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ICTP-IAEA joint workshop on vitrification

Chemical Durability of Vitreous Wasteforms

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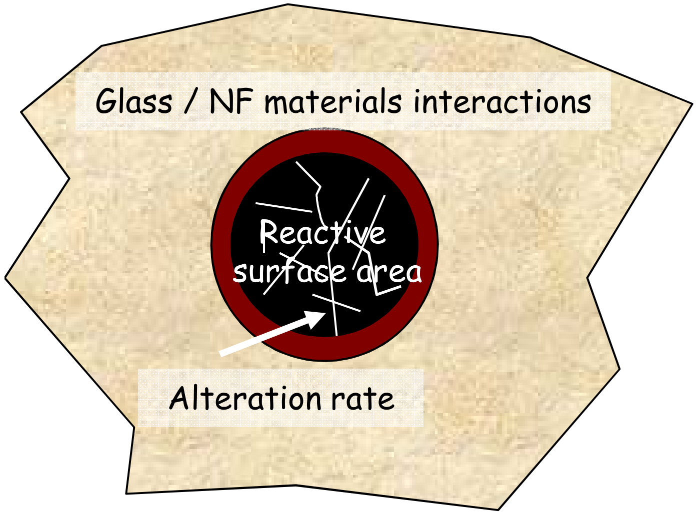
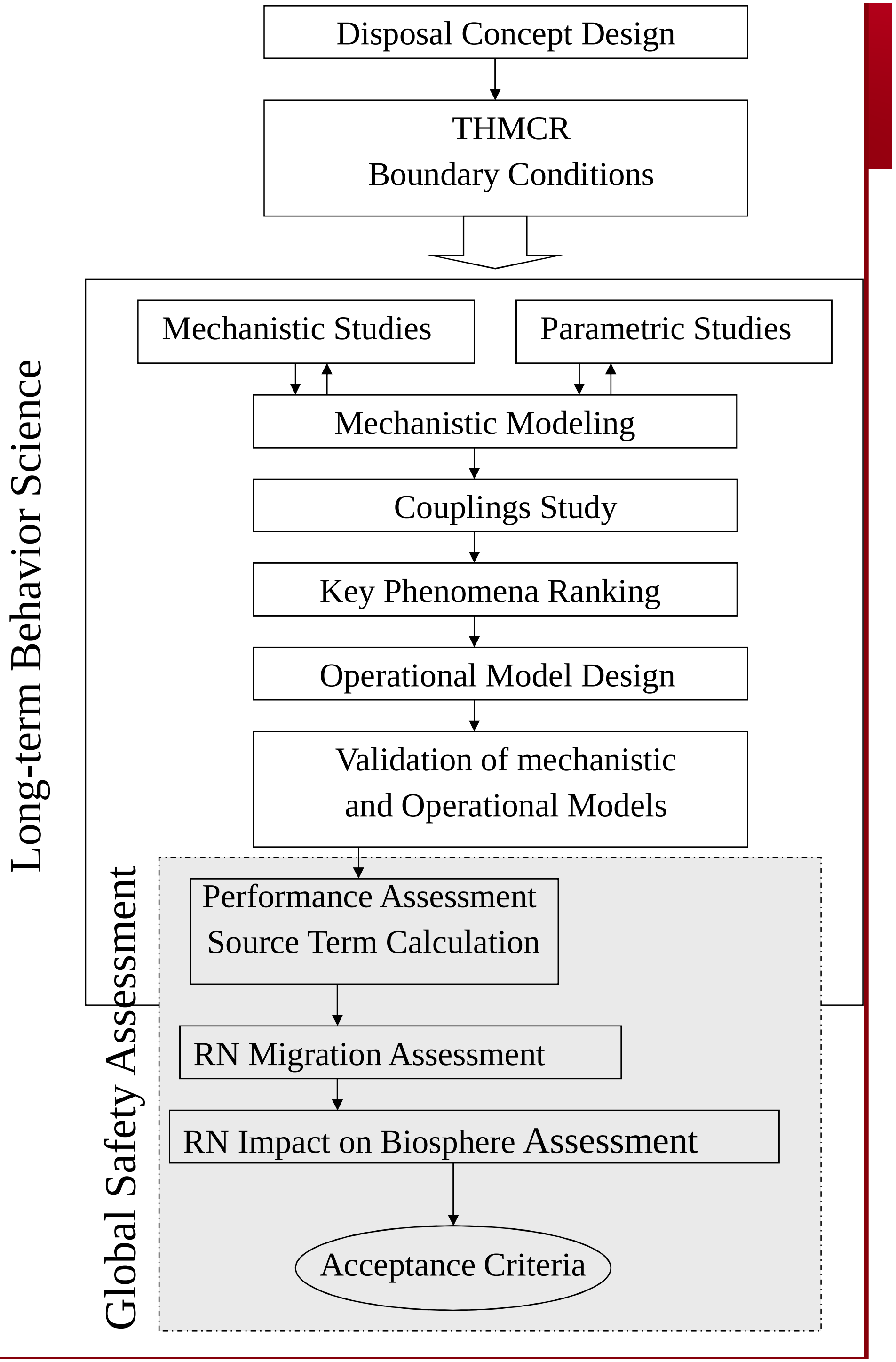
Glass durability?

$$\phi_{RN} \; \alpha \; M_{altered\ glass} = \iint r(t,s)dsdt$$



ASTM Standard C1174-07
Poinssot et al., JNM 2012



Disposal Concept Design

THMCR
Boundary Conditions

Long-term Behavior Science

Mechanistic Studies

Parametric Studies

Mechanistic Modeling

Couplings Study

Key Phenomena Ranking

Operational Model Design

Validation of mechanistic
and Operational Models

Global Safety Assessment

Performance Assessment
Source Term Calculation

RN Migration Assessment

RN Impact on Biosphere Assessment

Acceptance Criteria

Outline

1. Basic mechanisms of glass corrosion
2. Kinetic regimes
3. Ongoing studies to better understand how gel layer form and passivate the glass surface
4. Remaining challenges

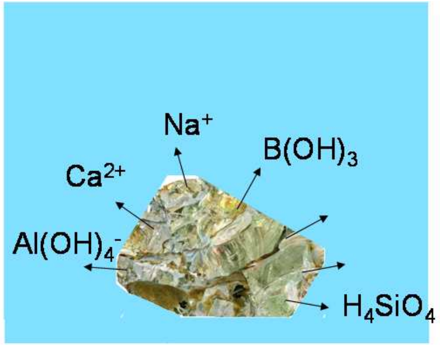
Can thermodynamic equilibrium between glass surface and solution be achieved?

- **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



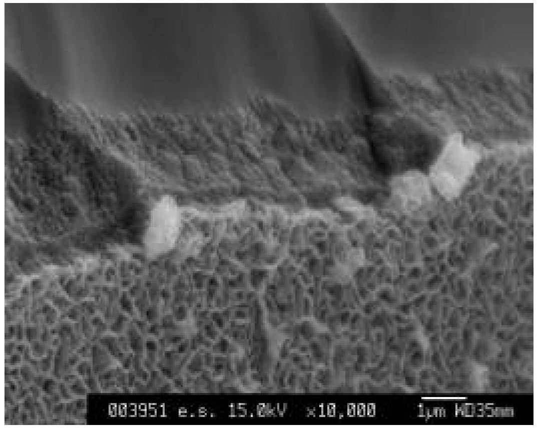
What are the key parameters to be considered?

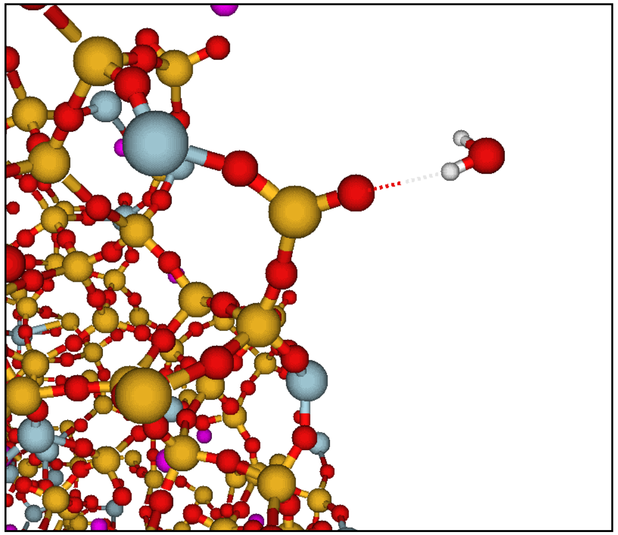
- **Intrinsic Parameters**
  - → Glass composition
  - → Glass structure (cooling rate, homogeneity)
  - → Reactive surface area, surface roughness and residual stress
  - → Self irradiation (in case of nuclear glasses)

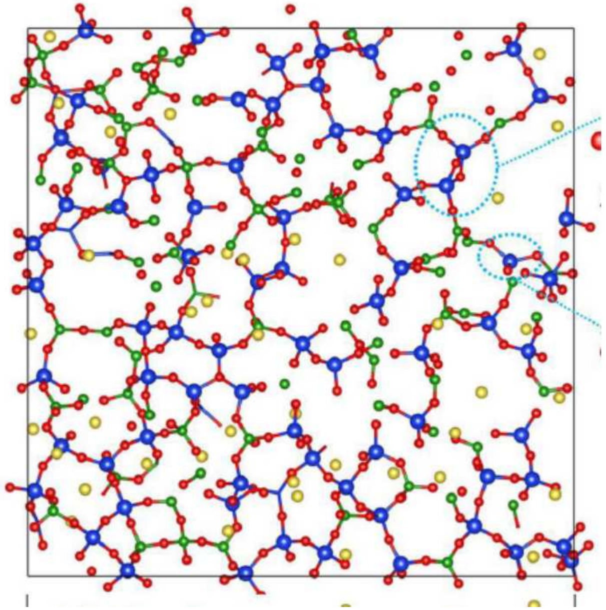
- **Extrinsic Parameters**
  - → Temperature
  - → Unsaturated (relative humidity) vs water saturated medium
  - → pH, water composition (itself modified by the surrounding solids)
  - → Flow rate
  - → (Pressure, Eh, microbial activity)

Basic mechanisms

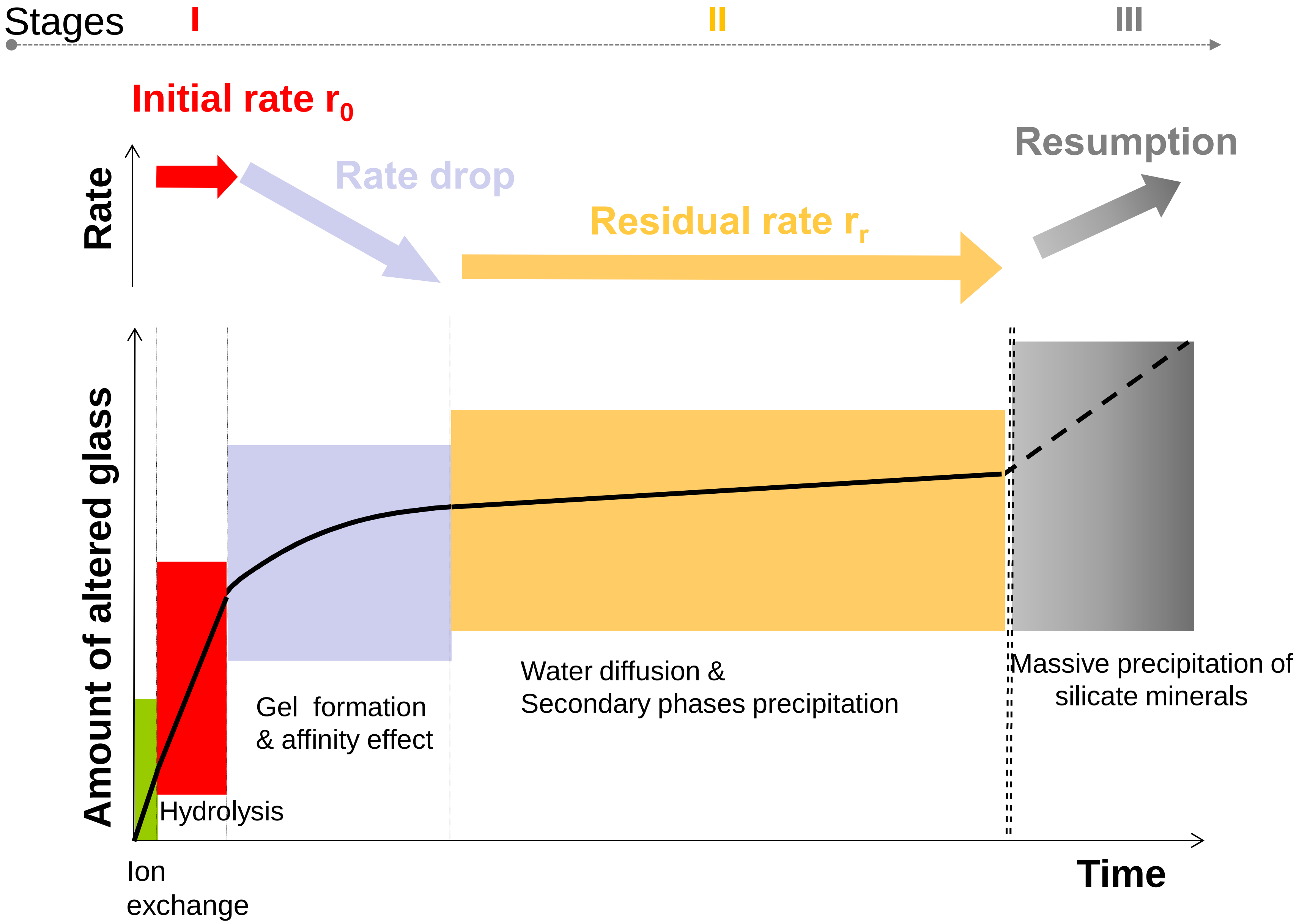
- Hydration / Interdiffusion
- Hydrolysis of glass formers
- Condensation of some hydrolyzed species (Si, Al, Ca…)
- Precipitation of secondary phases

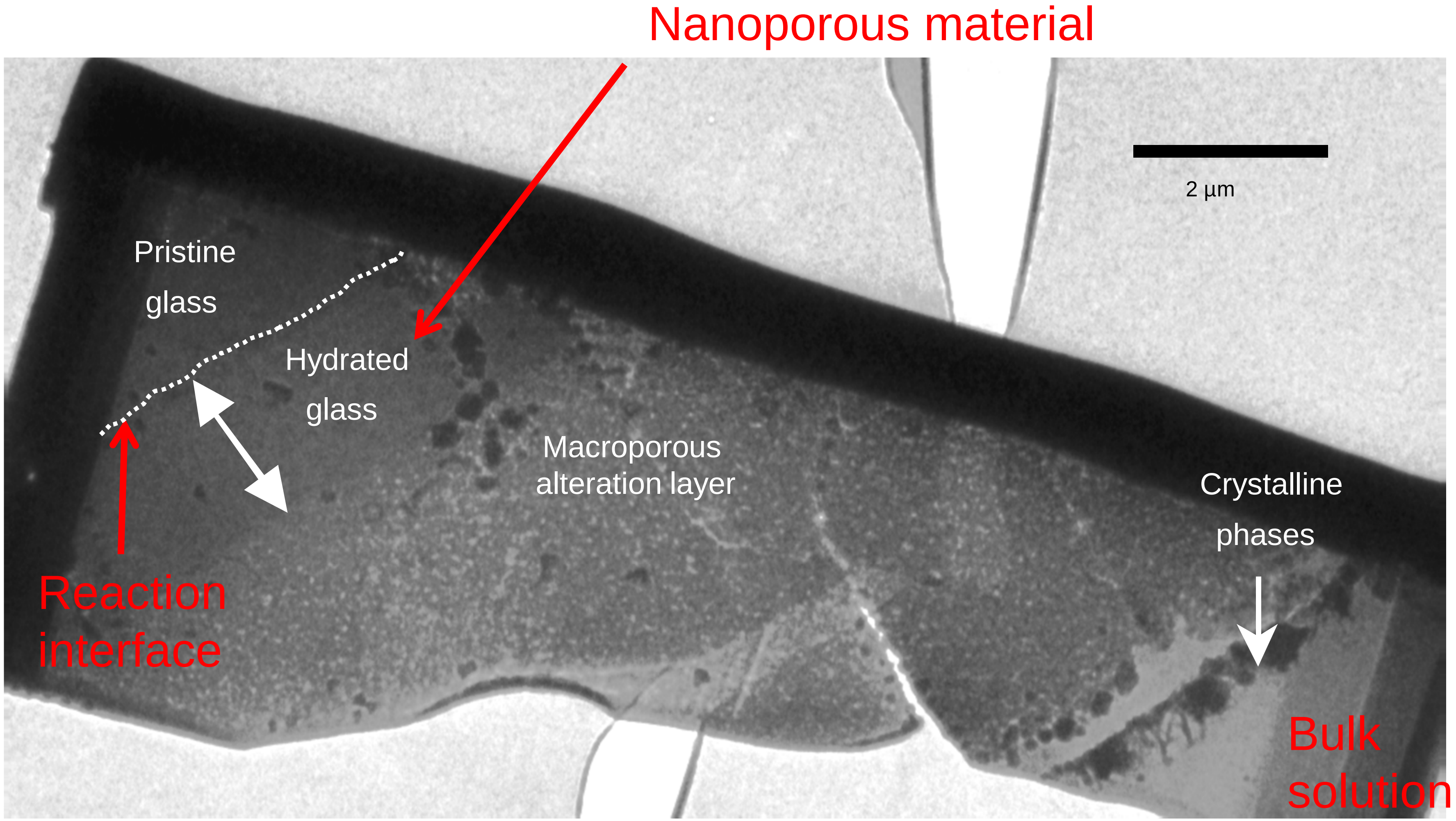






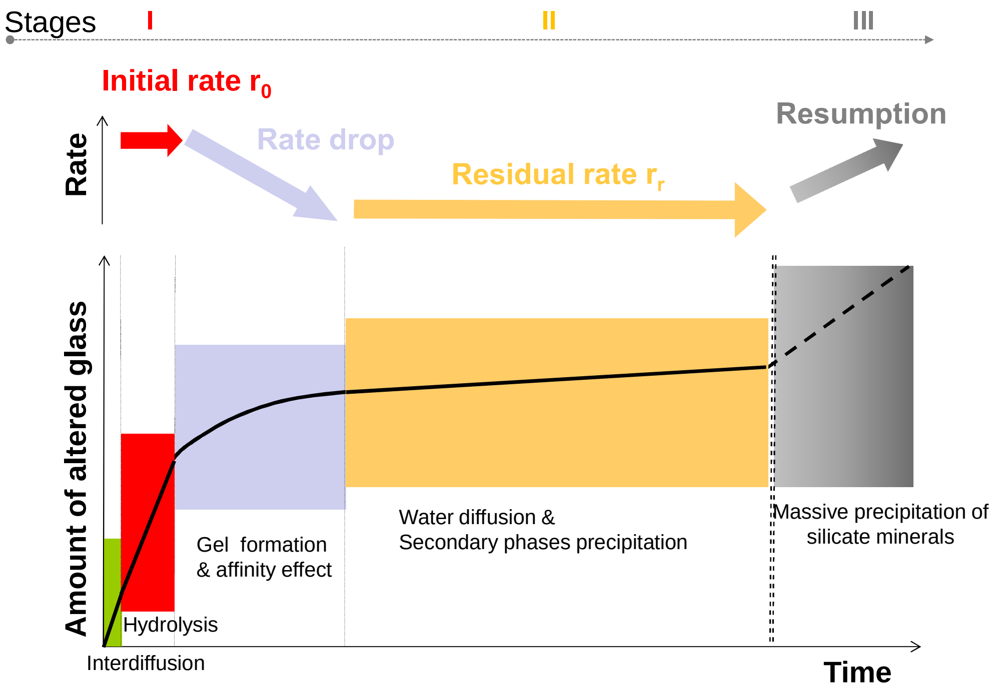
KINETIC REGIMES





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 with glass lifetime of a few 10^3 years…

Some key figures @ 90℃ for R7T7 type glass

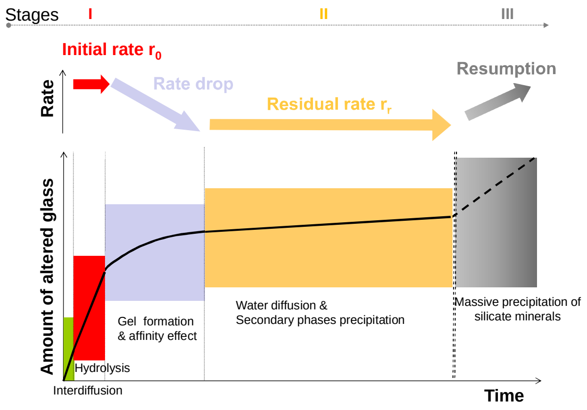
- Stage I : $r_0 \sim 0.5\ \mu.d^{-1}$ $D_{w\ \text{in pristine glass}} \sim 10^{-20}\ m^2.s^{-1}$
- Stage II : $r_0 \sim 10^{-4}\ \mu.d^{-1}$ $D_{w\ \text{in stage II}} \sim 10^{-23}\ m^2.s^{-1}$

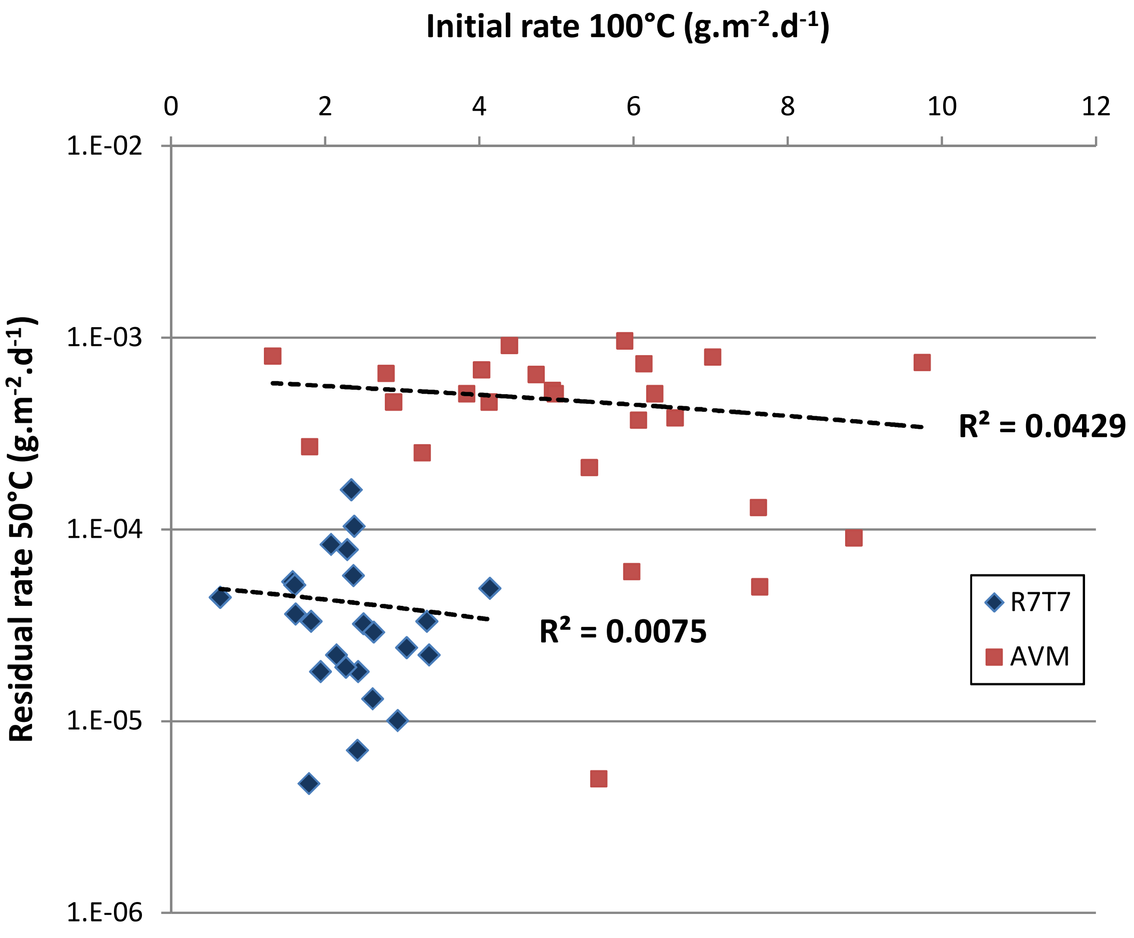
➢ What is behind these low apparent D?

➢ What is the effect of glass composition?

➢ How secondary phases disrupt passivating layers?

Relation between short-term & residual rate



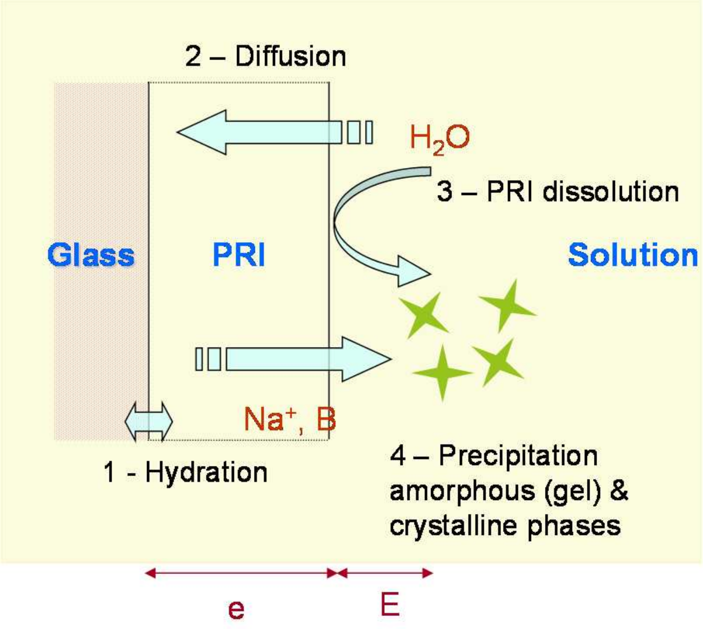


- *Measuring initial rates does not help understand what could happen at long term*
- *Same conclusion for PCT 7d*

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

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

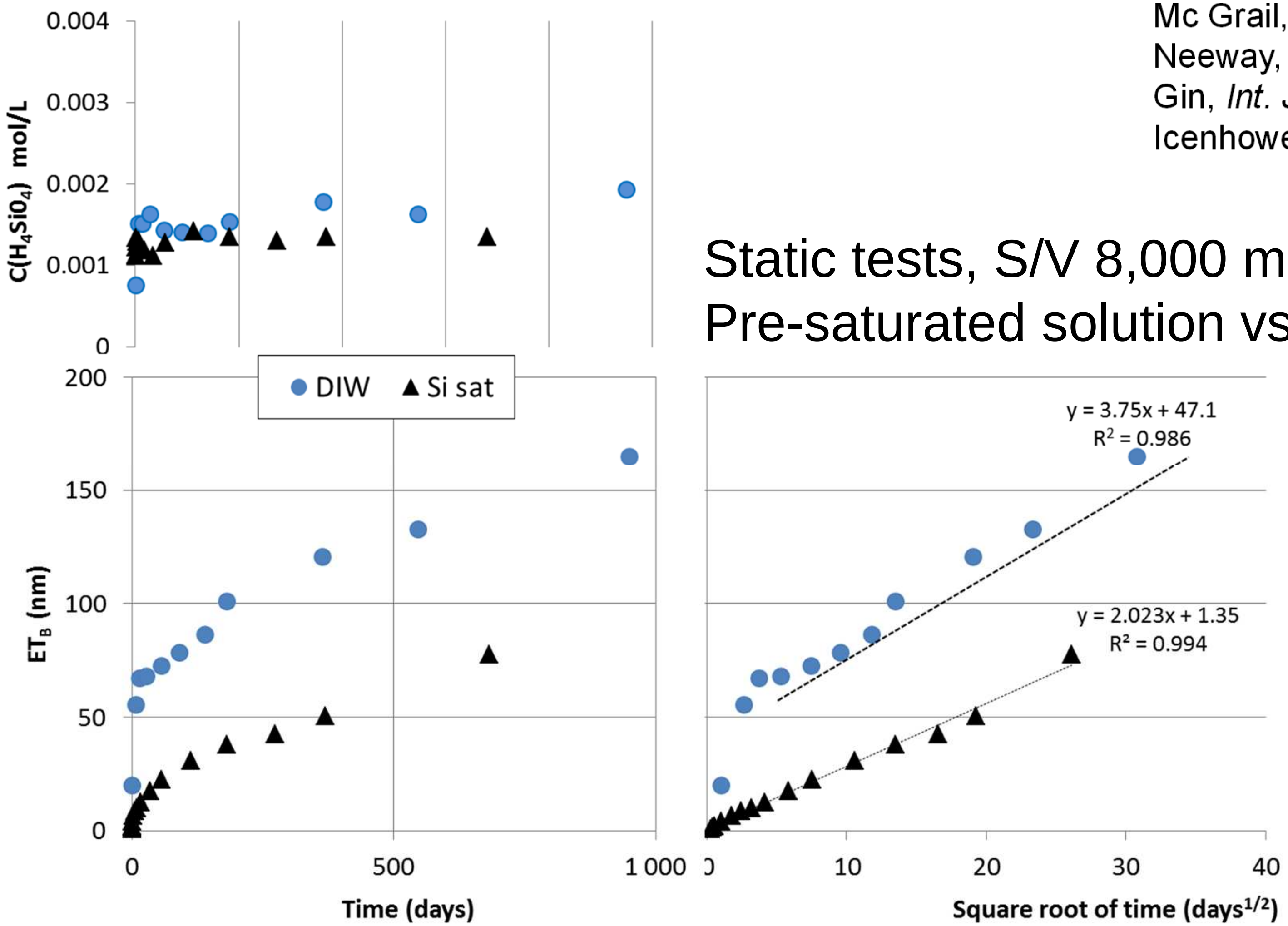
$$\frac{de}{dt} = \frac{r_{hydr}}{1+\frac{e\cdot r_{hydr}}{D_{PRI}}} - \frac{dE}{dt}$$ $\rightarrow$ **Macroscopic parameter**

- 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

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 8,000 m^{-1}, 90°C, 3y
Pre-saturated solution vs DIW

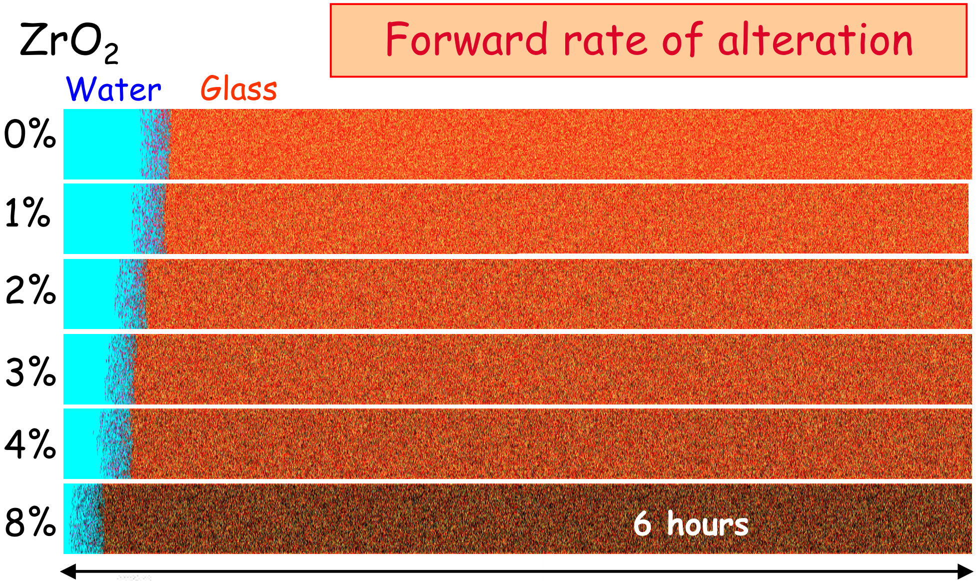


Pre-sat solution makes the RD stage much shorter (Si affects the rate of Si-O-Si hydrolysis) but does not impact the RR regime.

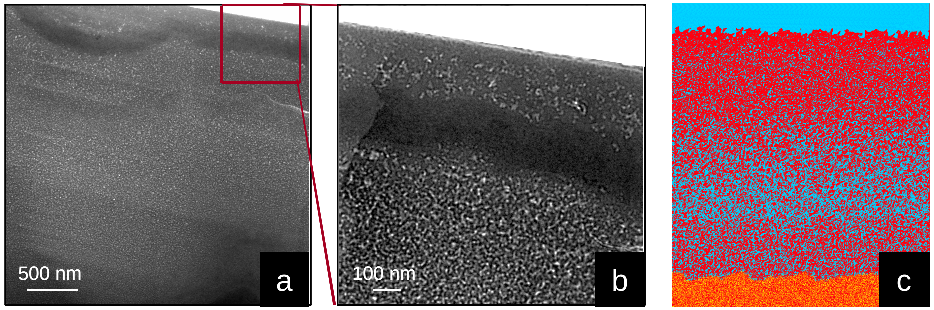
🟦 H_2O 🟨 B
🟥 Si ⬛ Zr
🟪 Condensed Si

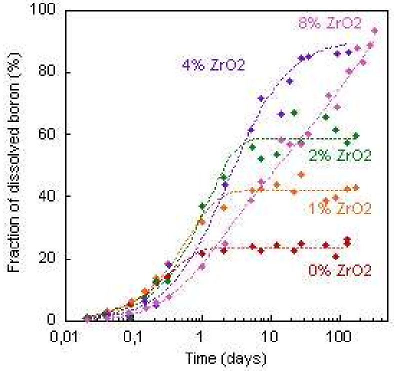
Processes causing the drop of the rate
2 : Formation of a diffusion barrier

Forward rate of alteration



Cailleteau, *Nature Materials* 2008



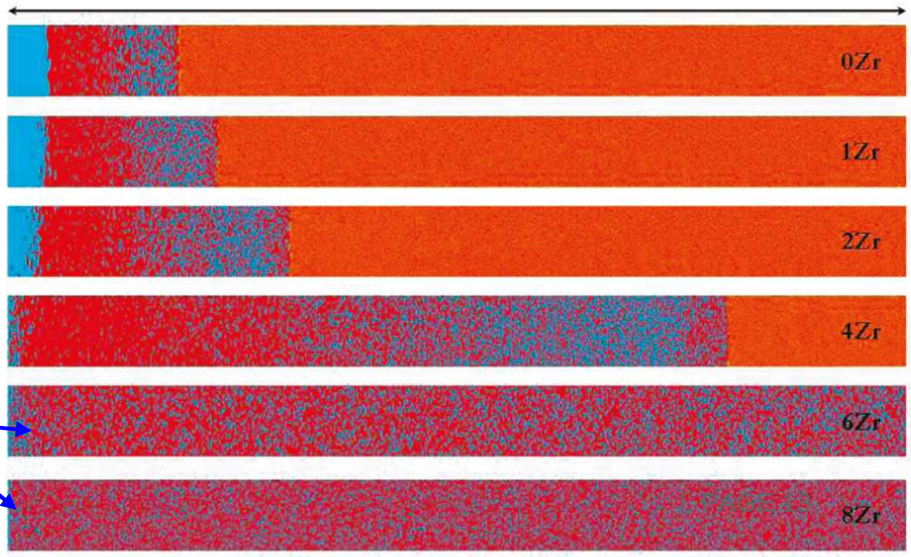


Zr at.: immobilize increasing numbers of Si

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

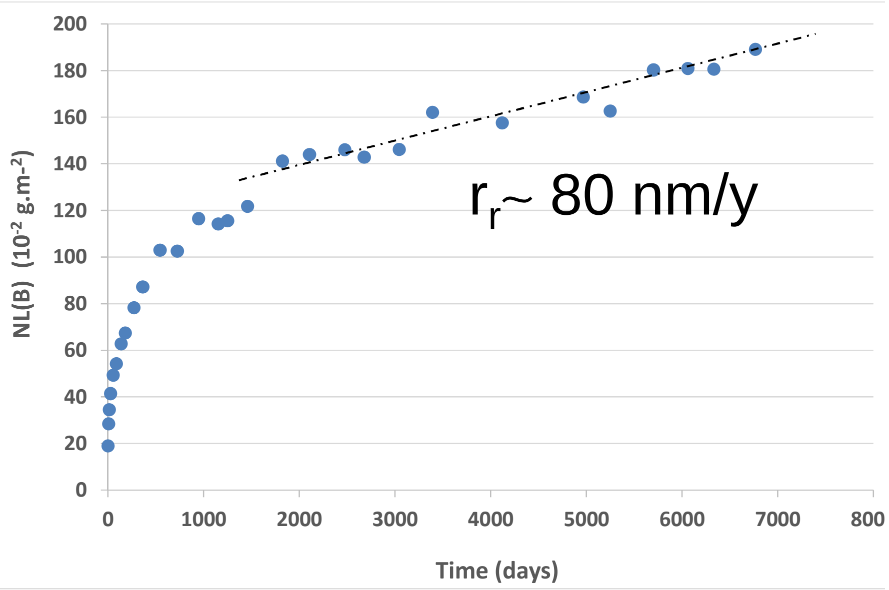
-> <u>percolation pathways</u>
(leaching sol. - pristine glass surf.)

Porosity clogging: up to 4% of ZrO_2



Why alteration does not stop in stage II?

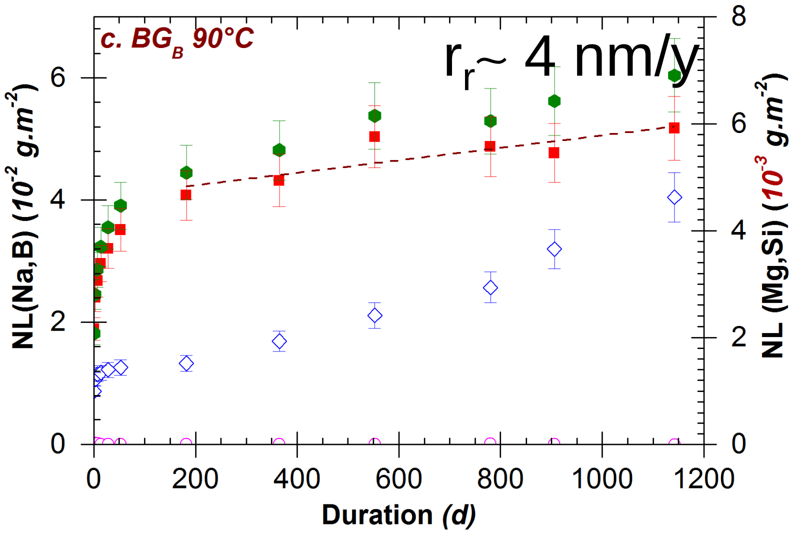
A rate never equal to zero: case of nuclear glass and basaltic glass



$r_r \sim 80$ nm/y

Nuclear glass (ISG - 6 oxides)

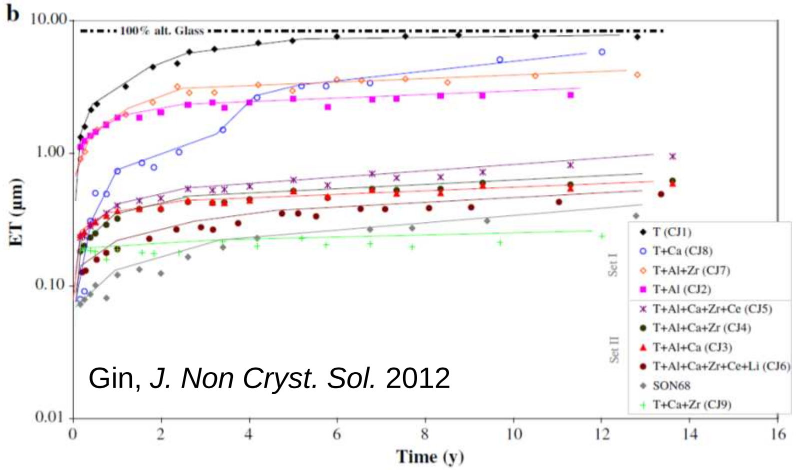
Alteration at 90℃, in deionized water, in static mode



$r_r \sim 4$ nm/y

Basaltic glass

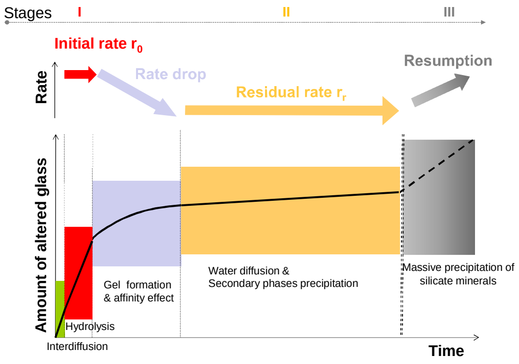
Why alteration does not stop in stage II?



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 5 and 10

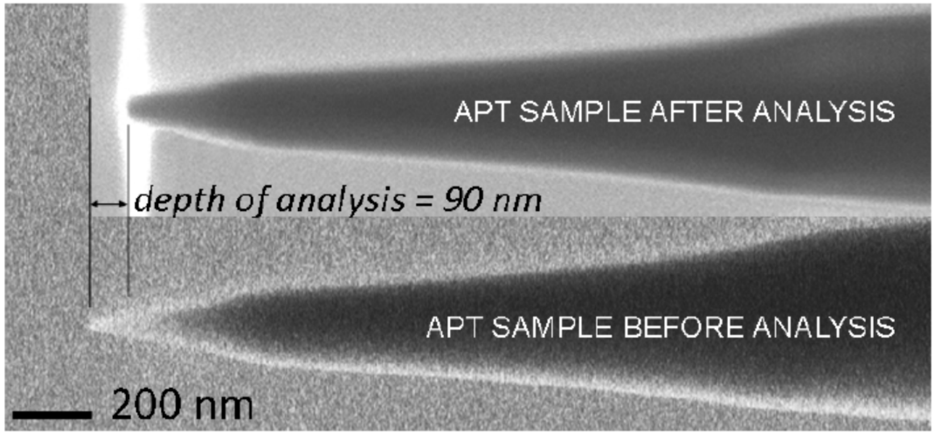
Hypothesis 2: because IX continues beyond the saturation of the solution w.r.t. SiO_2am (Grambow *MRS proc.* 1985 ; McGrail *J. Non Cryst. Sol.* 2001)
No, recent results show that Na and B profiles do not match a simple IX process

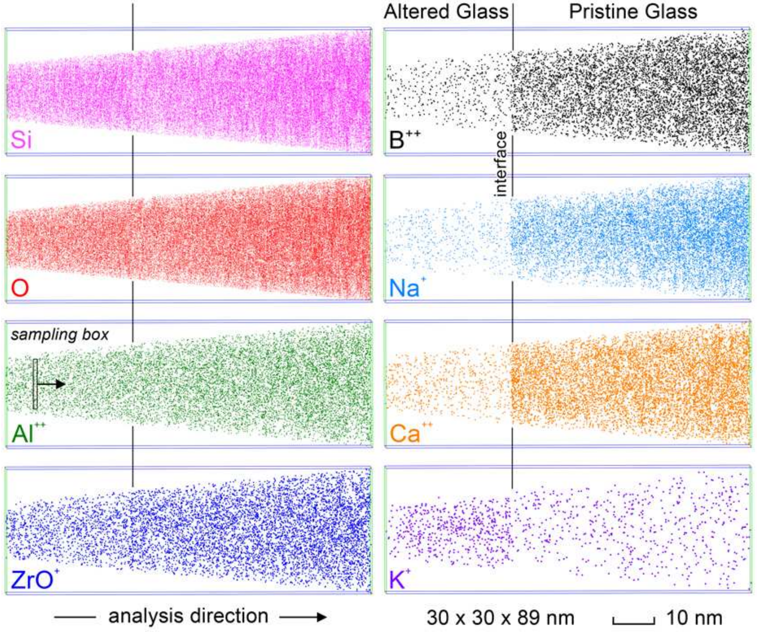


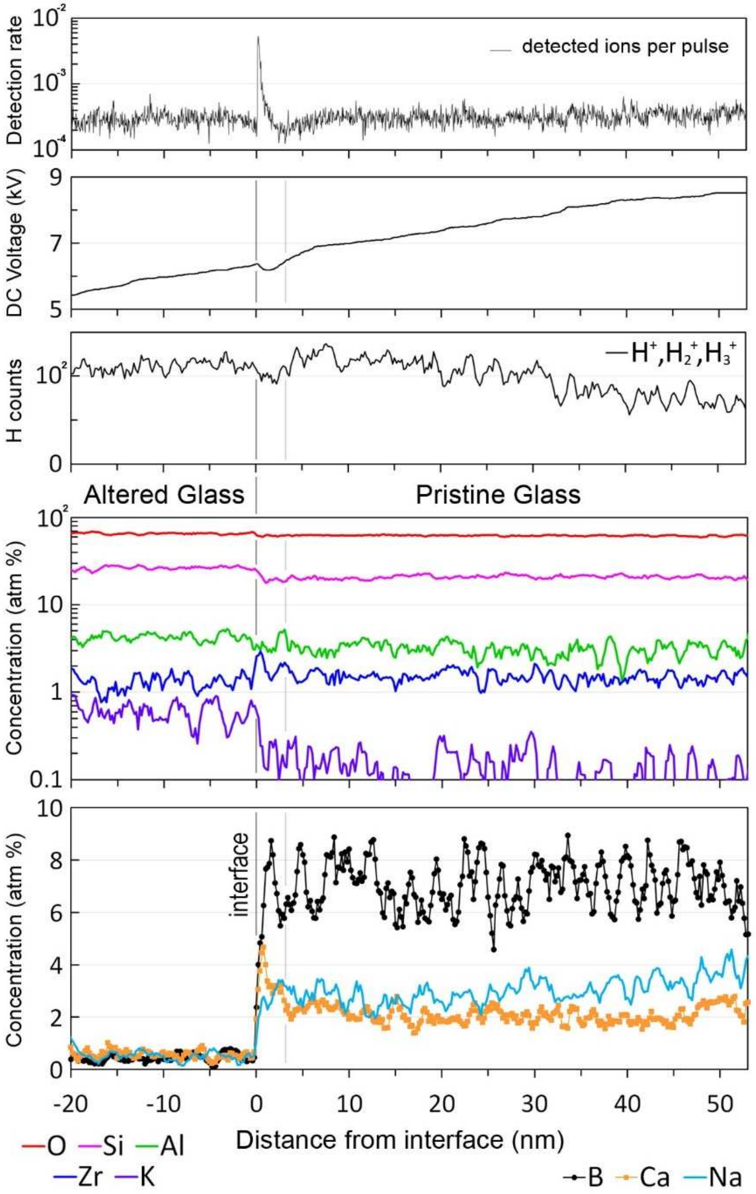
Hypothesis 3: water accessibility to reactive sites is hampered the the low porous gel formed by in-situ reoganization of the silicate network after the departure of mobile species
Need to be confirmed by a better understanding of water speciation and dynamics within the alteration layers (DOE - EFRC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

Results @ pH 9 – APT Profiles

Gin et al. *Geochim. Cosmochim. Acta*, 2017

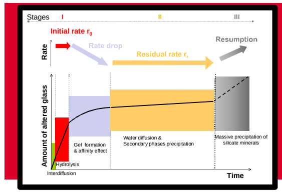


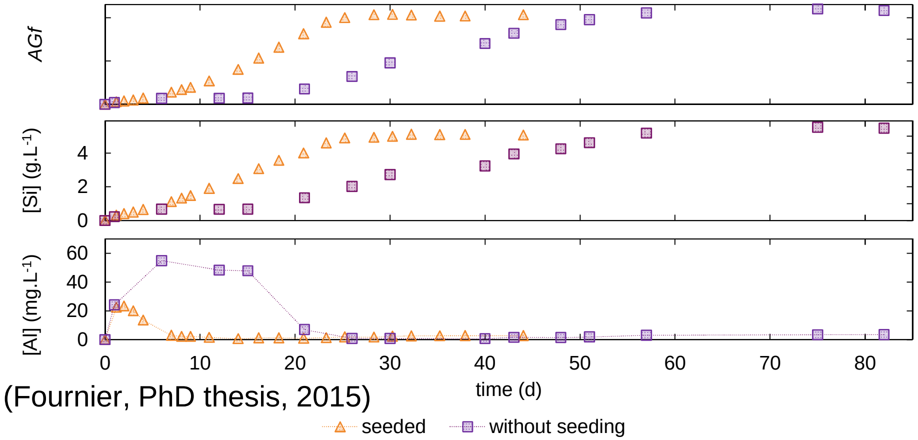




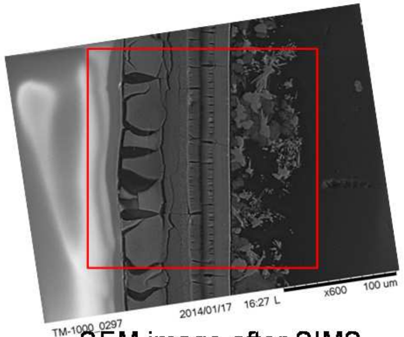
Why glass dissolution can turn into stage III?

Why dissolution can turn into stage III?

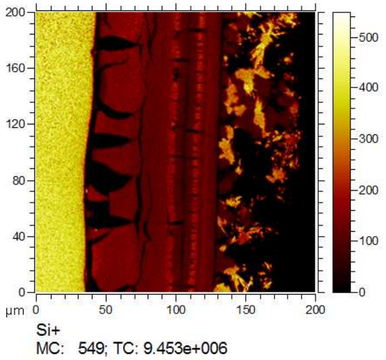


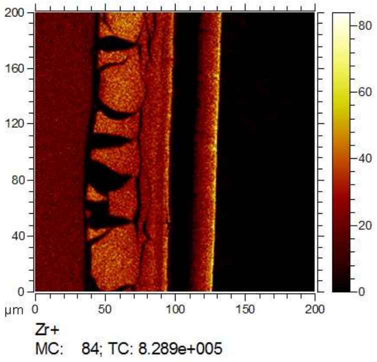


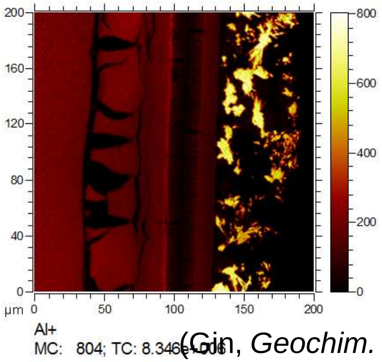
(Fournier, PhD thesis, 2015)

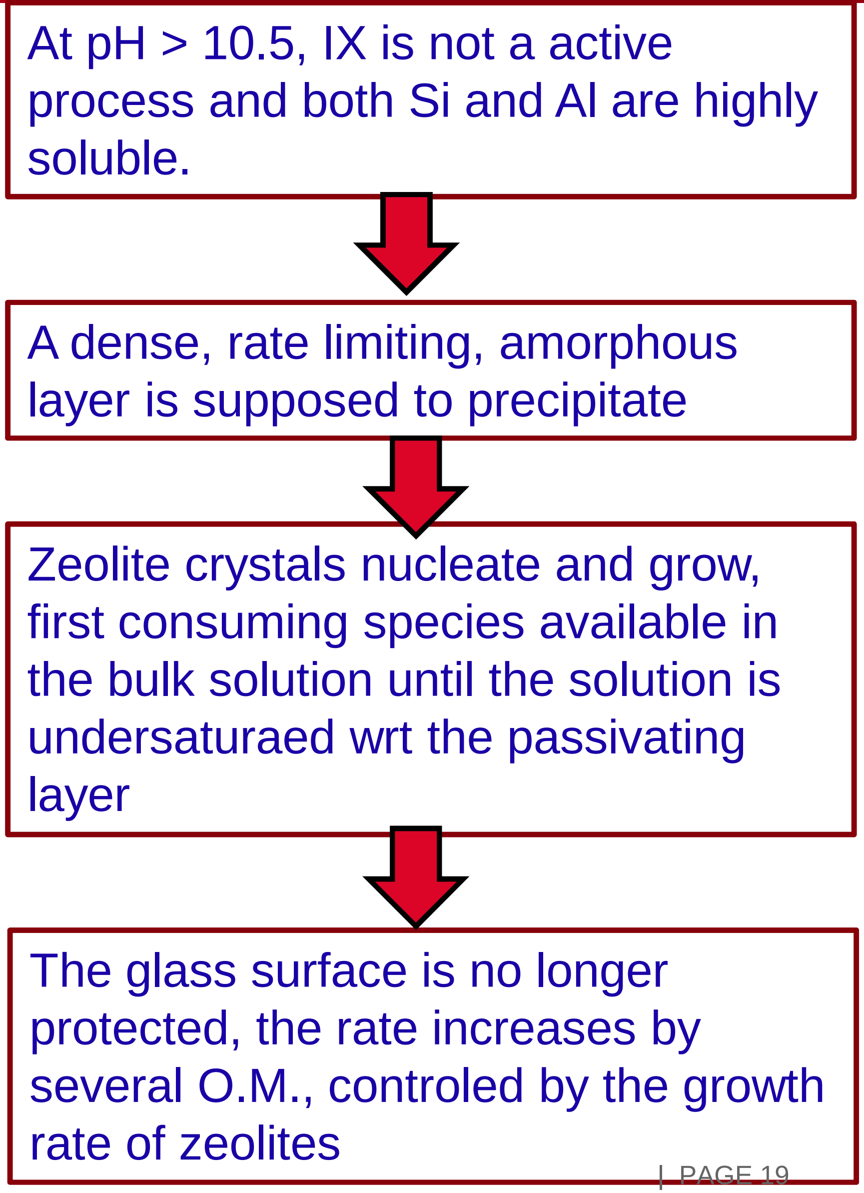


SEM image after SIMS









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

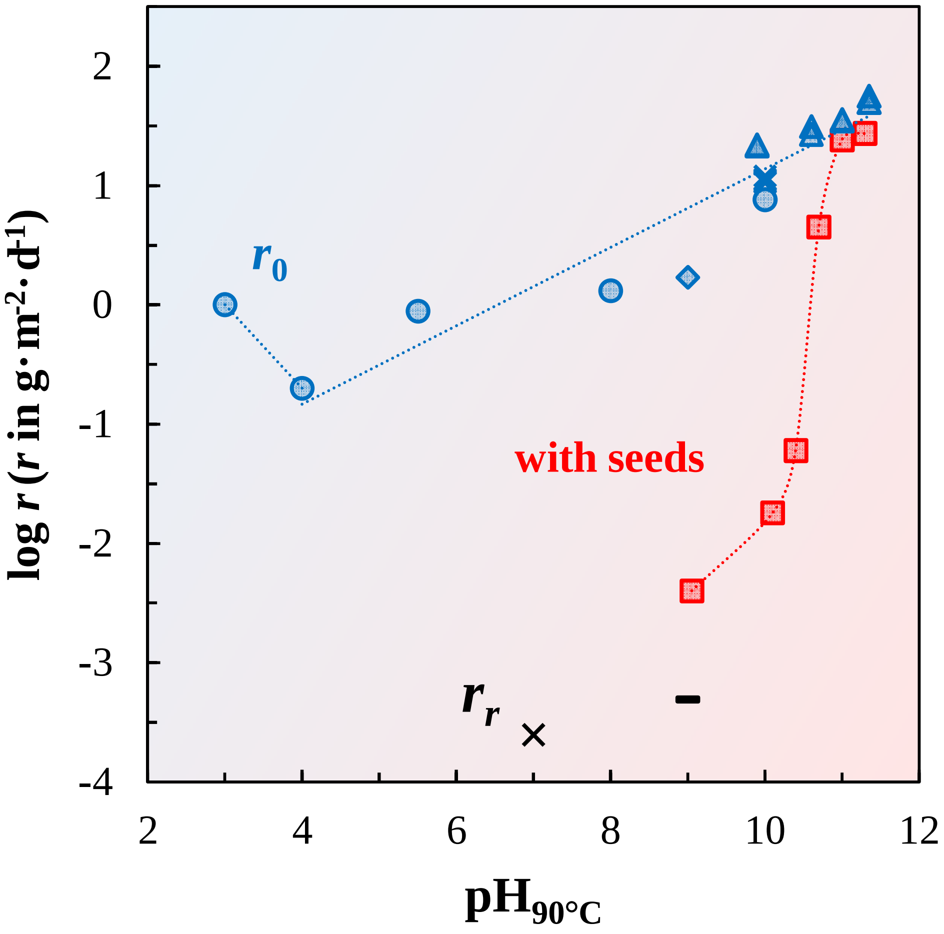
Zeolite crystals nucleate and grow, first consuming species available in the bulk solution until the solution is undersaturaed wrt the passivating layer

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

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

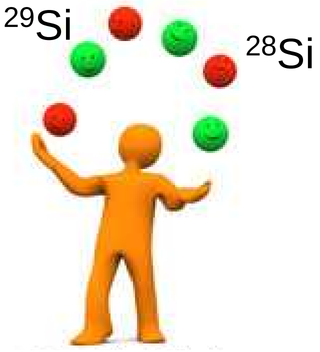
Seeding: a new tool to investigate long-term glass stability

ISG glass, 90℃, seeds: Zeolite P2



(Fournier et al., npj-Materials Degradation, accepted)

Ongoing studies at CEA on fundamentals in glass corrosion

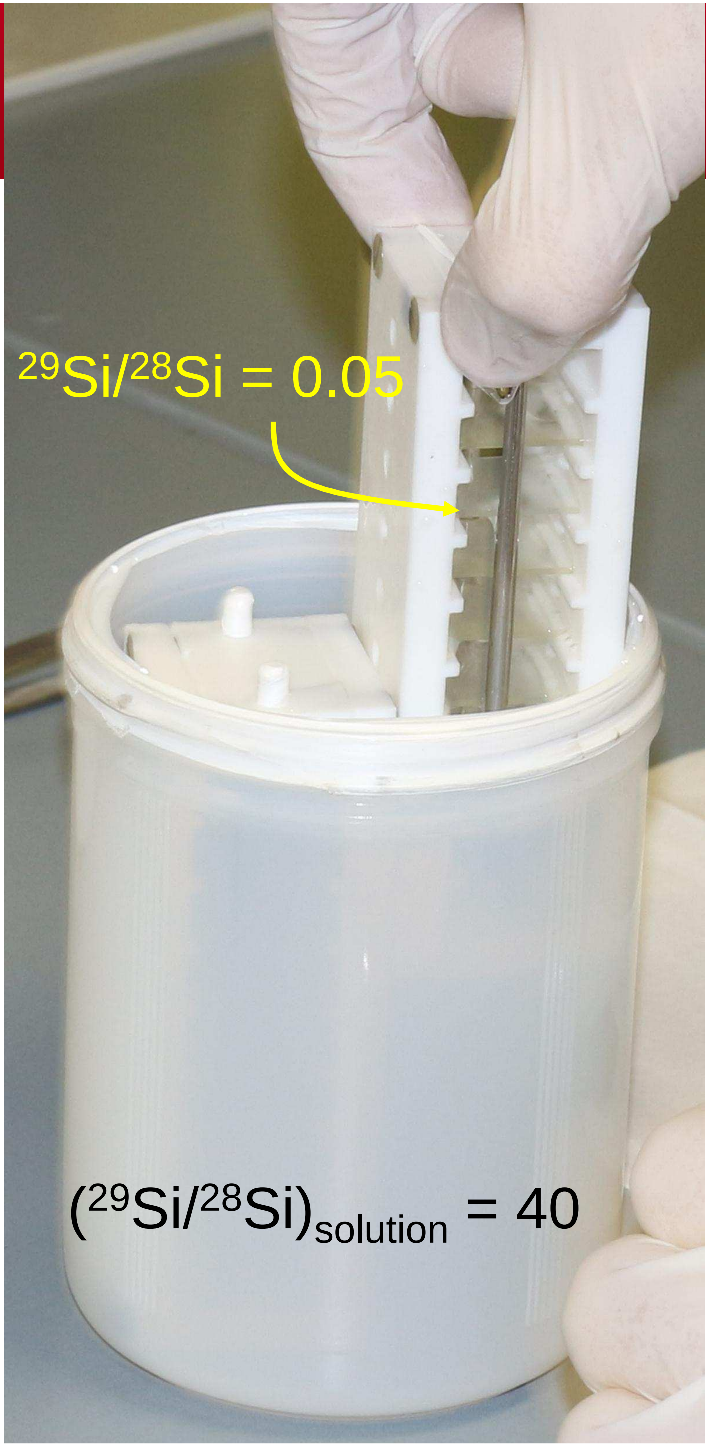


Experiments

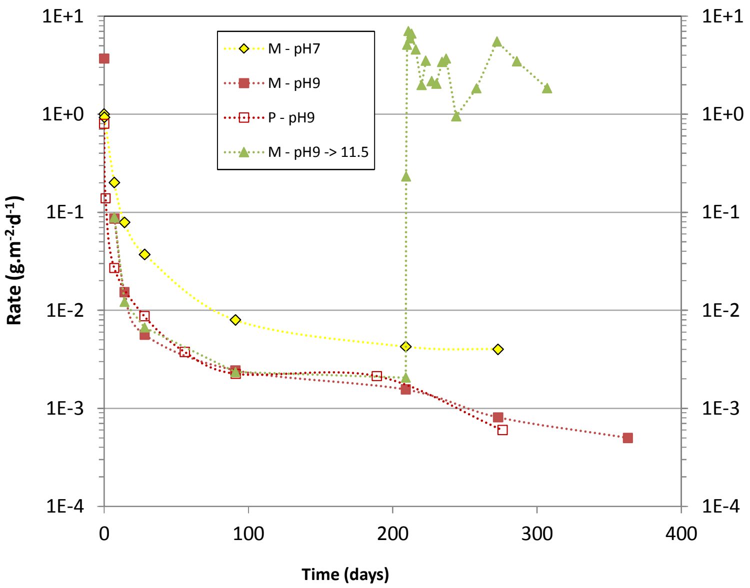
- ❑ International Simple Glass (ISG)
- ❑ 3 exp run in controlled conditions – Launching Feb. 2013
- ❑ 16 glass coupons (with one face polished) 90°C - 380 mL of solution initially saturated in $^{29}SiO_2$am (S/V= 0.6 cm^{-1})
  1. $pH_{90°C}$ 7 (Nat. Com., **6**, 2015)
  2. $pH_{90°C}$ 9 (Geochim Cosmochim. Acta, **202**, 2017)
  3. $pH_{90°C}$ 9 for 209d then 11.5 (Geochim Cosmochim. Acta, **151**, 2015)
- ❑ Coupon withdrawal: 7, 209, 363, 875, 1625… days
- ❑ Tracing experiments (room T – various probe molecules)
- ❑ Isotope sensitive analytical techniques: MC-ICP-MS and ToF-SIMS, APT + TEM

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

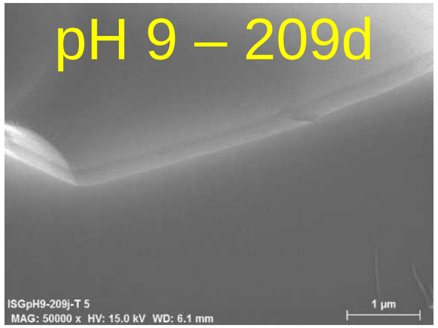


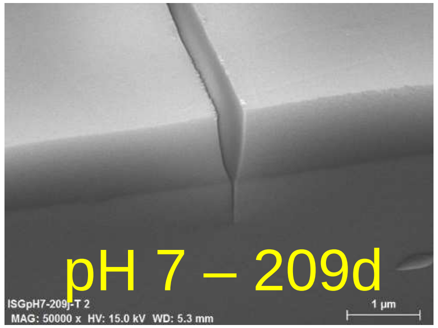
First set of observations



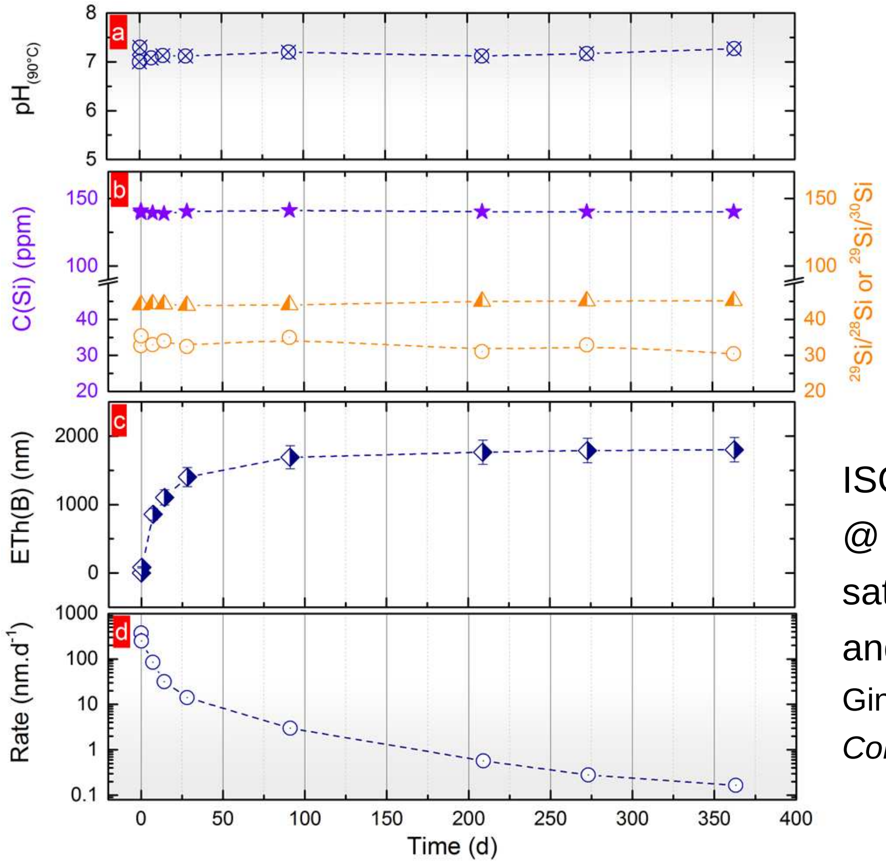
- *r* evolves similarly at 0.6 cm^{-1} and 500 cm^{-1}
- *r* drops by 3 O.M. in ~ 6 months
- $r_{(pH\ 7)} > r_{(pH\ 9)}$
- *r* “immediately” increases when the the pH is raised @ 11.5

- A uniform, “isovolumetric” gel layer forms at pH 7 and 9 (best conditions for ToF-SIMS depth profiling)
- No secondary phases precipitate at pH 7 and 9





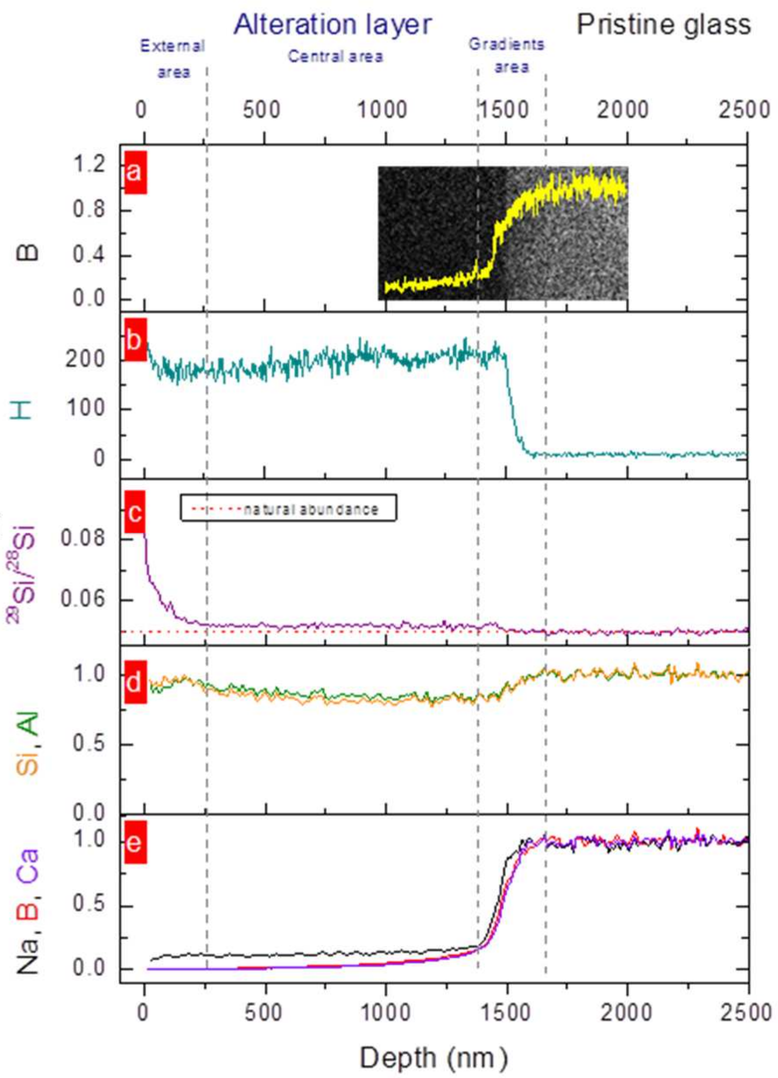
Evidence of the formation of a passivating layer by in situ reorganization of the silicate network



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

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

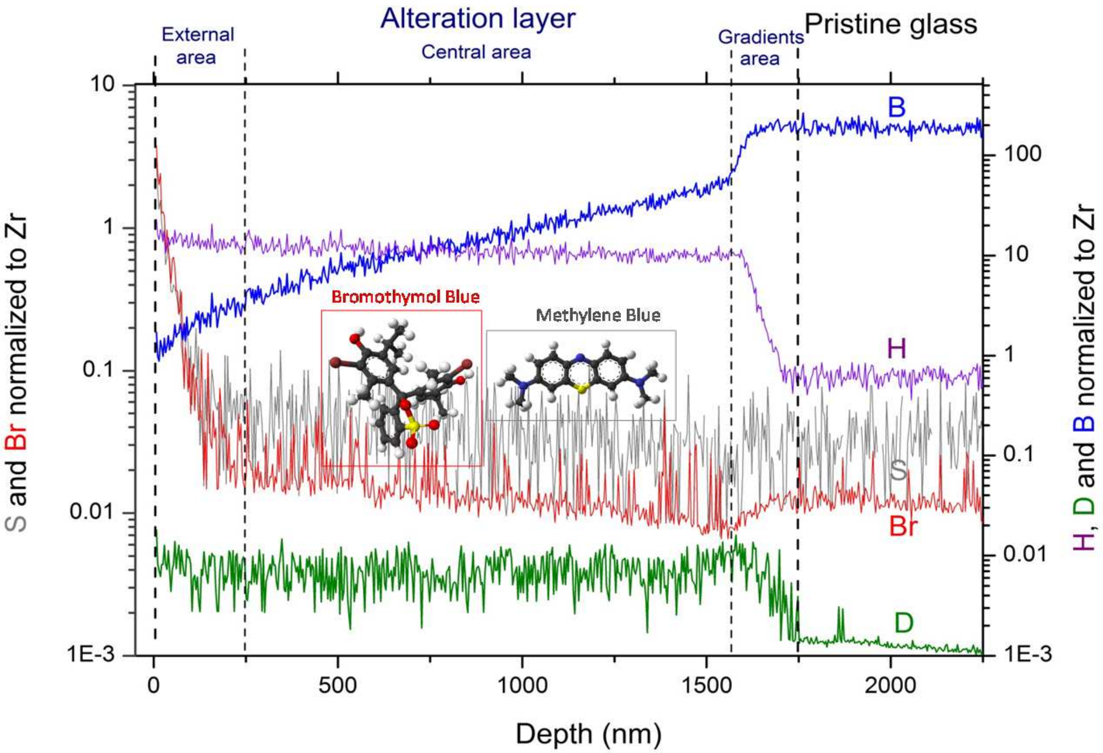
SiO_2	B_20_3	Na_20	Al_2O_3	Ca0	ZrO_2
56.2	17.3	12.2	6.1	5.0	3.3



Rate limiting mechanisms strongly depend leaching conditions

More discussion in Gin, *Chem. Geol* 2016

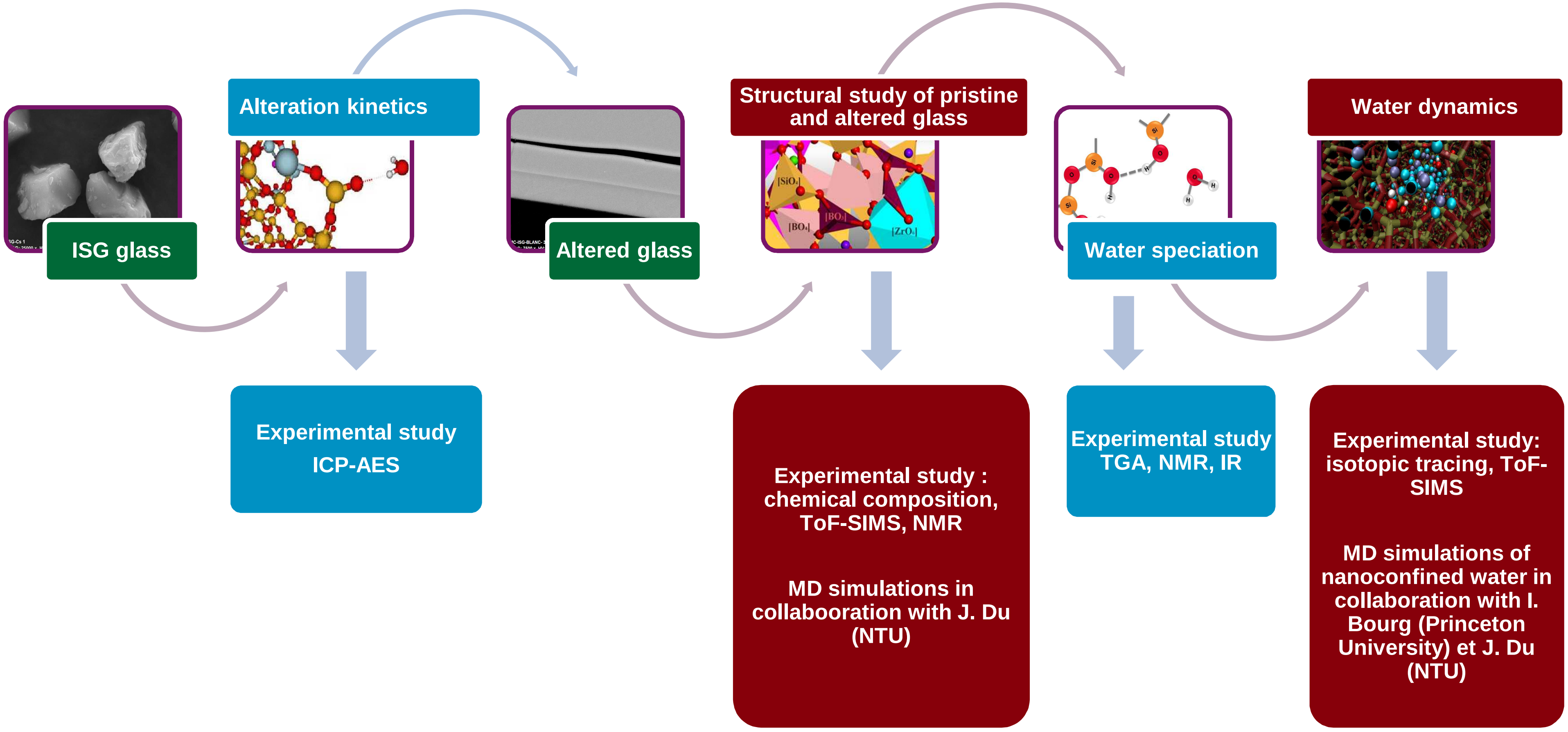
Evidence of the formation of a passivating layer by in situ reorganization of the silicate network



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

Gin, *Nature Comm.* 2015

ISG glass altered at pH 7 90℃ in SiO_2 saturation conditions



ISG glass

Alteration kinetics

Experimental study
ICP-AES

Altered glass

Structural study of pristine and altered glass

Experimental study : chemical composition, ToF-SIMS, NMR

MD simulations in collabooration with J. Du (NTU)

Water speciation

Experimental study TGA, NMR, IR

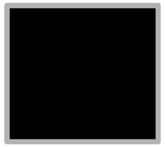
Water dynamics

Experimental study: isotopic tracing, ToF-SIMS

MD simulations of nanoconfined water in collaboration with I. Bourg (Princeton University) et J. Du (NTU)

Collin et al., *npj-Materials Degradation* accepted

Water dynamics in passivating layers

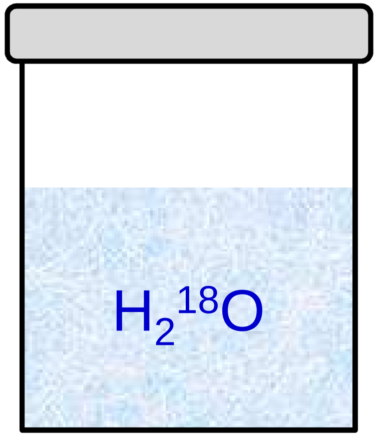


ISG glass coupon
altered for 1 year @
90℃, pH 7, Sisat

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

Porosity ~ 30%
Pore size ~ 1 nm
$O_{skeleton}$ = 0.71, O_{SiOH} = 0.13, O_{H20} = 0.16

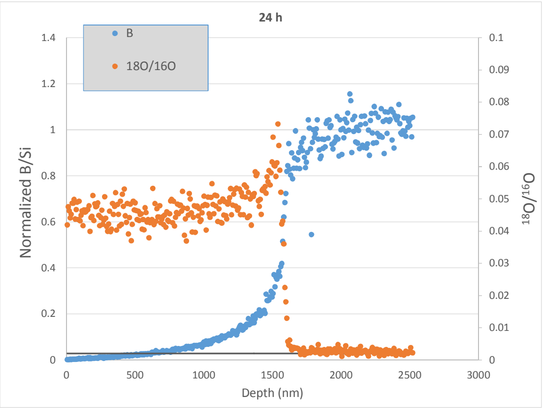
25℃



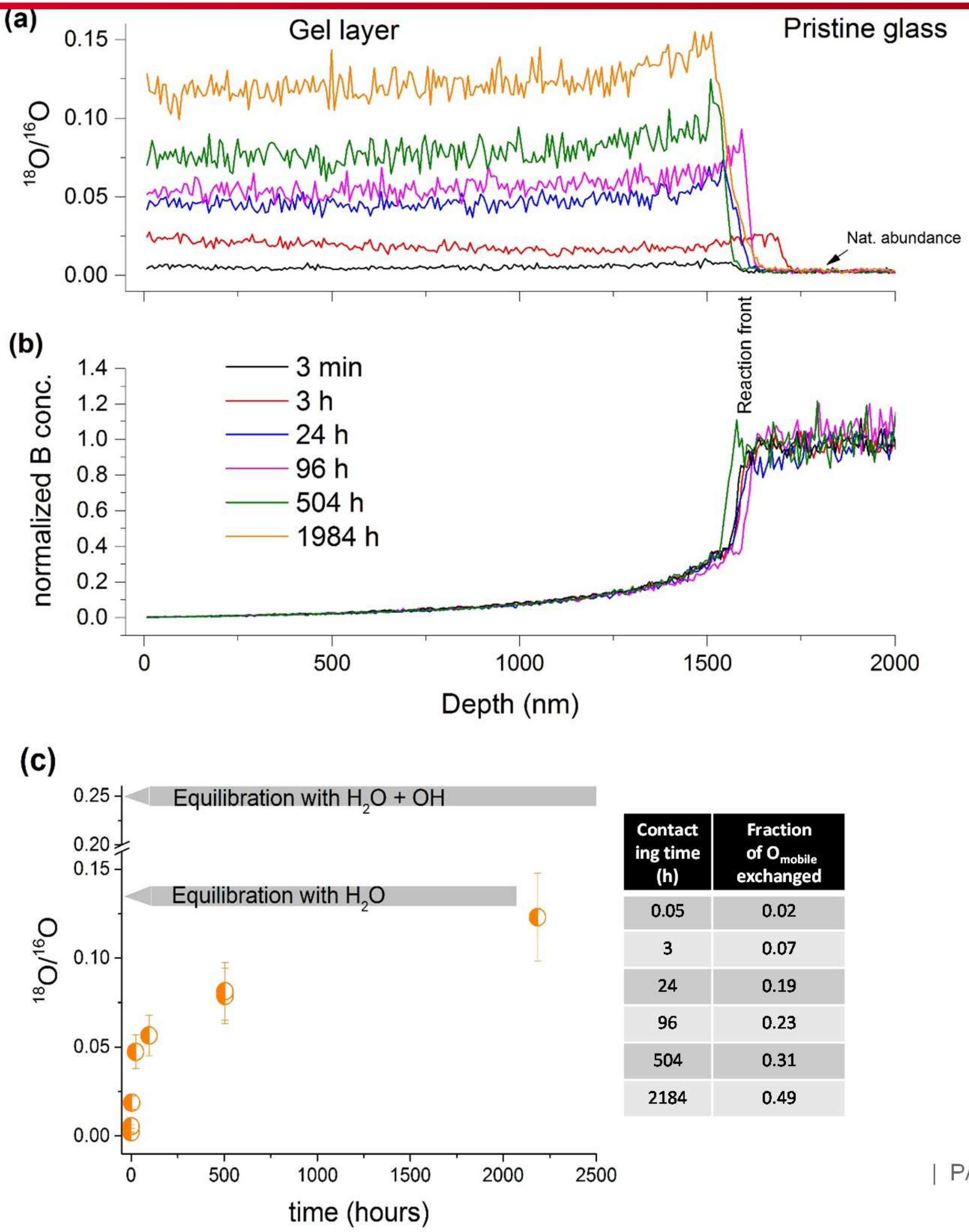
ToF-SIMS

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

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

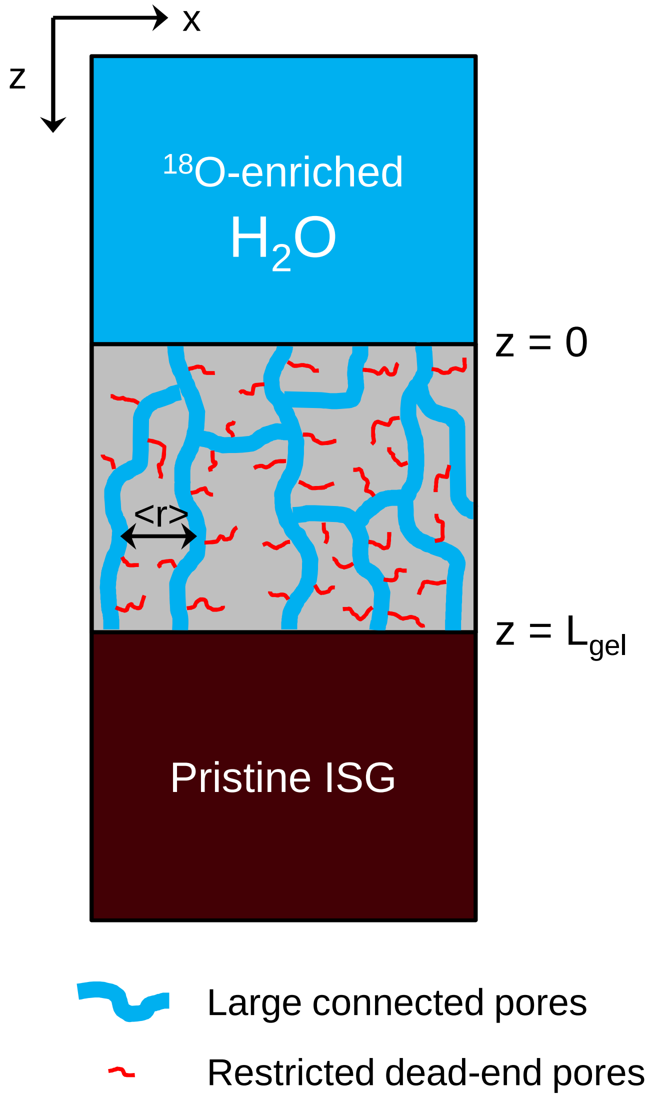


- Coupon of ISG altered @ 90°C, pH 7, SiO_2 sat solution for 363 days
- 1.5 µm thick alteration layer
- Equilibrium would be achieved in ~1 s in case of an open highly connected pore network



Contacting time (h)	Fraction of O_{mobile} exchanged
0.05	0.02
3	0.07
24	0.19
96	0.23
504	0.31
2184	0.49

Conceptual model



L_{gel} = gel thickness

<r> = mean distance between connected pores

Diffusion in connected pores

1D diffusion along z with D_c
Constant source: C_0 at z = 0
$z_{max.} = L_{gel}$

Diffusion in dead-end pores

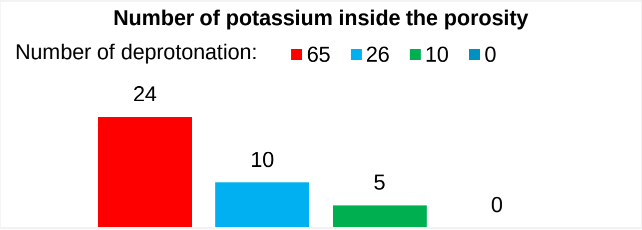
1D diffusion along x with D_d
Constant source: C_0 at x = 0
$x_{max.}$ = <r>

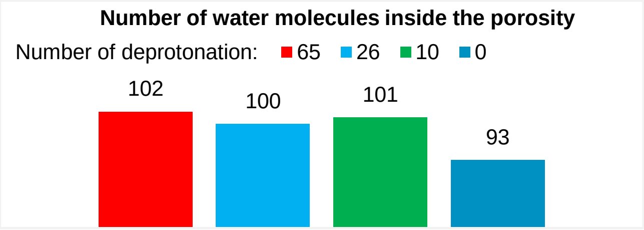
For 2% of H_20 D_{quick} ~10^{-12} $m^2.s^{-1}$
For 98% of H_20 D_{slow} ~ 10^{-20} – 10^{-24} $m^2.s^{-1}$

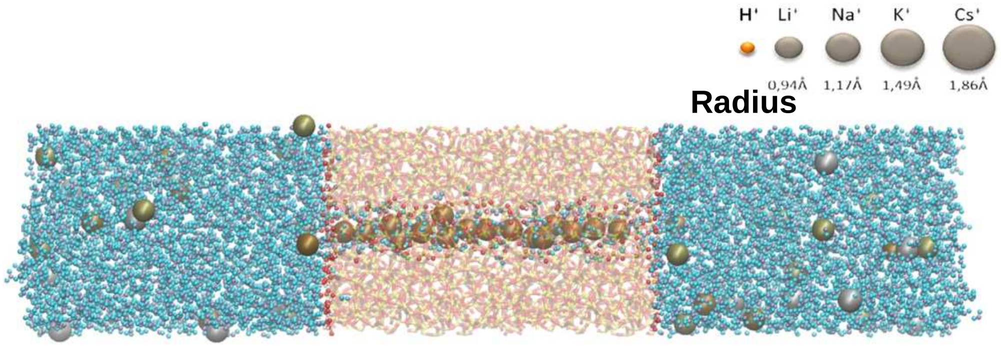
Can MD explain the peculiar behavior of water molecules?

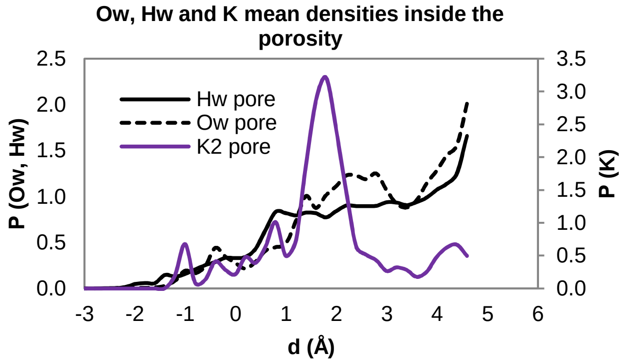
(Φ_{pore} 1 nm, CLAYFF, rigid water, collab. with Ian Bourg @ Princeton Univ and Jincheng Du)

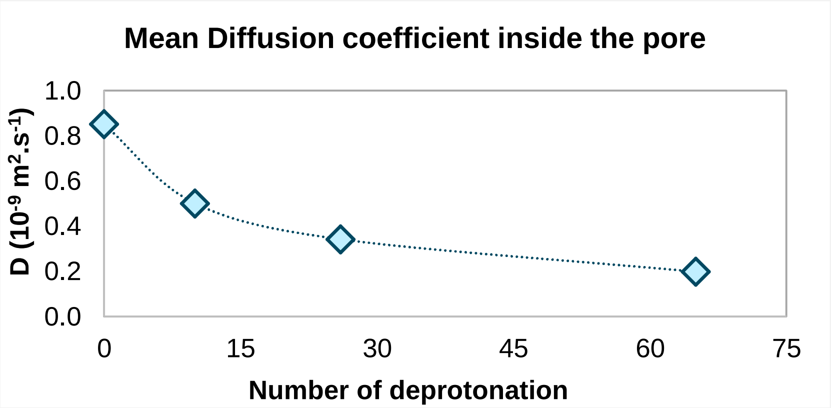
Deprotonation of silanols on the surface of a nanoporous silica bloc (potassium as charge compensator):

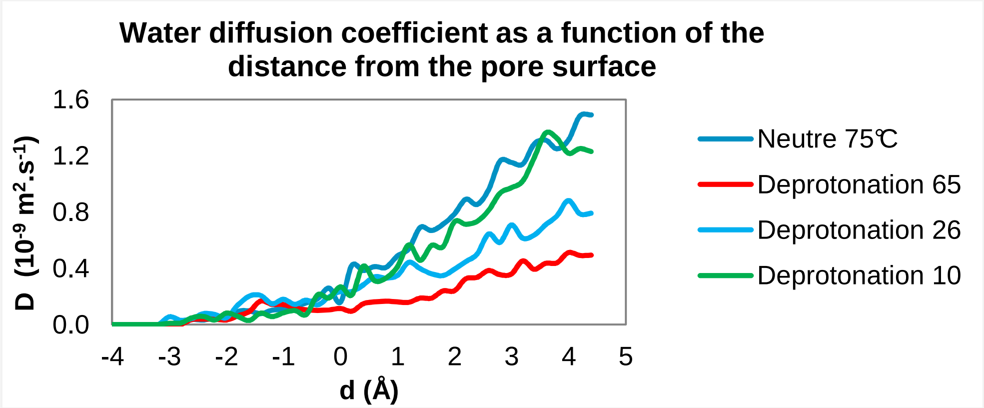

Number of potassium inside the porosity


Number of water molecules inside the porosity

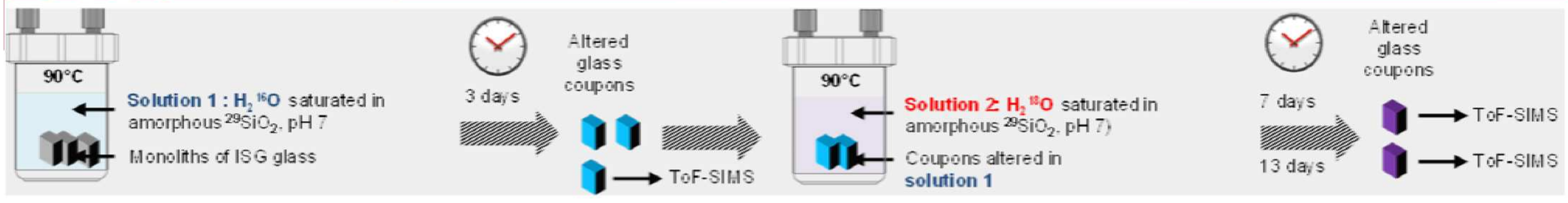



Ow, Hw and K mean densities inside the porosity


Mean Diffusion coefficient inside the pore


Water diffusion coefficient as a function of the distance from the pore surface

How passivating layer forms (ISG, 90°C, pH 7)?



Solution 1 : $H_2{}^{16}O$ saturated in amorphous $^{29}SiO_2$, pH 7

Monoliths of ISG glass

3 days

Altered glass coupons

ToF-SIMS

Solution 2: $H_2{}^{18}O$ saturated in amorphous $^{29}SiO_2$, pH 7)

Coupons altered in **solution 1**

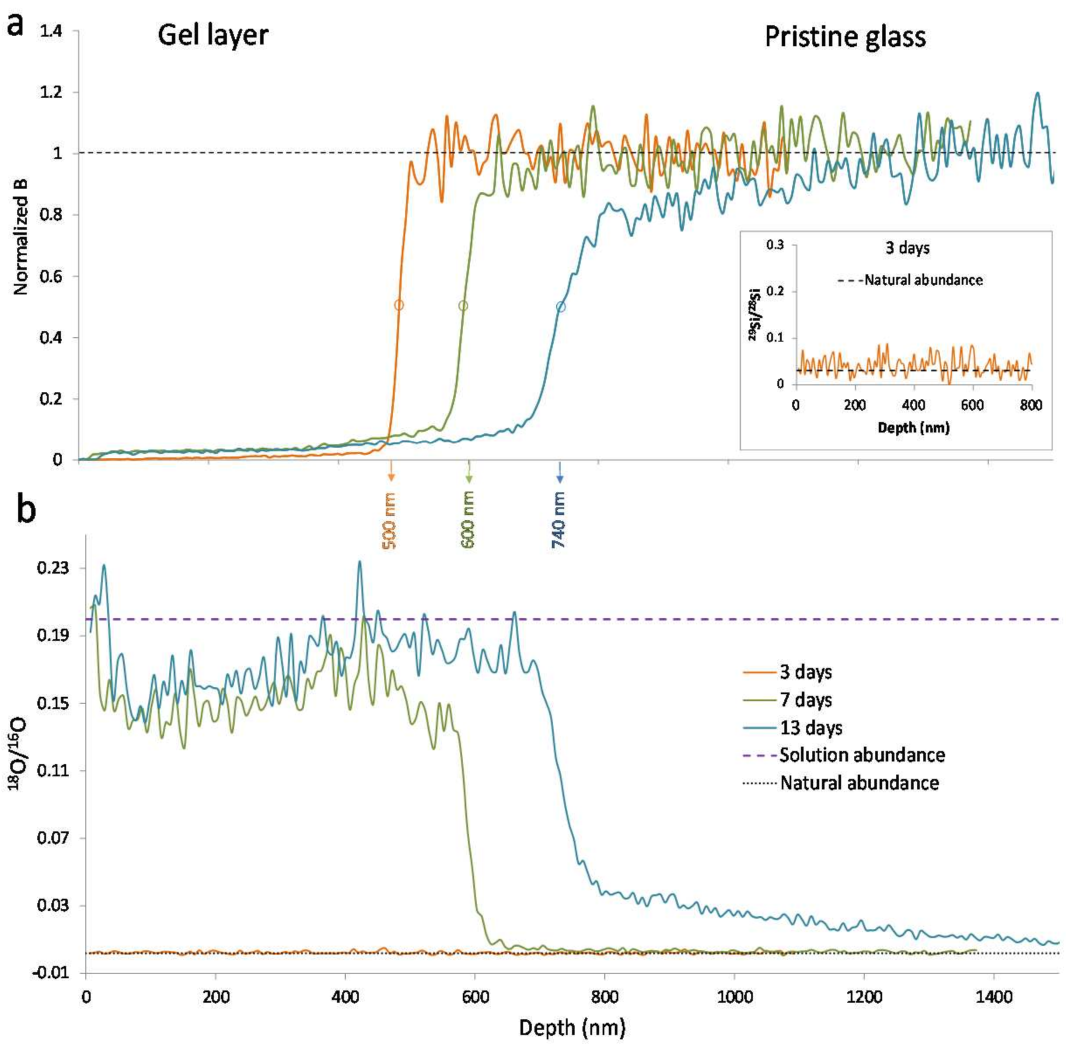
7 days

13 days

Altered glass coupons

ToF-SIMS

ToF-SIMS



65% of the bridging O of the gel network have been hydrolyzed and exchanged between day 3 and 7 and this figures becomes 79% at day 13.

The gel is a dynamic material but in the studied conditions Si is low mobile. Water mobility is dramatically affected by these H/C reactions

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 depends on the pH
- The origin of passivation needs to be better understood. It seems that reorganization of the silicate network following the release of mobile species is a major process controling the properties of the passivating layer
- Precipitation of Si-phases plays a major role in stage II and III

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