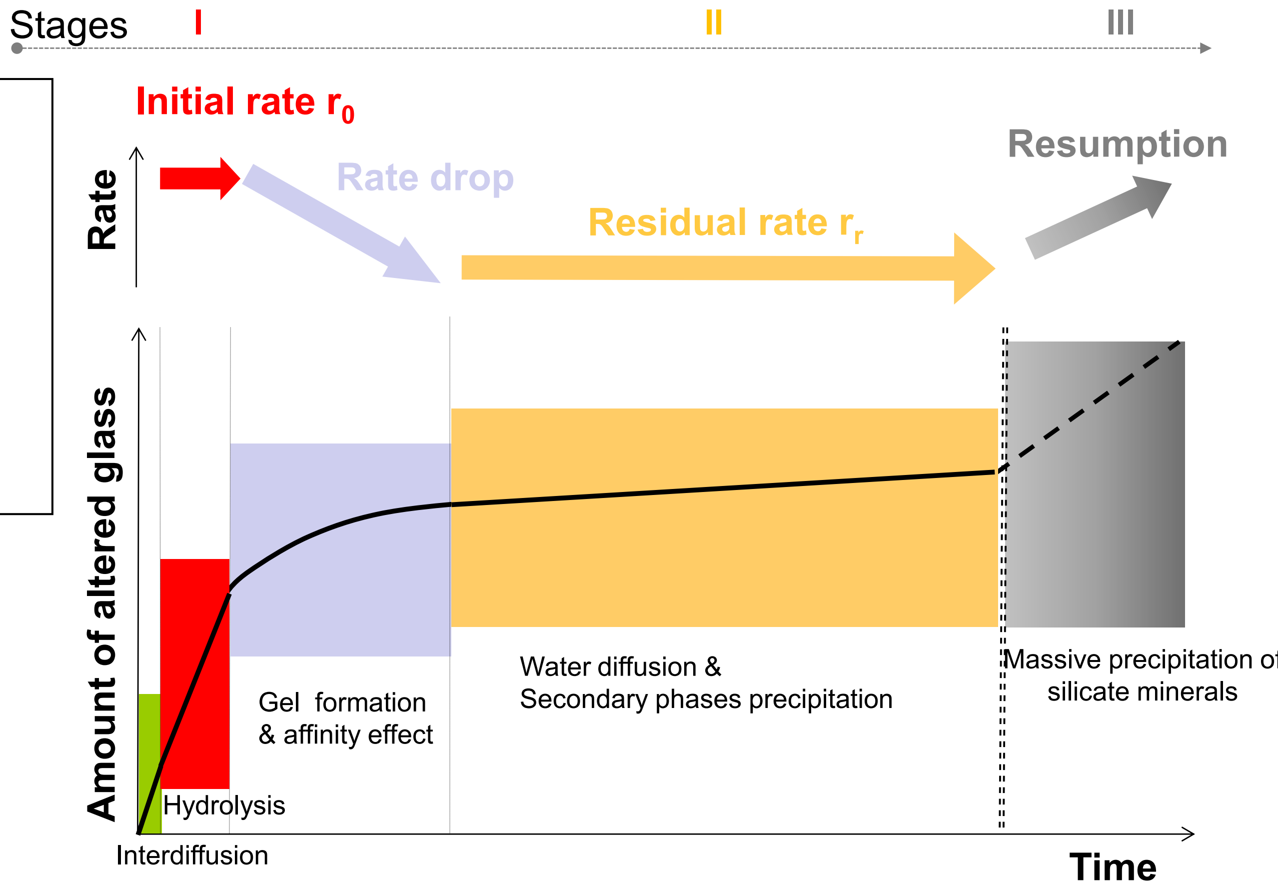
French high-level waste package and disposal cell [1]

[1] Andra 265 VA, 2006

State of knowledge



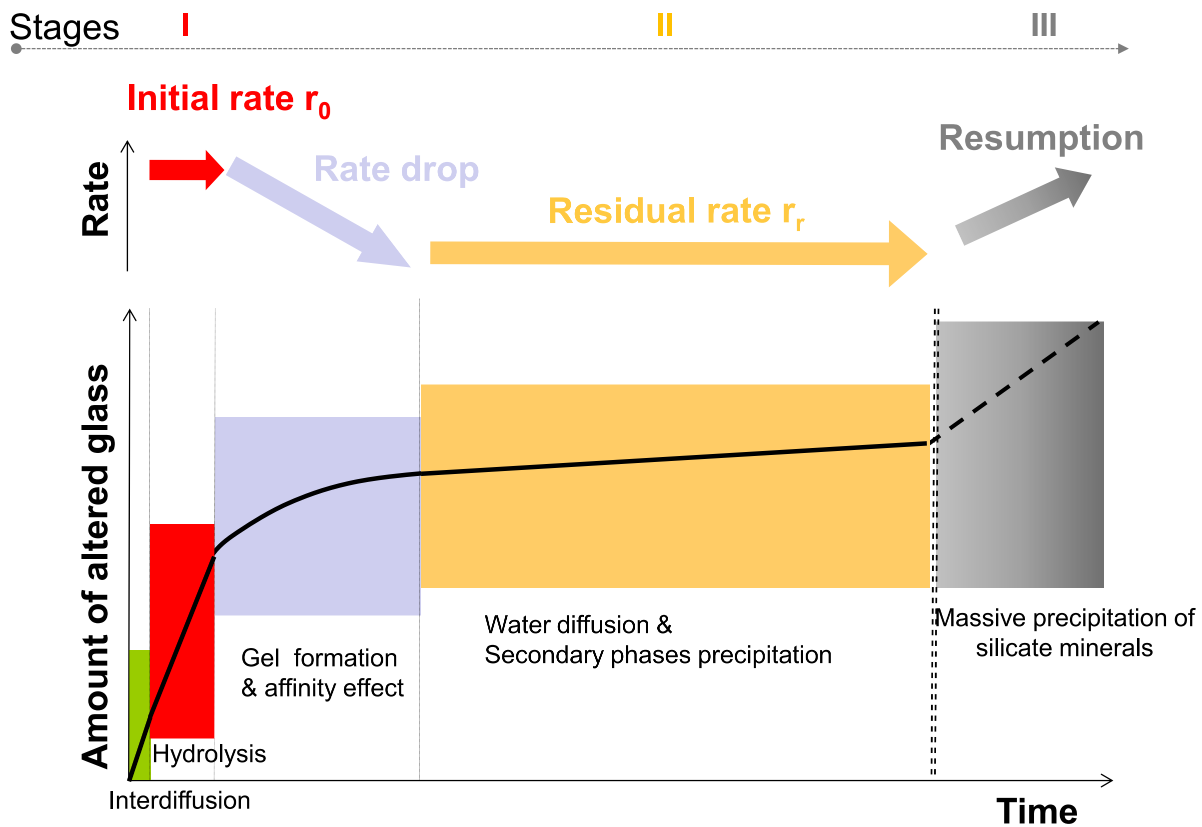




SON68 @ 90°C **~1 μm/d** **~ 10 nm/y**

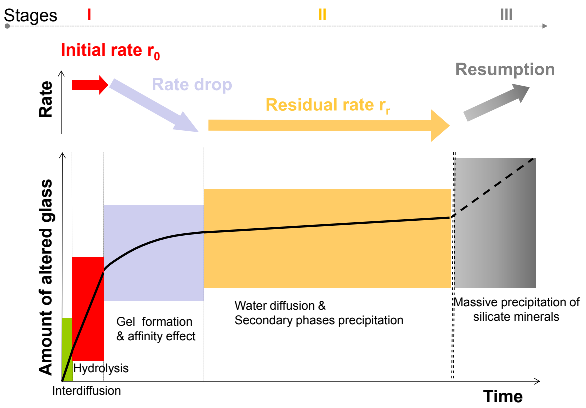
- Glass canisters could last over 10^6y if pH < 10, T < 90°C, high $C(Si_{aq})$ and low flow rate
- But several phenomena could shorten this duration

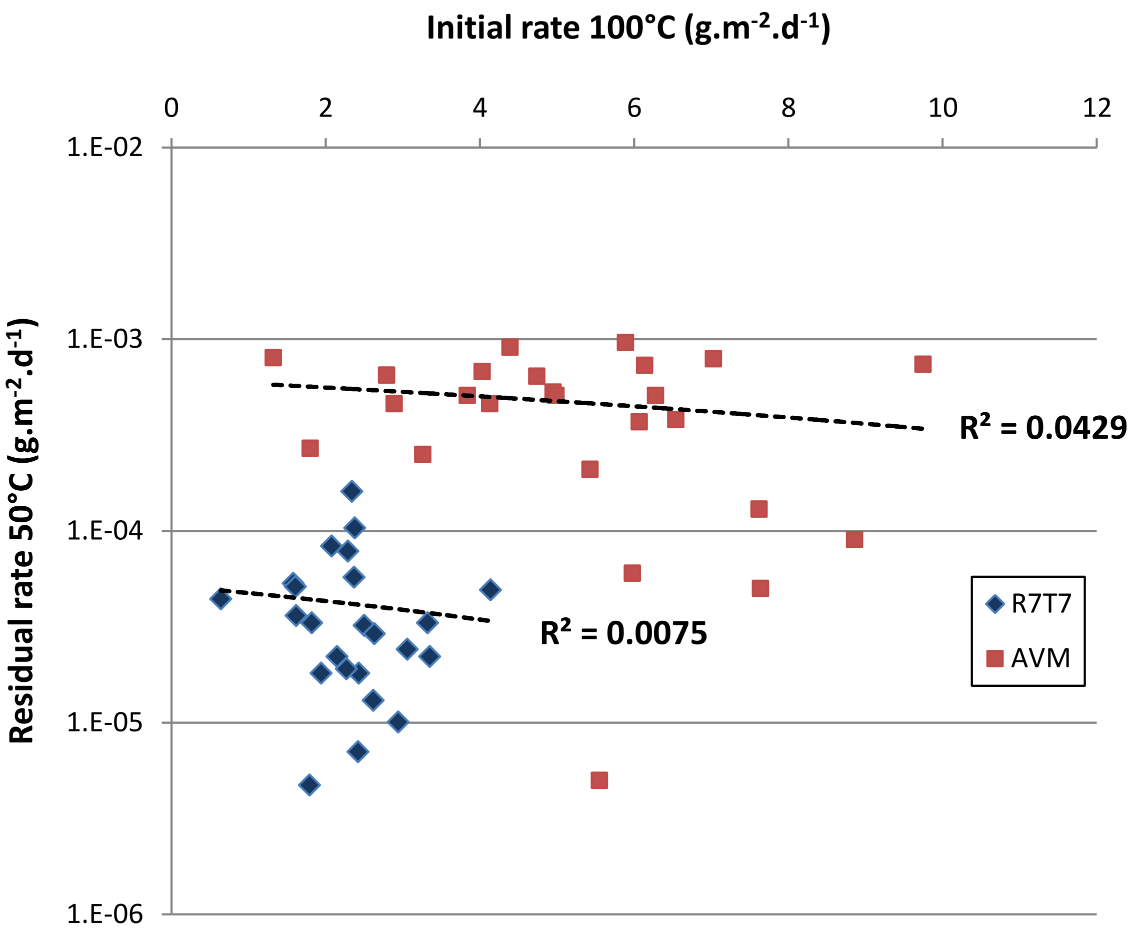
General needs



- Better understand the mechanisms responsible for the residual rate
- Assess the probablility and the consequences of a shift toward stage III
- Better quantify the effects of NF materials and radioactivity

Relation between short-term & residual rate



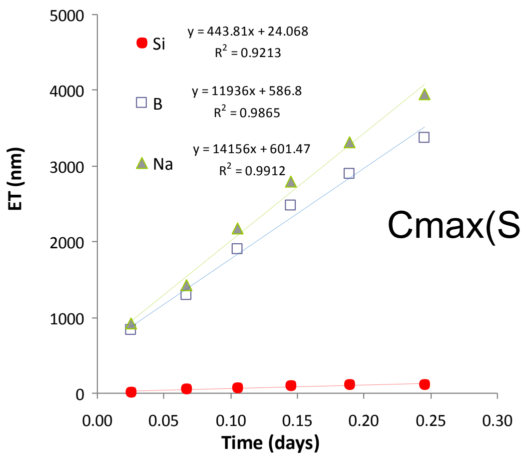


- Measuring initial rates does not help understand what could happen at long term
- Same conclusion for PCT 7d

Evidences of interdiffusion far from saturation

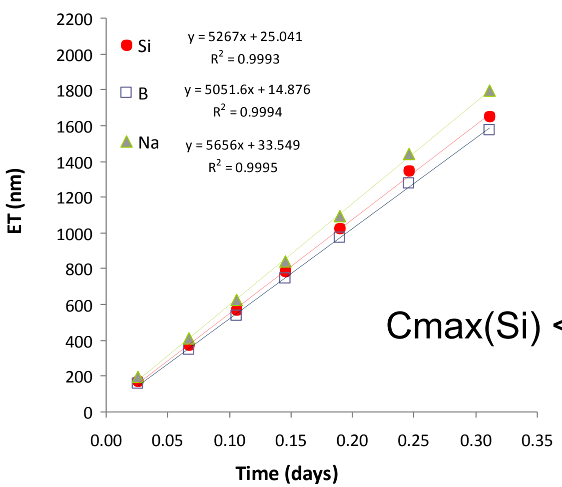
Glass (wt%) : SiO2 : 66% ; B2O3 : 20% ; Na2O : 14%
Static tests @ S/V 10 m^{-1} ; 30, 60 ; 90°C

90°C pH 4.2

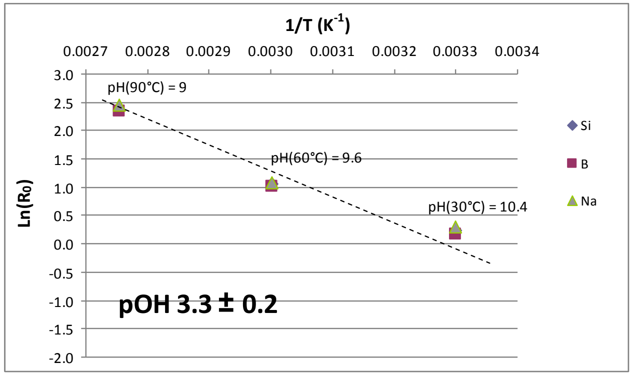


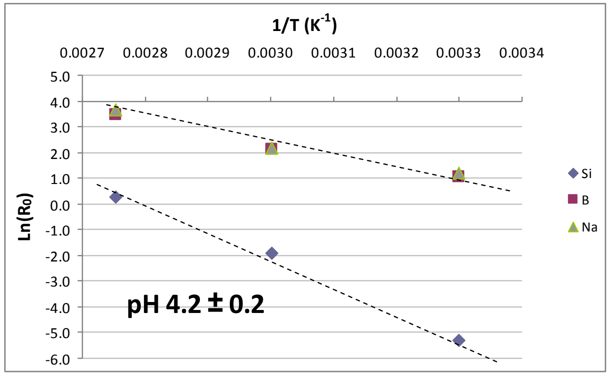
Cmax(Si) = 1% sat

90°C pOH 3.3



Cmax(Si) << 1% sat





Evidences of interdiffusion far from saturation

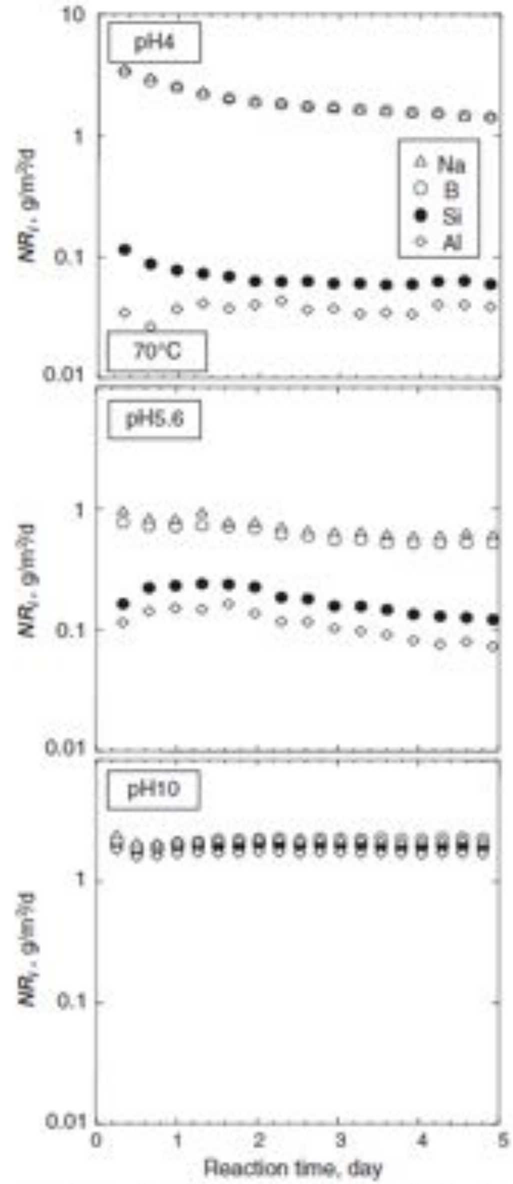


Fig. 4. Normalized dissolution rate of B, Na, and Al as well as Si at 70°C as a function of reaction time and pH.

International simple glass
Microchannel flow through test @ 70°C

ISG glass composition (wt%)

SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
56.2	17.3	12.2	6.1	5.0	3.3

$$\text{-Si-O-M}^+ + H^+ \rightarrow \text{-Si-O}^- + M^+ + OH^-$$

$$\text{-Si-O-M}^+ + H_3O^+ \rightarrow \text{-Si-OH} + M^+ + H_2O$$

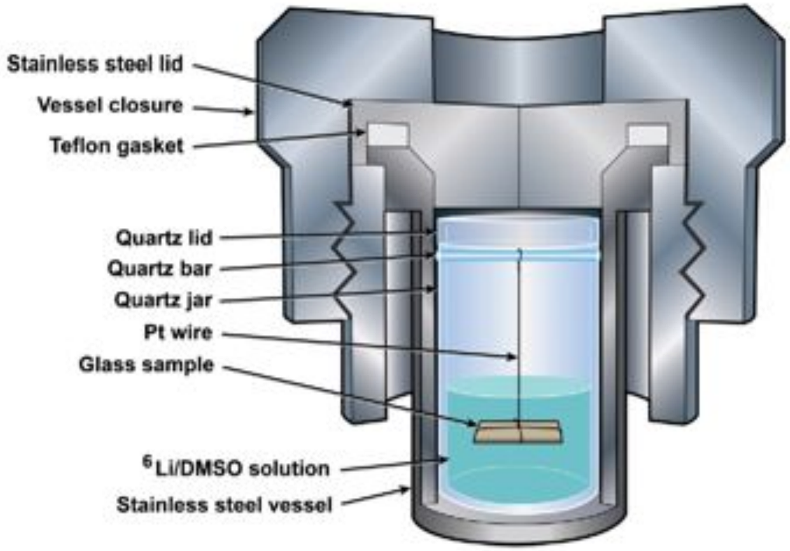
	E_a (kJ/mol)		
	Protonated	Neutral	Deprotonated
$^3B(Q^1)$-O-$^3B(Q^3)$	23	102	39
$^3B(Q^2)$-O-$^3B(Q^2)$	18	129	145
$^3B(Q^2)$-O-$^3B(Q^3)$	53	98	115
$^3B(Q^3)$-O-$^4B(Q^4)$	60	113	–
$^3B(Q^2)$-O-Si(Q^3)	60	106	108
$^3B(Q^2)$-O-Si(Q^4)	80	102	120
$^4B(Q^4)$-O-Si(Q^2)	72	151	–

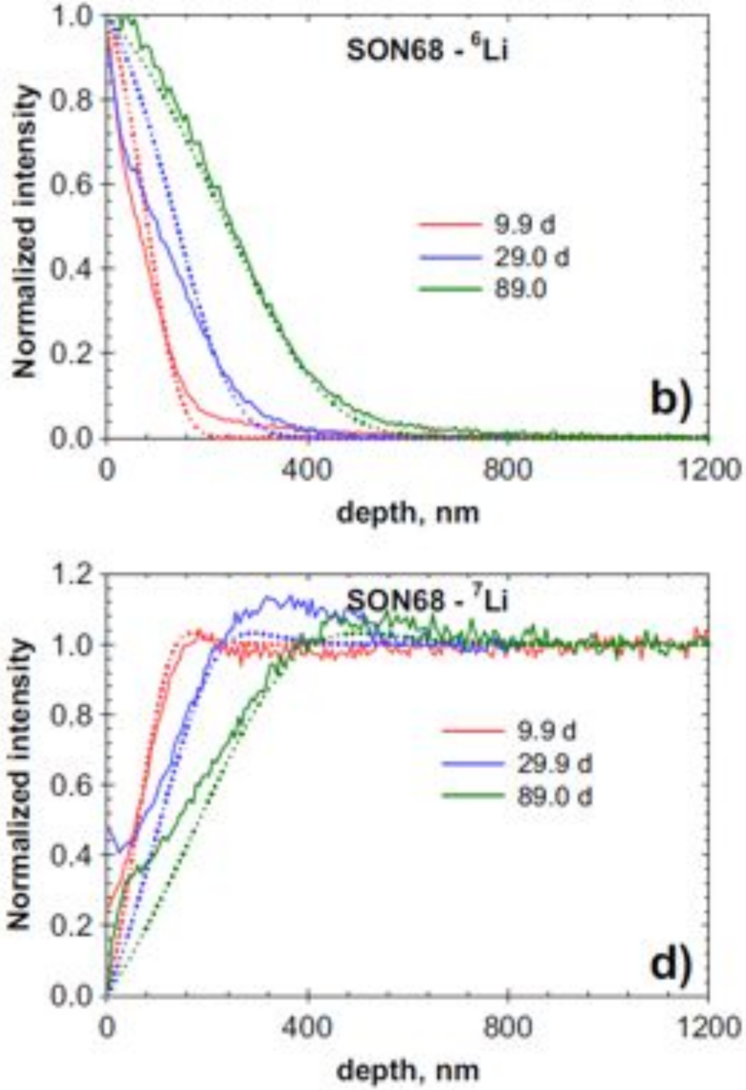
✶ Interdiffusion involves Alk, Alk earths and B

Inagaki et al., *Intern. J. Applied Glass Sci., 4* (2013)
Geneste et al., J. Non-Cryst Solids (2006)
Zapol, *Intern. J. Applied Glass Sci., 4* (2013)

Evidences of interdiffusion without water

^{7}Li-doped SON68 glass in DMSO solution tagged with ^{6}Li





$$D_{interdiff} = 2\text{-}4 \times 10^{-20}\ m^{2}.s^{-1}$$

Neeway et al., J. Non-Cryst Solids 405 (2014)

Evidences of interdiffusion far from saturation

SON68 glass coupons altered @ 50°C and characterized by XRR

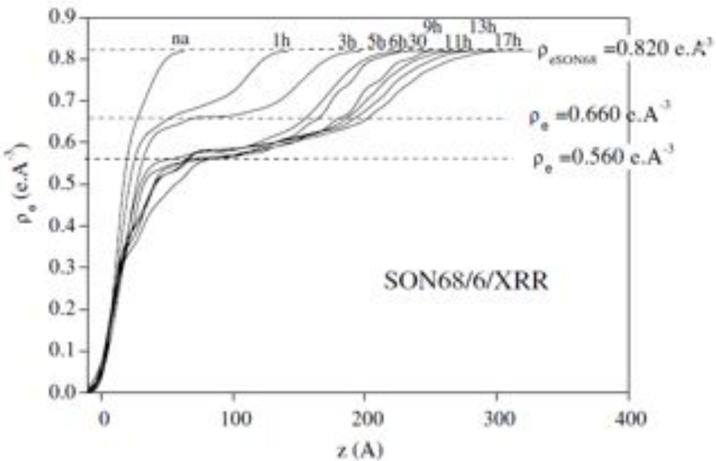


Fig. 11. Evolution of the electron density ρ_e of the altered glass for the SON68/6/XRR test.

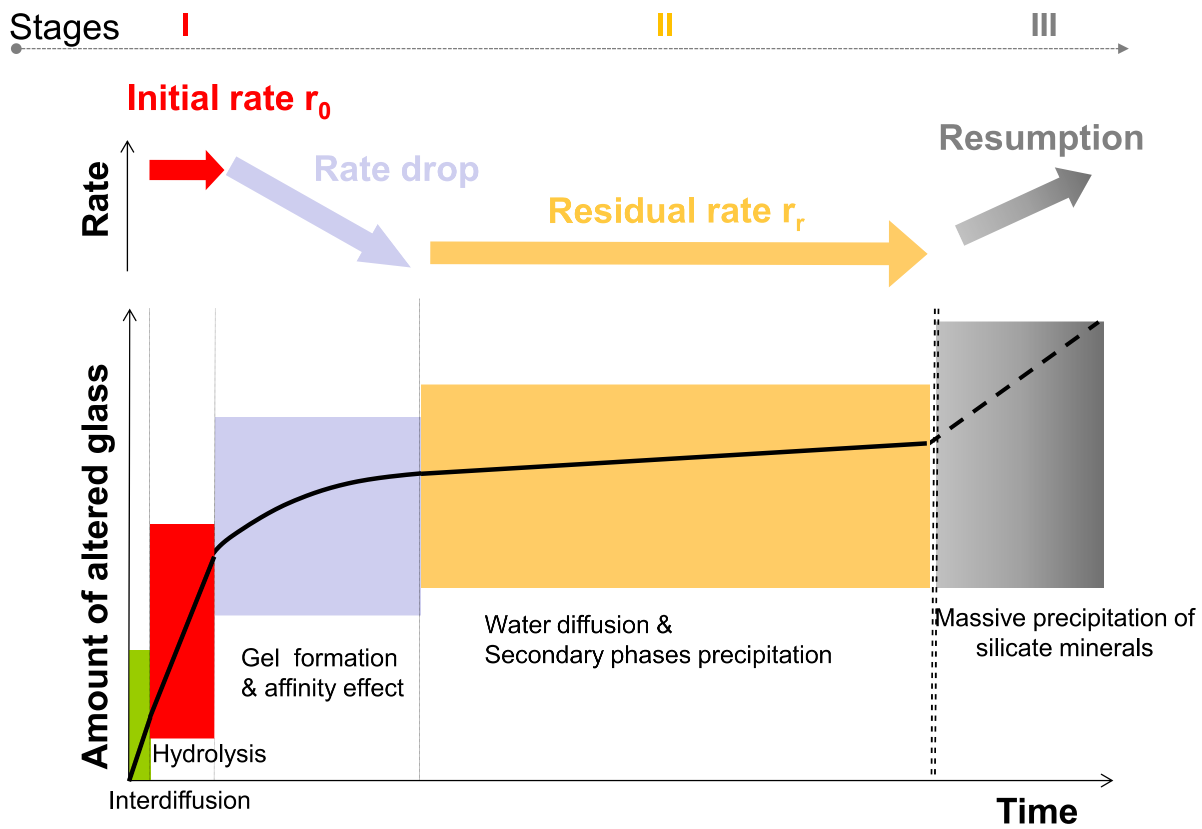
Water Diffusion coefficient in glass 1, 2 and SON68 at pH 3.2 and 5.7 at 50 °C

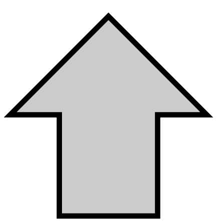
	pH/pD	3.2	5.7
H_2O	Glass 1		$(1.5 \pm 0.2) \cdot 10^{-19}\ m^2\ s^{-1}$
	Glass 2	$(9.8 \pm 0.5) \cdot 10^{-20}\ m^2\ s^{-1}$	$(3.5 \pm 0.7) \cdot 10^{-20}\ m^2\ s^{-1}$
	SON68	$(5.1 \pm 0.4) \cdot 10^{-20}\ m^2\ s^{-1}$	$(6.5 \pm 0.7) \cdot 10^{-21}\ m^2\ s^{-1}$
D_2O	Glass 1	–	–
	SON68	$(1.5 \pm 0.4) \cdot 10^{-20}\ m^2\ s^{-1}$	–

- Interdiffusion involve alkali, alkaline earths and B
- It is favoured under acidic conditions
- For SON68 glass *Dw* is of the order of 10^{-20} m^2/s at 50°C and 10^{-19} m^2/s at 90°C

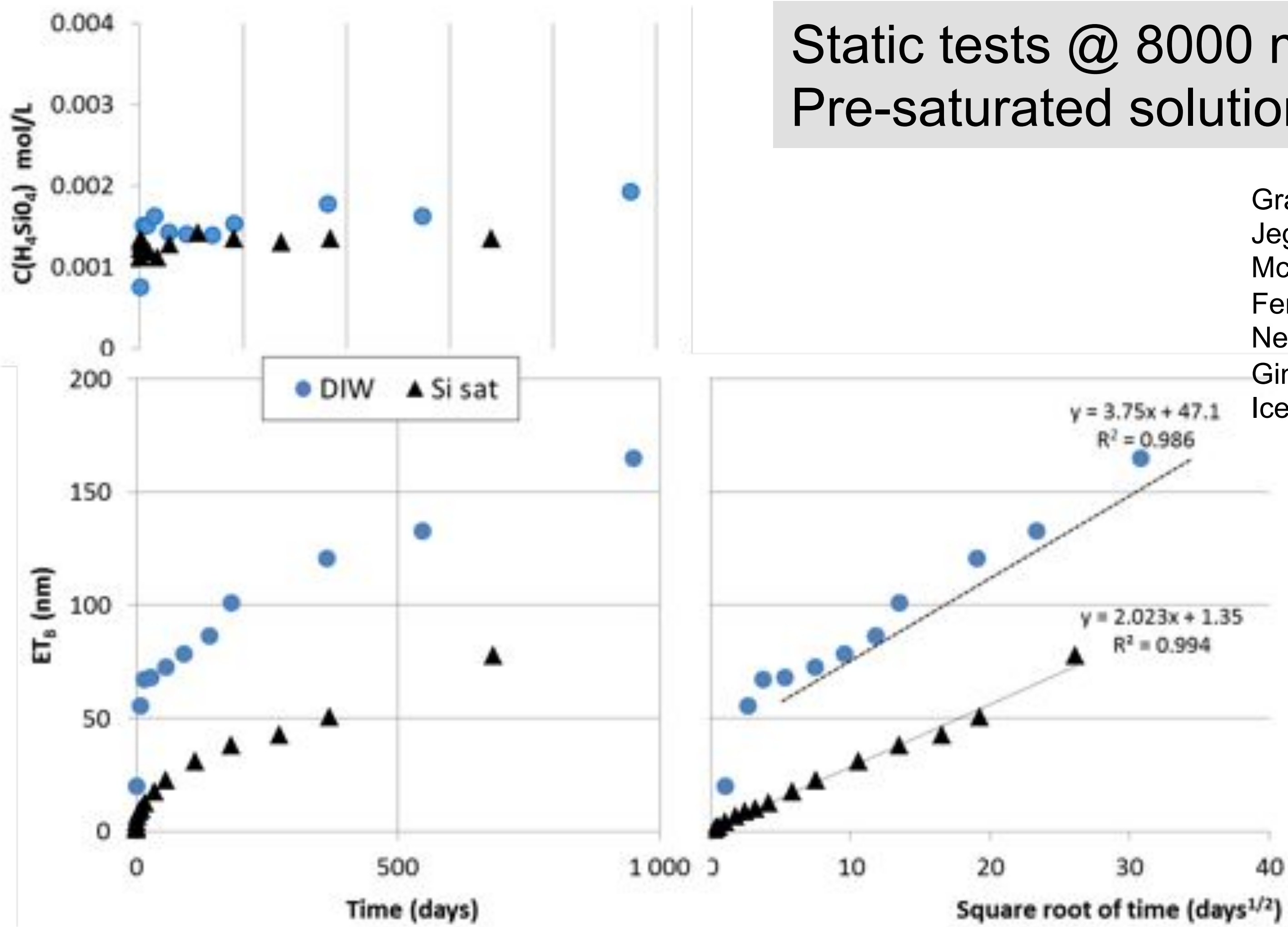
Rebiscoul et al., J. Non-Cryst Solids *353* (2007)

What happens 'close to equilibrium'?





3 processes causing the drop of the rate
1 : Effect of Si

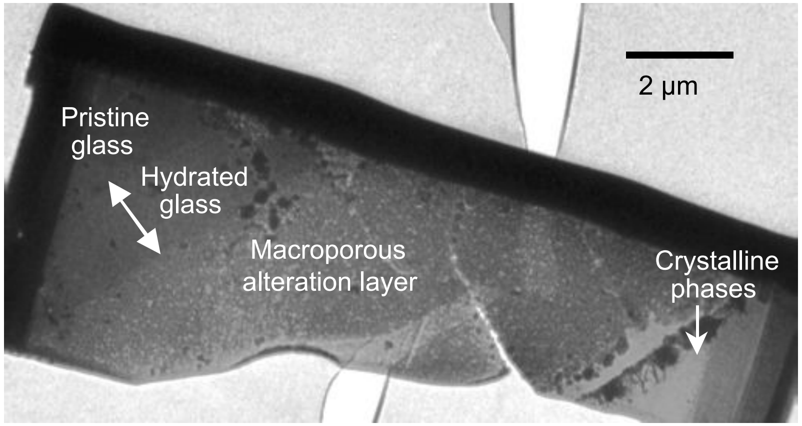


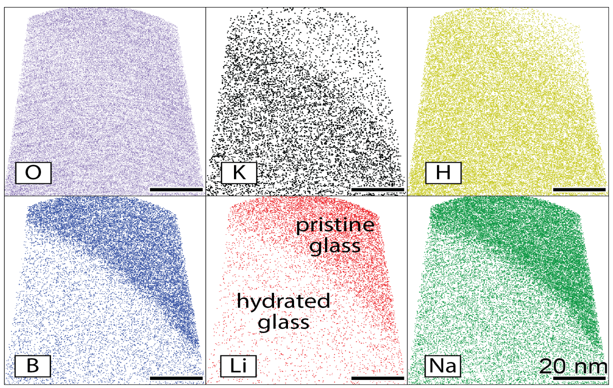
Static tests @ 8000 m^{-1}, 90°C, 3y
Pre-saturated solution vs DIW

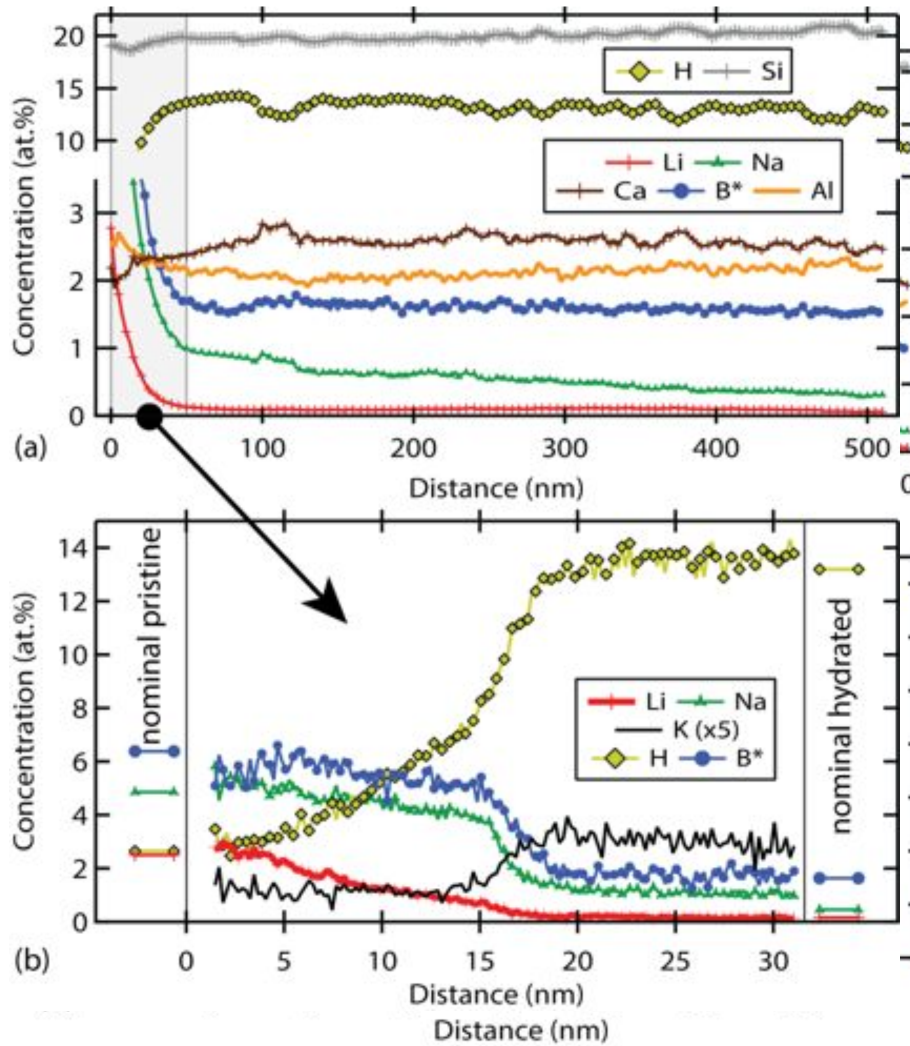
Grambow et al., MRS proc. 1985
Jegou, Thesis 1998
Mc Grail et al., JNCS 2001
Ferrand et al., JNM 2006
Neeway et al., JNM 2011
Gin et al., IJAGS 2013
Icenhower et al, JNM 2014

Pre-sat solution makes the RD stage much shorter but does not impact the RR regime. The first hundreds of days are dominated by interdiffusion

3 processes causing the drop of the rate
2 : formation of a PRI







- Thin (15 nm) diffusion profile of Li, H within the hydrated glass layer: D = $1.5.10^{-22}$ m^2/s (in agreement with GRAAL)
- 2 OM < $D_{interdiffusion}$ at the begining of the dissolution process

Gin et al., Chem. Geol 2013

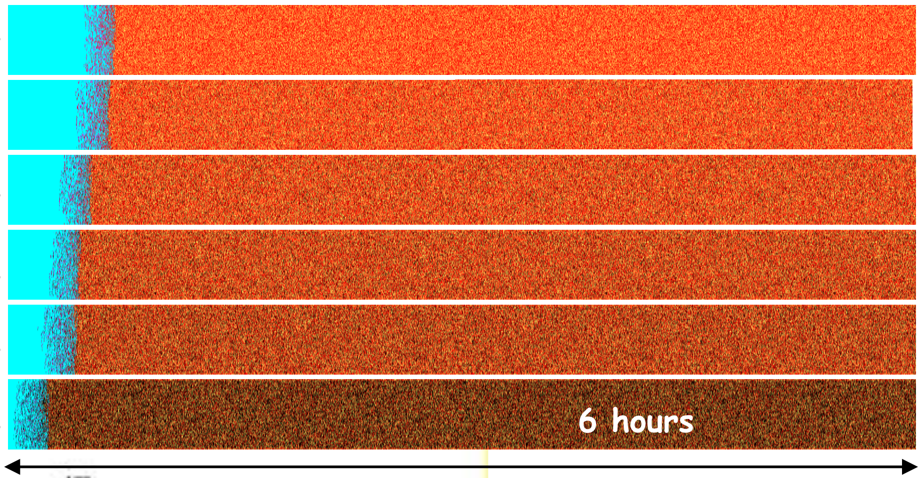
H_2O B
Si Zr
Condensed Si

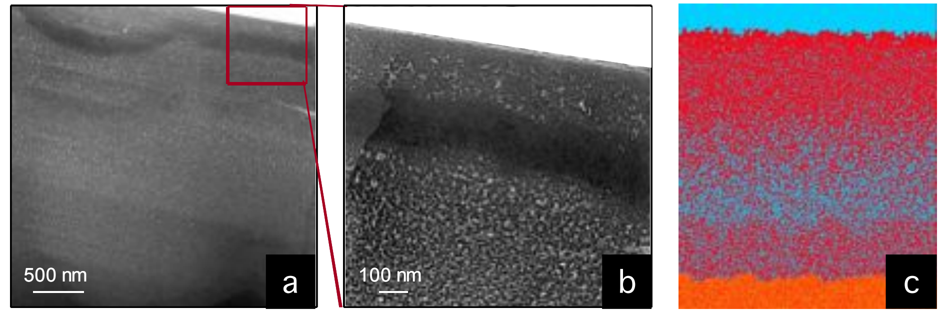
3 processes causing the drop of the rate
3 : Effect of porosity clogging

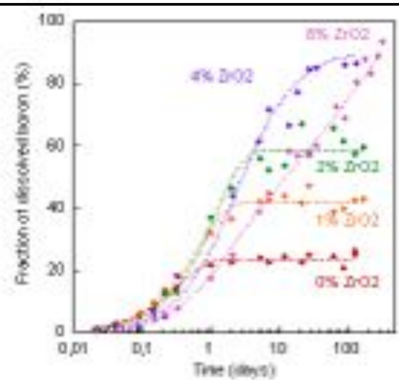
ZrO_2

Forward rate of alteration

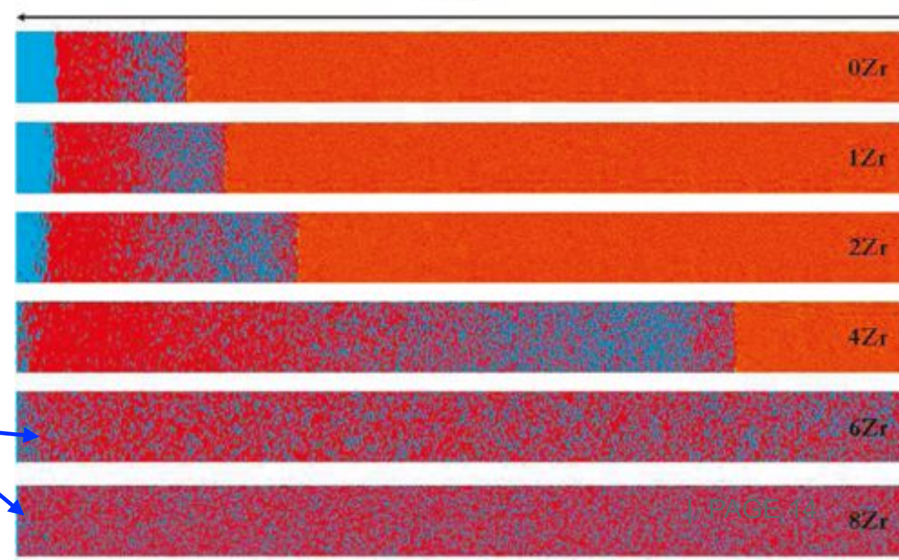
Cailleteau et al. Nature Materials 2008







Porosity clogging: up to 4% of ZrO_2

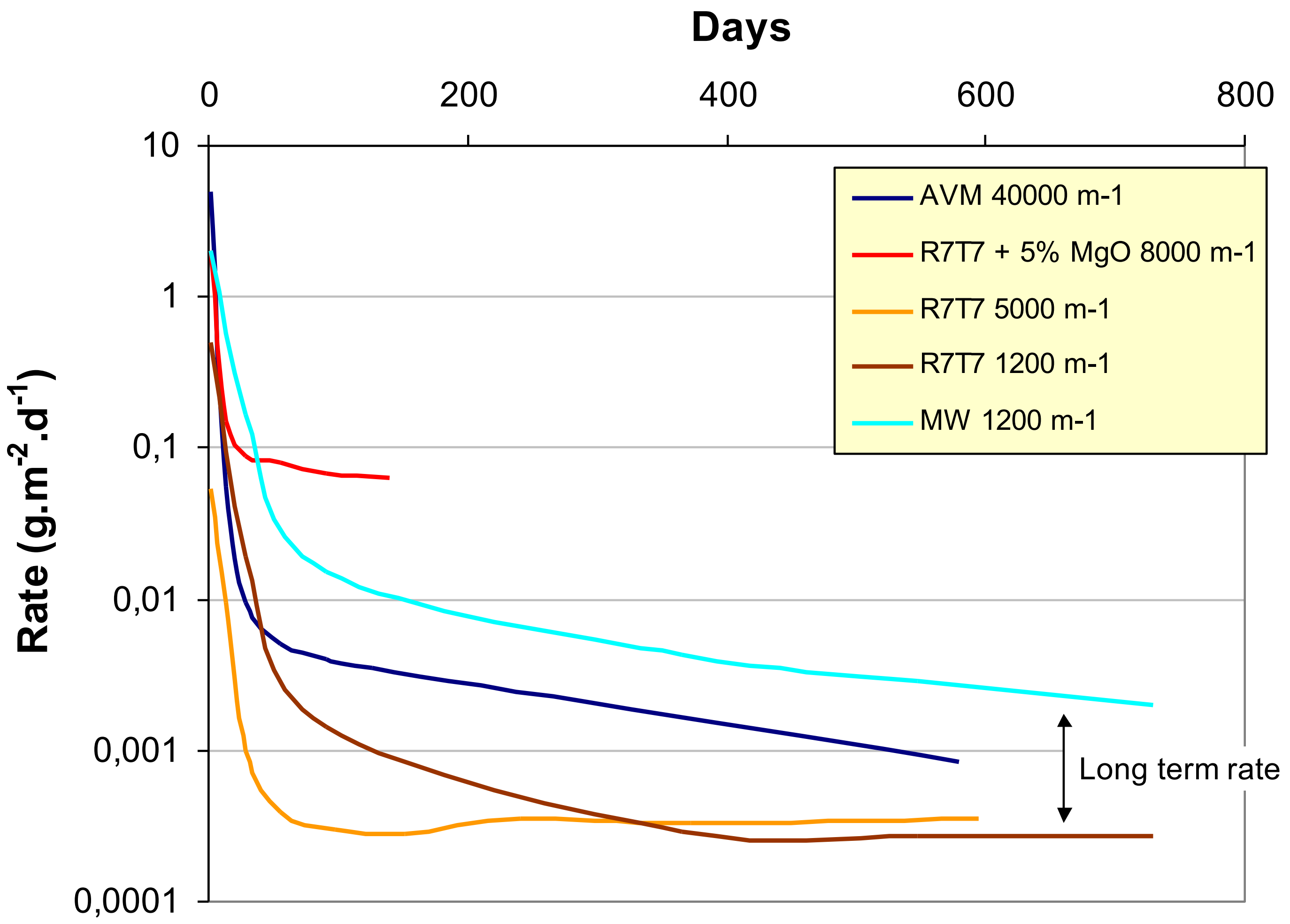


Zr at.: immobilize increasing numbers of Si

-> <u>prevents any reorganization</u>

-> <u>percolation pathways</u>
(leaching sol. - pristine glass surf.)

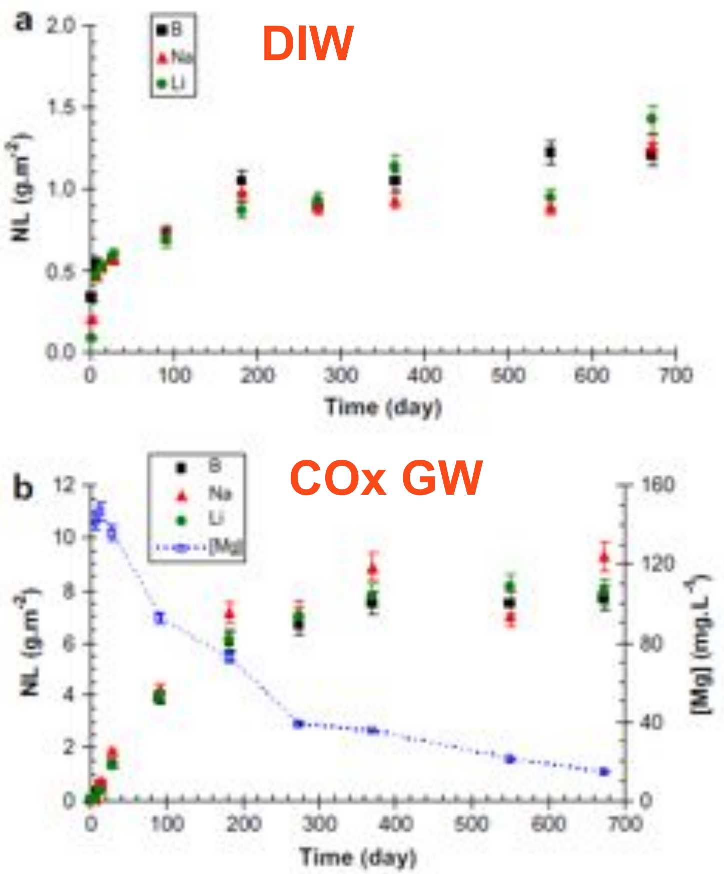
Effect of glass composition on the dissolution rate



Static test
90°C

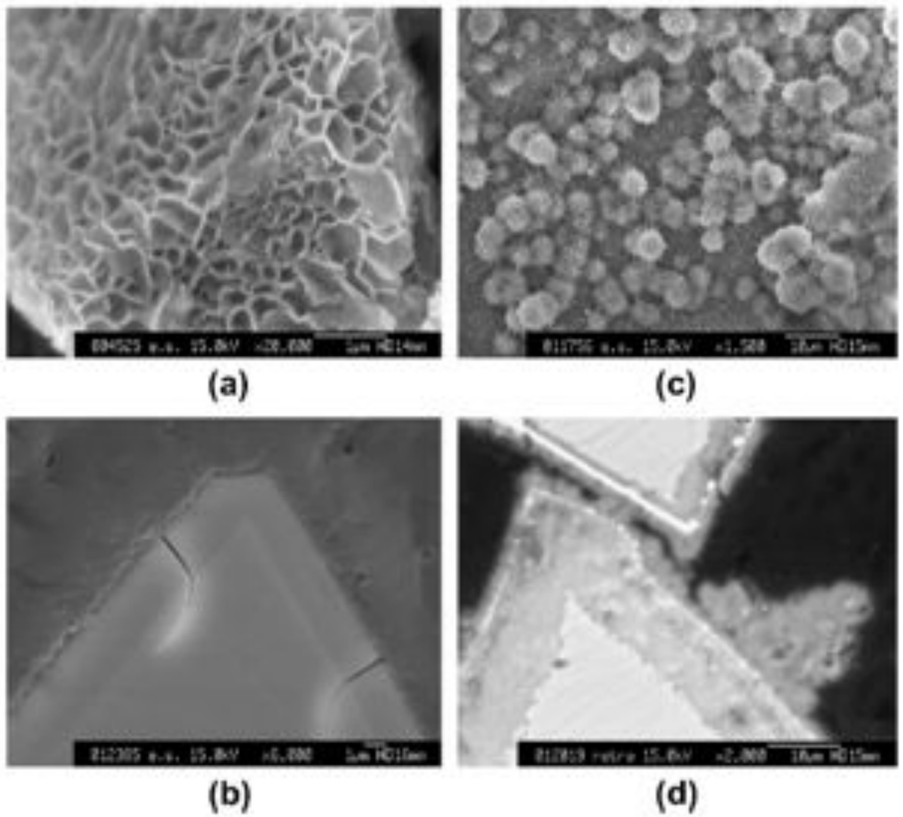
Glass dissolution kinetics strongly depends glass composition (Frugier, JNM 2005)

Effect of COx GW on SON68 glass dissolution rate



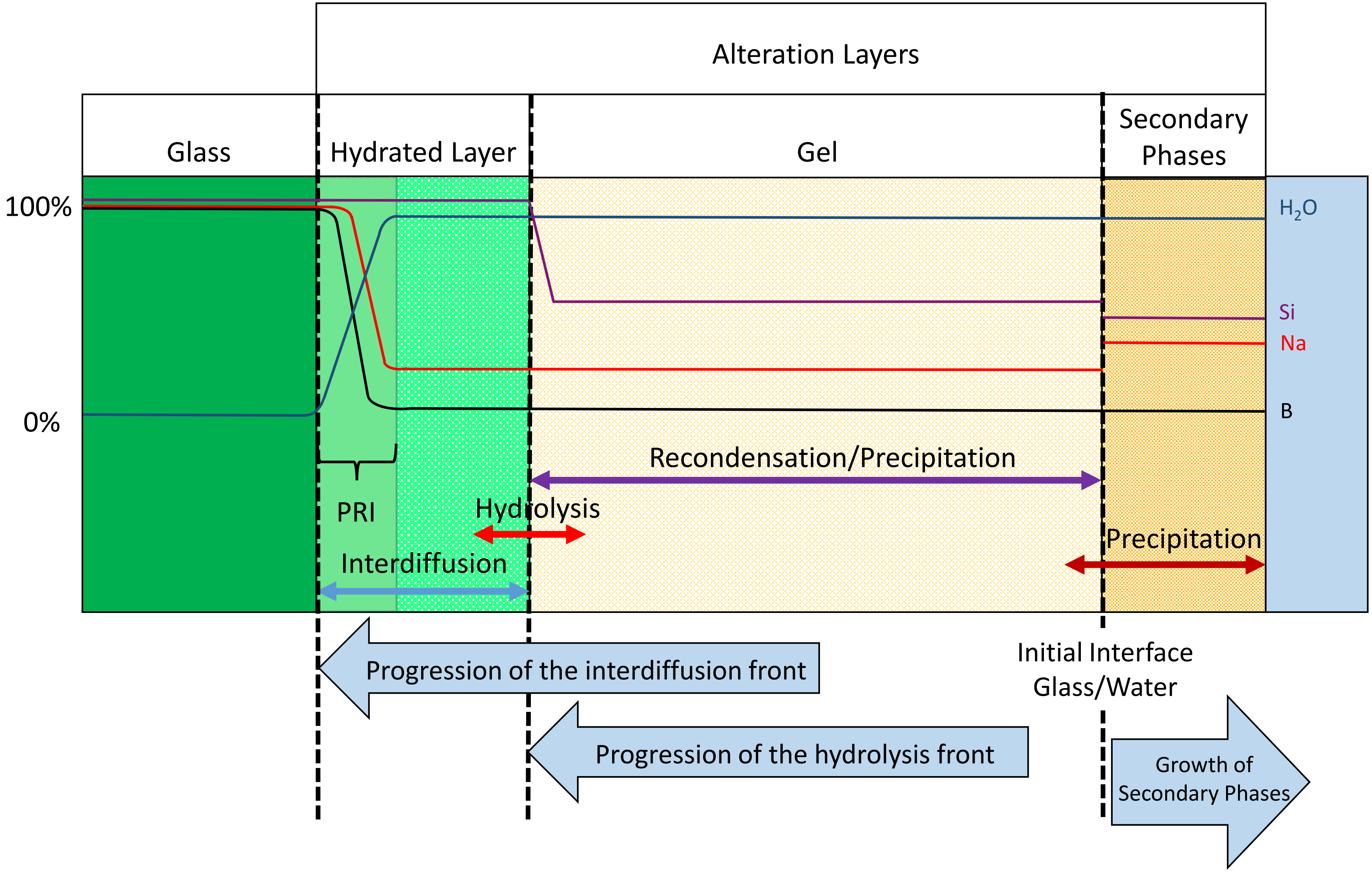
Static tests @ 300 m^{-1}, 90°C

DIW COx GW



★ Mg-silicate precipitation sustains glass corrosion despite similar concentrations of Si

Jollivet et al., J. Nucl. Mater, 420 (2012)



Alteration Layers
Glass
Hydrated Layer
Gel
Secondary Phases
100%
0%
H_2O
Si
Na
B
Recondensation/Precipitation
PRI
Hydrolysis
Interdiffusion
Precipitation
Progression of the interdiffusion front
Initial Interface Glass/Water
Progression of the hydrolysis front
Growth of Secondary Phases

Current controversy

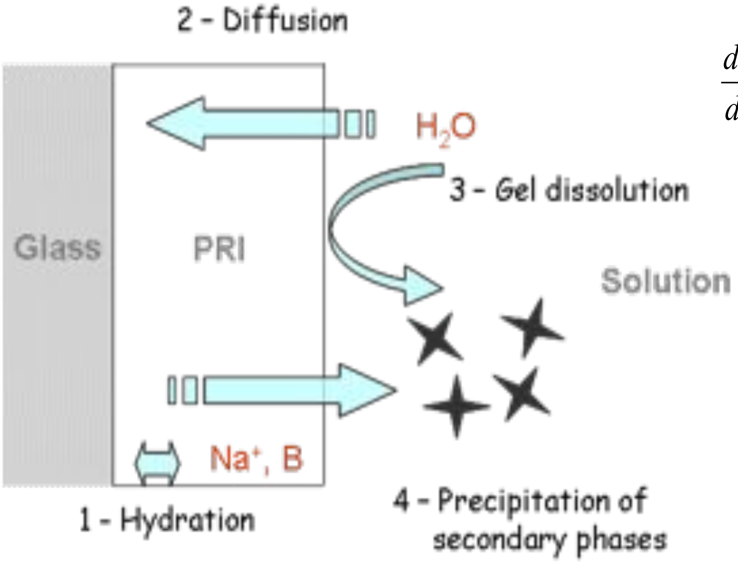
Diffusion / Hydrolysis Condensation / Precipitation

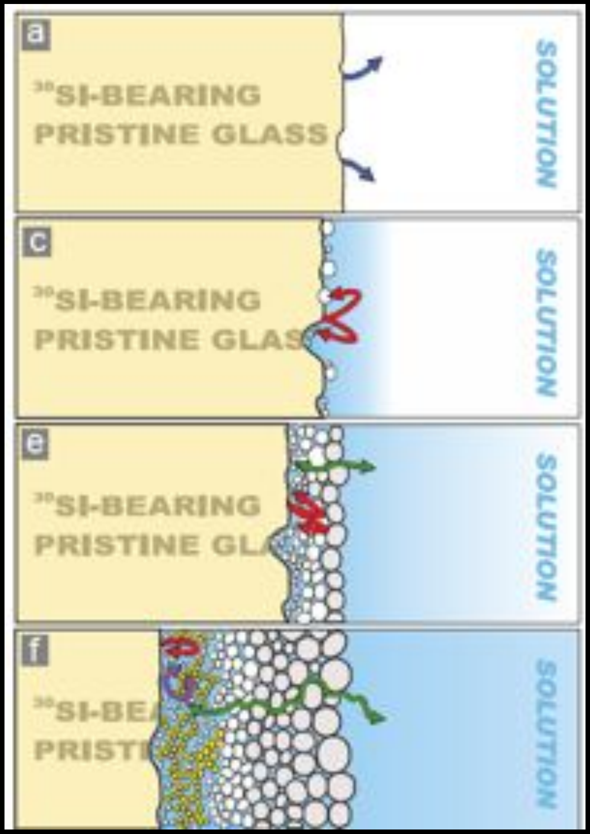
Glass → Hydrated Glass → Gel → Crystalline Phases

Frugier et al., *J. Nucl. Mater.* (2008)
Frugier et al., *J. Nucl. Mater.* (2009)

$$\frac{dE}{dt} = r_{disso}\left(1 - \frac{Q_{PRI}}{K_{PRI}}\right)$$

$$\frac{de}{dt} = \frac{r_{hydr}}{1 + \frac{e \cdot r_{hydr}}{D_{PRI}}} - \frac{dE}{dt}$$





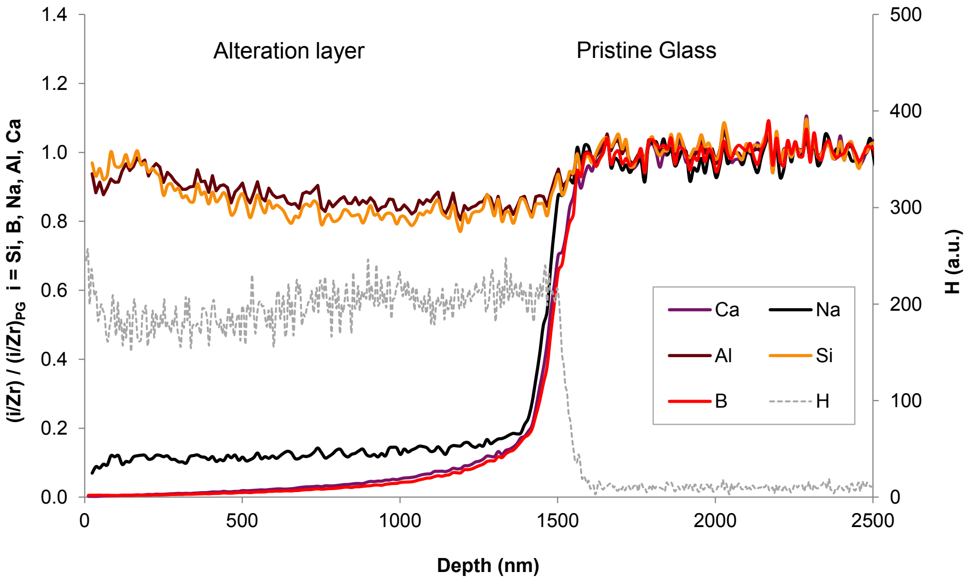
Dissolution / Precipitation

Glass → Gel + Crystalline Phases

Geisler et al., *J. non-Cryst. Solids* 356 (2010)
Hellmann et al., *Nat. Mater,* (2015)

About the interfacial film of water

- Under silica saturation conditions it is impossible to separate the hydrated glass from the pristine glass (micro-scratch test). PhD Thesis of Diane Rebiscoul
- There is a significant decrase of H in the interfacial zone (PRI)



★ ISG, altered 6 months at pH 7 90°C, Si sat solution

- Under silica saturated conditions, there is no isotopic evidence of interfacial precipitation of silica

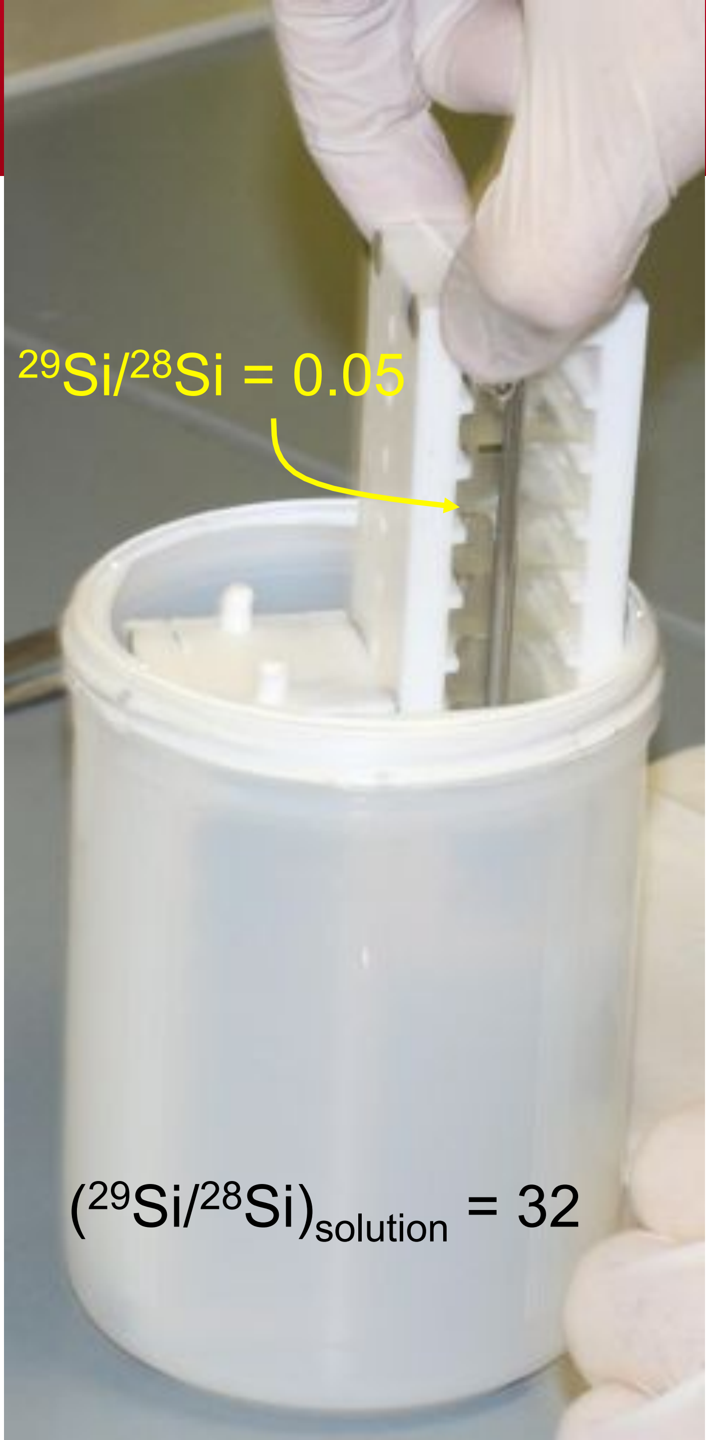
New experiments

Gin et al., *Nature Comm. 6* (2015)

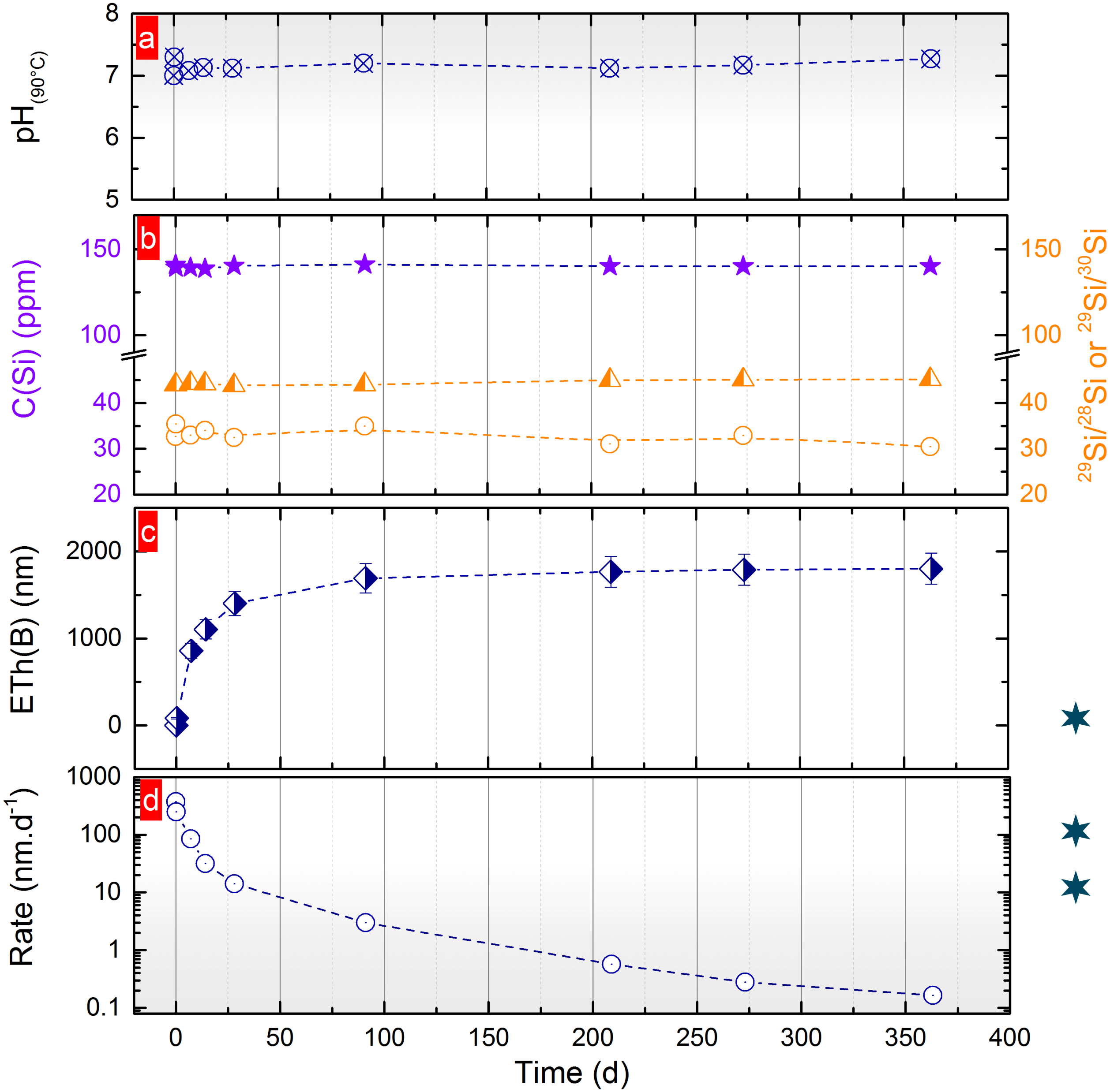
- International Simple Glass (ISG)
- 16 glass coupons have been altered at 90°C in 380 mL of solution initially saturated / ($^{29}SiO_2$)am at $pH_{90°C}$ 7
- $S/V = 0.6\ cm^{-1}$
- Isotope sensitive analytical techniques: MC-ICP-MS and ToF-SIMS, NMR
- Similar experiments run at $pH_{90°C}$ 9 and 11.5
- For NMR studies, similar exp. with a 5μm glass powder

ISG glass composition (wt%)

SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
56.2	17.3	12.2	6.1	5.0	3.3

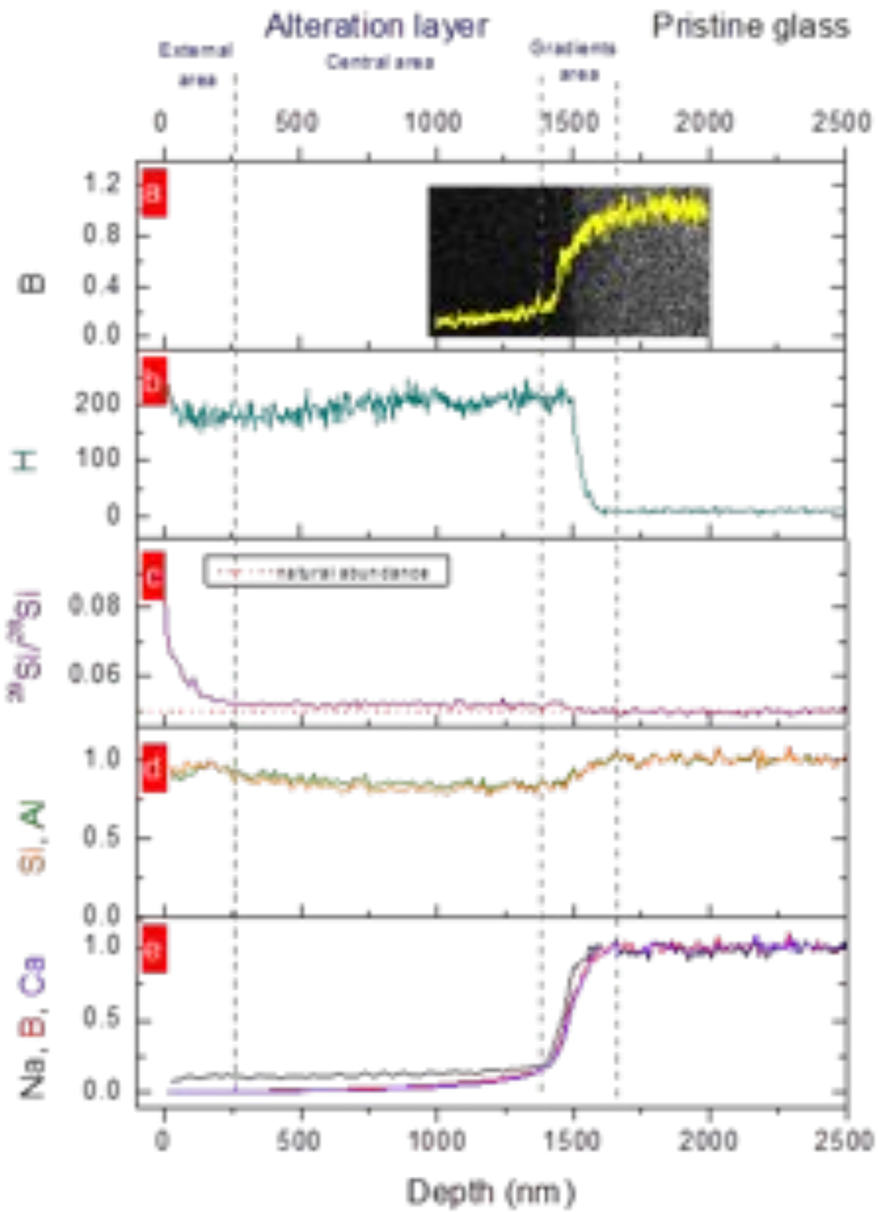


Solution data

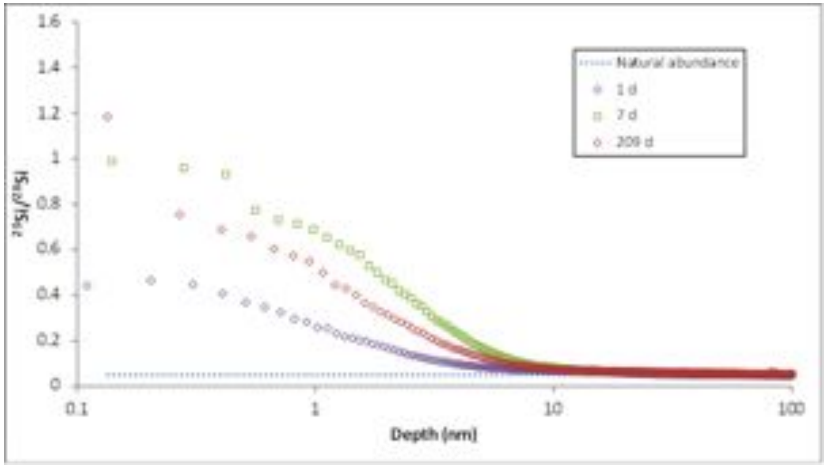


- pH and $C^{tot}(Si)$ and $C(^{29}Si)$ are stable
- The rate drops by 3 OM
- ETh reaches 1.5 µm

Solid analysis of the 209d sample

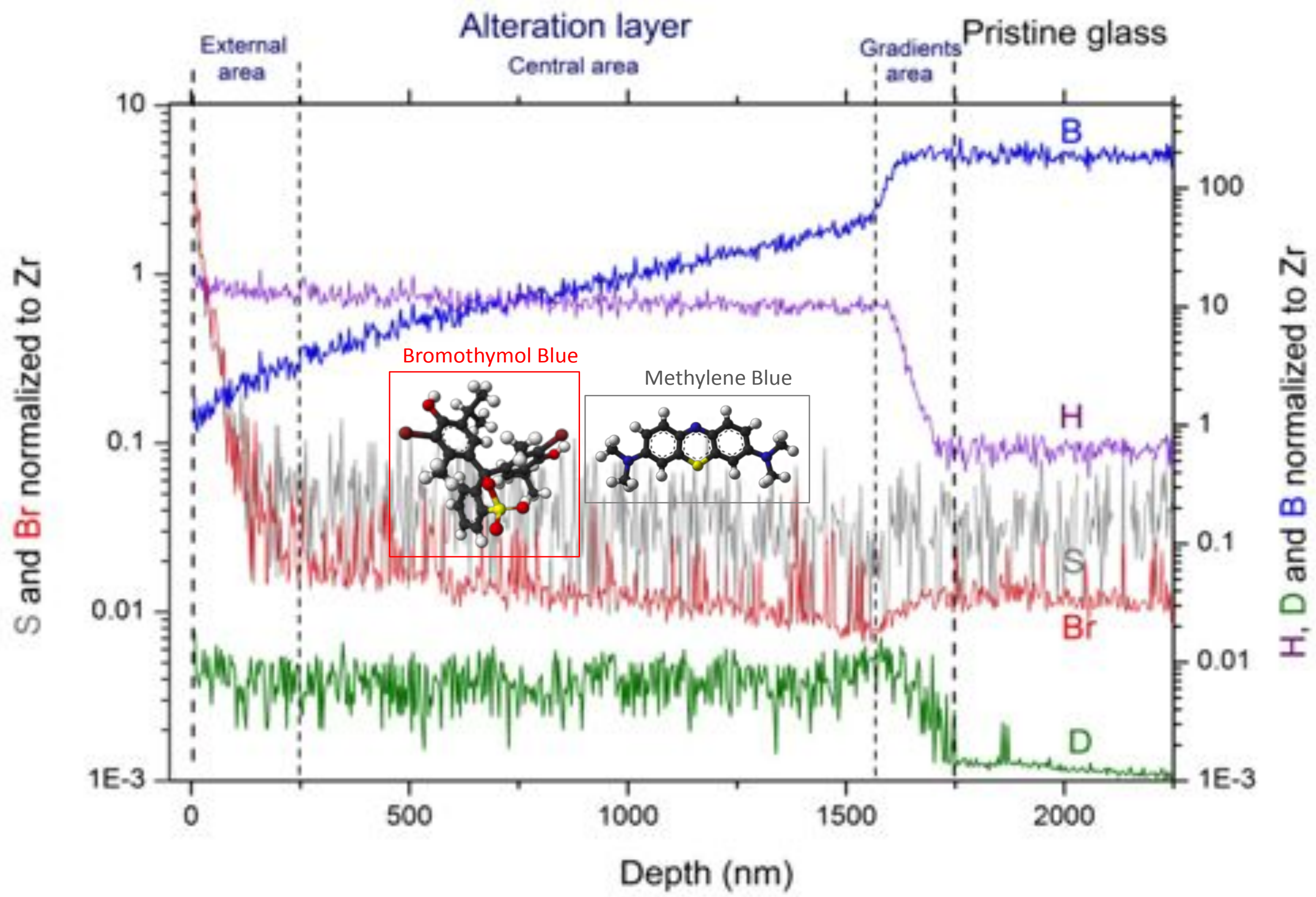


- B, Na, Ca are released congruently
- H displays an opposite profile
- A tiny amount of ^{29}Si diffuses into the AL
- No Si isotopes equilibration
- ToF SIMS profiles are confirmed by TEM



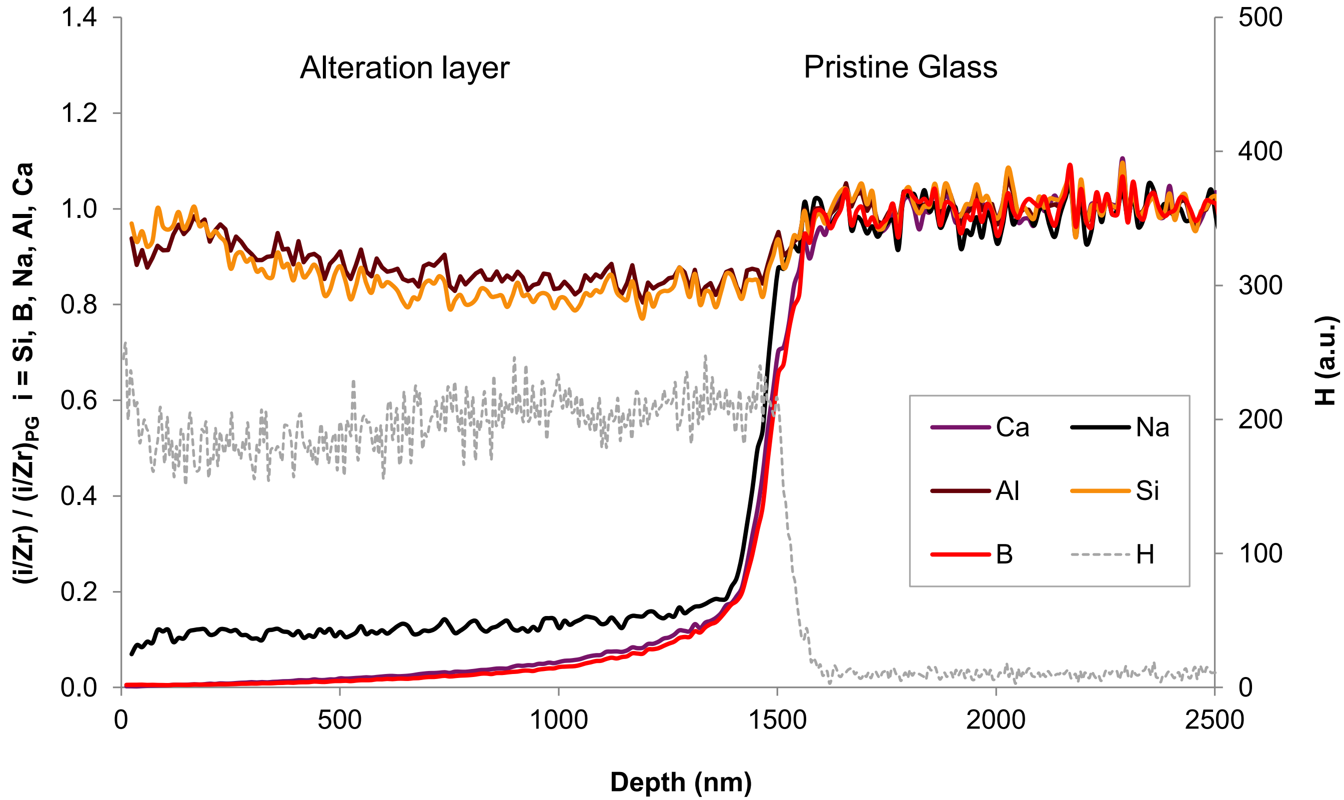
$[^{29}Si/^{28}Si]_{sol} = 32$

How exogenous molecules diffuse through the AL?



- Only small molecules can diffuse up to the corrosion front
- Pore size is < 1nm
- No free water molecules within the alteration layer

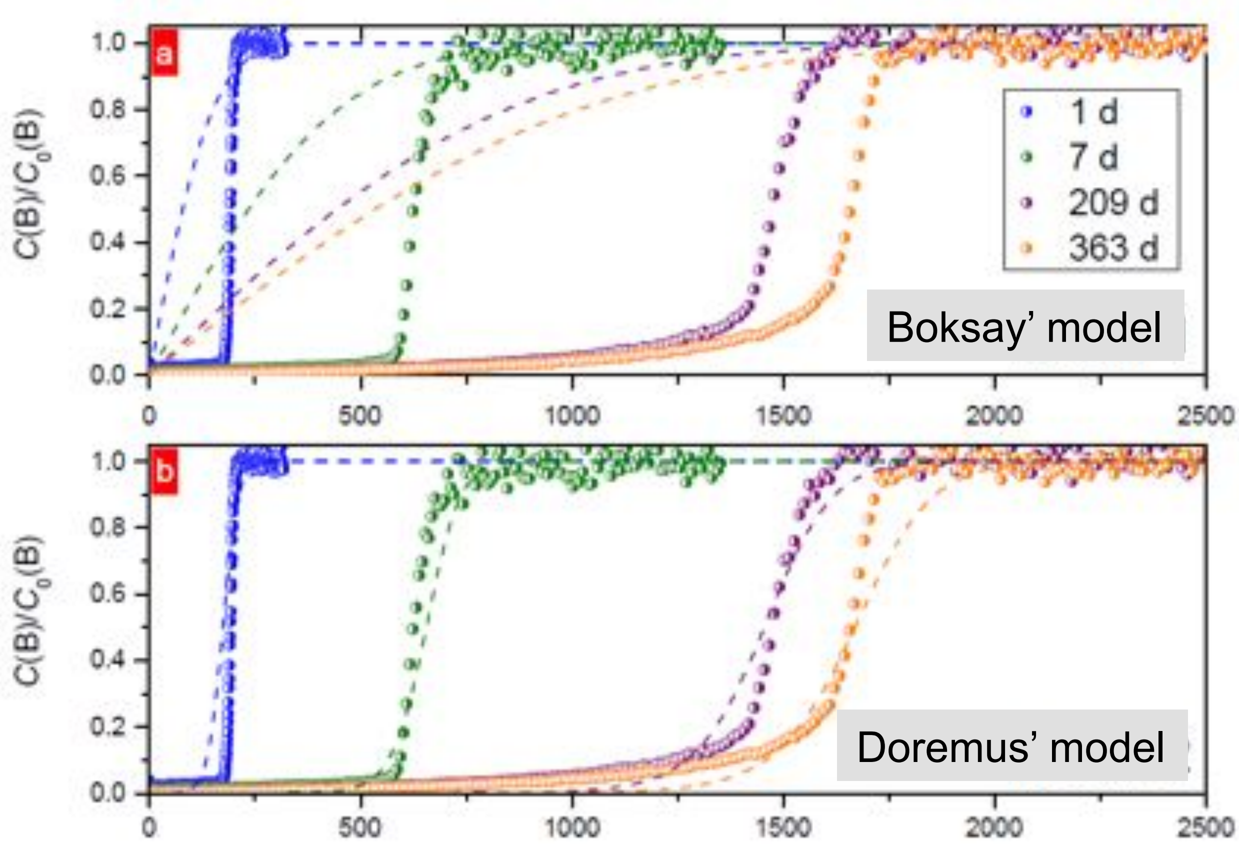
Why AL passivates glass?



- B, Na, Ca are released congruently (despite their different structural role)
- H displays an anticorrelated profile
- Dw in the pristine glass (90°C and pH 7) ~ 6 10^{-19} $m^2.s^{-1}$ (from Rebiscoul work)

B profiles
ISG Glass altered @ 90°C, pH 7 in SiO_2am sat solt

Gin et al., *Nature Com. 6* (2015)



$C(\mathrm{B})/C_0(\mathrm{B}) = \mathrm{erf}(z/2$

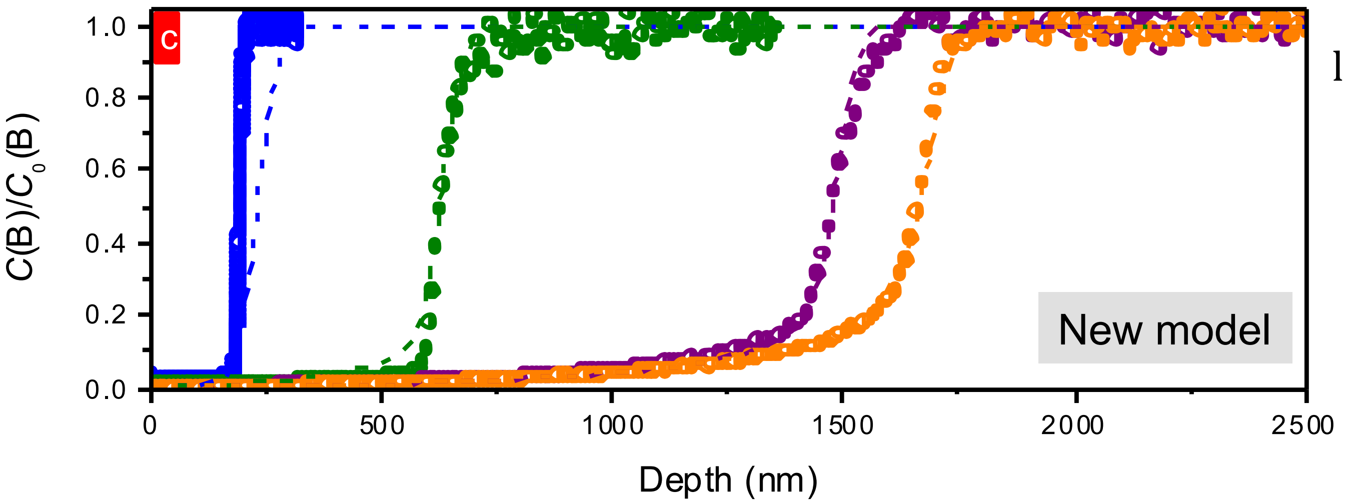
D = 6 10^{-19} $m^2.s^{-1}$

$C(\mathrm{B})/C_0(\mathrm{B}) = 1 - \mathrm{erfc}(z$

$b = D/D_w - 1$

$D_w = 10^{-21}$ $m^2.s^{-1}$
b = 40000

✶ Classical diffusion models fail to fit experimental profiles

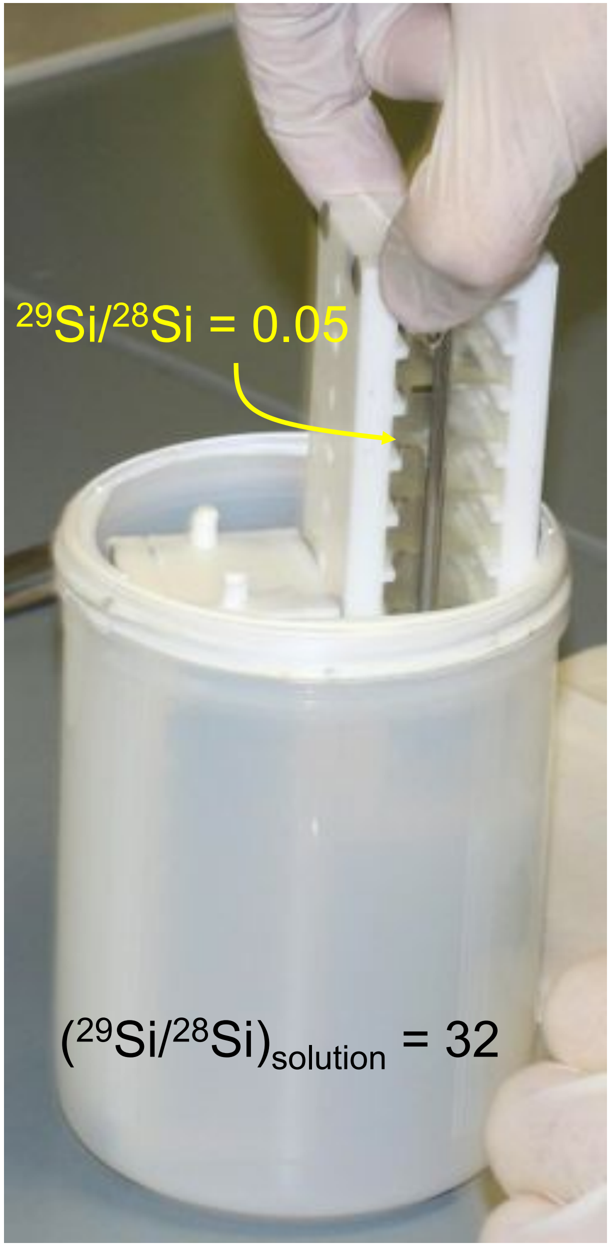


$$\log_{10}\frac{D}{D_{\max}} = -\beta\left(\frac{C(\mathrm{w})}{C_0(\mathrm{w})}\right)^{-\frac{1}{\alpha}}$$

D_{max} = 7 10^{-19} $m^2.s^{-1}$
α = 1.9
β = 4.6

- ✶ *D* drops by about 5 O.M. from the outermost AL to the reactive interface
- ✶ *D* remains 5 to 9 O.M. lower than D_{He} in the pristine glass

- ✶ Reactive transport at nanoscale must be better understood



Consequences of the pH rise?

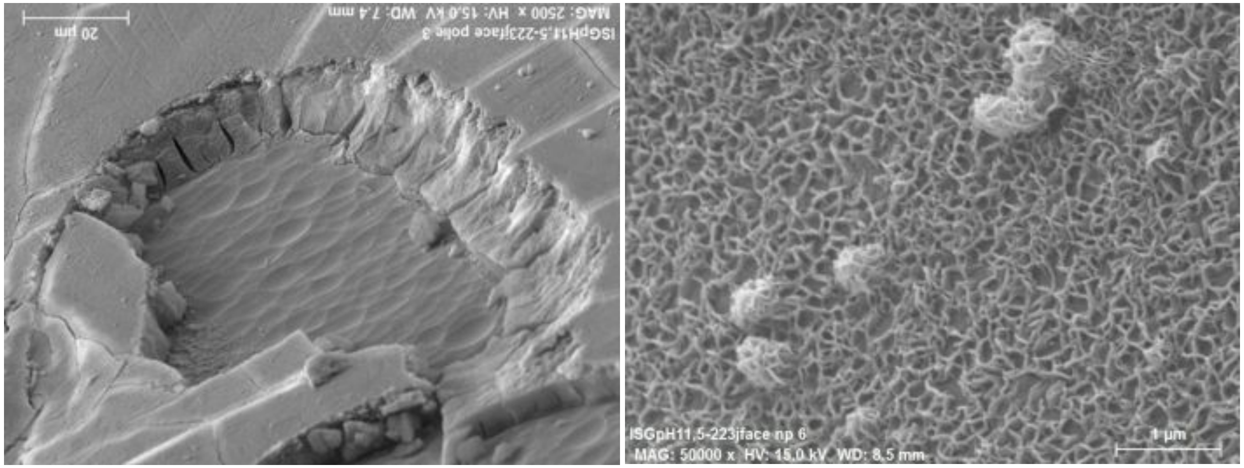
ISG glass altered à 90°C
in a SiO_2am sat solution

Stage 1 : 209d @ pH 9

Stage 2 : pH raised to 11.5

Gin et al., *Geochim. et Cosmochim. Acta* (2015)

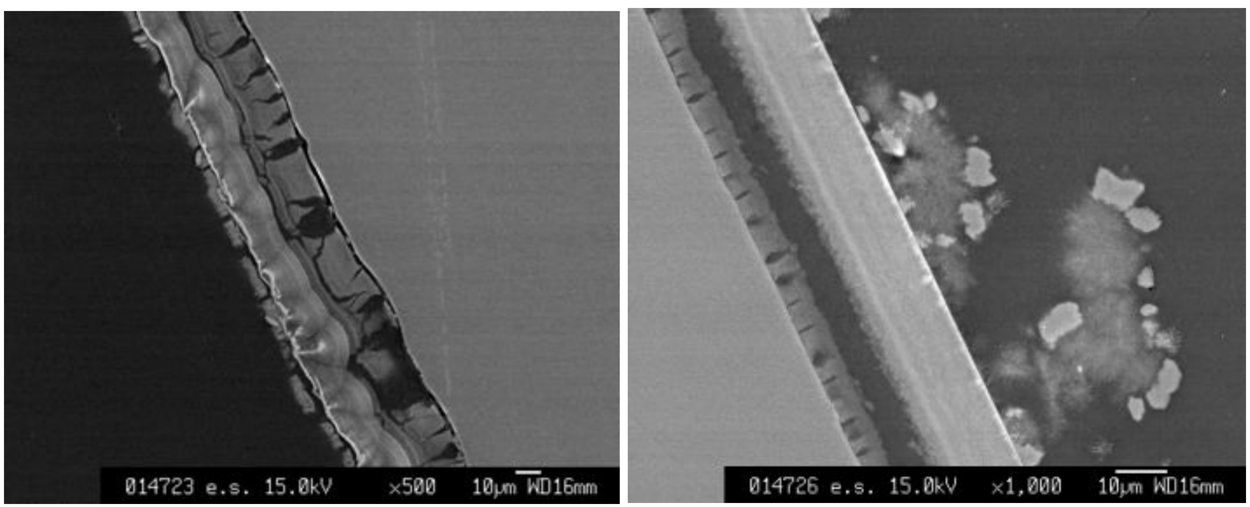
Morphological evolutions (pH$_{90°C}$ 11.5)



Δt = 14 d

E = 10 µm

CSH

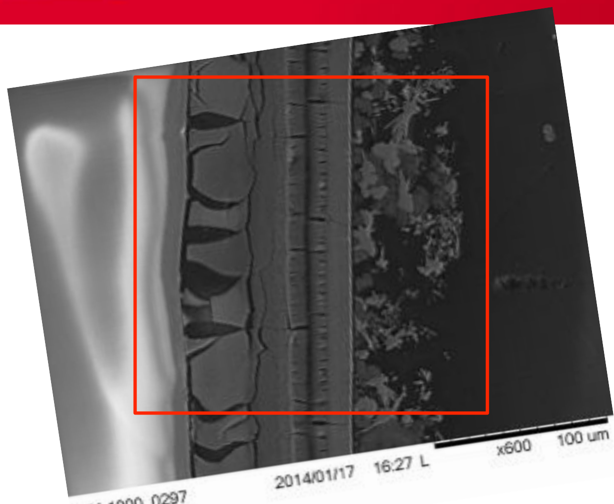


Δt = 52 d

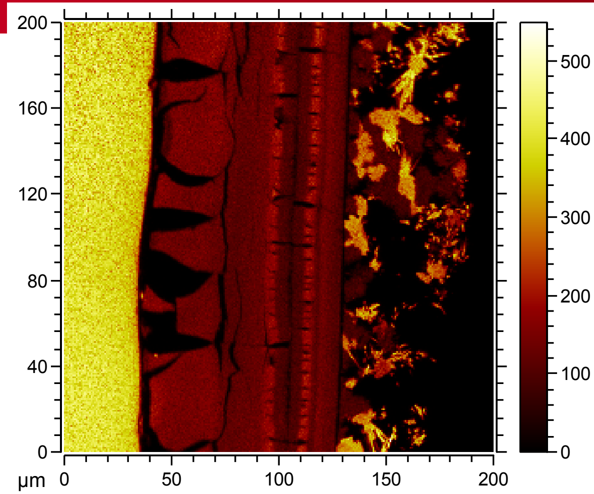
E = 25-35 µm

CSH, Zéolithes

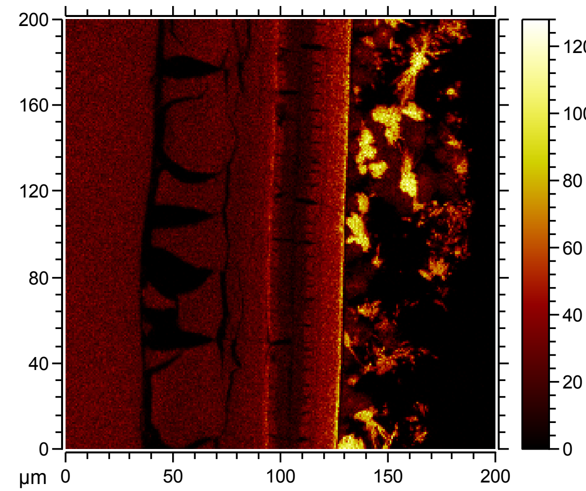
ToF-SIMS elemental & isotopes mapping ($pH_{90°C}$ 11.5)



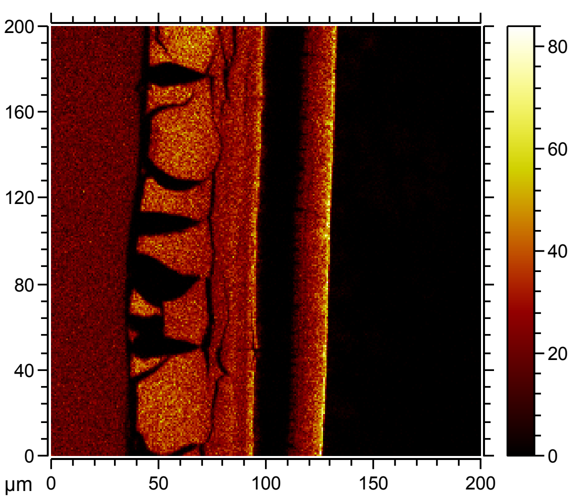
SEM image after SIMS



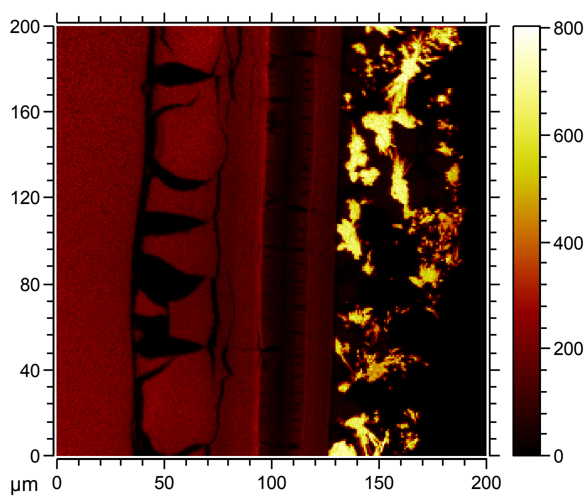
Si+
MC: 549; TC: 9.453e+006



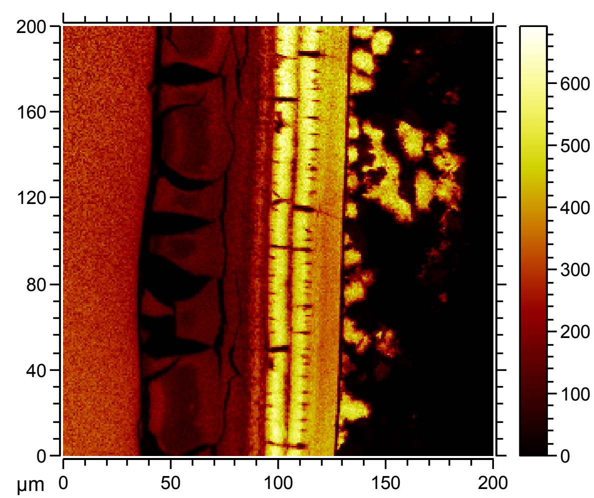
$^{29}Si+$
MC: 128; TC: 1.227e+006



Zr+
MC: 84; TC: 8.289e+005

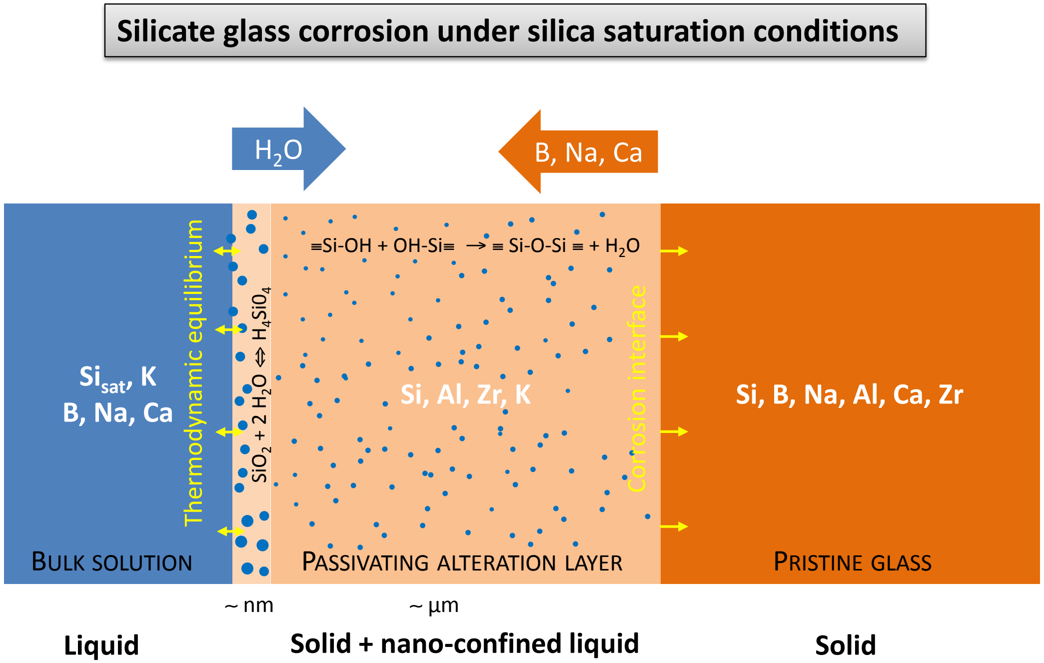


Al+
MC: 804; TC: 8.346e+006



Ca+
MC: 693; TC: 1.175e+007

Conclusion - Outlook



- At $pH_{90°C}$ < 10: passivation (tied to nanoconfinement of water) is the main mechanism controlling the glass dissolution rate. The properties of nanoconfined water must be better understood.
- At $pH_{90°C}$ > 10: the 'new' dissolution/precipitation paradigm proposed by Hellmann, Geisler, Puntnis is likely valid.

Conclusions

- Passivation means that water access to the pristine glass is hindered by the alteration layer
- Under Si sat solution the alteration layer forms by interdiffusion and self-reorganization of the hydrated silicate network
- The hydrated glass slowly transform into more stable amorphous and crystalline phases
- Water diffusion through the altered glass = solid state diffusion.
- The gradient area can be seen as a reaction front but there is no evidence of a film of water
- Controversy or not controversy?

Initiatives at the international level

Workshops

Seattle (2009), Warrington (2010), Savannah (2011), Saint Louis (2012), San Diego (2013), Aachen (2014), Miami (2015). **Next: Madison (May 2016)**

Publications

General paper published in Materials Today

Special issue of IJAGS (by the end of 2013)

International Simple Glass (6 oxide borosilicate glass)

Synthesis (SRNL): 2012

Ongoing studies: SRNL, PNNL, ORNL,

Penn State Univ., Kyushu Univ., CEA, Subatech,

SCK, AMEC, Sheffield Univ., Cambridge Univ.

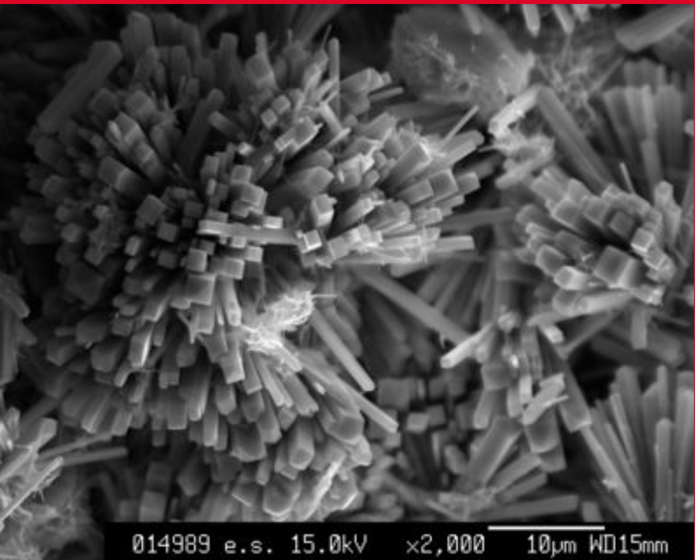
Several Bilateral collaborations

PNNL / CEA, PNNL/SCK, Kyushu Univ. / LBNL

Other

Visit of scientists, joint thesis, Coordinated Research Project

IAEA International Atomic Energy Agency



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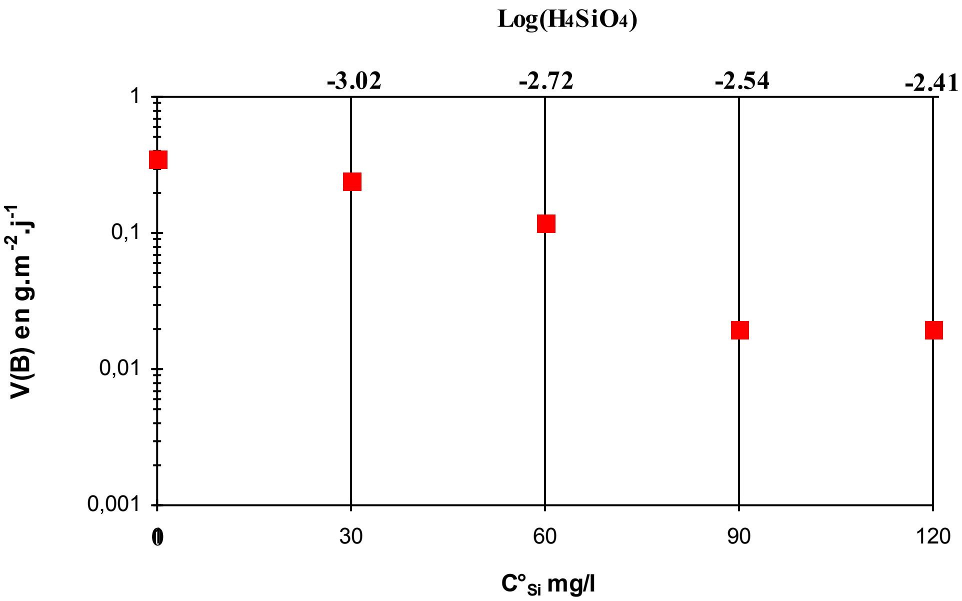
Areva, Andra, EdF

THANK YOU!

Effects of Si on the glass dissolution rate

SON68 glass
SPTF test with solutions spiked with Si, pH 8
Q/S = 10^{-2} m/d

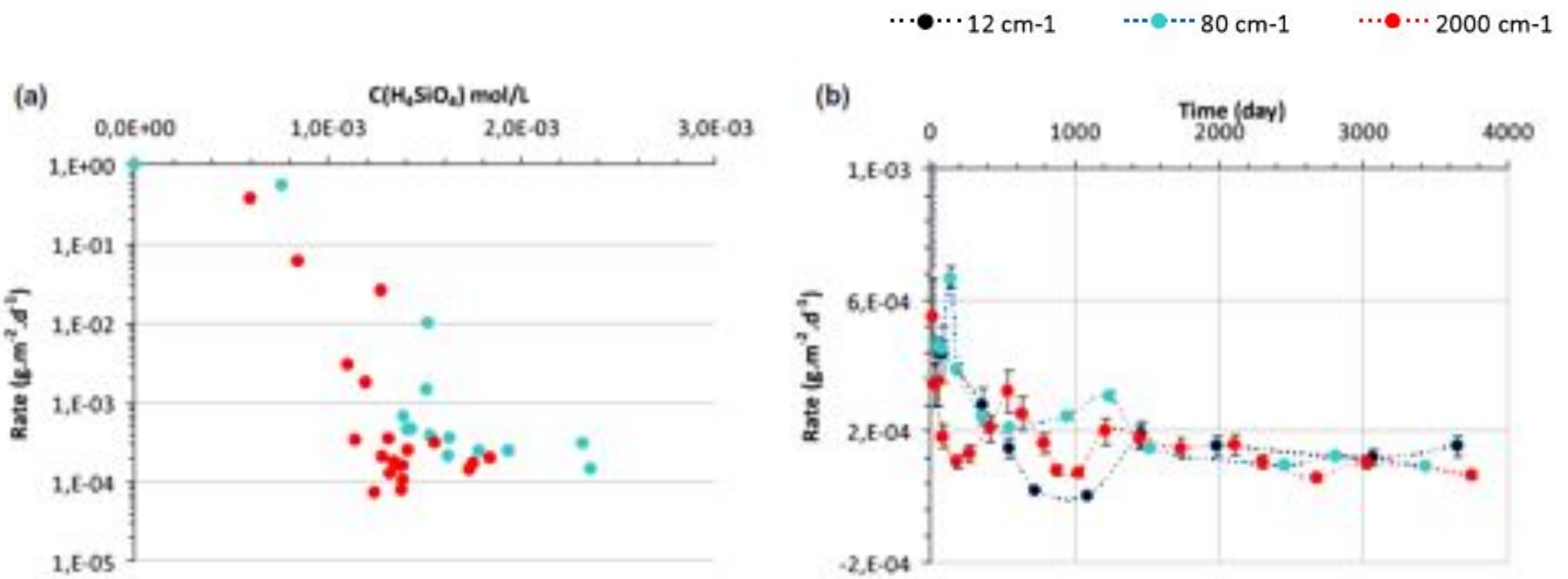


★ Dissolved silica account for a rate drop of 2 O.M.

Jegou, PhD Thesis 1998

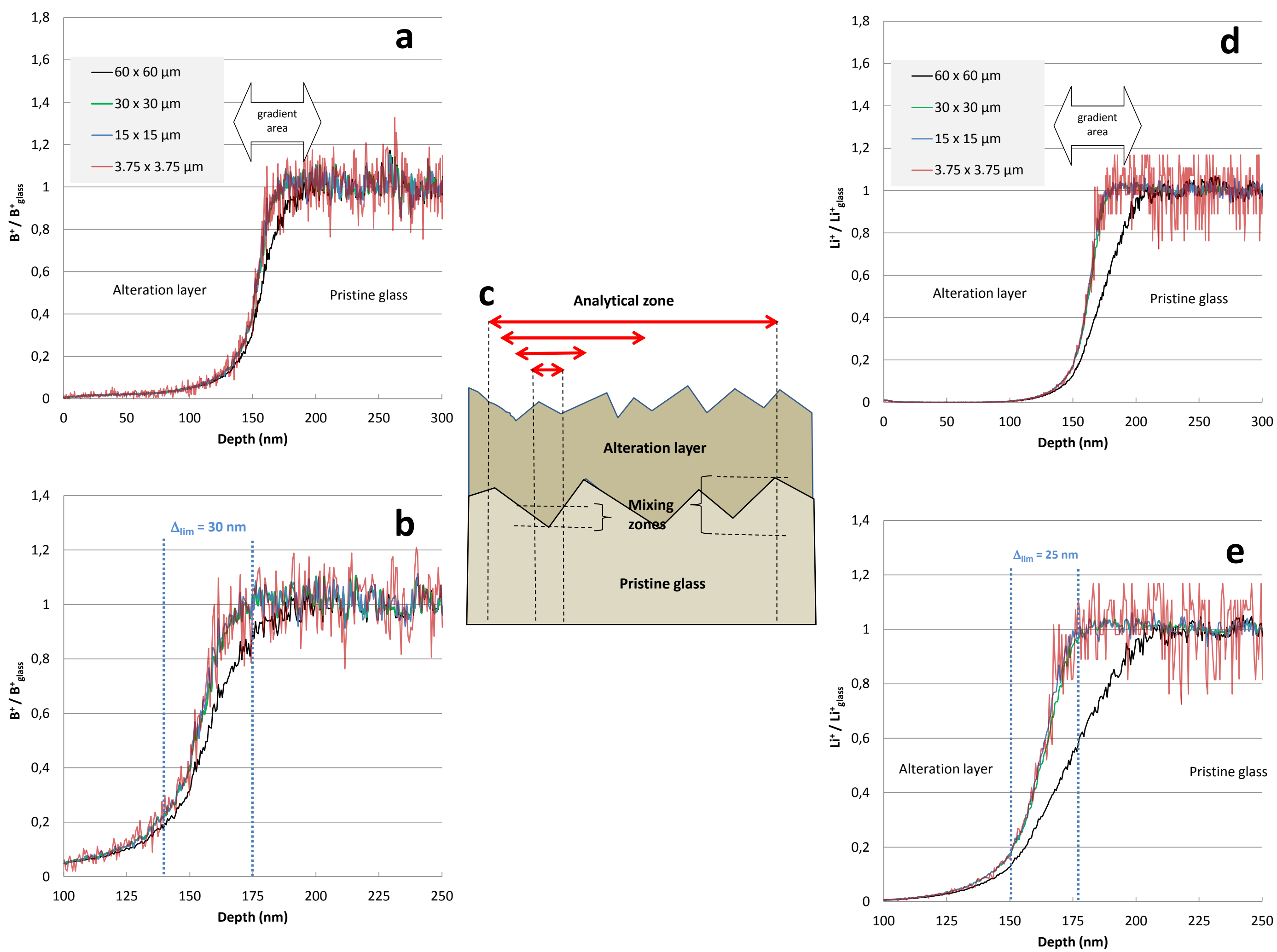
Solution chemistry and glass dissolution rate near equilibrium

SON68 glass
Static tests @ 90°C, DIW, various S/V



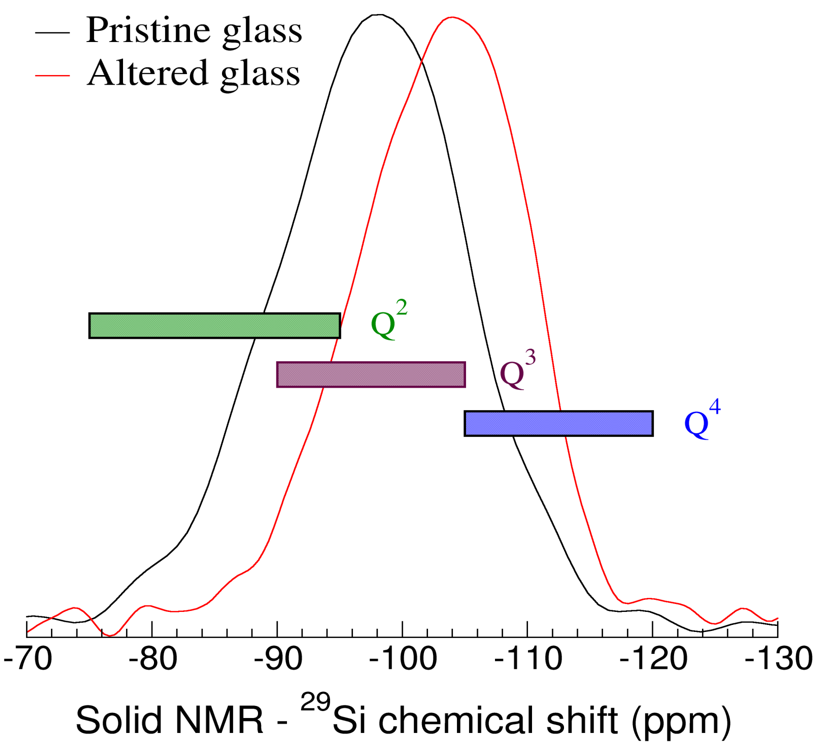
Gin et al., *Intern. J. Applied Glass Sci., 4* (2013)
Curti et al., Appl. Geochem. 21 (2006)

ToF-SIMS analysis of the Roland's sample (180d)



Structure of the AL

- 5 µm glass powder altered at pH 7 in Si-saturated solution until complete release of B, Na, Ca
- ^{29}Si NMR MAS and ^{1}H-^{29}Si CPMAS NMR analyses



- ✶ Partial repolymerization of the altered glass following the release of B, Na and Ca
- ✶ The resulting material should be less soluble than the glass