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NWTRB meeting

Current understanding and remaining challenges in measuring and modeling long-term performance of borosilicate nuclear waste glass

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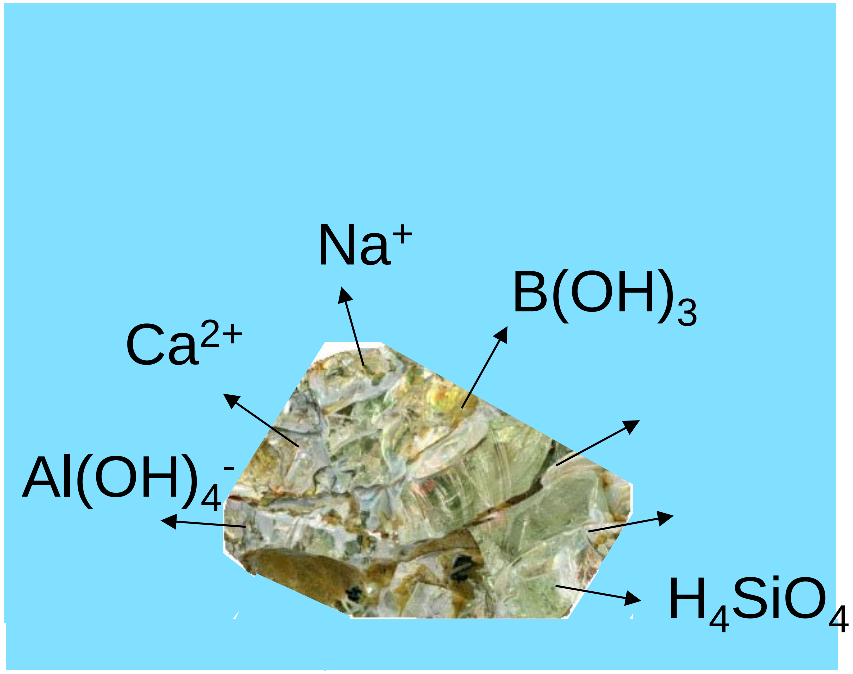
June 21, 2017 — Richland, WA

Outline

1. Basic mechanisms of glass corrosion
2. Kinetic regimes
3. Very brief overview of the effects of environmental parameters (T, pH, solution composition, NF materials…)
4. Remaining challenges

- **For thermodynamic reasons**
  - $\mu_{glass} \neq \mu_{solution} \rightarrow \Delta G_{reaction} < 0$
  - Distance to equilibrium = Affinity: $A = - RT \ln (Q/K_{eq})$
  - Dissolution rate: $r = r_0 (1 – Q/K)$



Can thermodynamic equilibrium between glass surface and solution be achieved?

- **No**, for thermodynamic & kinetic reasons
  - → K_{eq} (glass) >> K_{eq} (crystal) due to structural disorder
  - → Secondary phases with low solubility AND fast precipitation kinetics control the solution chemistry

Ostwald rule of stages

Glass → Hydrated Glass → Gels → Crystalline Phases

Grambow, *J. Nucl. Mater.* 2001
Frugier, *J. Nucl. Mater.* 2008
Gin, *Nature Com.* 2015

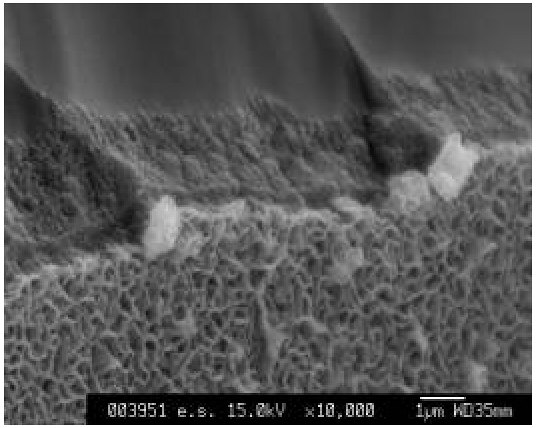
What are the key parameters to be considered?

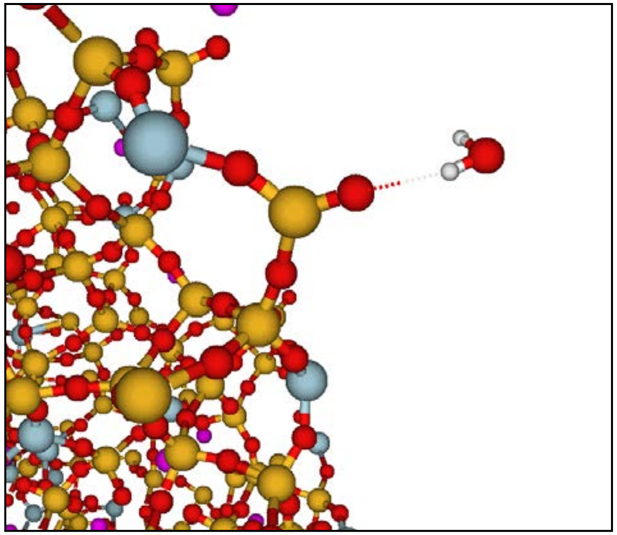
- **Intrinsic Parameters**
  - → Glass composition
  - → Glass structure (cooling rate, homogeneity)
  - → Reactive surface area, surface roughness and residual stress
  - → Self irradiation (in case of nuclear glasses)

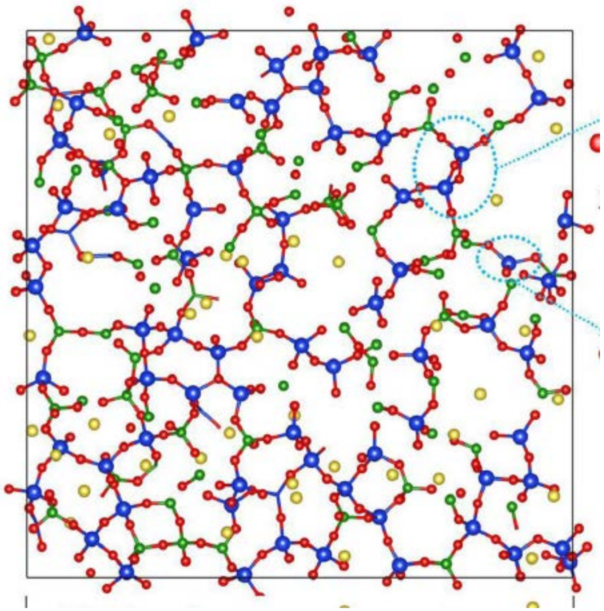
- **Extrinsic Parameters**
  - → Temperature
  - → Unsaturated (relative humidity) vs water saturated medium
  - → pH, water composition (itself modified by the surrounding solids)
  - → Flow rate
  - → (Pressure, Eh, microbial activity)

Basic mechanisms

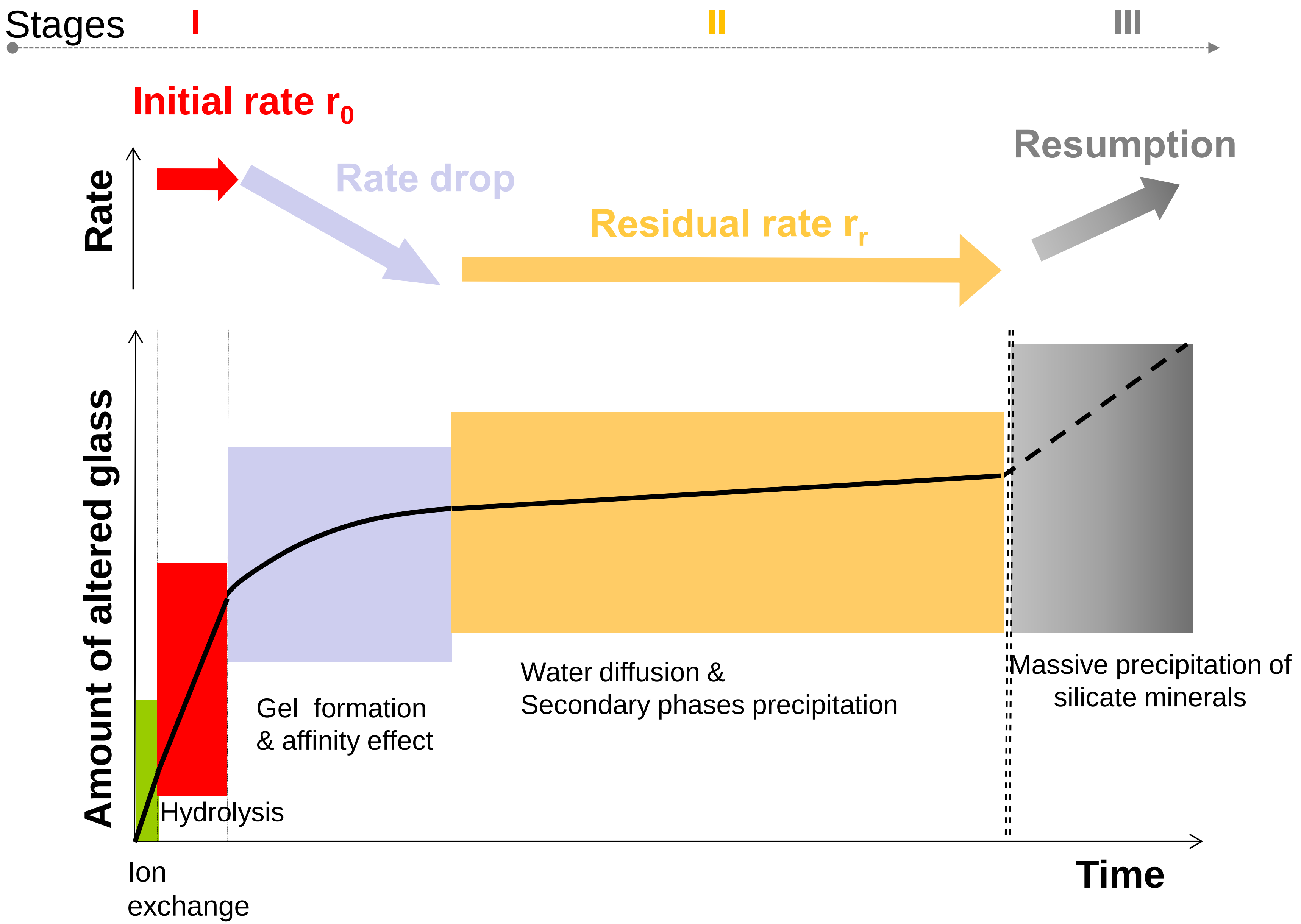
- Hydration / <u>Interdiffusion</u>
- <u>Hydrolysis</u> of glass formers
- <u>Condensation</u> of some hydrolyzed species (Si, Al, Ca…)
- <u>Precipitation</u> of secondary phases

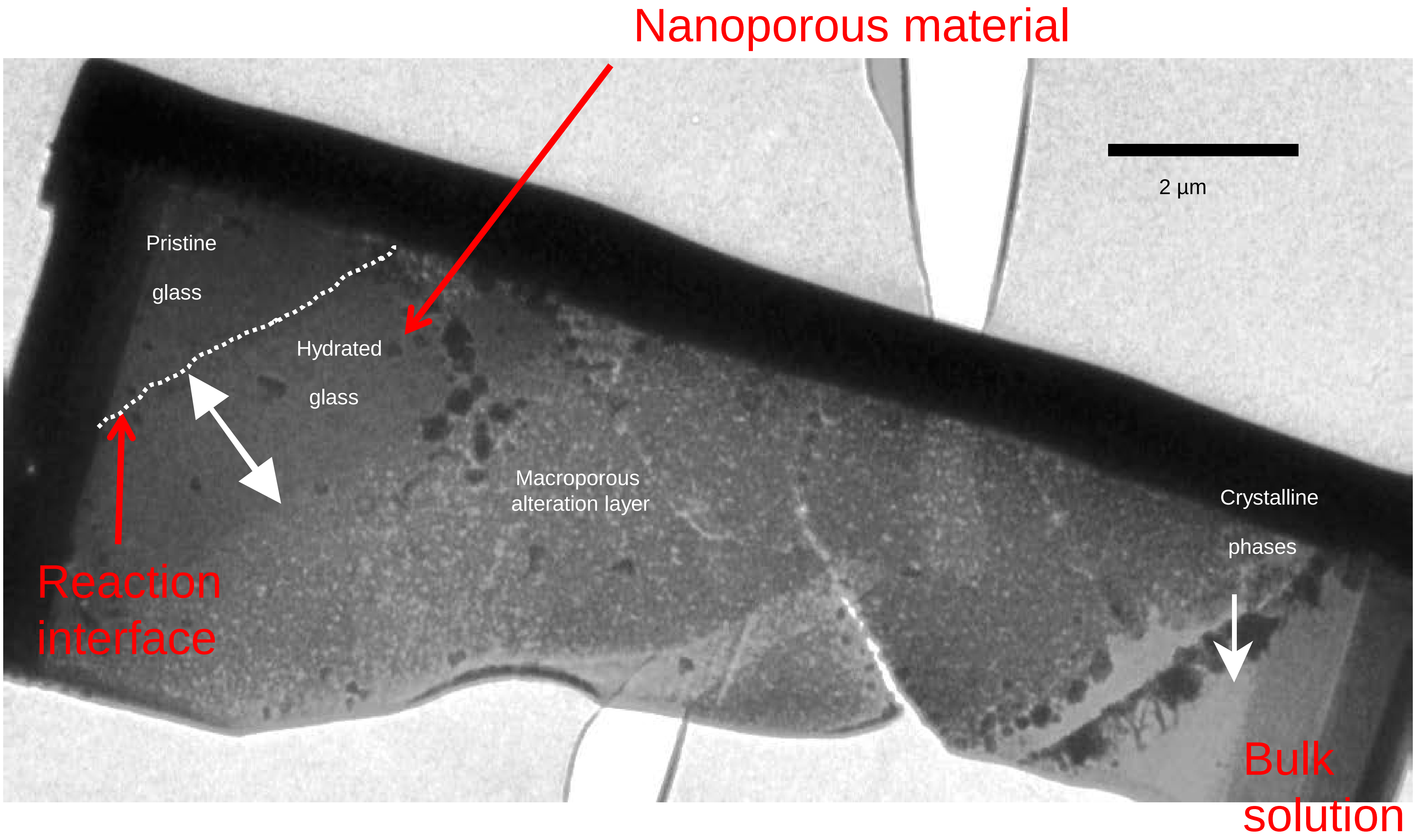






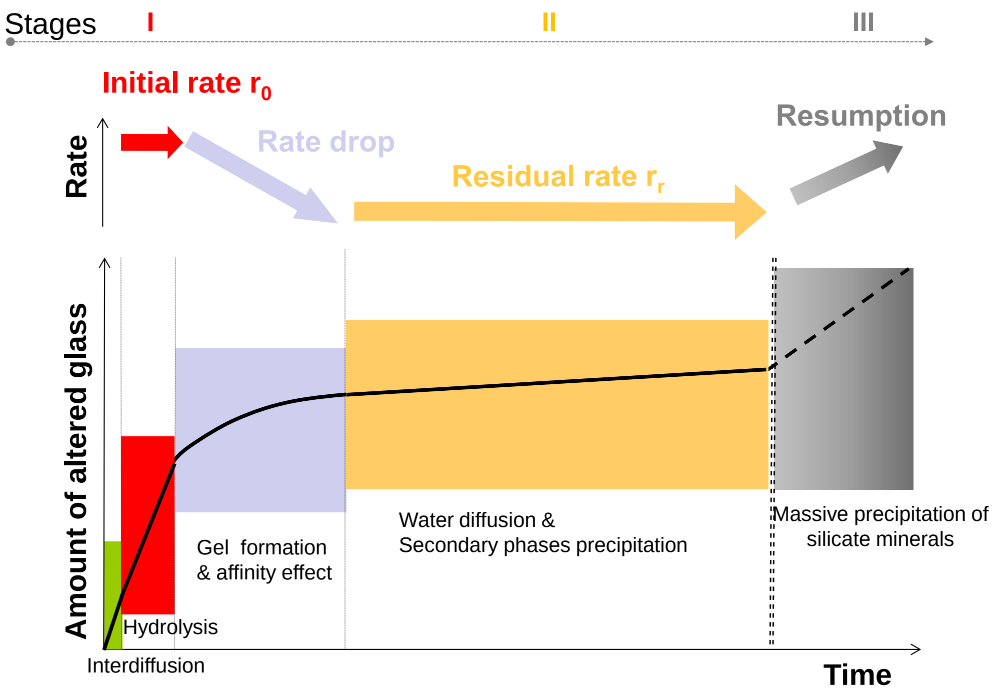
Kinetic Regimes





No free water in pores of 1 nm: e.g. Bourg, *J. Phys. Chem. C* 2012

A few orders of magnitude



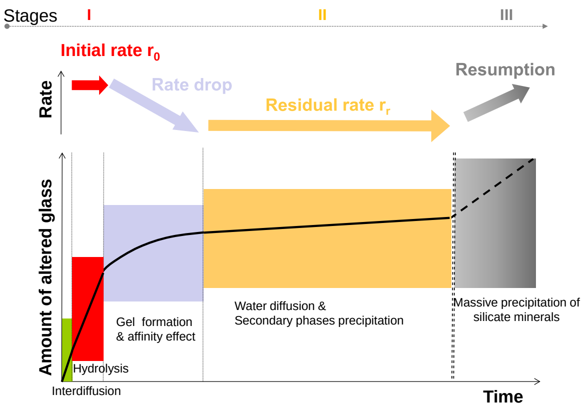
r_0 depends on glass composition, T, pH and to a lesser extent to the solution composition (Jollivet *Chem. Geol*. 2012)

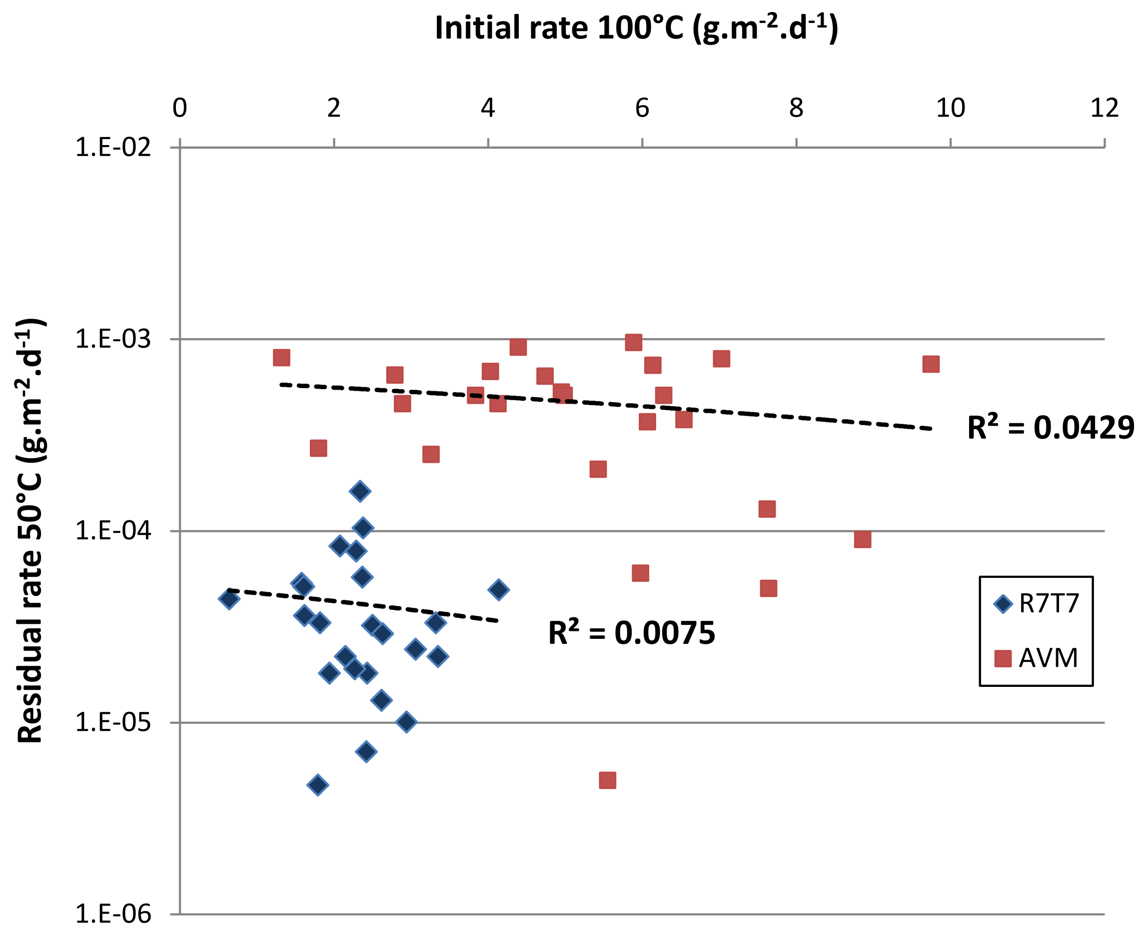
PA relying on r_0 ends up to glass lifetime of a few 10^3 years…

Some key figures @ 90°C for SON68 or ISG glass

- 10^{-20} m².s⁻¹ < $D_{W\ \text{in pristine glass}} \sim D_{B,\ Na\ \text{at}\ t_0}$ < 10^{-17} m².s⁻¹
- $r_0 \sim 0.2 - 5\ \mu.d^{-1}$
- $r_r \sim 10^{-3} - 10^{-5}\ \mu.d^{-1}$
- $10^{-23}\ m^2.s^{-1} < D_{W\ \text{in stage II}} < 10^{-20}\ m^2.s^{-1}$
- Time to form a passivating layer: [days – years] depending on exp. conditions
- In case of zeolite precipitation r ~ [1-1/10] r_0

Relation between short-term & residual rate



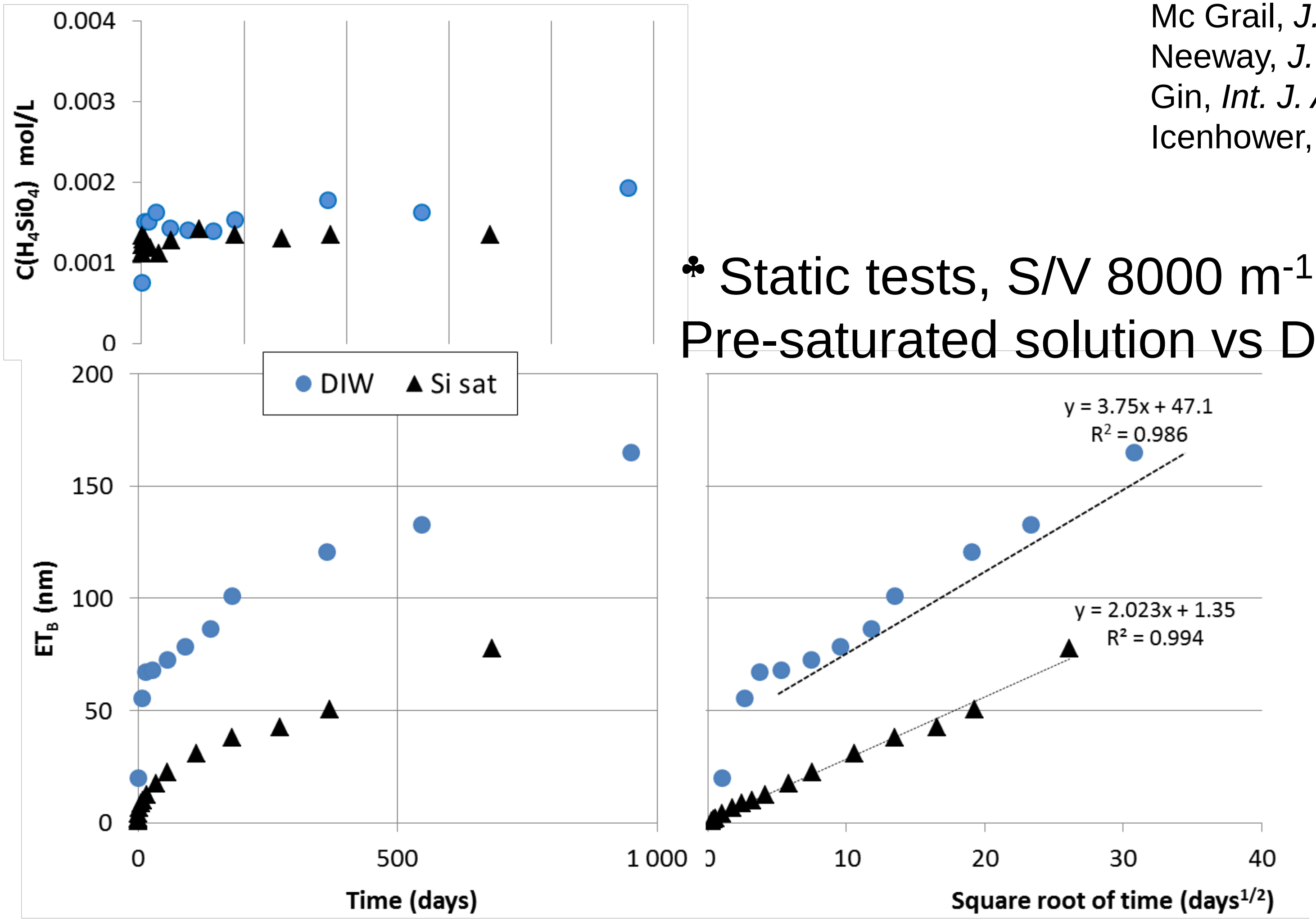


- Measuring initial rates does not help understand what could happen at long term
- Same conclusion for PCT 7d

3 processes causing the drop of the rate
1 : Effect of Si (affinity effect)

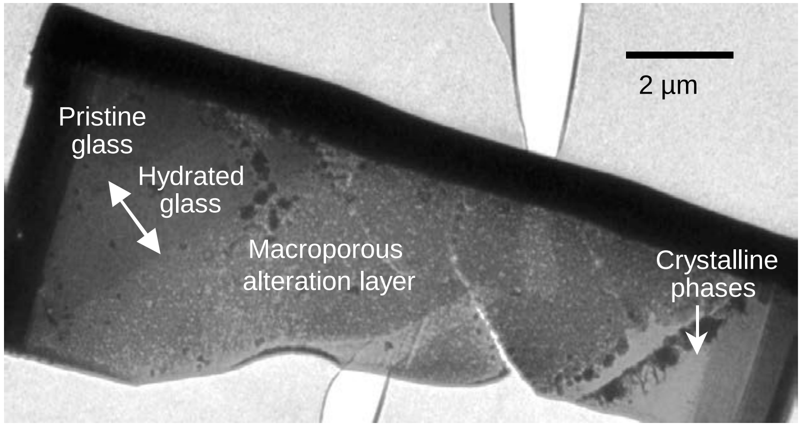
Grambow, *MRS proc.* 1985
Mc Grail, *J. Non-Cryst. Sol.* 2001
Neeway, *J. Nucl. Mater.* 2011
Gin, *Int. J. Appl. Glass Sci.* 2013♣
Icenhower, *J.Nucl.Mater.* 2013

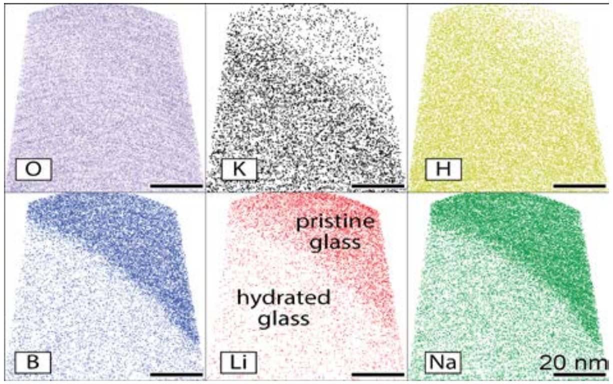
♣ Static tests, S/V 8000 m^{-1}, 90°C, 3y
Pre-saturated solution vs DIW

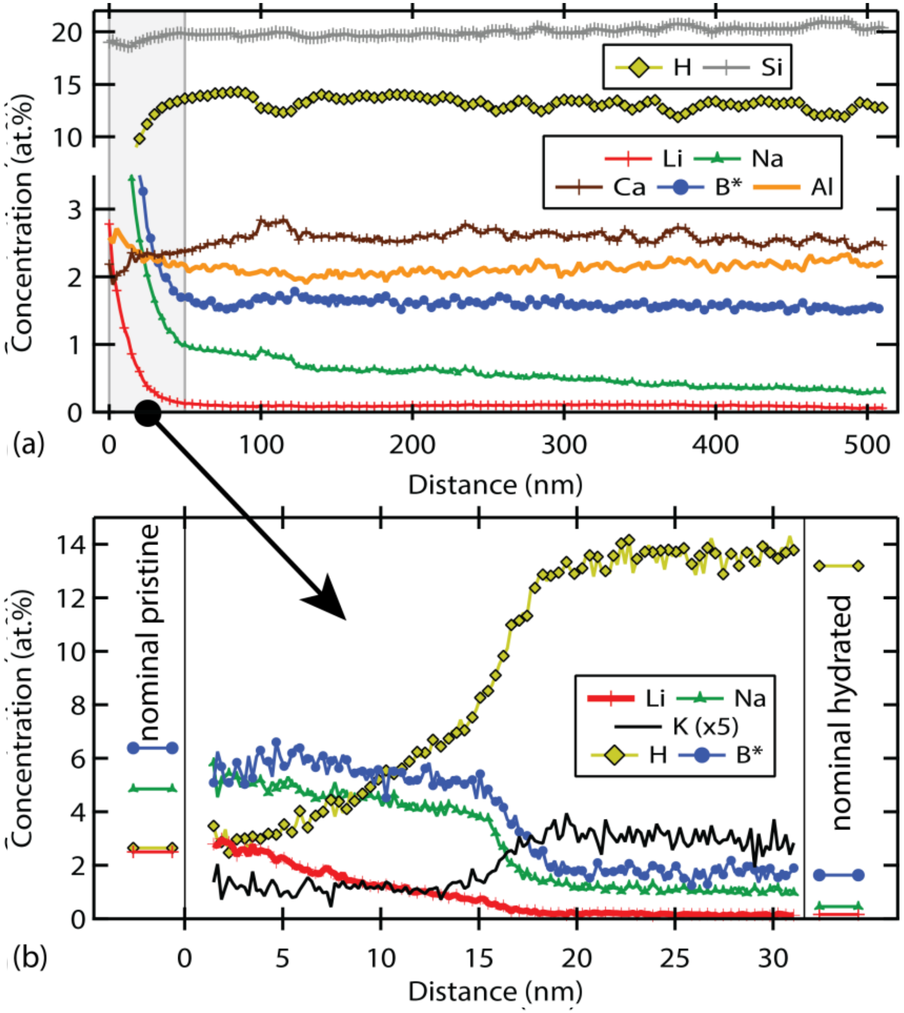


Pre-sat solution makes the RD stage much shorter but does not impact the RR regime.

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







- ❑ Very sharp reaction front
- ❑ $D_{water \rightarrow hydrated}$ glass « $D_{water \rightarrow glass}$ at the beginning of the dissolution process

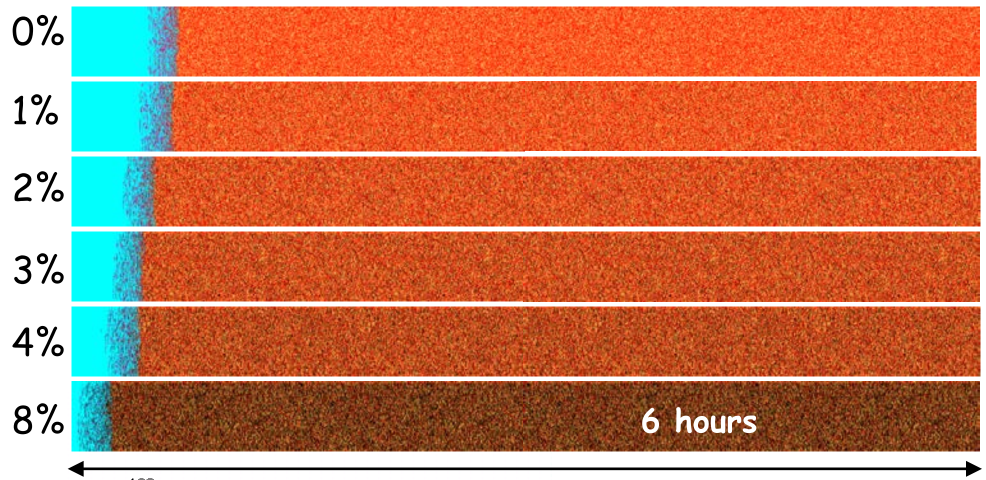
Gin *et al.*, *Chem. Geol* 2013♣, *Nature Comm.* 2015, *Geochim. Cosmochim. Acta* 2017
Hellmann, *Nature Mater.* 2015, Geisler, *Geochim. Cosmochim. Acta* 2015

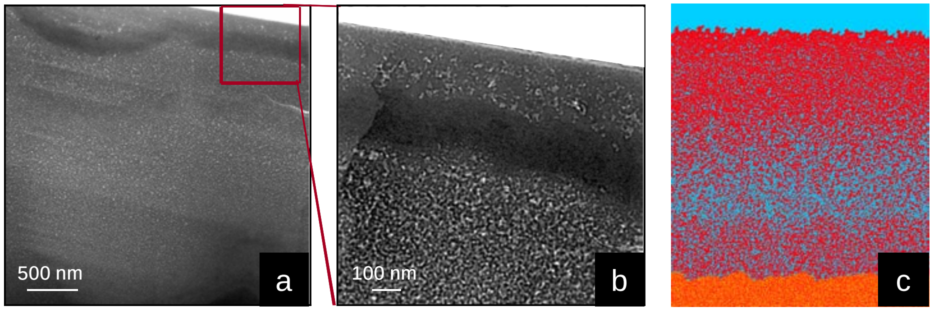
3 processes causing the drop of the rate
3 : Effect of porosity clogging

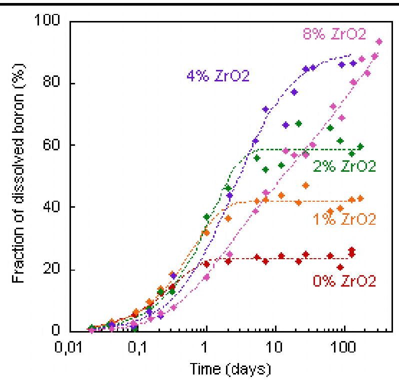
ZrO_2

Forward rate of alteration

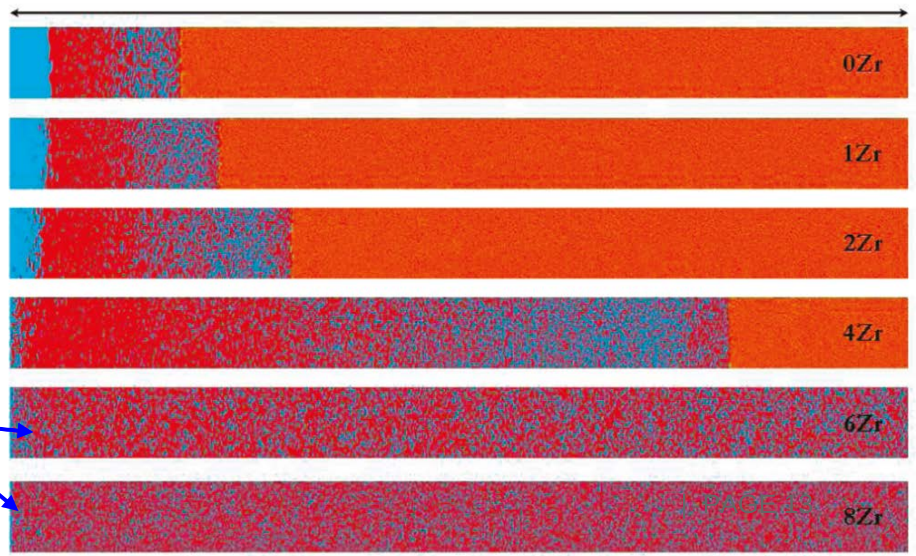
Cailleteau, *Nature Materials* 2008







Porosity clogging: up to 4% of ZrO_2

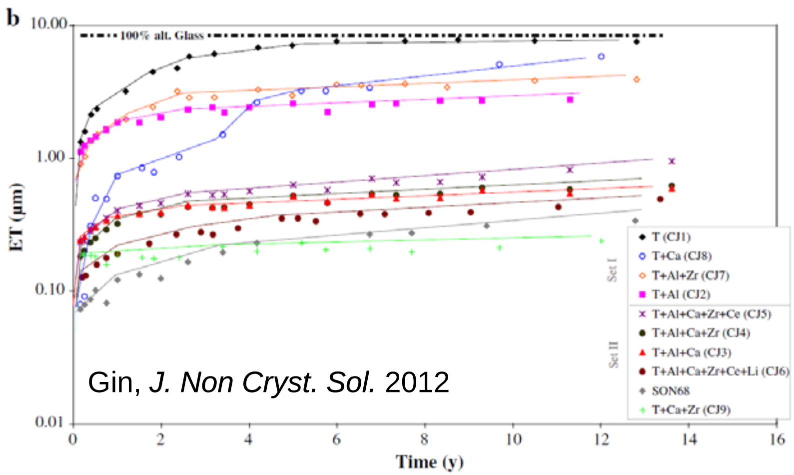


Zr at.: immobilize increasing numbers of Si

-> prevents any reorganization

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

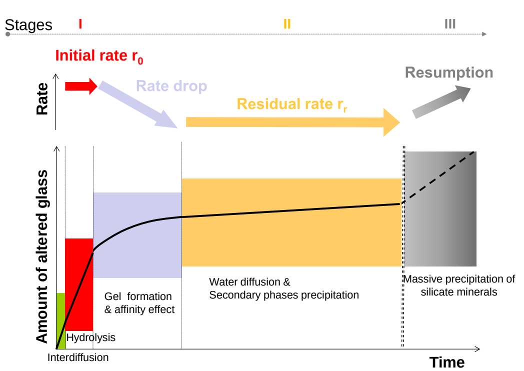
Why alteration does not stop in stage II?



Gin, *J. Non Cryst. Sol.* 2012

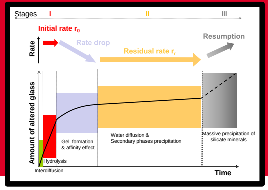
Hypothesis 1: because precipitation of secondary phases consumes elements form the passivation layer.
Yes for some cases but not necessarily!
Most of simple glasses do not form secondary phases between pH 7 and 9

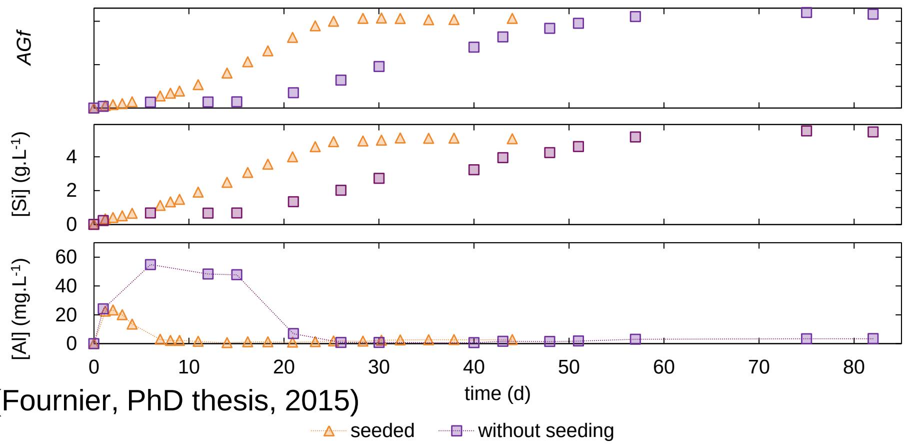
Hypothesis 2: because IX continues beyond the saturation of the solution w.r.t. SiO_2am (Grambow *MRS proc.* 1985 ; McGrail *J. Non Cryst. Sol.* 2001)
No, recent results show that Na and B profiles do not match a simple IX process



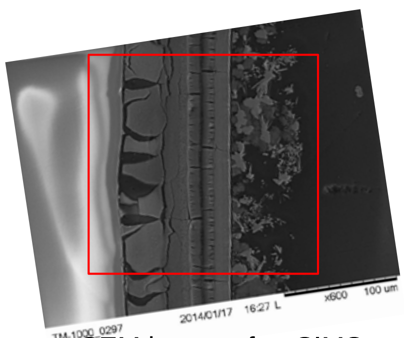
Hypothesis 3: water accessibility to reactive sites is hampered the the low porous gel formed by in-situ reoganization of the silicate network after the departure of mobile species
Need to be confirmed by a better understanding of water speciation and dynamics within the alteration layers (EFRC WastePD project)

Why dissolution turns into stage III?

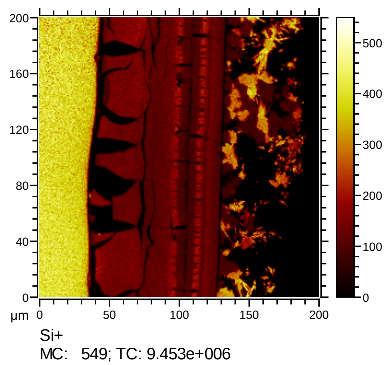




(Fournier, PhD thesis, 2015)



SEM image after SIMS

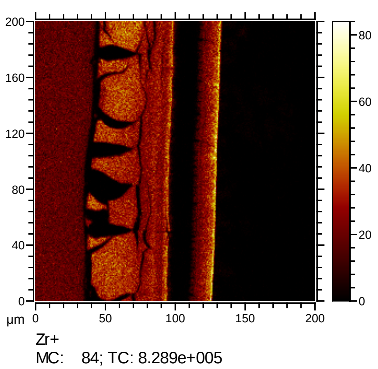


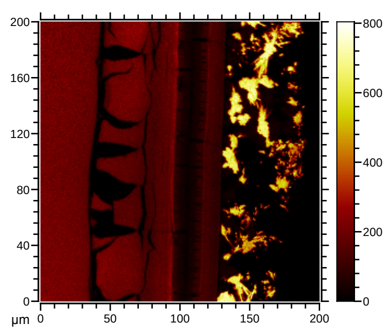
At pH > 10.5, IX is not a active process and both Si and Al are highly soluble.

A dense, rate limiting, amorphous layer is supposed to precipitate

Zeolite crystals nucleate and grow, first consuming species available in the bulk solution until the solution is unsaturaed wrt the passivating layer

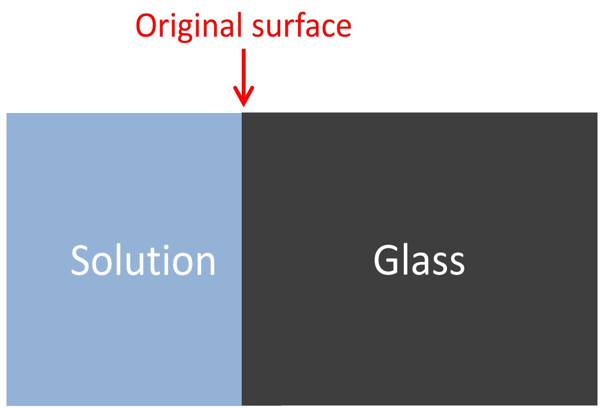
The glass surface is no longer protected, the rate increases by several O.M., controlled by the growth rate of zeolites





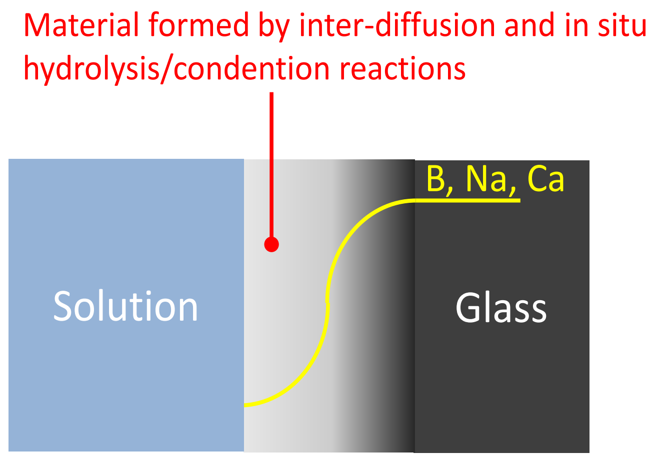
(Gin, *Geochim. Cosmochim. Acta* 2015♣, Ribet, *J.Nucl.Mater.* 2004, Fournier, *J.Nucl.Mater.* 2014)

Two different models for the same thing!



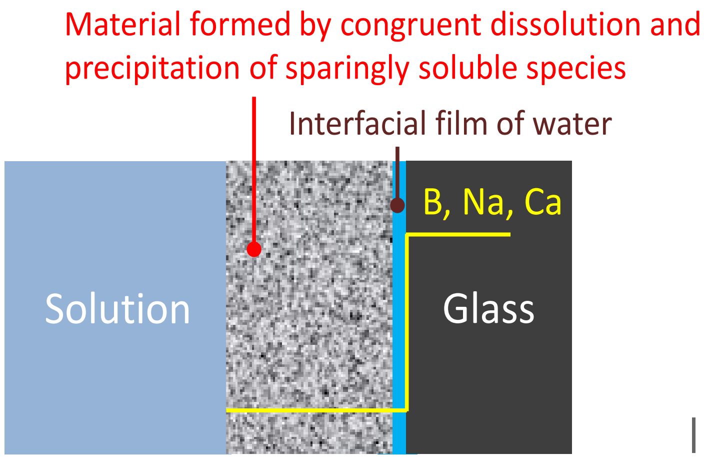
Classical theory involving inter-diffusion

Ferrand, *J.Nucl.Mater.* 2006
Frugier, *J. Nucl. Mater.* 2008

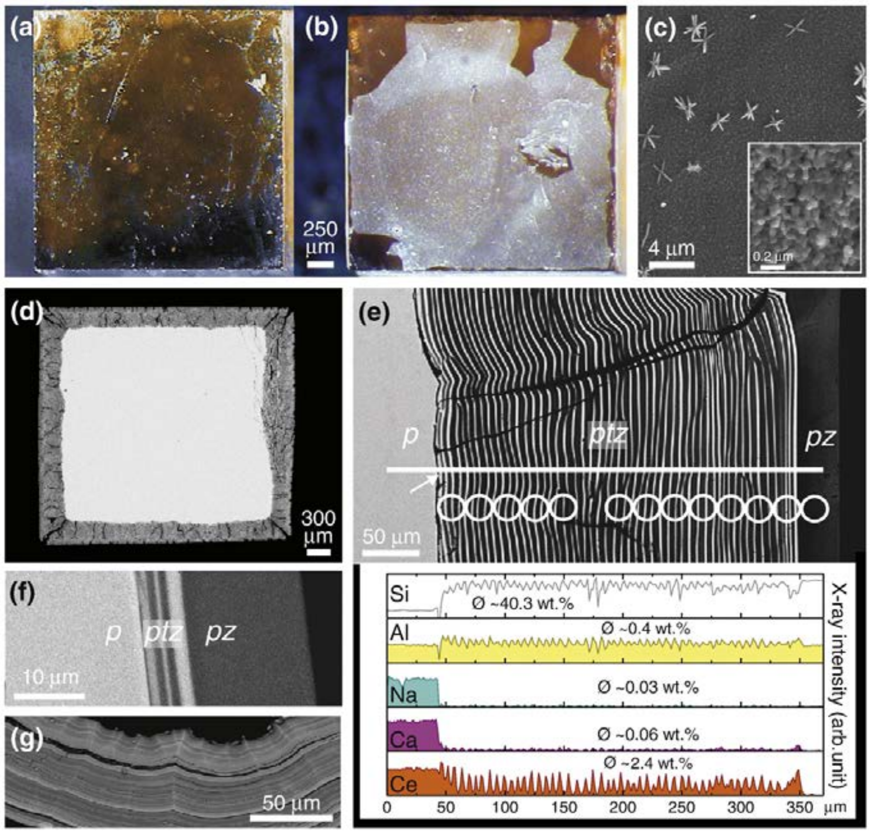


Interfacial Dissolution/precipitation theory

Hellmann, *Nature Mater.* 2015

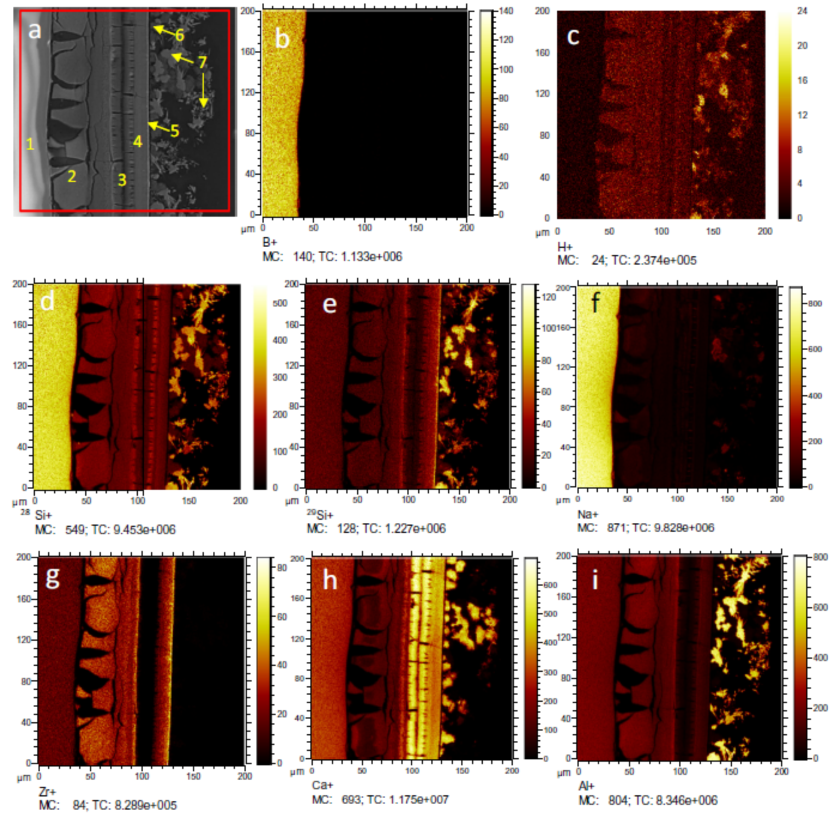


Evidence of dissolution - precipitation



9 Ox Borosilicate glass altered @ 150°C pH ~ 0

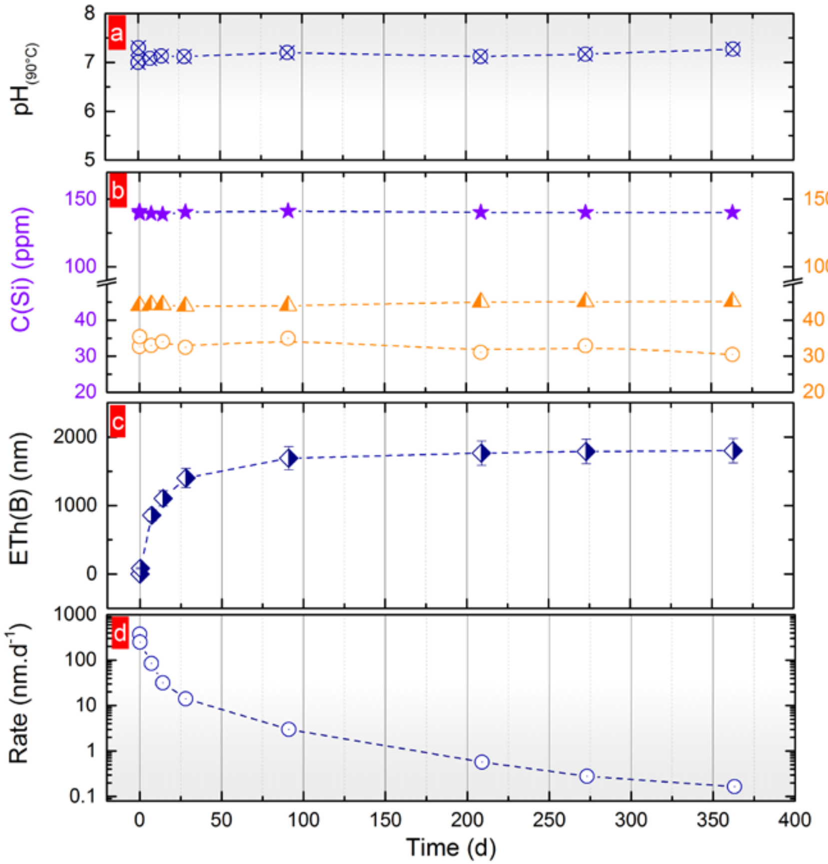
Geisler, *J. Non Cryst. Sol.* 2010



ISG glass altered @ 90°C pH ~ 11.5

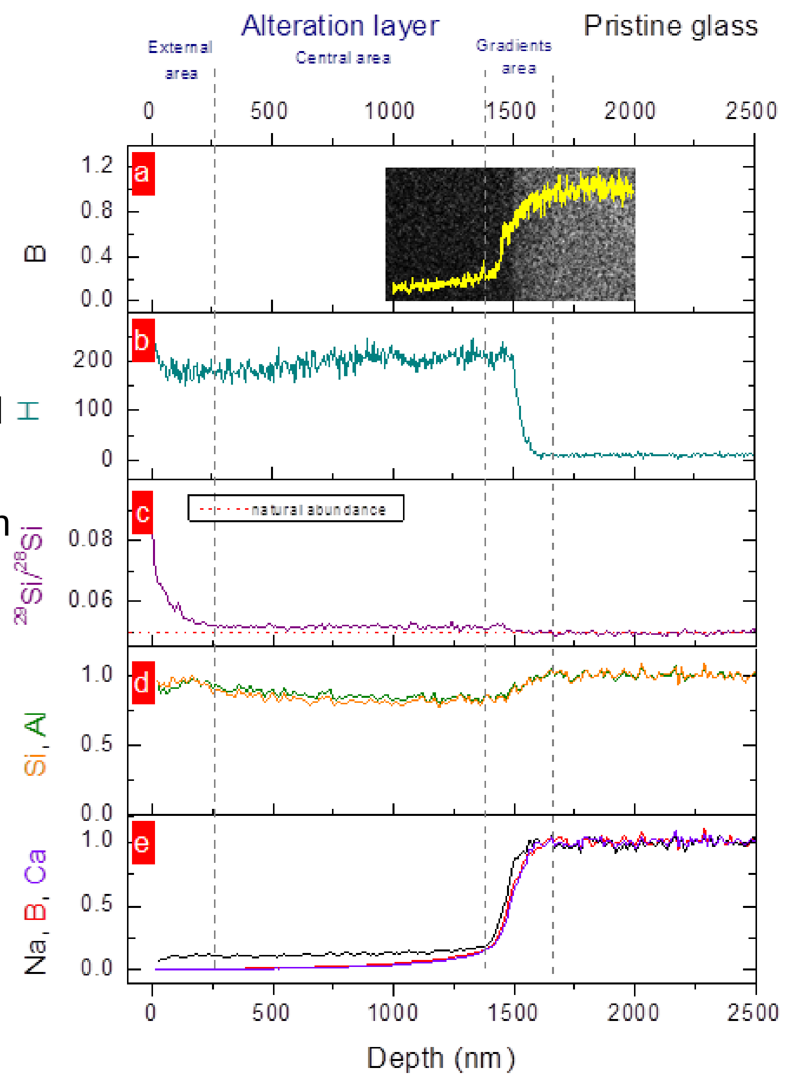
Gin, *Geochim. Cosmochim. Acta* (2015)

Evidence of the formation of a passivating layer by in situ reorganization of the silicate network



ISG glass altered @ 90°C, Si saturated solution and pH 7

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

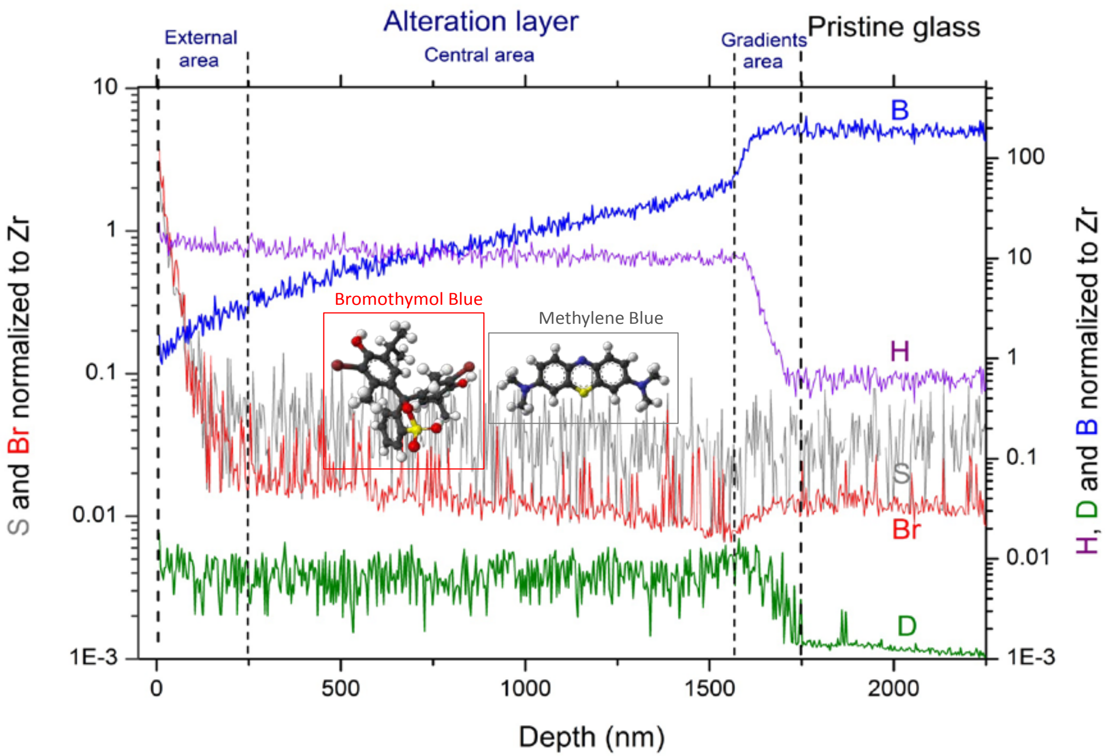


SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
56.2	17.3	12.2	6.1	5.0	3.3

Rate limiting mechanisms strongly depend leaching conditions

More discussion in Gin, *Chem. Geol* 2016

Evidence of the formation of a passivating layer by in situ reorganization of the silicate network



ISG glass altered @ 90°C, Si saturated solution and pH 7

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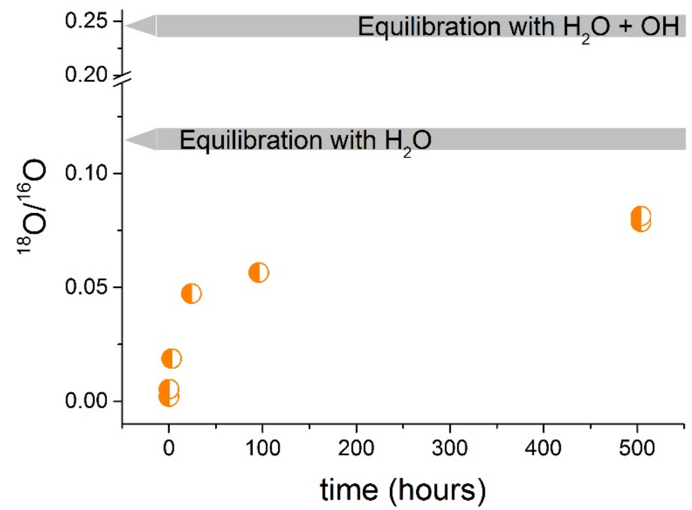


New evidence of ultra-slow mobility of water molecules in passivating layer (Collin et al., in prep.)

BRIEF SUMMARY

- The initial dissolution rate is controlled by the hydrolysis of the silicate network. It is the fastest rate for a given glass under given T and pH conditions
- The rate drops because $A_{hydrolysis}$ ↘ and a passivating layer forms
- The mechanisms by which passivating layers and non passivating gels (dissolution/precipitation vs in situ reorganization) form strongly depend on the pH
- The origin of passivation needs to be better understood
- Precipitation of Si-phases plays a major role in stage II and III

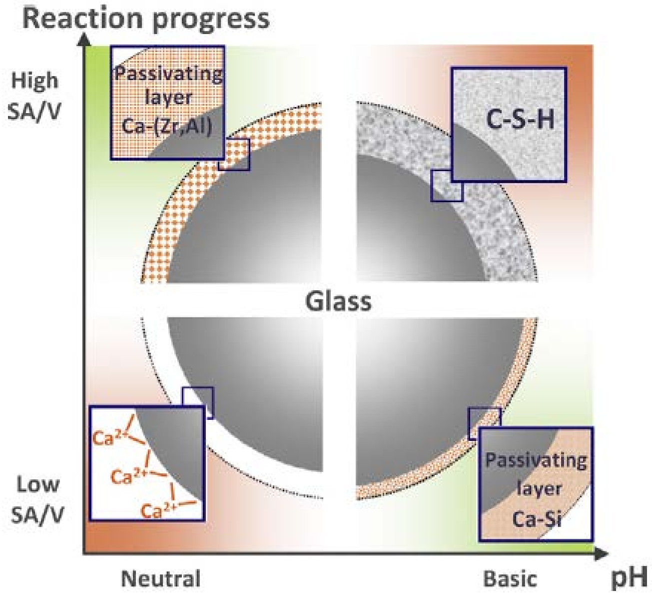
A few examples of the effect of environmental parameters on glass alteration

Example: effect of Ca supplied by the solution

Mercado-Depierre, *J. Nucl. Mater.* 2012

Stage II
(passivation competeing with
mineral precipitation)

Stage I
(hydrolysis of the silicate netwrok)

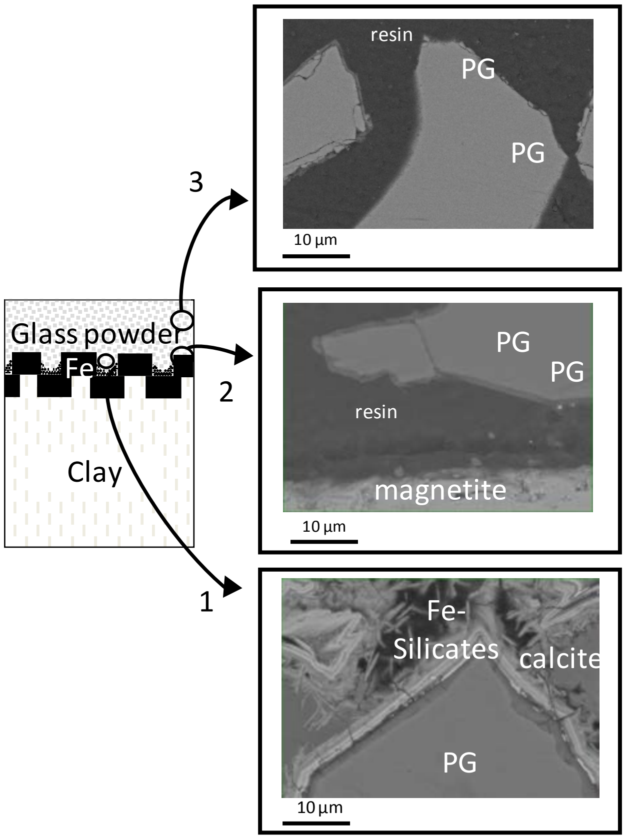


Cement water: pH 11-13

Clayey ground water: pH ~ 7

Effect of near-field materials

Chemical reactions & Transport must be considered



Glass altered thickness

~ 1 µm → At few mm from the iron source

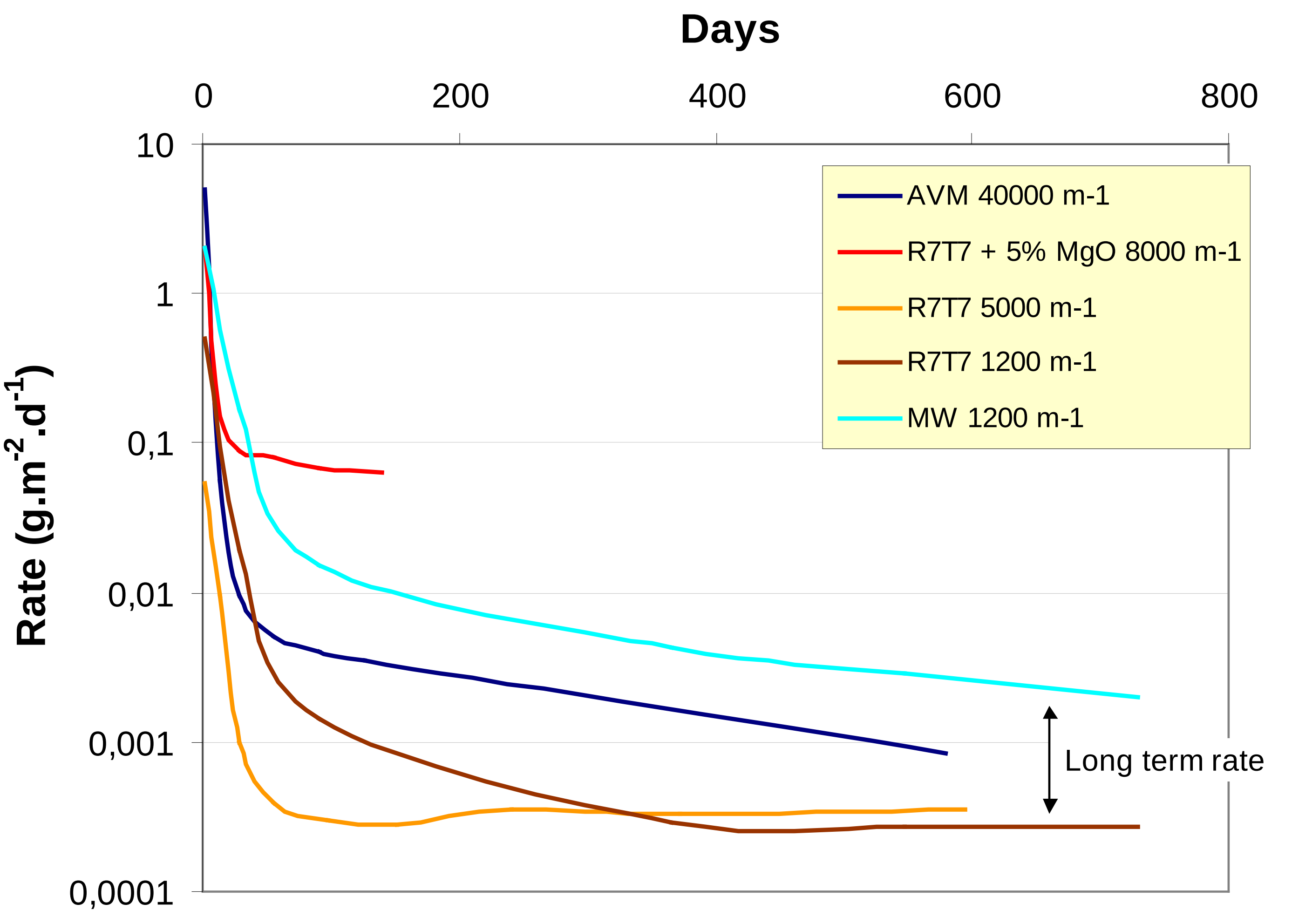
~ 2 µm → In between

~ 5 µm → Direct contact

SON68, 50°C, synthetic GW, anoxic conditions, low flow rate, 2y

Michelin, *Env.Sci.&Tech.* 2013
Burger, *Appl. Geochem.* 2013

INFLUENCE OF GLASS COMPOSITIONS



Static test
90°C

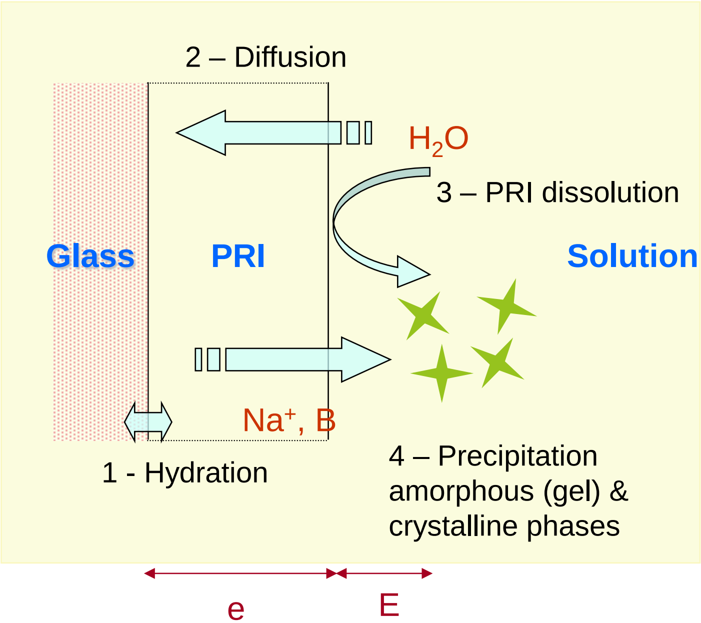
Glass dissolution kinetics strongly depends glass composition (Frugier, *J. Nucl. Mater.* 2005)

Synergetic effects: **experimental design methodology, simple glasses**

Modeling glass alteration in an open and reactive environment

Frugier et al. *J. Nucl. Mater.* (2008) **380** ; Minet et al., *J. Nucl. Mater* (2010) **404**; Debure et al., *J. Nucl. Mater.* (2013) **443**

- GRAAL has been developed to predict the rate of glass dissolution as a function of environmental conditions.
- GRAAL relies on the properties of a passivating layer called PRI
- Equations are implemented either in a reactive transport code (HYTEC)



E(t) : Thickness of the dissolved PRI
e(t) : Thickness of the PRI

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

→ **Empirical parameter**

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

→ **Macroscopic parameter**

- Recent applications : evaluate the effect of COx ground water, the effect of flow rate, the effect of Mg bearing minerals, simulate the resumption of alteration
- Under development: complete parameterization between RT and 90°C, 2 PRIs, construction of a simplified tool to assess the effect of corrosion products on glass durability

Toward a new mechanistic model

Step 1: in-depth understanding of the rate limiting mechanisms controlling stage II and the transition toward stage III → **General equations**

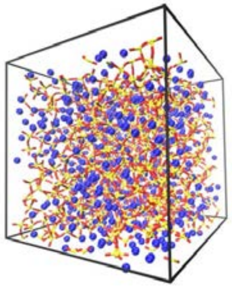
Step 2: understanding of glass composition effects

Step 3a: understanding of irradiation effects

Step 3b: understanding of nearfield materials effects

→ **Parameterization**

Step 1: Rate limiting mechanisms



NEED

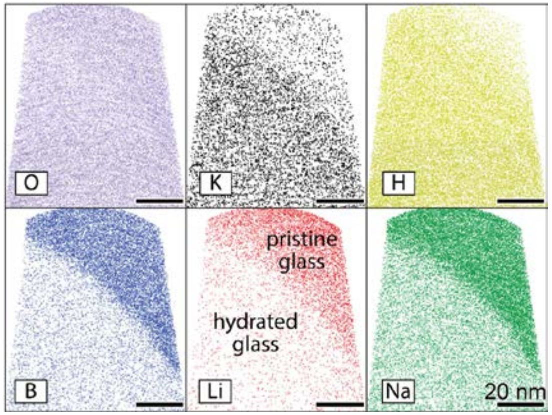
- Role/properties of gels
- Role/properties of secondary phases
- Role of solution chemistry (bulk and in nanoporous gels)
- Need to bridge the various scales (molecular -> macroscopic)

MEANS

- Smart experimental designs on model glasses (e.g. glass or solution spiked with isotopes)
- Advanced analytical techniques (cryo-APT, cryo-SIMS, in situ Raman…)
- Molecular Dynamics, Kinetic Monte Carlo simulations

OUTCOMES

- Fundamental understanding of basic processes
- Set of equations



Step 2: Effects of glass composition

NEED

- Link glass composition & rate limiting mechanisms

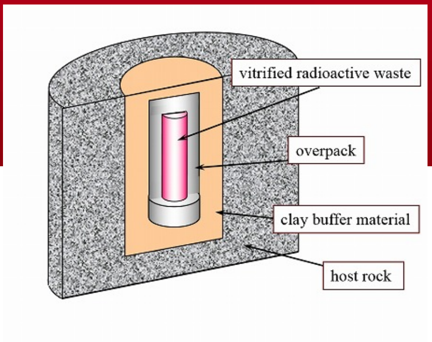
MEANS

- Explore the ISG domain with Molecular Dynamics (Si, B, Na, Al, Ca, Zr) + experimental validation
- By substitution or addition study the effects of other elements (Mg, Fe, REE…)

OUTCOMES

- Parameterization of the model
- New rules to improve glass formulation

Step 3: Effects of irradiation and NF materials



NEED

- Understand various disruptive effects

MEANS

- Irradiation: experiments + MD/KMC simulations
- NF effects: experiments + geochemical calculations

OUTCOMES

- Parameterization of the model
- New suggestions to improve the design of the multi-barrier system

ACKNOWLEDGEMENTS

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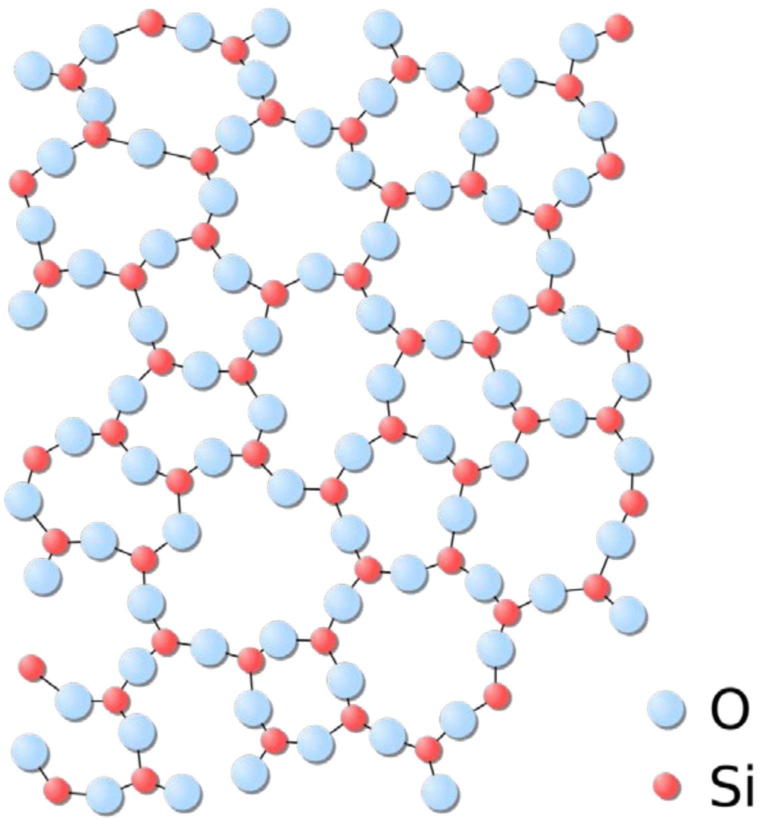
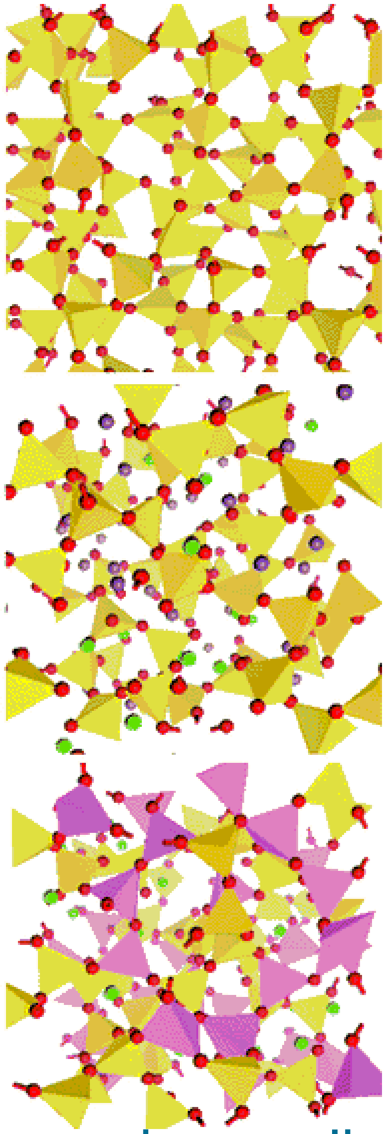
BACKUP SLIDES

Assembly of connected polyhedra with no long range order (> 1 nm)



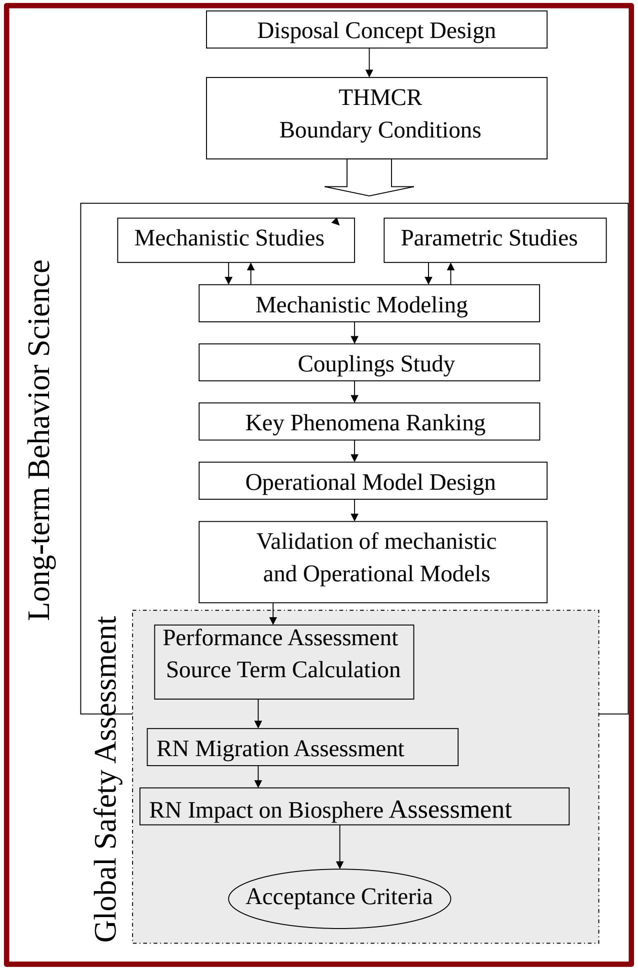


Distribution of angles, rings statistic …

The degree of disorder increases with increasing cooling rate

Outline

Long-term behavior science is an iterative process involving THMCR couplings between glass and the geological disposal design

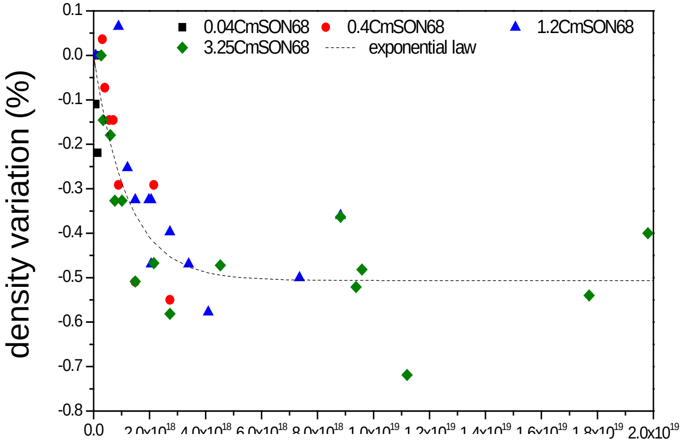


ASTM Standard C1174-07
Poinssot et al., *J. Nucl. Mater.* (2012)

1. Improvement in understanding effects of irradiation on glass
2. Improvement in understanding glass corrosion mechanisms
3. Conclusions and Open questions

Understanding the effects of alpha decays in glass (1/2)

- Slight modification of density and mechanical properties
- Glass is still homogeneous (SEM and TEM scale)
- No effect on initial dissolution rate
- Modification of glass Short Range Order (B coordination, NBO …)
- Modification of Medium Range Order (ring statistic, angle distribution)

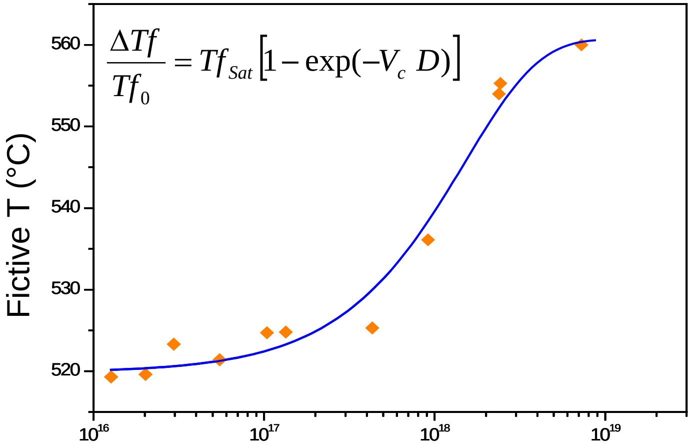


Modifications observed in the first $4x10^{18}$α/g according to a direct impact model …

Model of accumulation of ballistic disordering fast quenching events

Stabilization of a new glass structure when all the volume has been damaged one time

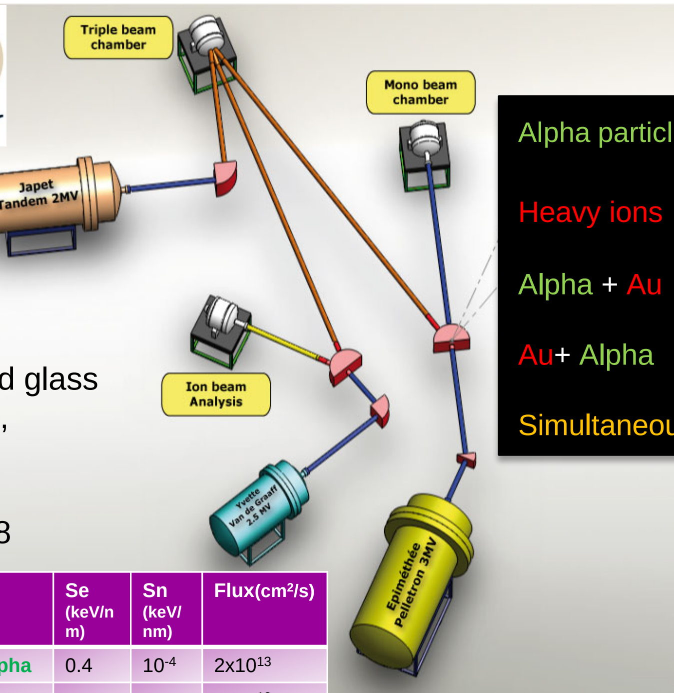
Peuget *et al., J. Nucl. Mater.* **444** (2014) 76-91
Maugeri *et al.* J. Amer. Soc. **95** (2012) 2869



Understanding the effects of alpha decays in glass (2/2)

Charpentier et al., Scientific Reports (2016); Mir et al., *Eur. Phys. Lett.* (2015) 112 ; Mir et al., *J. Nucl. Mater.* (2016) 469

- How to simulate α decay in glass in a short time? (external irradiation of inactive glass, α doped glass with short live emitters, MD simulation)



Alpha particles **2 MeV He, Se**

Heavy ions **14MeV Au, Sn**

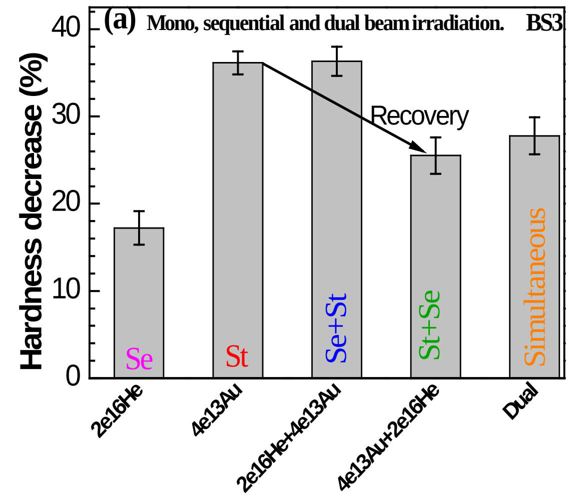
Alpha + Au

Au+ Alpha

Simultaneous

Studied glass
a-SiO_2,
CJ1,
ISG,
SON68

Ion	Se (keV/nm)	Sn (keV/nm)	Flux(cm²/s)
2 MeV Alpha	0.4	10^{-4}	$2x10^{13}$
14 MeV Au	2.5	2	$1x10^{10}$

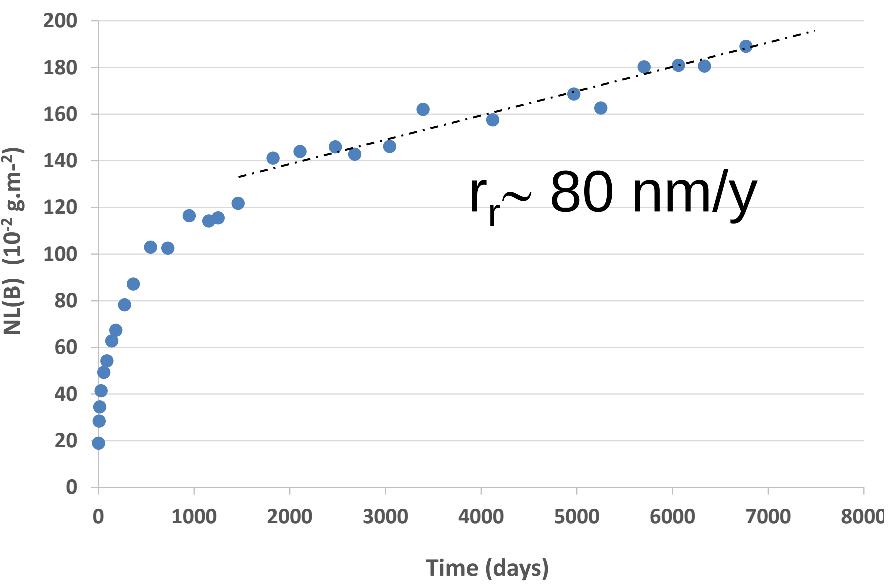


Role of both nuclear and electronic stopping powers

- **Heavy ions: main damage (~ supervitrification)**
- **Alpha particle: recovery effect due to electronic energy loss**

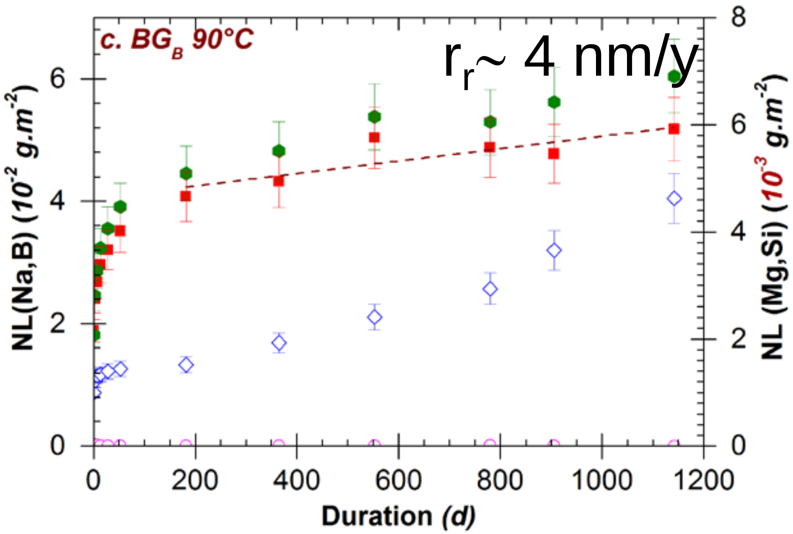
- Explain the lower property variation observed on actinide doped glass compared to heavy ions irradiated glass
- Alpha decay effects should be simulated by dual beam irradiation !

A rate never equal to zero: case of nuclear glass and basaltic glass



Nuclear glass (ISG - 6 oxides)

Alteration at 90°C, in deionized water, in static mode

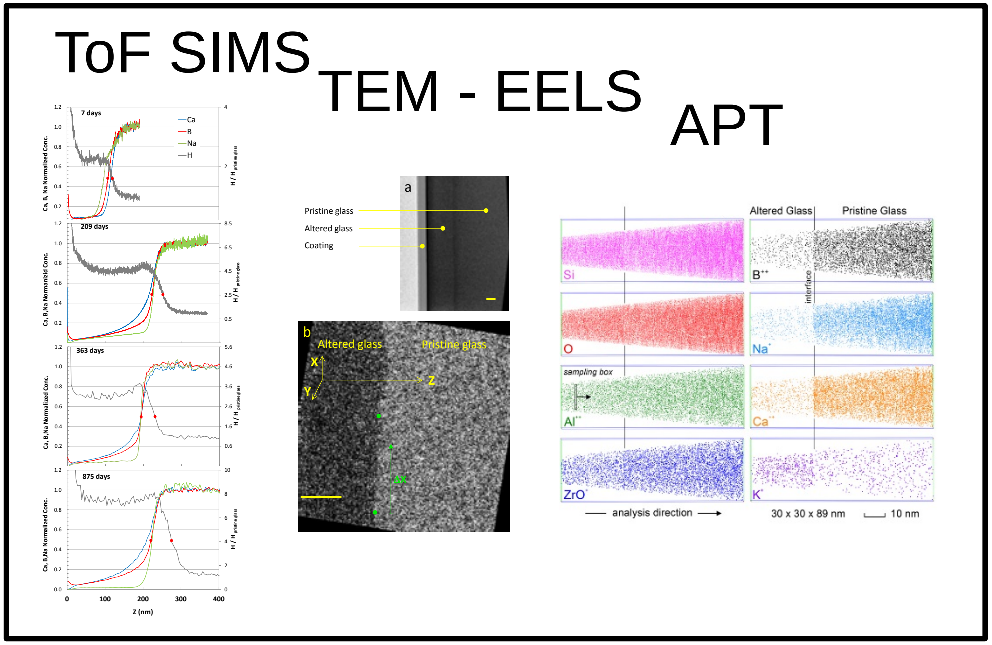


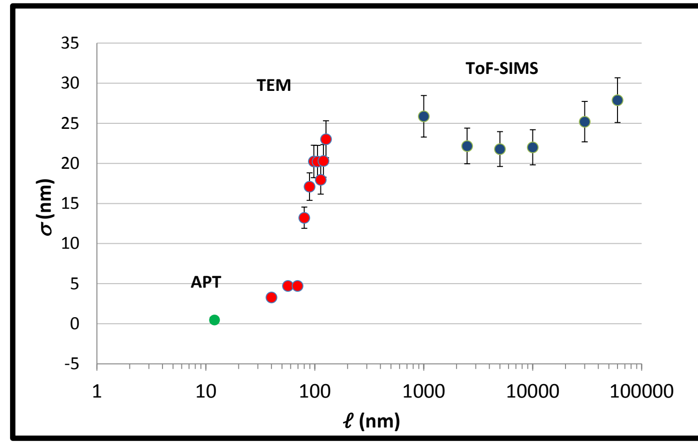
Basaltic glass

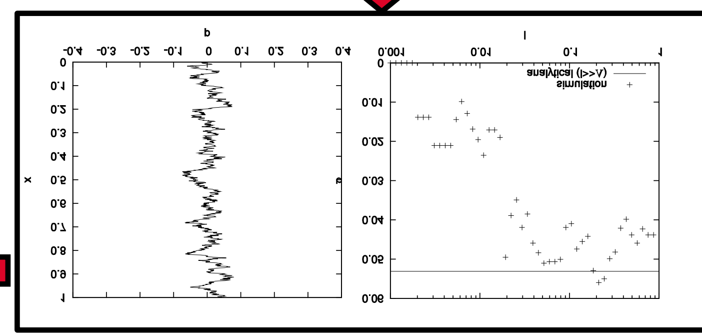
How glass surface is passivated?

Gin et al. *Nature Comm.* 2015 ; Gin et al. Geochim. Cosmochim. Acta, sub.

- Reconstruction of the reactive interface from a multiscale analysis of the alteration layer formed under residual rate conditions







ω = 15 nm
Λ = 100 nm

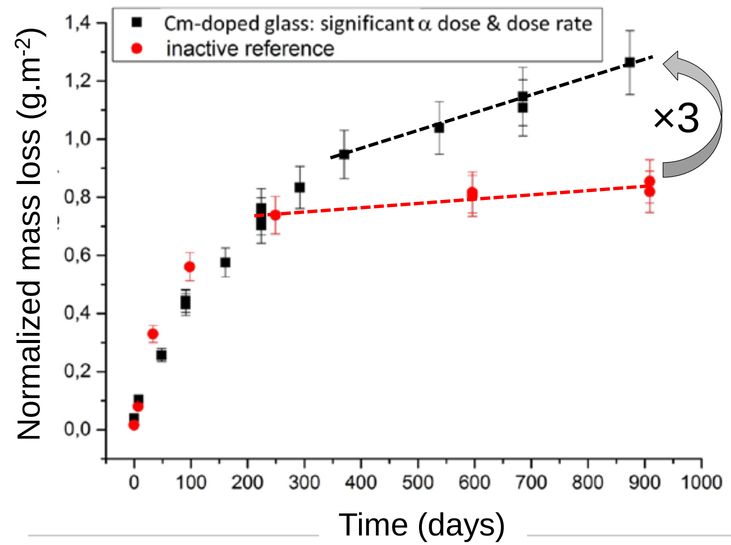
- New paradigm: the rough interface if created in the early stage of glass corrosion and propagates into the material at a rate limited by the accessibility of water molecules to the reactive interface.
- Water molecules are confined in pores of ~1 nm.
- With the passivating layer the diffusivity of water is decreased by 3 O.M. (10^{-23} $m^2.s^{-1}$)

Effect of irradiation on glass alteration

- α and β/γ dose rate and cumulative dose effects studied
  - Both on doped glasses & by external irradiation
  - In pure water, and high reaction progress (residual rate

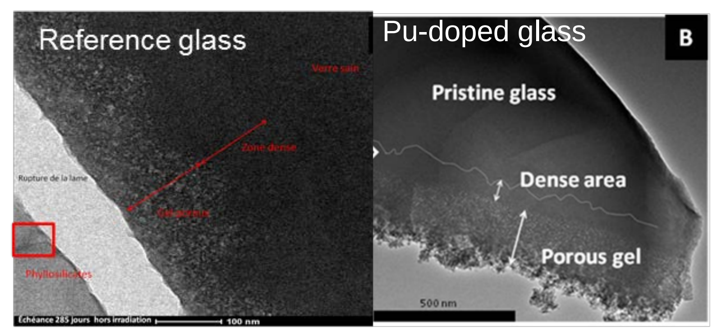
→ First order impact : alpha cumulative dose (around ×3)[1]

→ Second order impact (in prospect) : high alpha dose rate[1] ?



→ No significant impact of irradiation

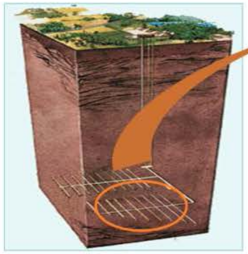
- → On initial rate value[4,5]
- → Of β/γ dose rate on residual alteration rate value[2,3]
- → Of β/γ cumulative dose on both rate and “gel” structure[1]
- → Of α dose rate ≤ 150 Gy/h (i.e. after 1,000 years)[3]

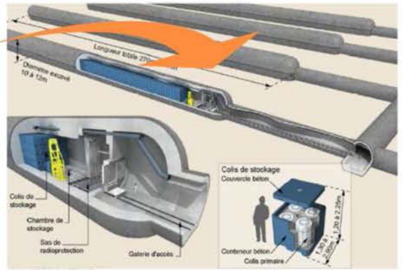


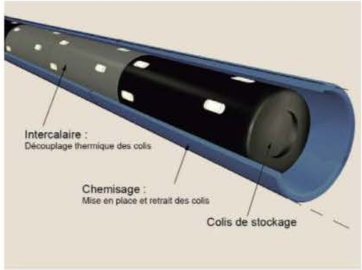
[4]Advocat et al., *J. Nucl. Mater* (2001)

[5]Peuget et al., *J. Nucl. Mater* (2014)

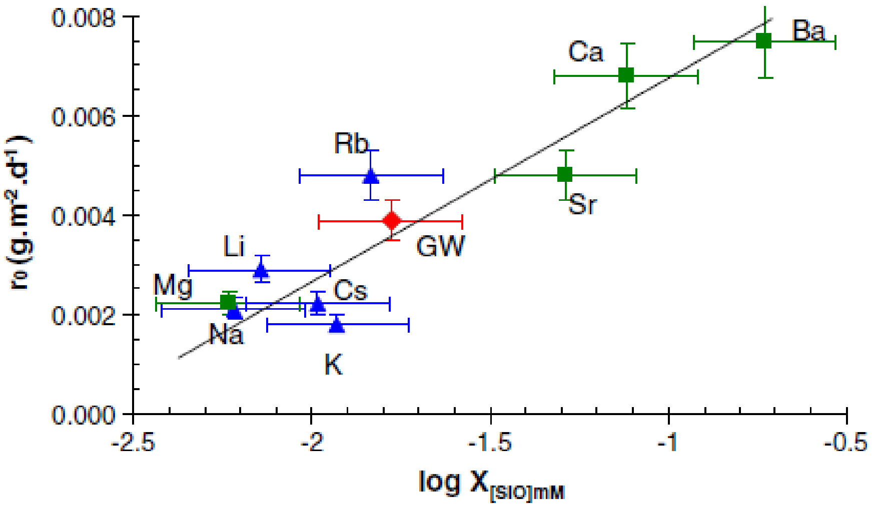
Glass durability = f(glass composition & environment)





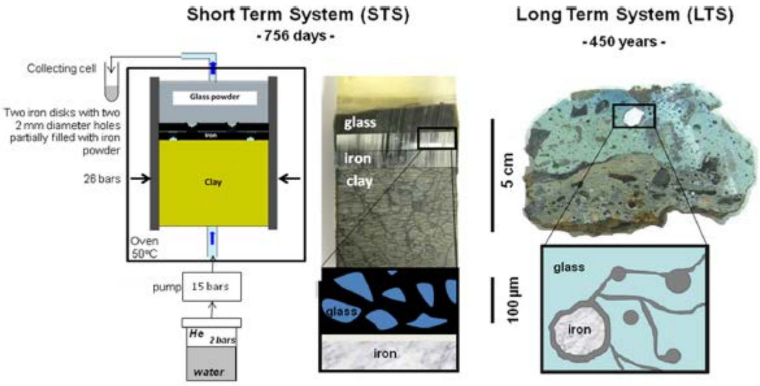


The ground water and large amounts of Fe in the vicinity of glass could impact the source term



► The COx ground water increases by a factor of 5 the initial dissolution rate of the glass

Jollivet et al. *Chem. Geol.* 2012, **330**



► Fe^0 & iron corrosion products strongly affect the fate of Si and thus delay the formation of a passivating layer. Reactive transport modeling in progress,

Michelin et al. *Env. Sci. & Tech.*. 2013, **47**

TST-based Rate Laws (used for PA in the US)

$$r = k_0 \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \bullet (1 - Q/K)$$

k_0 rate coefficient for glass composition

η accounts for pH dependence

E_a accounts for temperature dependence

(1 - Q/K) affinity term accounts for solution feed-back effects

Q is activity of orthosilicic acid

K is activity of orthosilicic acid at “equilibrium”

Main limitation: passivation not taken into account (several implications for the residual rate regime and stage III)

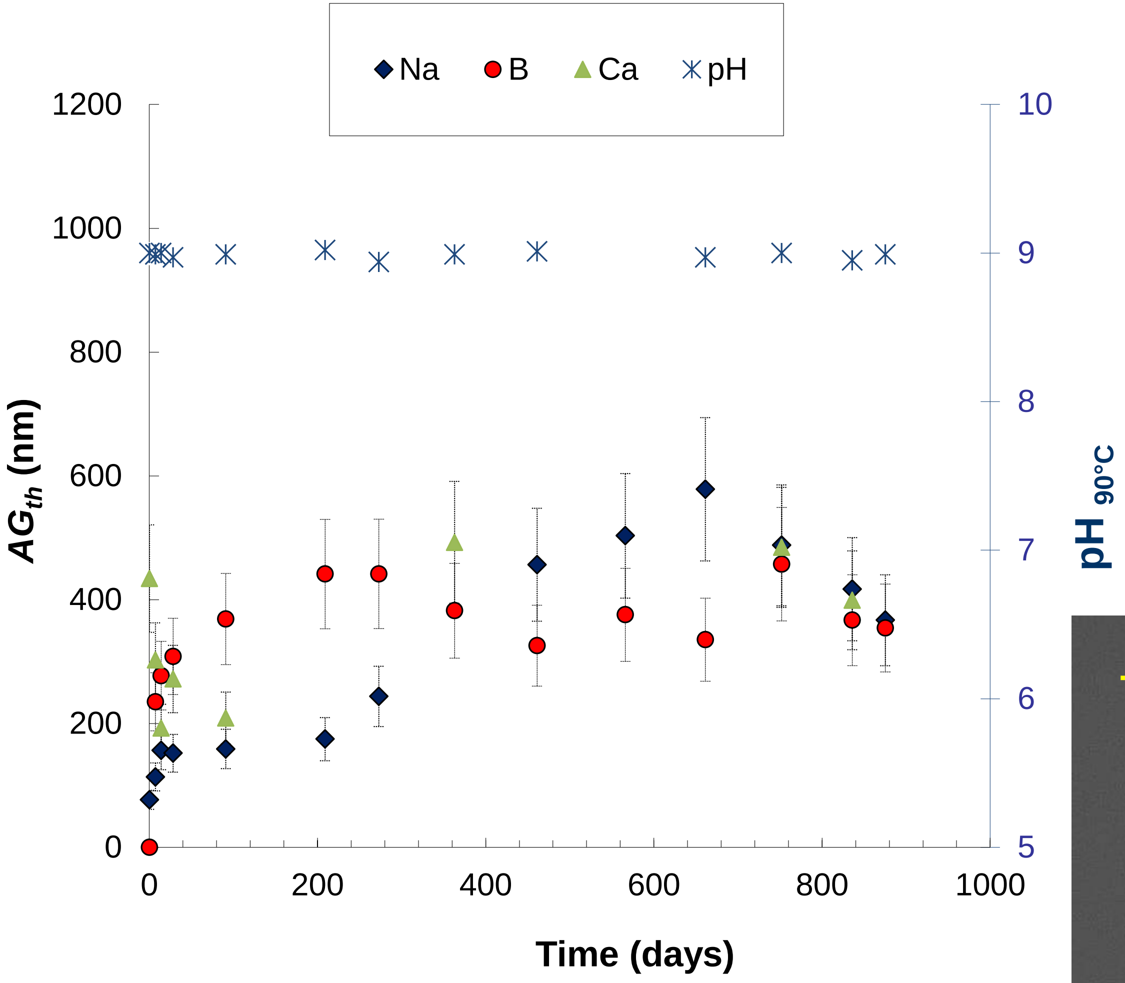
Experiments

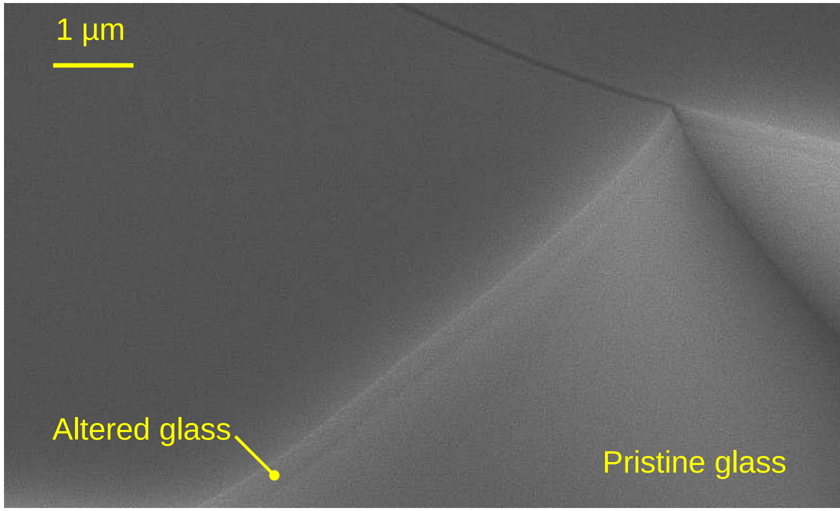
- International Simple Glass (ISG)
- 16 glass coupons have been altered at 90°C in 380 mL of solution initially saturated / $(^{29}SiO_2)$am at $pH_{90°C}$ 9
- $S/V = 0.6\ cm^{-1}$
- Isotope sensitive analytical techniques: MC-ICP-MS and ToF-SIMS, TEM, APT
- Coupon withdrawal: 7, 209, 363, 875 days
- 2 additional experiments with the 875d sample

ISG glass composition (wt%)

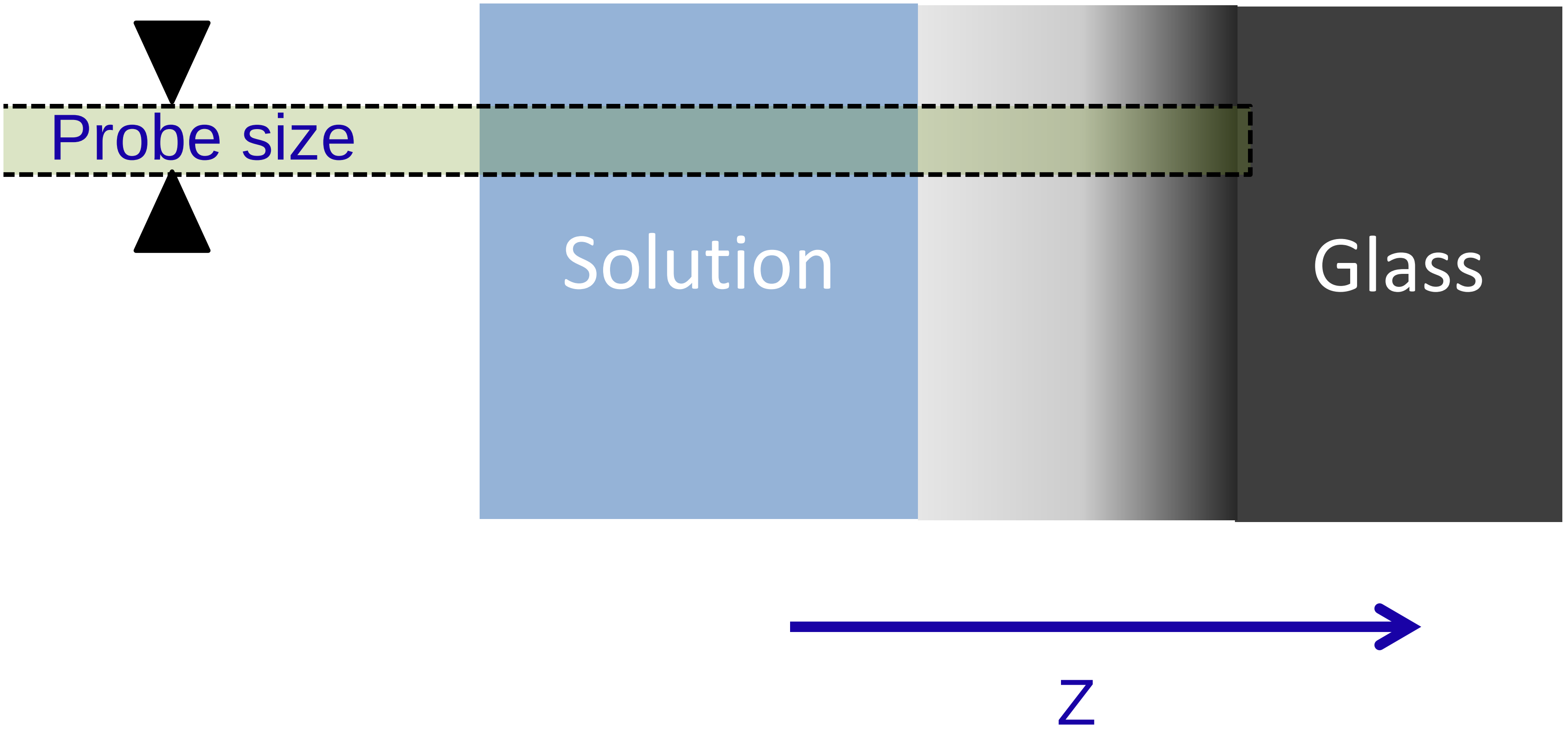
SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
56.2	17.3	12.2	6.1	5.0	3.3

Solution data

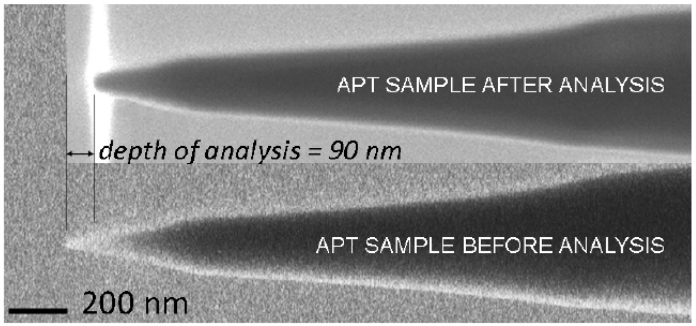




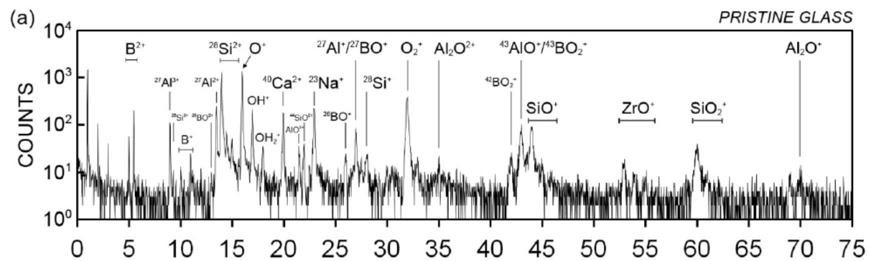
Probing chemical gradients at various scales



★ Atom Probe Tomography (3DAP CAMECA-LaWaTAPV)



Z resolution: 0.2 nm
Probe size: 12 nm



★ EFTEM (dual beam FIB prep and FEI TITAN 200 kV)

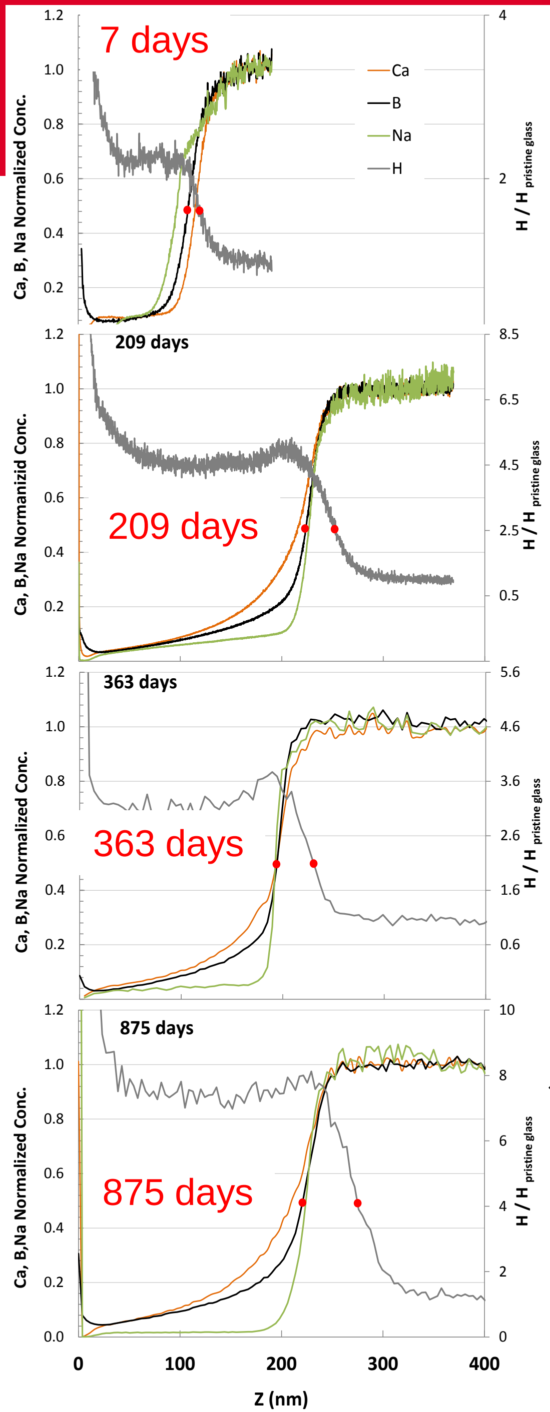
Z resolution: 2 nm
Probe size: 40 -150 nm

★ TOF-SIMS (TOF.SIMS5, IONTOF)
Low energy abrasion beam and reprocessing of data in order to get various rastered areas

Z resolution: 2 nm
Probe size: 1 - 30 µm

ToF-SIMS data

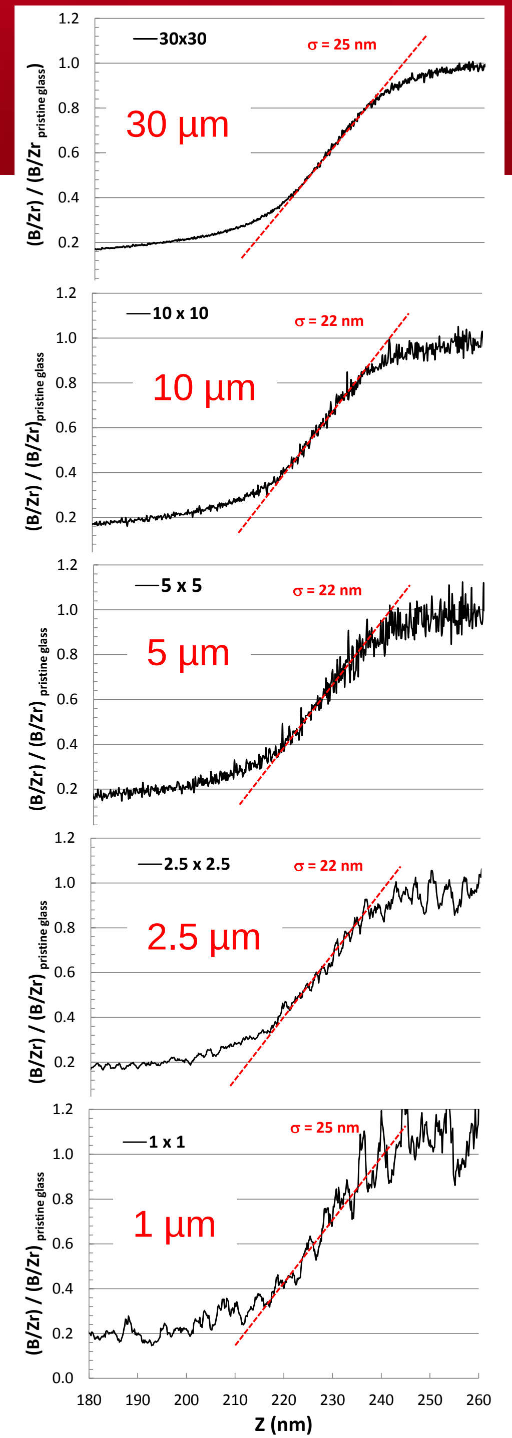
Z resolution: 2 nm
Probe size: 1-30 µm



209d sample B profiles

$$C_{\mathrm{B}}(z) = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{2\,\operatorname{erf}^{-1}(0.6)\,z}{\sigma}\right)\right)$$

Time-dependance profiles



Reconstruction of the chemical profiles

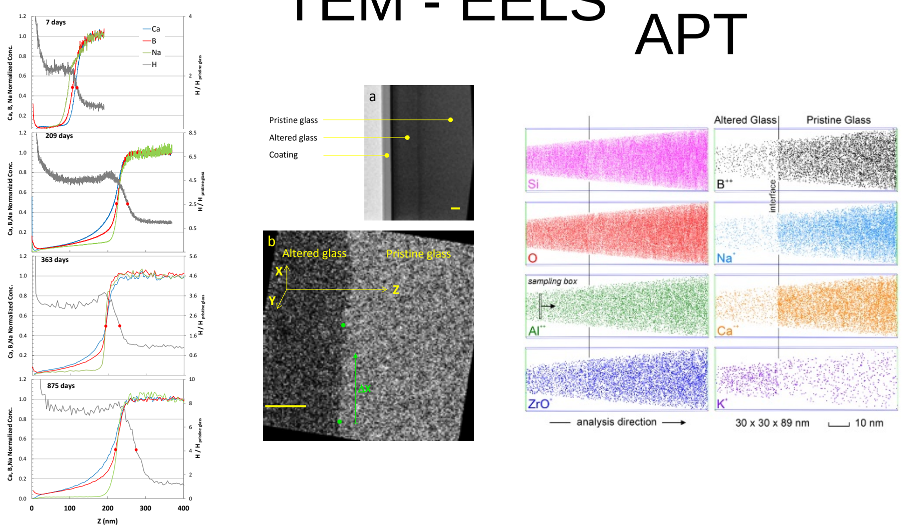
Gin et al. *Nature Comm.* 2015 ; Gin et al. *Geochim. Cosmochim. Acta* 2017

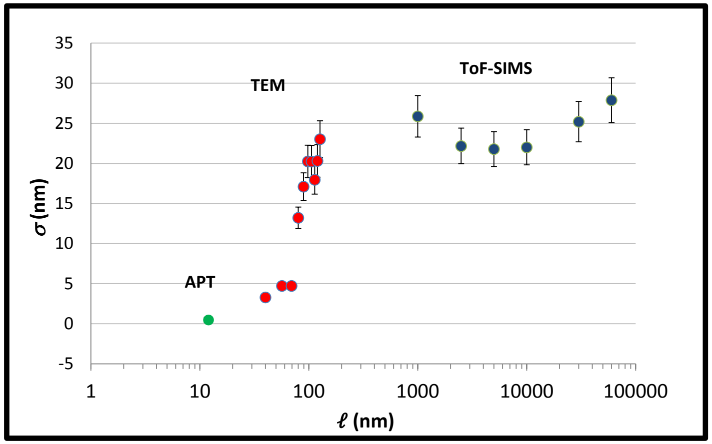
- Reconstruction of the reactive interface from a multiscale analysis of the alteration layer formed under residual rate conditions

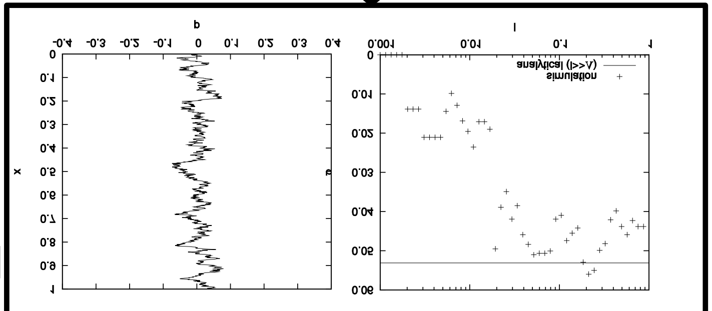
ToF SIMS

TEM - EELS

APT







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- New paradigm: the rough interface if created in the early stage of glass corrosion and propagates into the material at a rate limited by the accessibility of water molecules to the reactive interface.
- Water molecules are confined in pores of ~1 nm.
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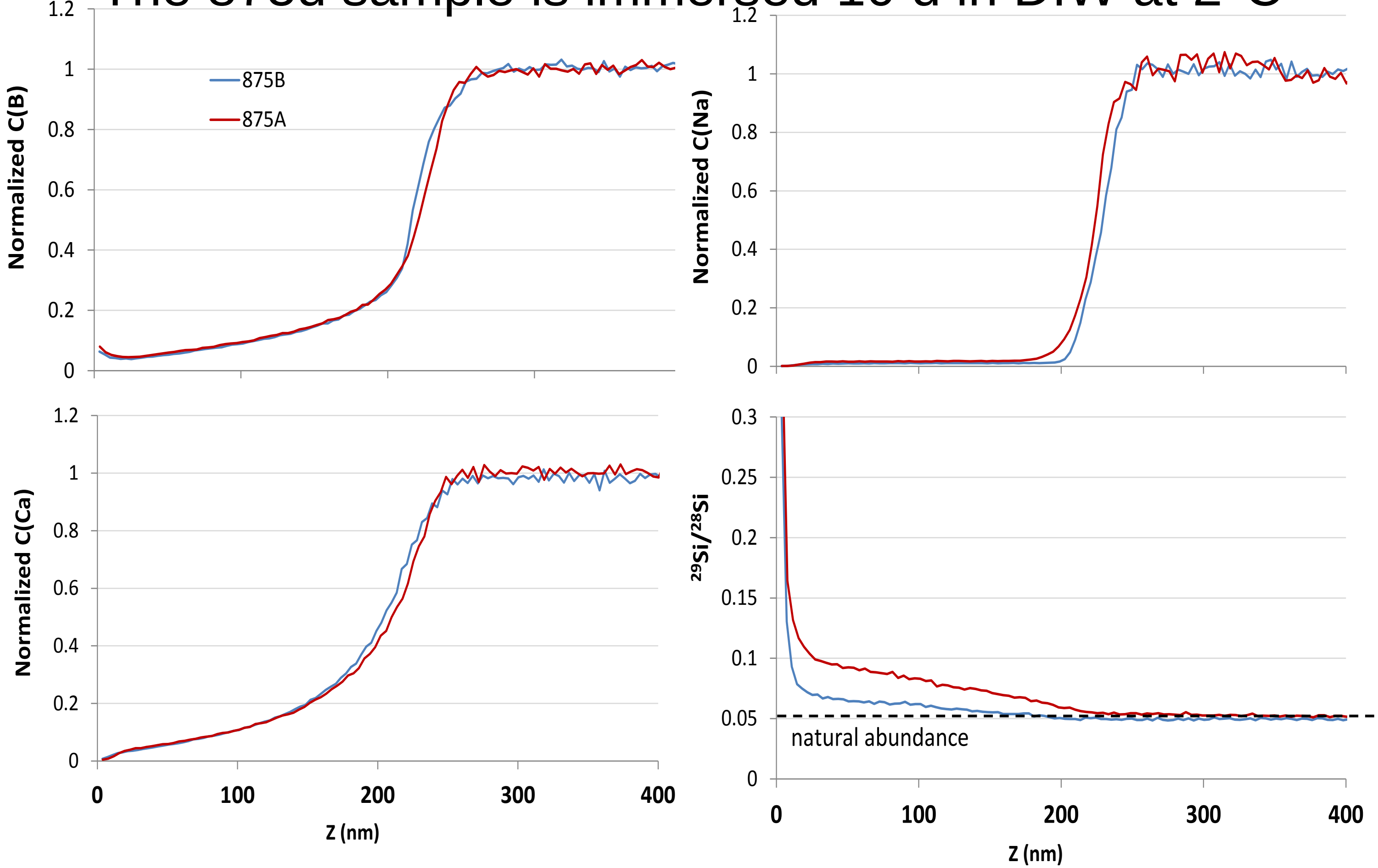
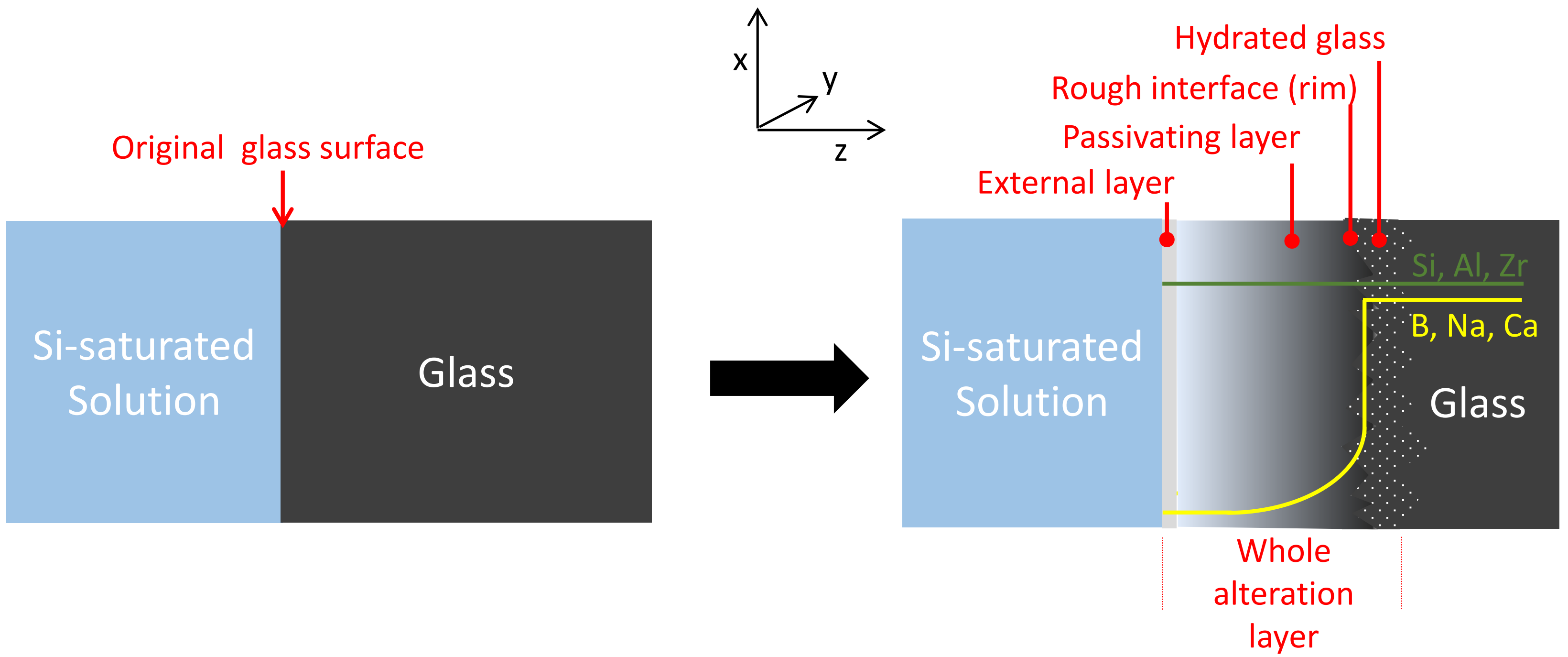
Mobility of “mobile” species

The 875d sample is immersed 10 d in DIW at 2°C

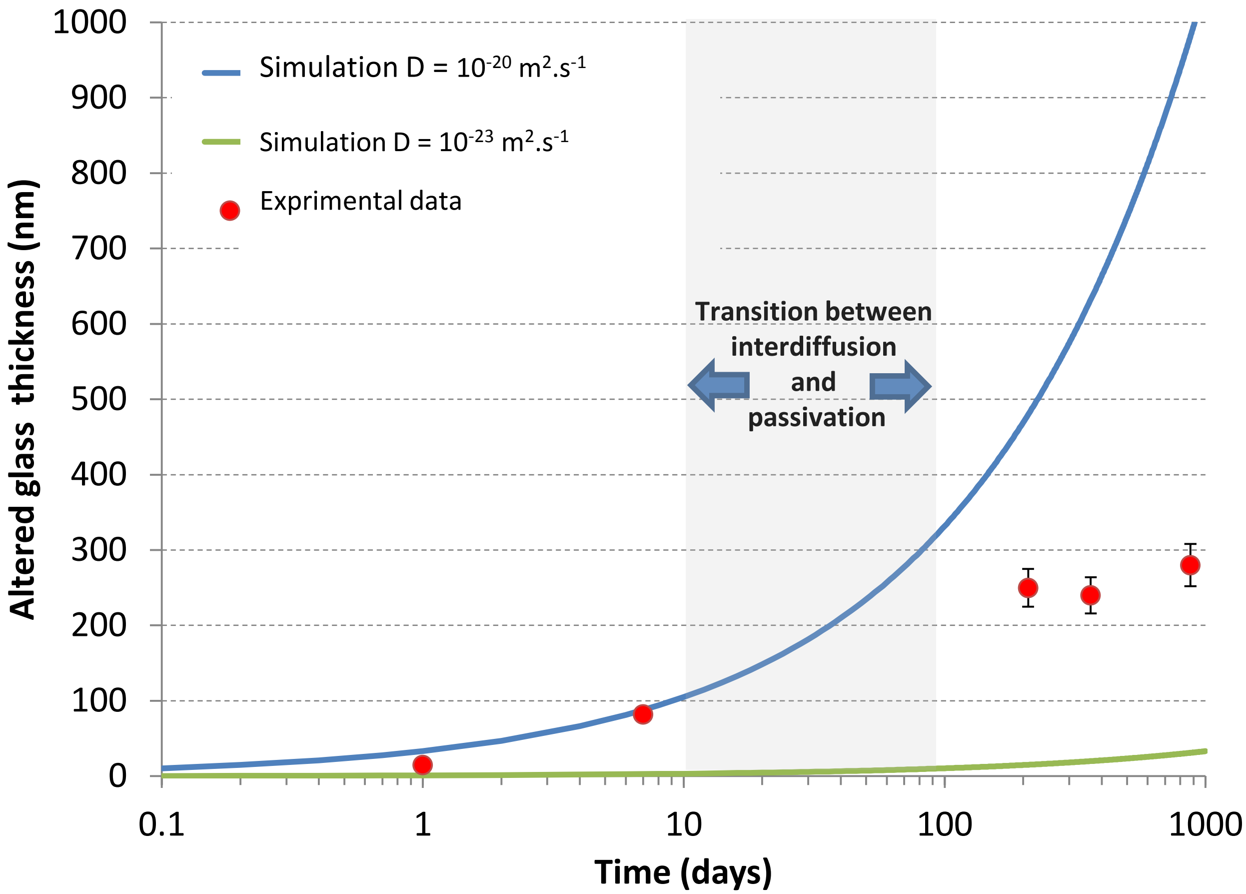


- ★ B and Ca remain trapped in the alteration layer ⟹ those species might be present in highly durable clusters
- ★ Unexpectedly ^{29}Si is mobile



Original glass surface
Si-saturated Solution
Glass
x
y
z
Hydrated glass
Rough interface (rim)
Passivating layer
External layer
Si, Al, Zr
B, Na, Ca
Si-saturated Solution
Glass
Whole alteration layer

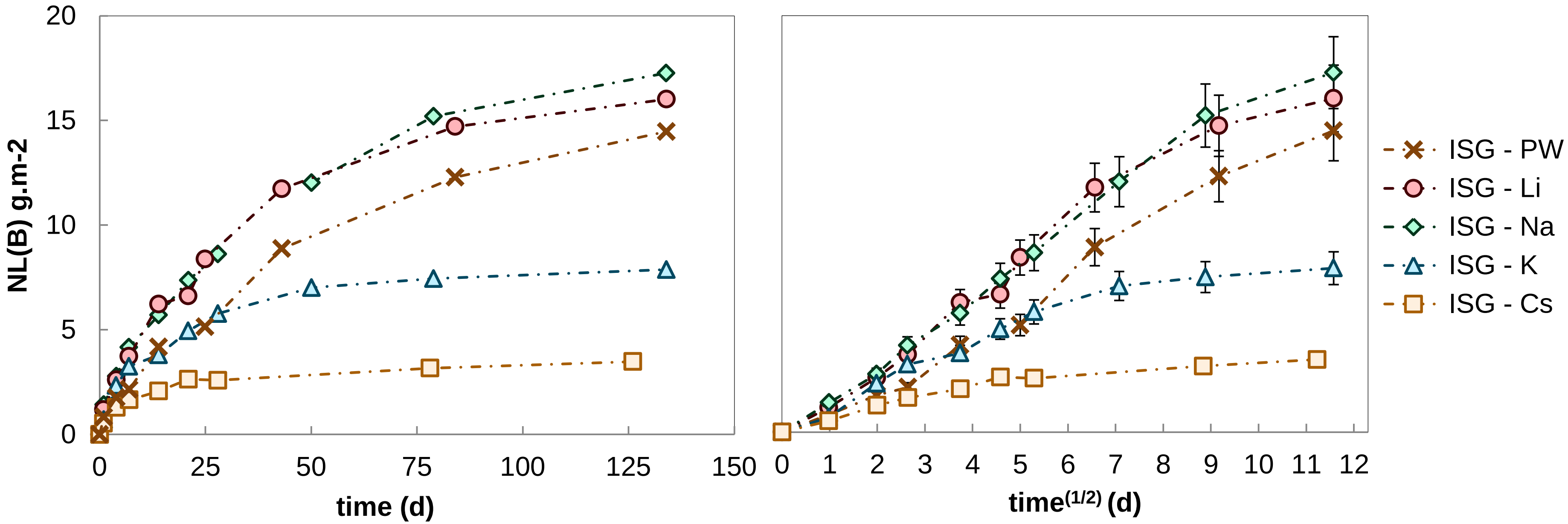
Apparent Diffusivity of the Passivating layer

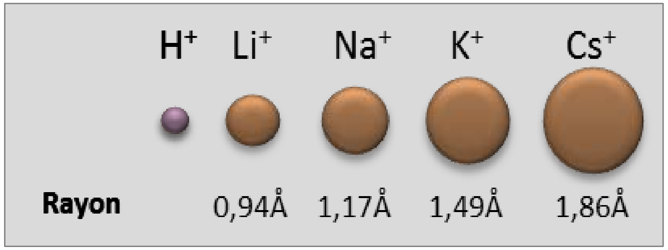


- ✶ Passivation occurs within the first tens of days
- ✶ D_{app} drops by 3 O.M.

Effect of alkali

The effect of counter ions in the solution is currently being studied :

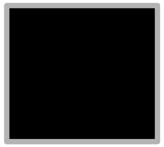




Size of the alkali[2].

(2) Conway et al., Journal of Solution Chemistry,1999,

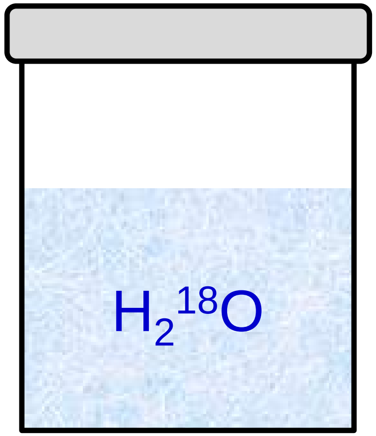
Water dynamics in passivating layers (1/3)



ISG glass coupon altered for 1 year @ 90°C, pH 7, Sisat

In depth characterization of the passivating layer (water content, porosity, pore size, speciation)

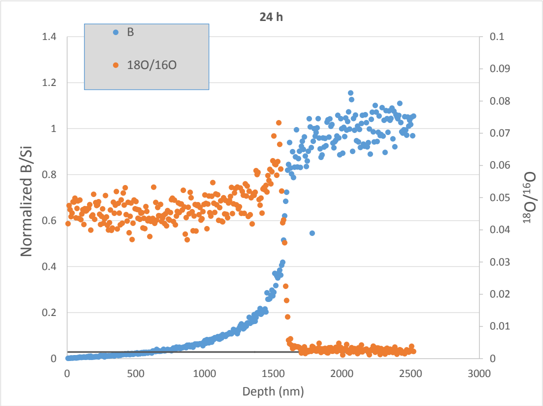
Porosity ~ 30%
Pore size ~ 1 nm
$O_{skeleton} = 0.75$, $O_{SiOH} = 0.12$, $O_{H20} = 0.12$



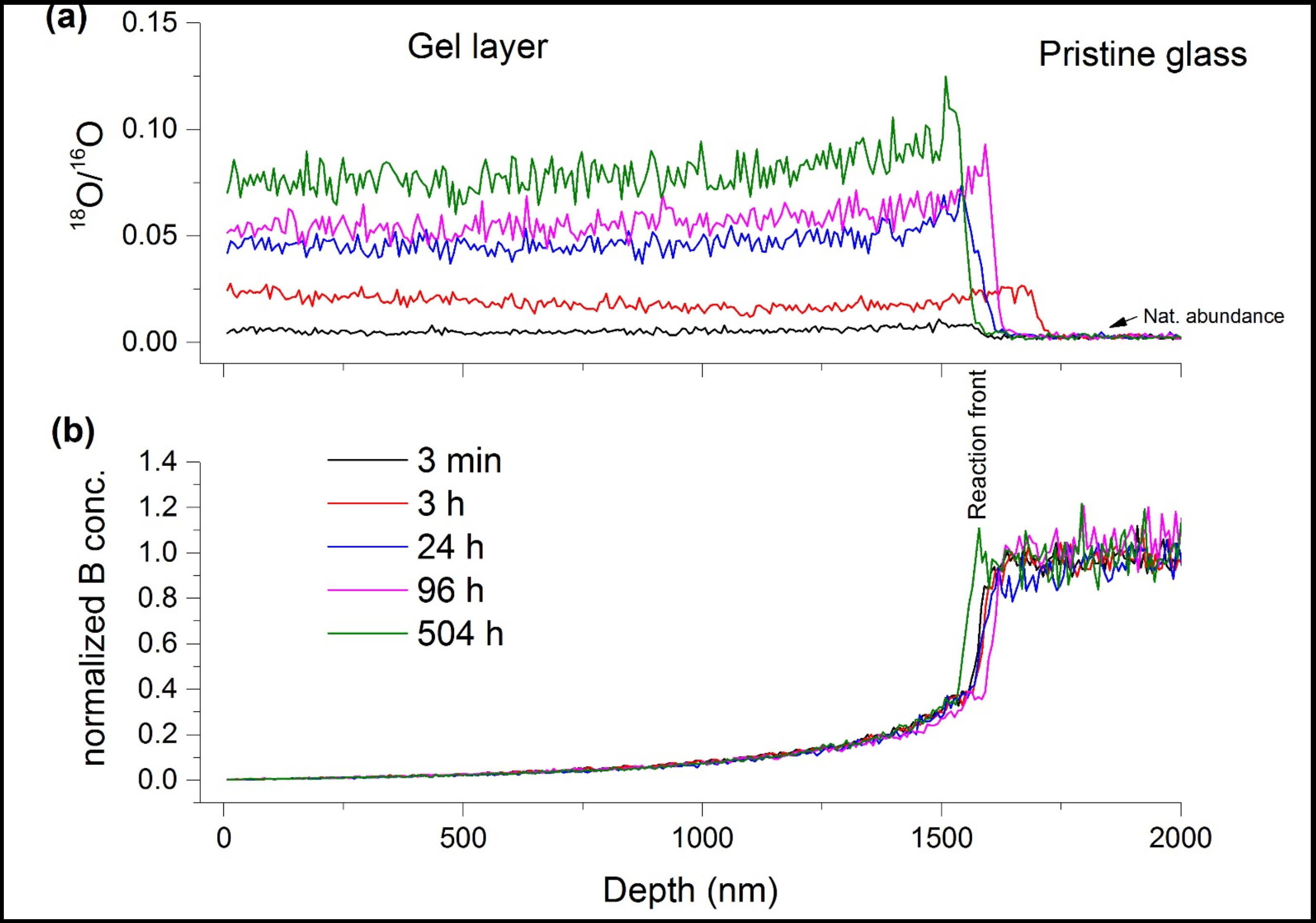
ToF-SIMS

Quantitative analysis of $^{18}O/^{16}O$ profiles with the passivating layer

- Mass balance
- Flux of water reaching the pristine glass surface



ToF SIMS profiles at various contacting time



Water budget based on O isotopes