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APPROCHE MULTI-ECHELLES DE L'ALTERATION EN PHASE AQUEUSE DES VERRES SILICATÉS

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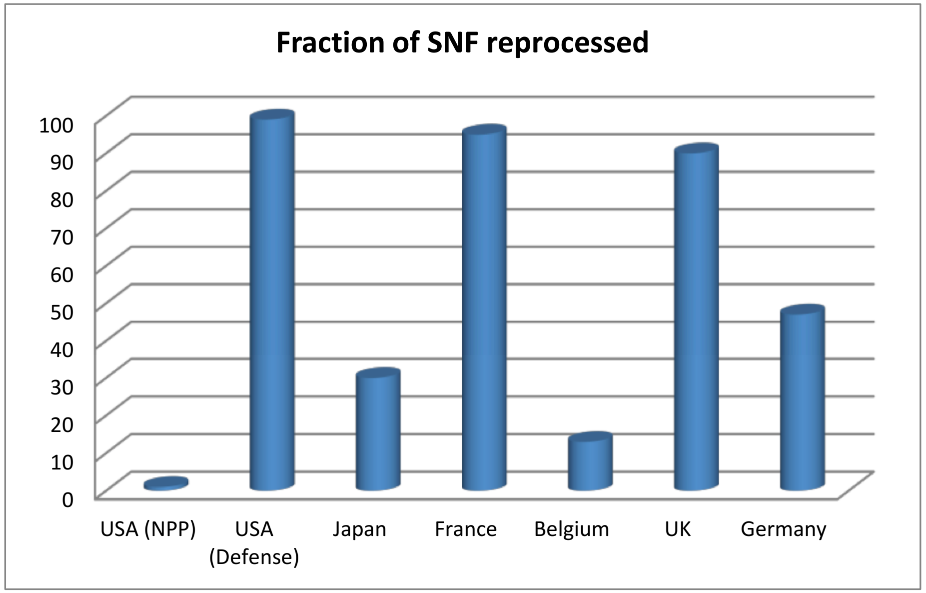
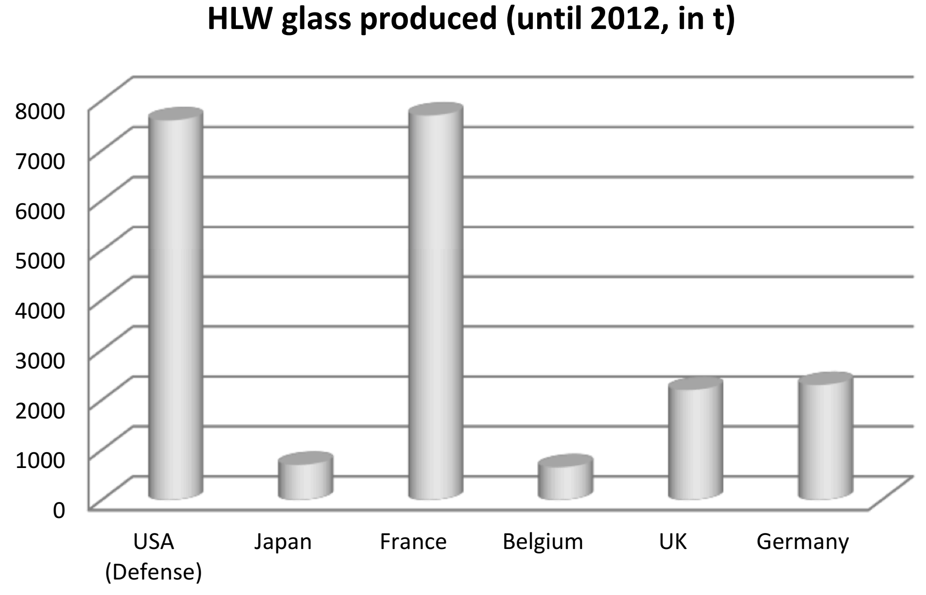
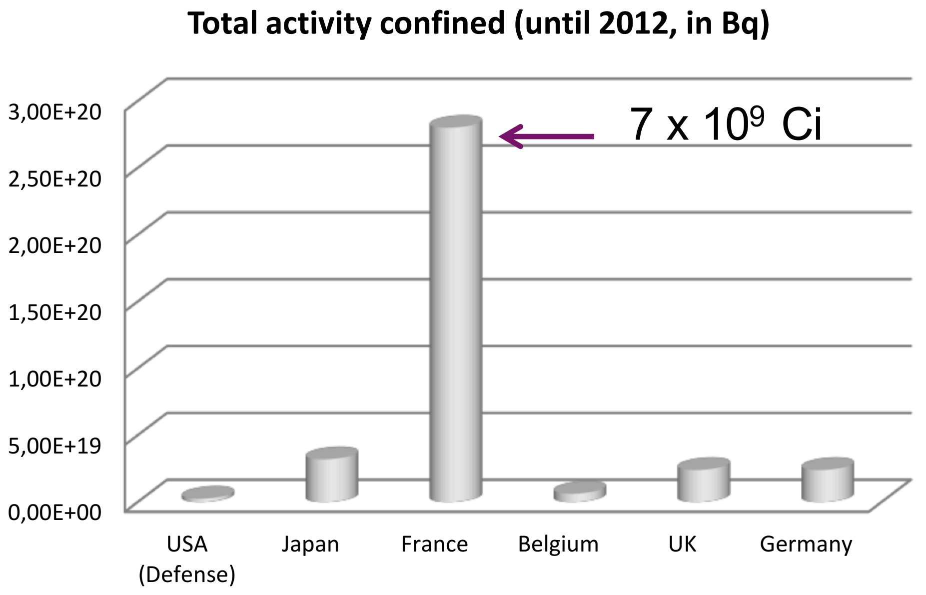
GDR VERRES
25-26 novembre 2013, Paris

International situation regarding vitrification of HLW







Various situations but a common need for safe geological repositories

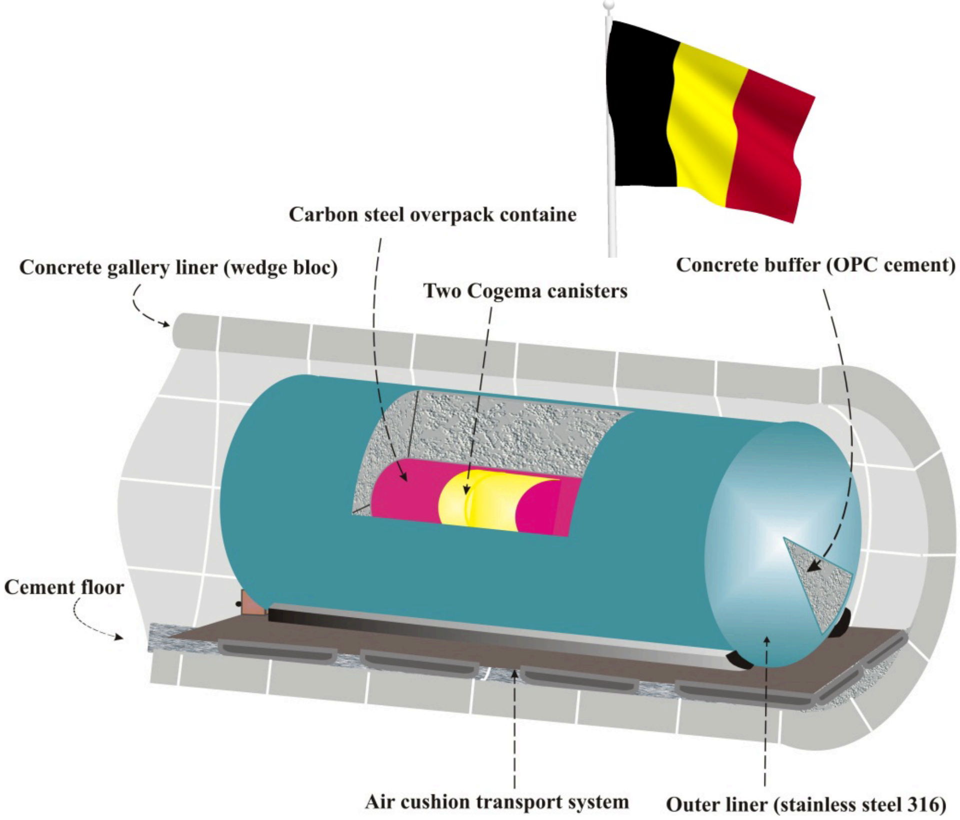
Typical HLW glass compositions

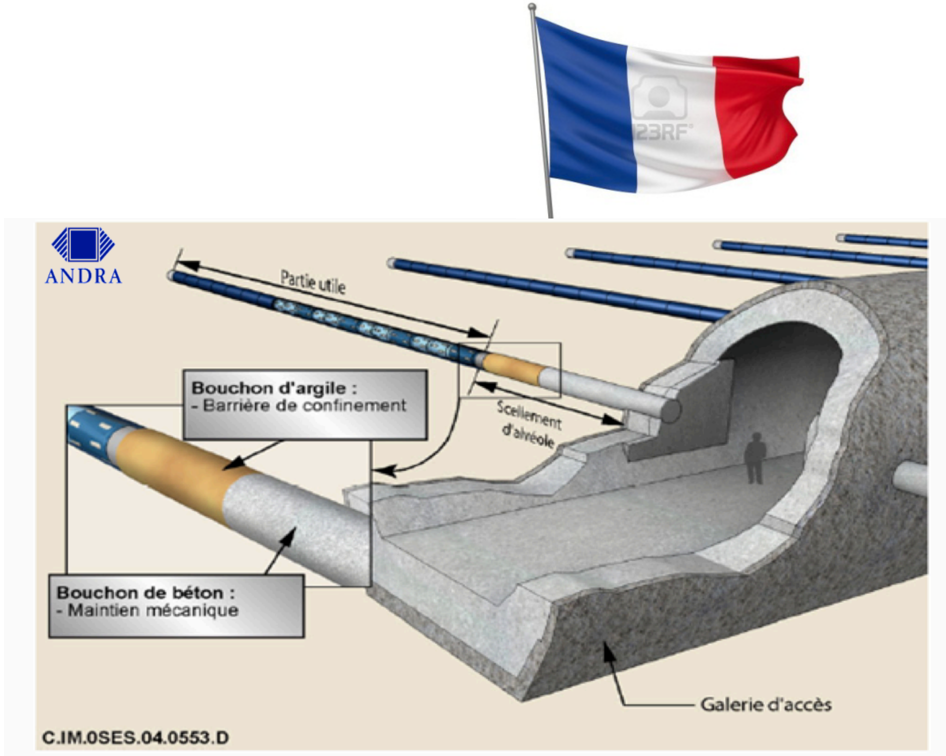
Type	Nb canisters	Country	SiO_2	$B2O_3$	Al_2O_3	Alc	MgO	FP+An	Other
R7T7	14000	France	45	14	5	12	0	15	
AVM	3000	France	40	17	10	17	5	6	
WAK	130	Germany	50	15	2.7	14	2	?	
Pamela	2200	Belgium	38	20	19	10	0	2	
MW	1500	England	47	14	5	12	2-5	?	
West Valley	285	USA	41	13	6	12	1	?	12% Fe2O3
SRL	1400	USA	56	8	12	18	0	?	
Al-P	4500	Russia	Phosphatic glass						

Des compositions différentes

	Verre Nucléaire (R7T7)	Verre basaltique	Laitiers	Verre romain (Embiez)
SiO_2	45,5	**45-50**	**65**	**70**
B_2O_3	13,9	**-**	**-**	**-**
Al_2O_3	4,9	**10-17**	**8**	**2**
Σ Alc	13,1	**2-5**	**2**	**20**
CaO	4,0	**9-12**	**17**	**5**
MgO	-	**4-9**	**1**	**<1**
Fe_2O_3	3,0	**9-16**	**8**	**<1**
TiO_2	-	**1-3**	**-**	**-**
Autres	15,6			**3**

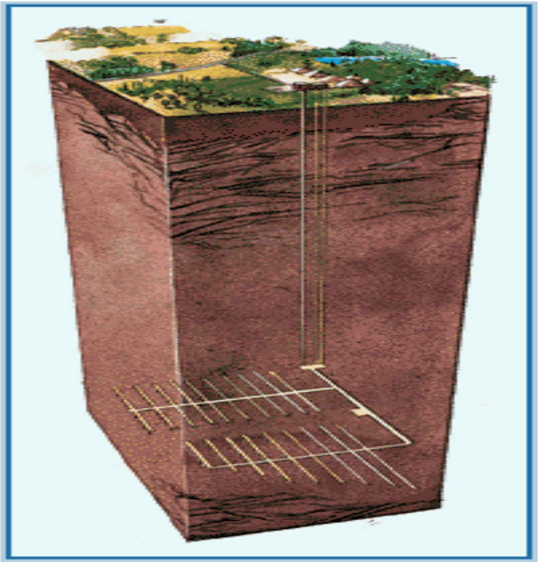
Various concepts for geological repository

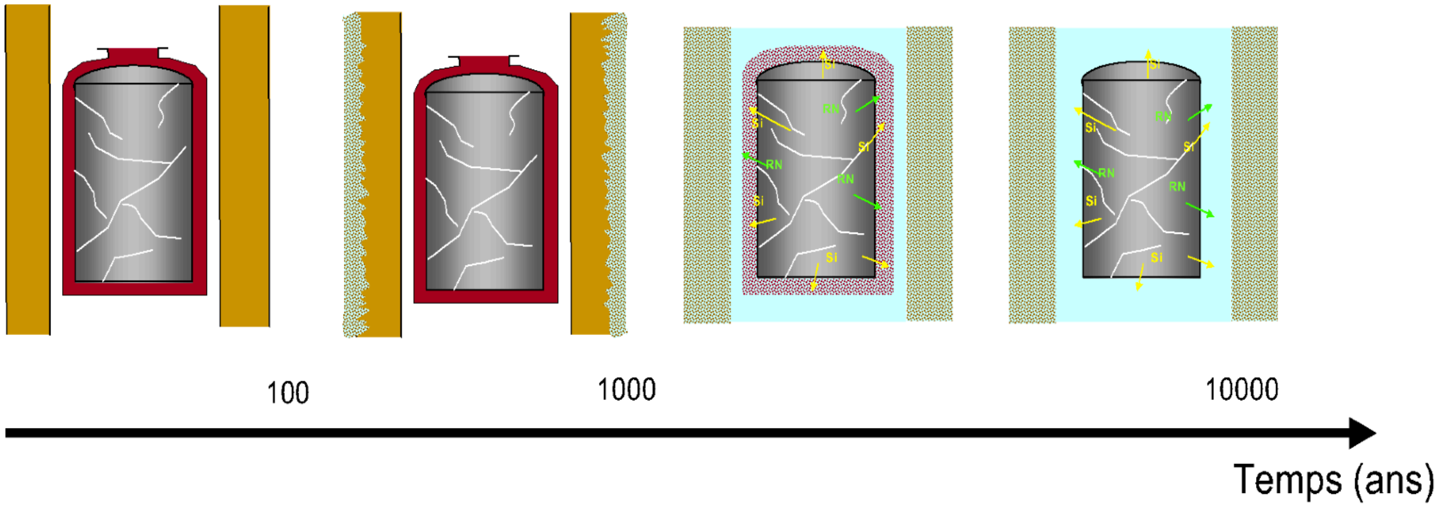




Various concepts but a common need of reliable long-term predictions ($\sim 10^6$ y)

Main boundary conditions in the French case





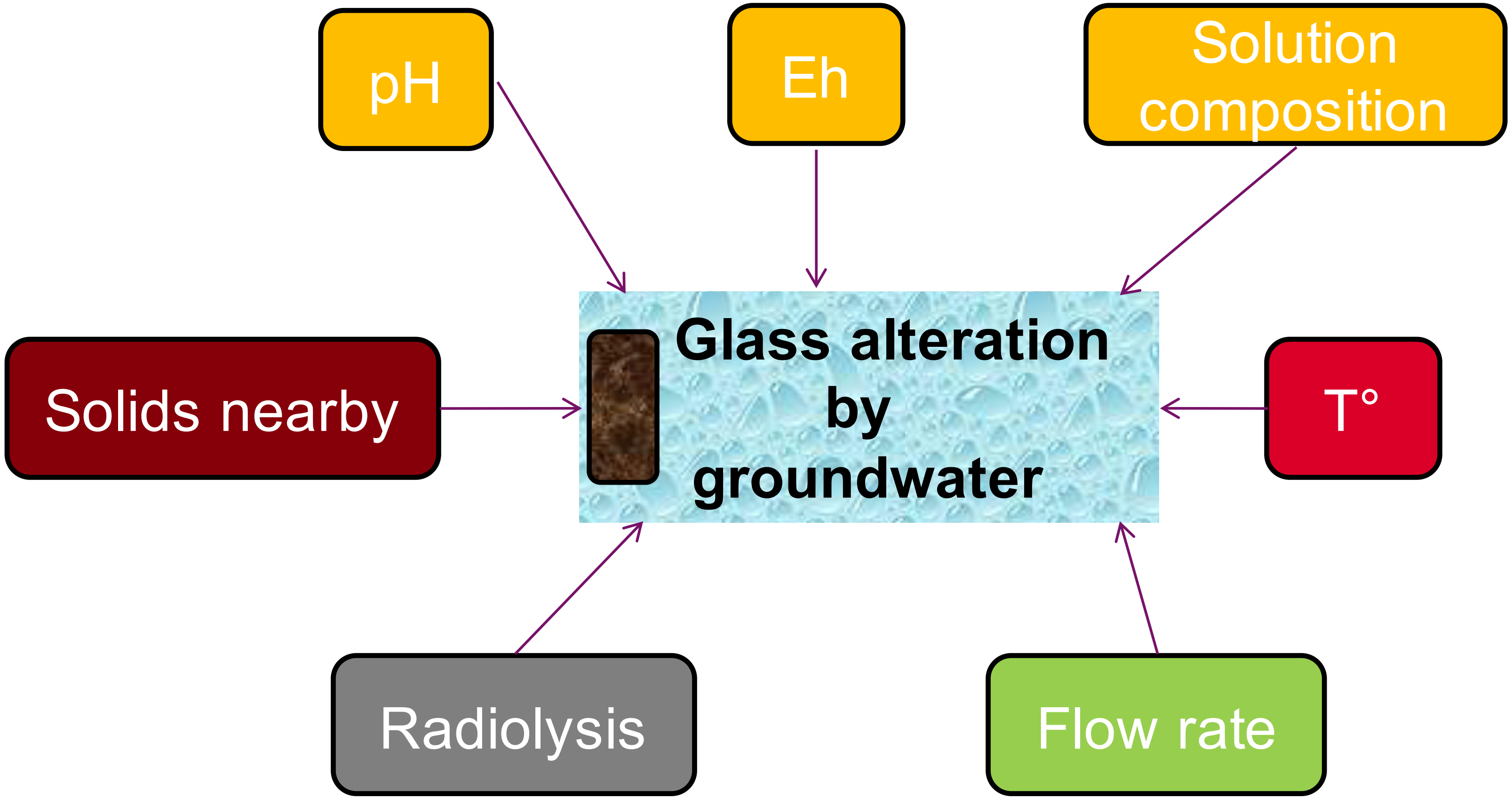
← - Water vapor - - →

← - - Water saturated medium - - →

Temperature → **90°C** → **50°C** → **25°C**

Key scientific issues

A highly durable glass (low source term) = a smart composition in a smart engineered barrier system



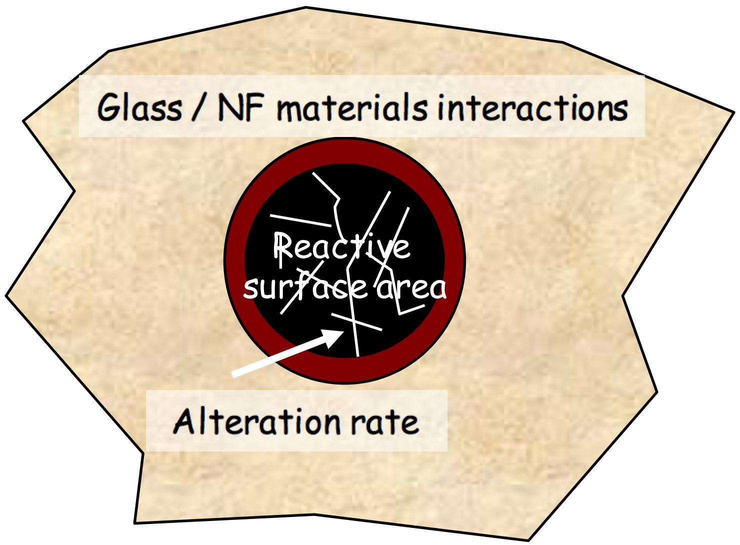
Reactive surface area

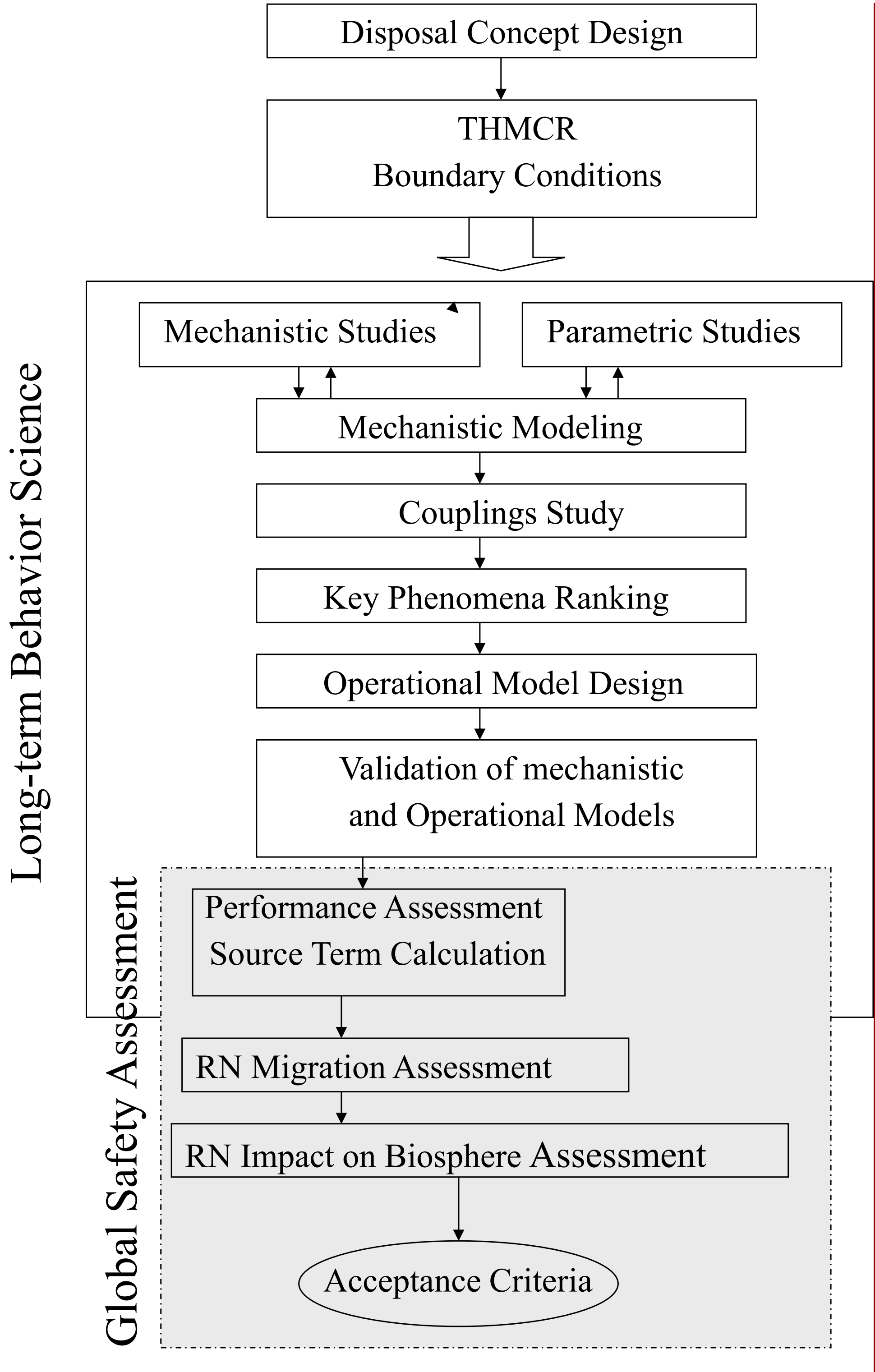
A complicated geometry due to the fracturation (rapid cooling following the pouring)

Reactive surface area ~ 50 S_{geo}

Methodology

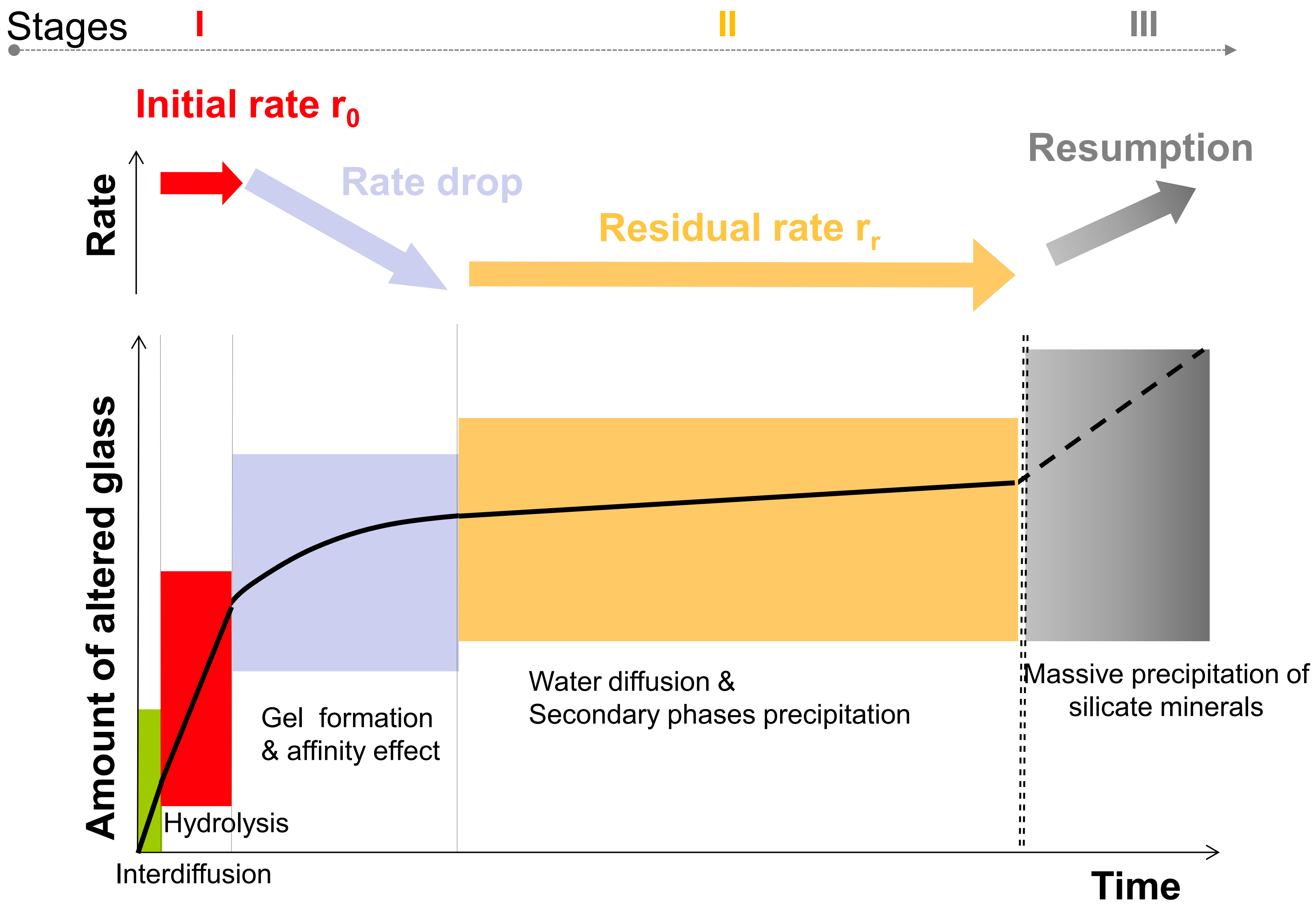
$$\varnothing_{RN} \; \alpha \; M_{altered\ glass} = \iint r(t,s)\,ds\,dt$$



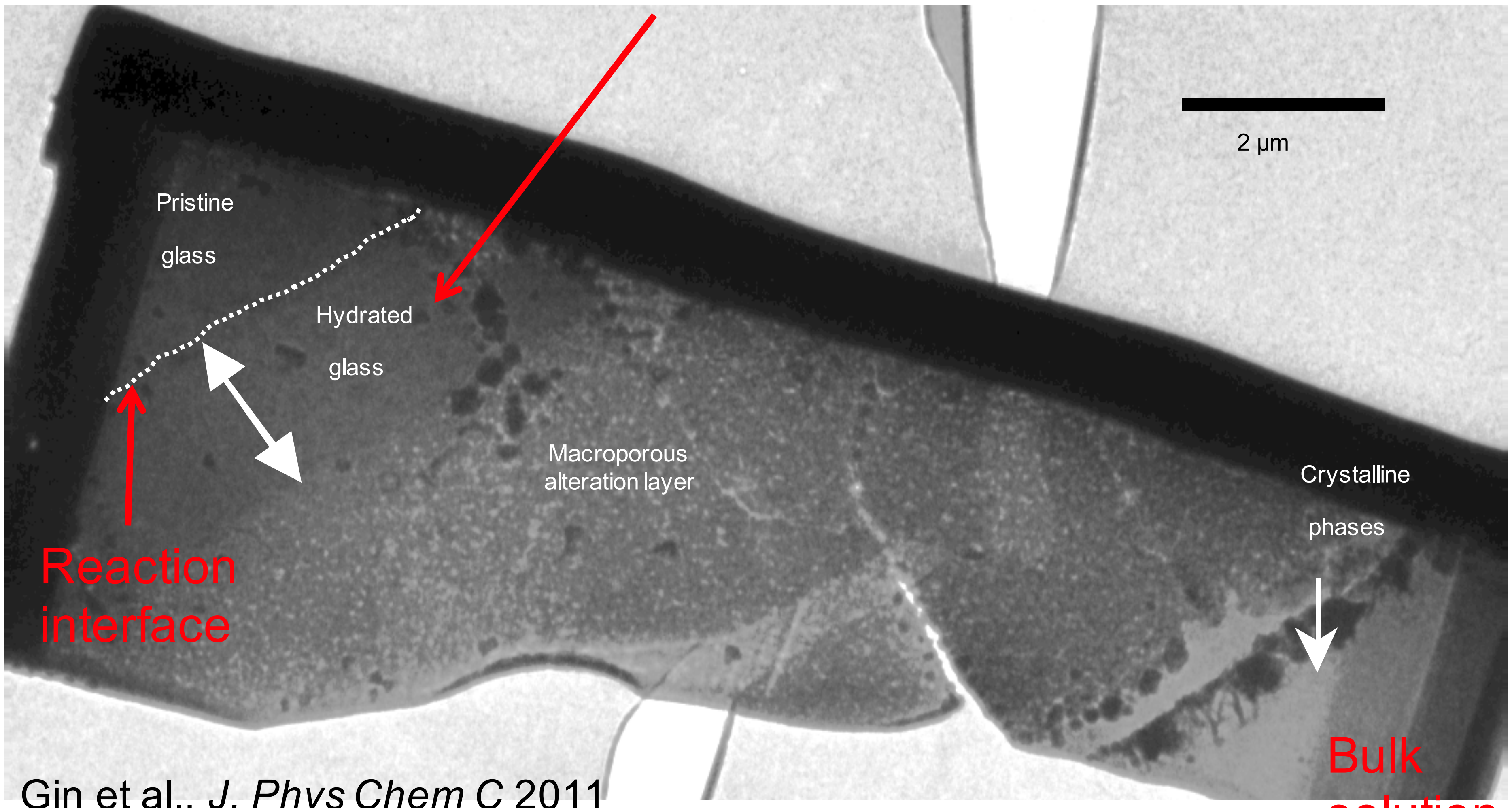


ASTM Standard C1174-07
Poinssot et al., JNM 2012

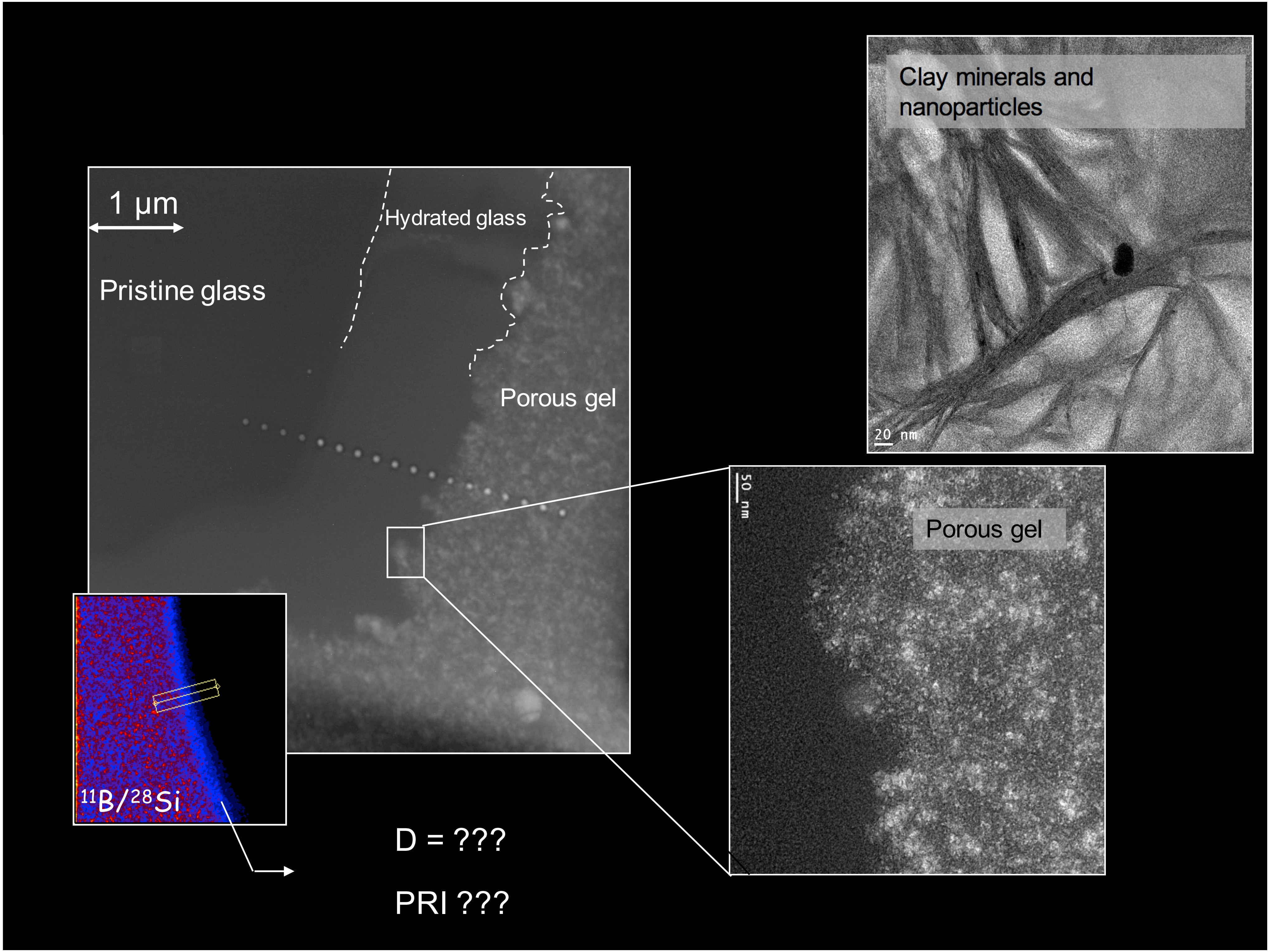
Glass dissolution kinetics



SON68 glass after 25y at 90°C

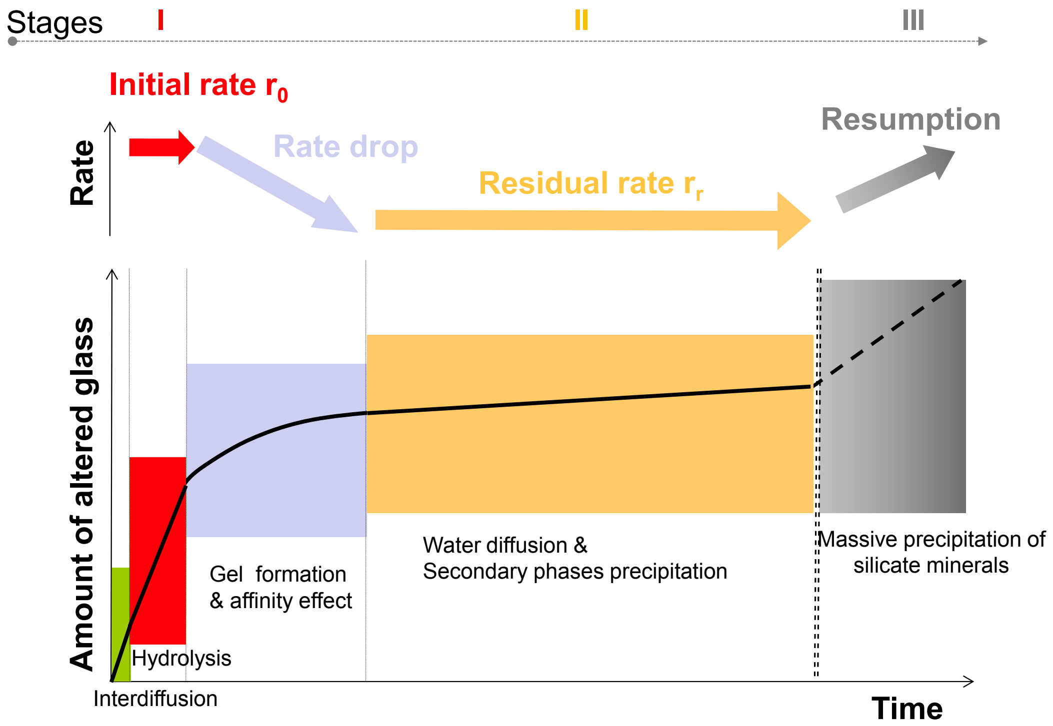


Gin et al., *J. Phys Chem C* 2011



Clay minerals and nanoparticles
20 nm
1 µm
Hydrated glass
Pristine glass
Porous gel
50 nm
Porous gel
$^{11}B/^{28}Si$
D = ???
PRI ???

Glass dissolution kinetics



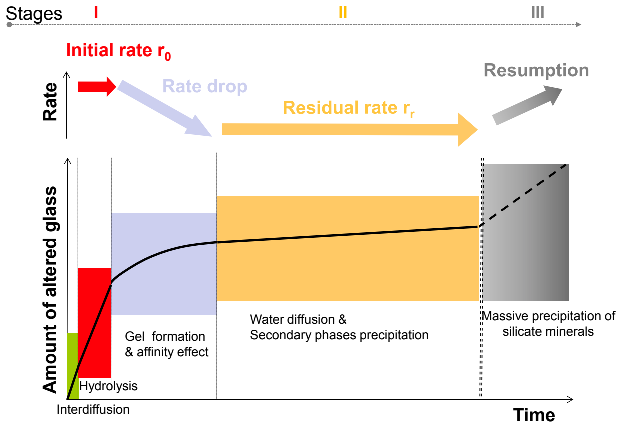
R_0 depends on glass composition, T, pH and to a lesser extent to the solution composition (Jollivet *Chem. Geol*. 2012)

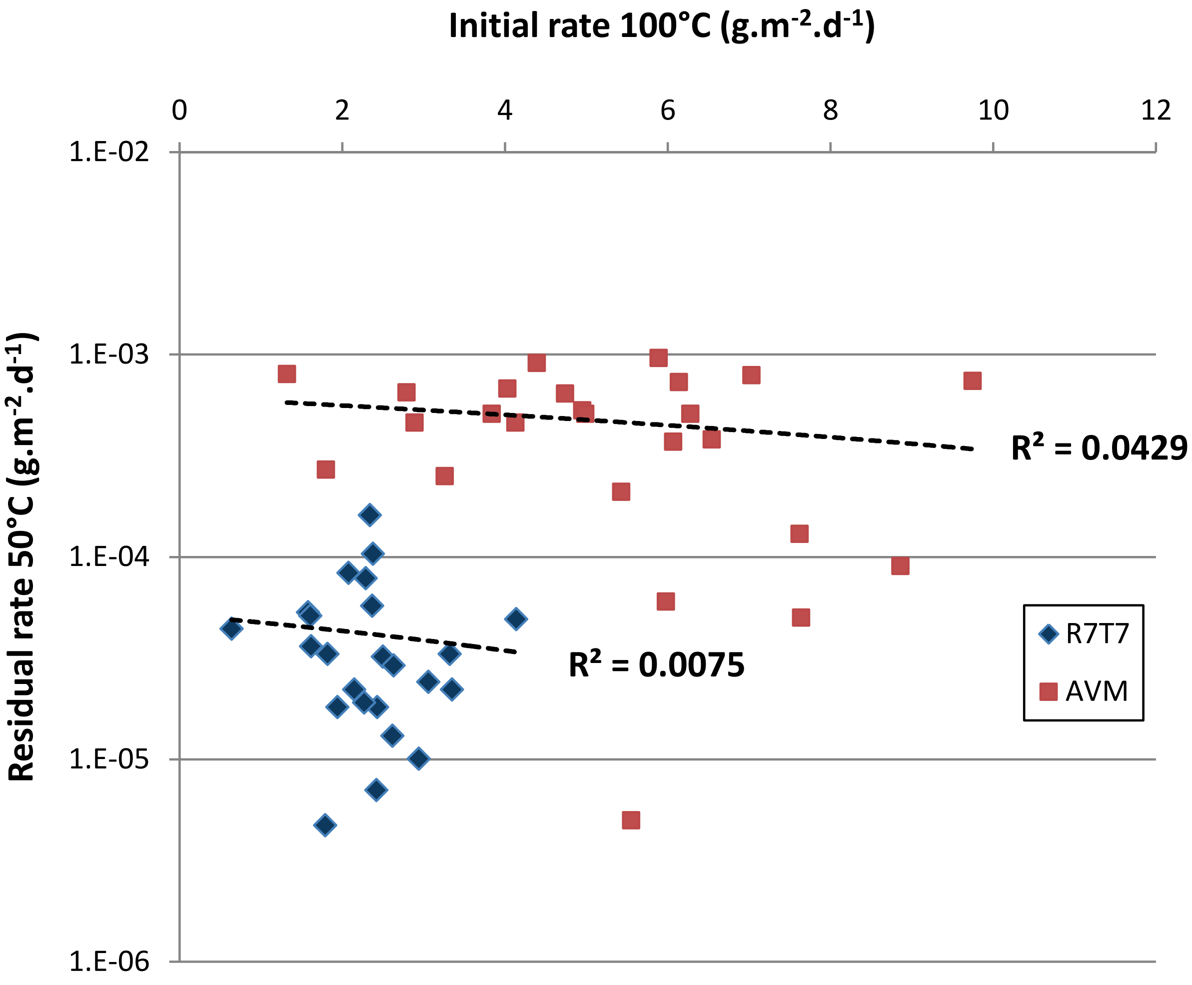
PA relying on R_0 ends up to glass lifetime of few ky

No impact on the safety

So….

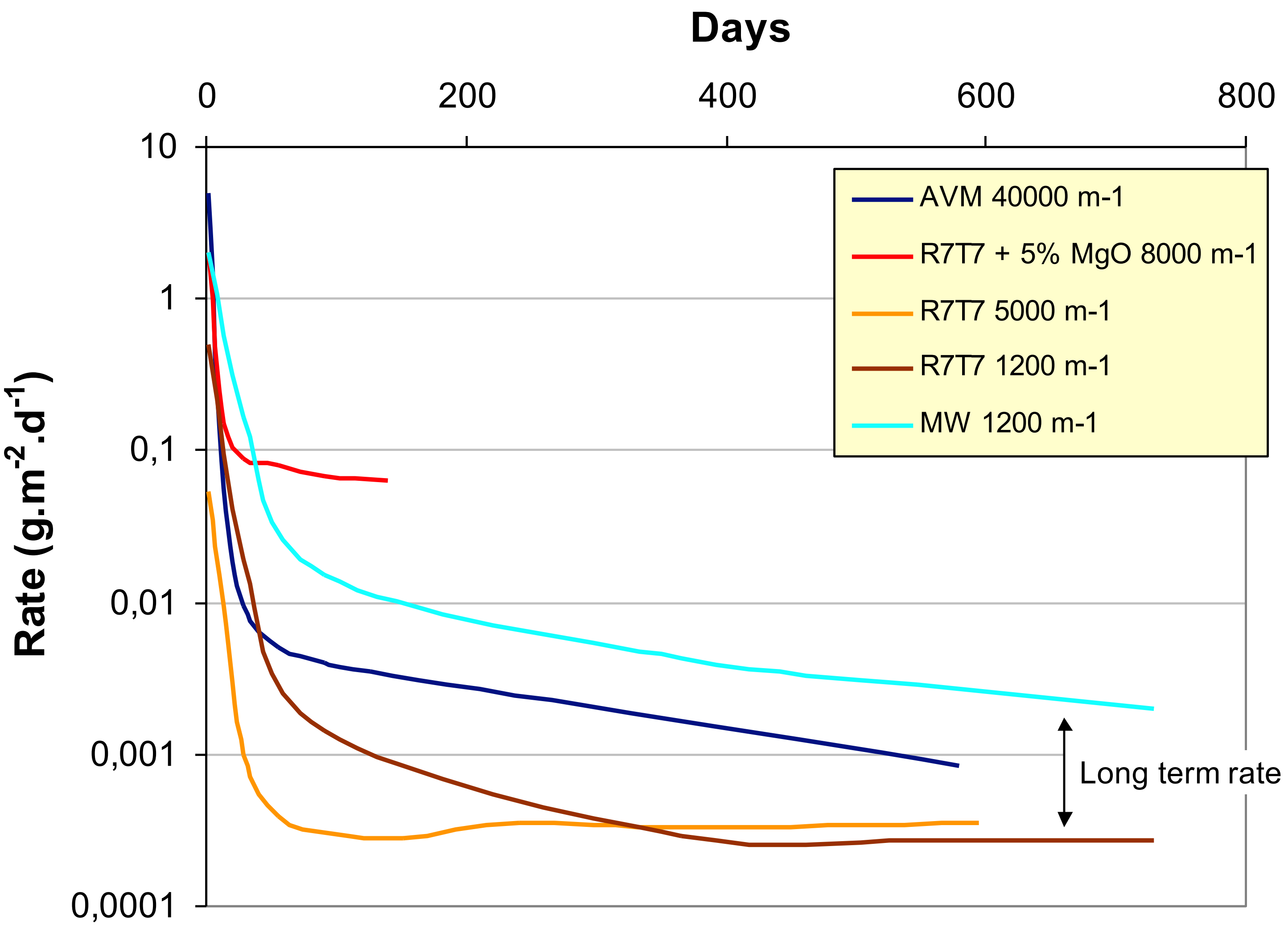
Relation between short-term & residual rate





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

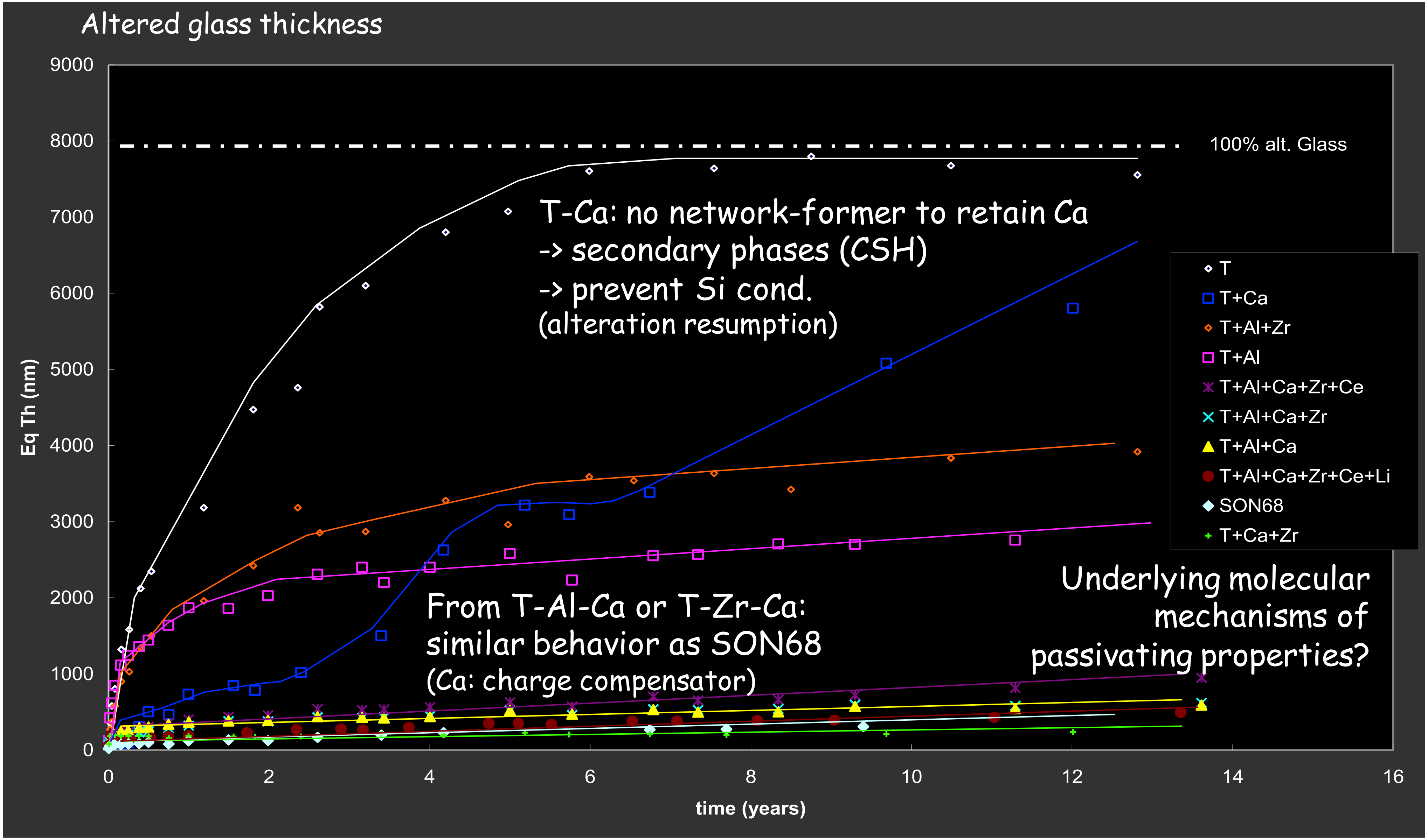
Effect of glass composition on the dissolution rate



Static test
90°C

Glass dissolution kinetics strongly depends glass composition (Frugier, JNM 2005)
Synergetic effects: **experimental design methodology, simple glasses**

Influence of glass composition on long-term alteration rate - 14 years of alteration

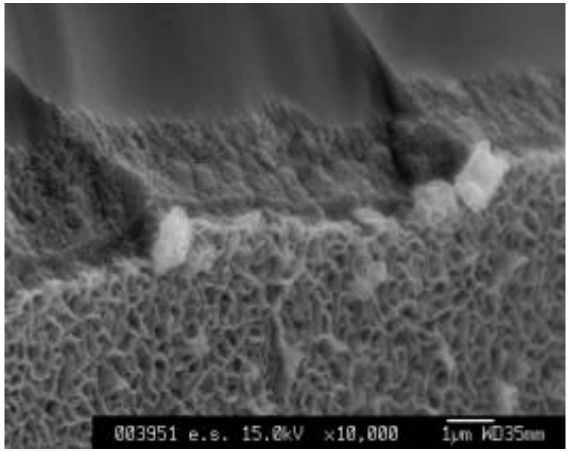


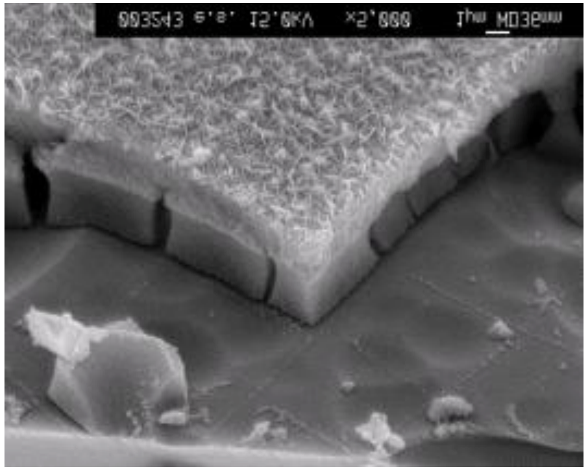
T : ternary Si,B,Na -> progressive adding of major elements up to SON68

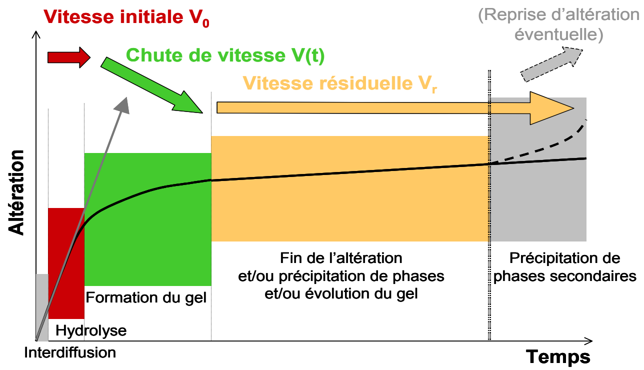
Gin et al. (2012) *J. Non Cryst. Sol.*

Basic Mechanisms

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







Glass → (Diffusion) Hydrated Glass → (Hydrolysis, Condensation) Gel → (Precipitation) Crystalline Phases

Glass → (Dissolution, Precipitation) Gel + Crystalline Phases

Grambow, JNM 2001
Frugier, *JNM 2008*

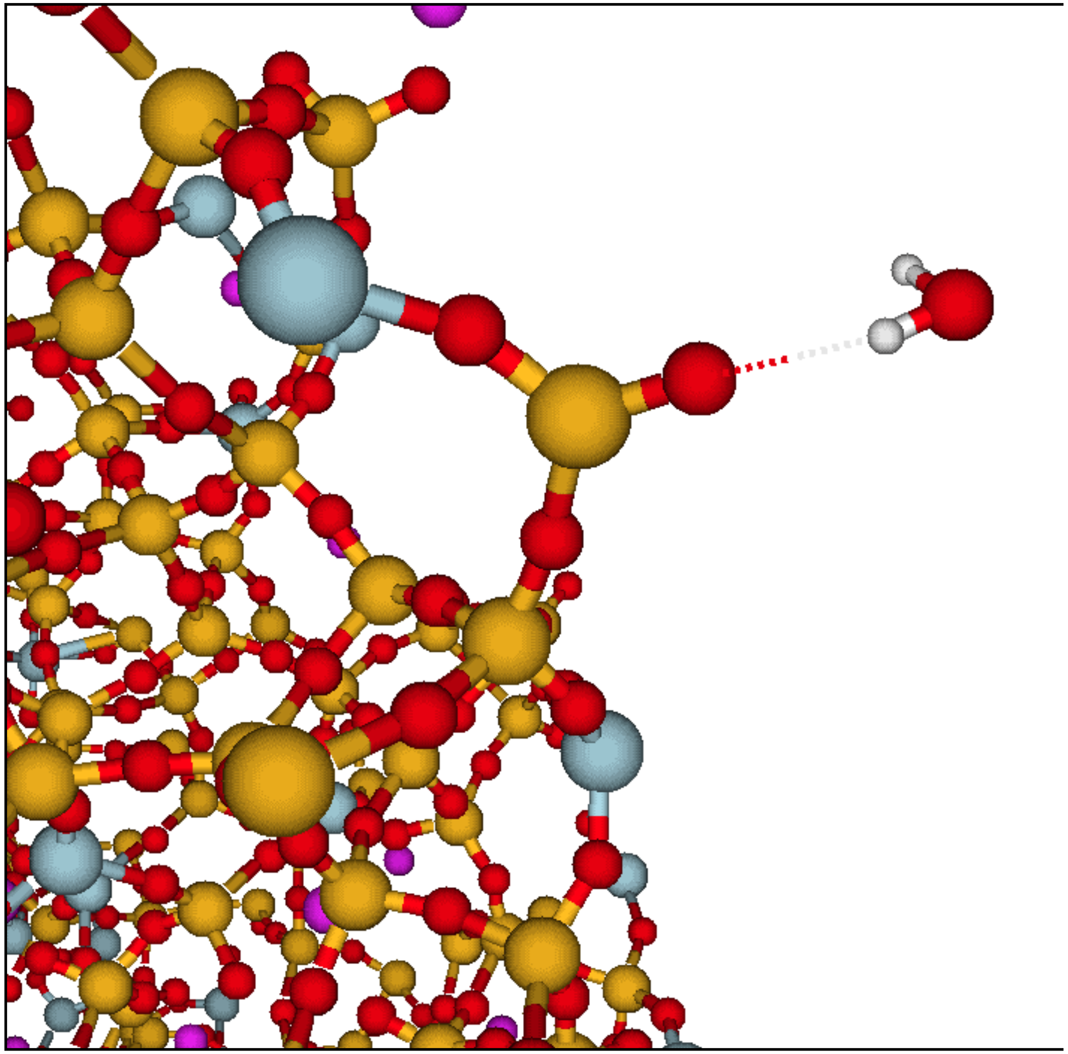
Geisler, JNCS 2011
Hellmann, Chem. Geol 2012

Few orders of magnitude (R7T7-type glass)

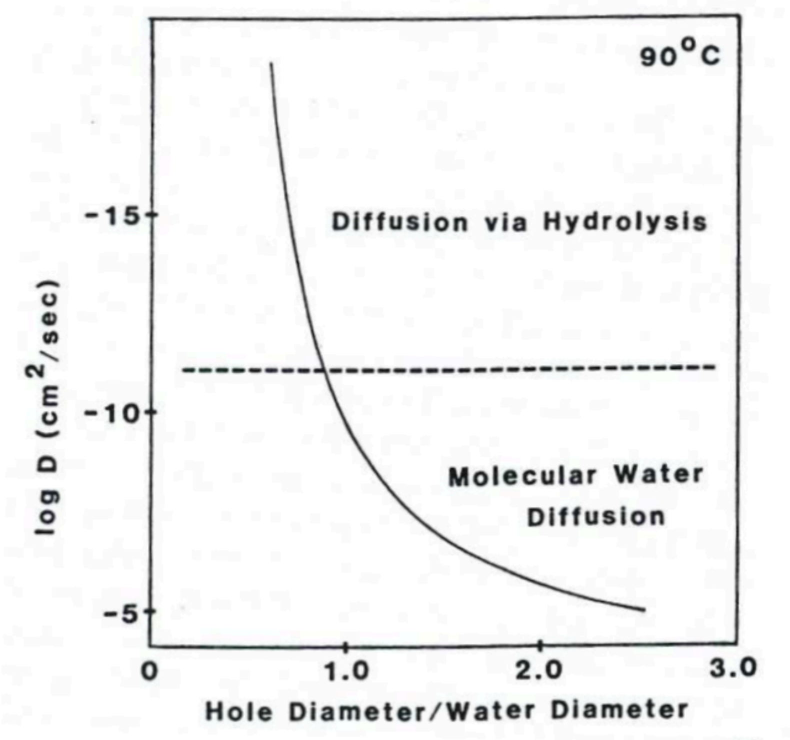
- $10^{-23}\ m^2.s^{-1} < D_{H20} < 10^{-19}\ m^2.s^{-1}$
- $r_{hydrolysis}$ (r_0) ~ 0.2 - 5 µm.d^{-1} @ 90°C
- Dynamic of recondensation: [days – years] depending on elements present in the glass (Al, Ca, Zr, REE…)
- $r_r \sim 10^{-3} - 10^{-5}$ µm.d^{-1} @ 90°C
- In case of Zeolite precipitation r ~ [1-1/10] $r_{hydrolysis}$

Basic Mechanisms

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



Hydration/Interdiffusion



(Bunker. *JNCS*, 1994)

General eq : $\equiv$ **Si-O-M** + **H**$^+$ $\rightarrow$ $\equiv$ **Si-OH** + **M**$^+$

What are the hydrogenated species that diffuse in the glassy structure ?

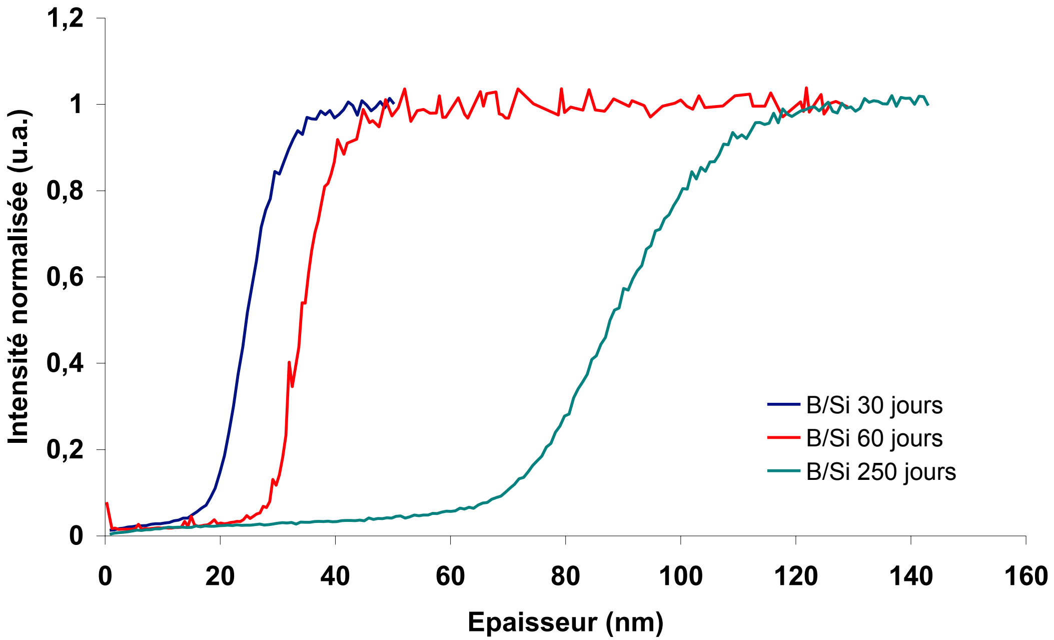
Ref	Glass	H/Na
Lanford et al. (1979)	SiO_2, Na_2O, CaO	2.9 ± 0.3
Houser et al. (1980)	SiO_2, Na_2O	1.75
Tsong et al. (1981)	SiO_2, Na_2O	2.0 ± 0.3 or 3.2 ± 0.4 depending % Na
Dran et al (1989)	SiO_2, Na_2O, CaO	~ 2 near surface, ~ 1 near diss front
Ferrand et al. (2006)	SON68	2.6 ± 0.3

Hydration/Interdiffusion

Concentration profile in the solid $$\frac{C - C_1}{C_0 - C_1} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Concentration of *i* in the solution $$C_i = 2\sqrt{\frac{Dt}{\pi}}\rho\, x_i \frac{S}{V}$$

(Frugier et al., *JNM*, 2008)



	ICP-AES	TOF-SIMS
30 d	32	24
60 d	38	35
250 d	83	87

(Chave et al., *JNM*, 2007)

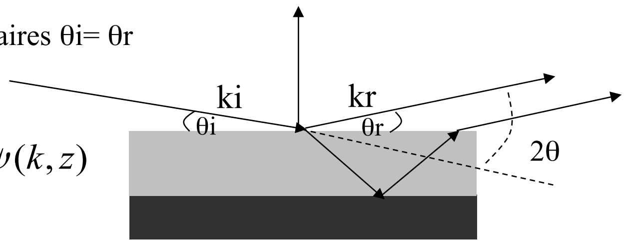
X-Ray Reflectometry

Principe

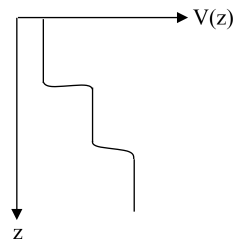
$$q = \frac{4\pi \sin\theta_i}{\lambda}$$ Vecteur de diffusion

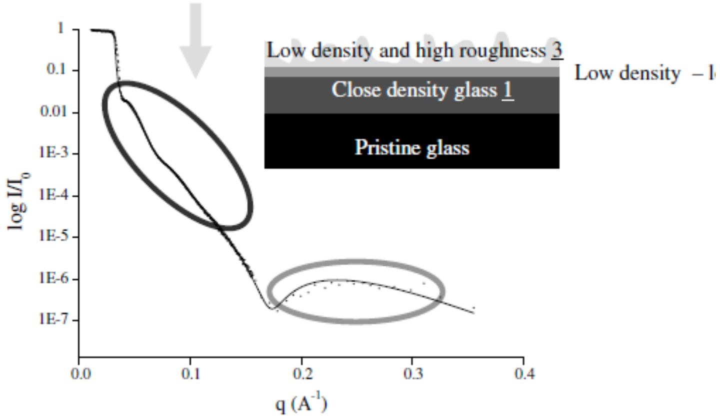
Conditions speculaires θi= θr

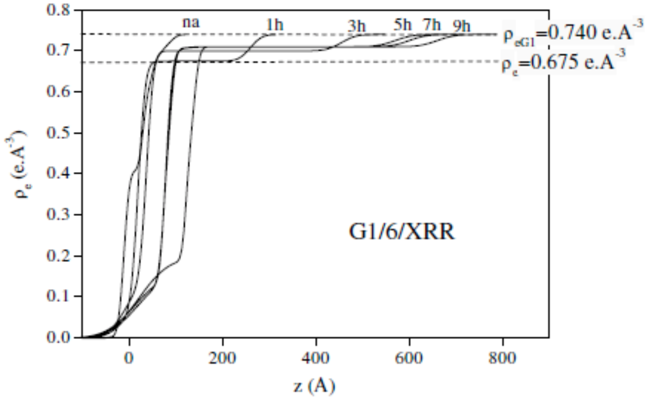
$$\psi''(k,z) + k^2\psi(k,z) = V(z)\psi(k,z)$$



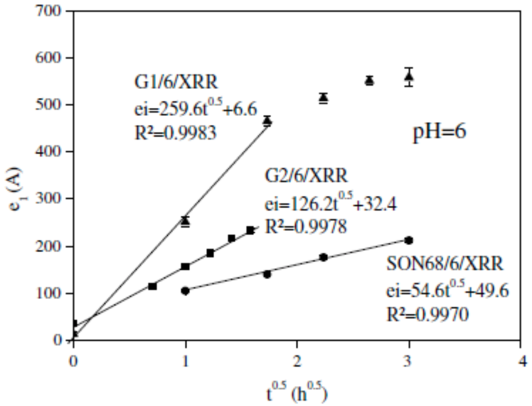
Potentiel de diffusion







SON68	ρ_m (g cm^{-3})	ρ_e (e A^{-3})
Glass	2.72	0.810
$Na^+ \rightarrow -$	2.55	0.745
$Na^+ \rightarrow H^+$	2.56	0.751
$Na^+ \rightarrow H_3O^+$	2.72	0.845
$(Na^+, Li^+, Cs^+) \rightarrow H^+$	2.50	0.737
$(Na^+, Li^+, Cs^+) \rightarrow H^+$ $B^3 \rightarrow 3H^+$	2.48	0.734
$(Na^+, Li^+, Cs^+) \rightarrow H^+$ $B^4 \rightarrow 4H^+$	2.45	0.733
$(Na^+, Li^+, Cs^+) \rightarrow H^+$ $B^3 \rightarrow 3H^+$ $B^4 \rightarrow 4H^+$	2.42	0.728
$(Na^+, Li^+, Cs^+) \rightarrow H^+$ $B^3 \rightarrow 2H^+ + H_3O^+$ $B^4 \rightarrow 4H^+ + H_3O^+$	2.62	0.851

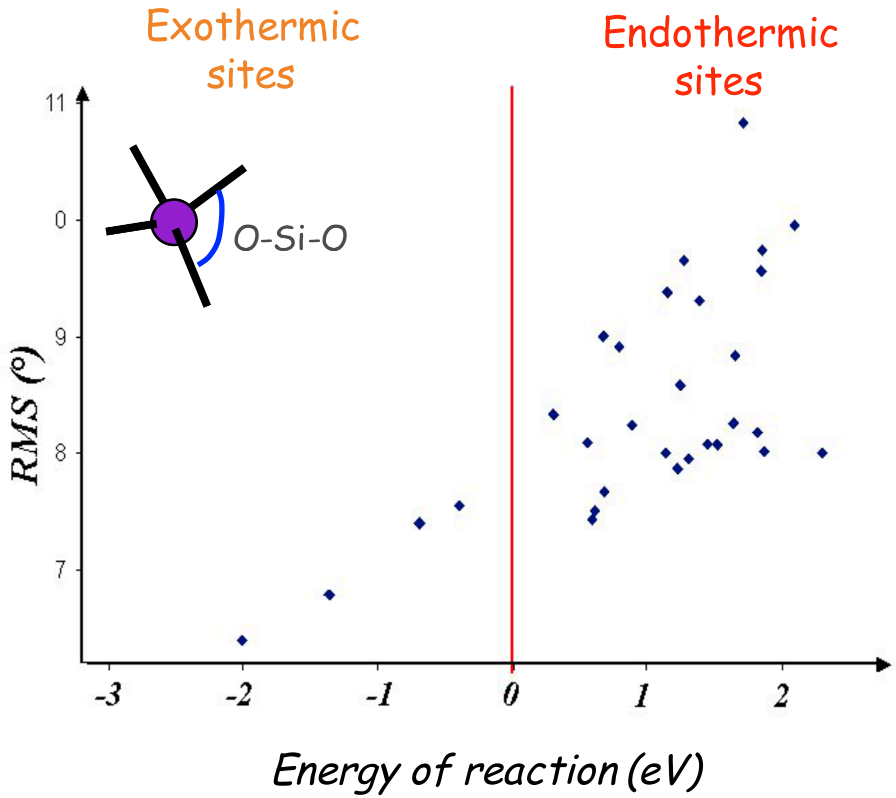


(Rebiscoul et al., *JNCS*, 2007)

Hydrolysis mechanisms by *ab initio*

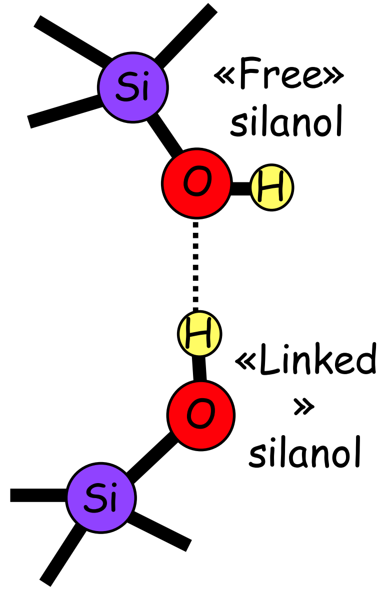
Vitreous network is non-homogeneous towards aqueous reactivity:
favorable/unfavorable sites for hydrolysis reaction

Distribution of the final O-Si-O angles (after hydrolysis)

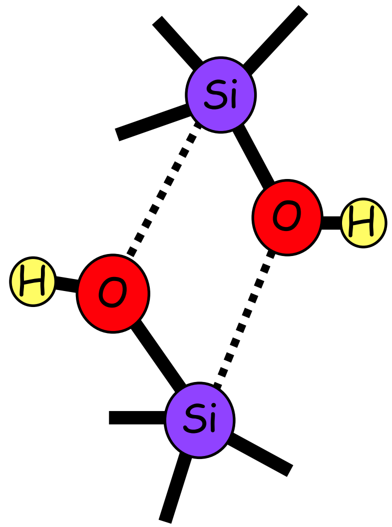


- number of favorable sites is lower
- decrease of their angle distribution

Exothermic sites
Si-O-Si bond
« stretched »



Endothermic sites
Si-O-Si bond
« compressed »



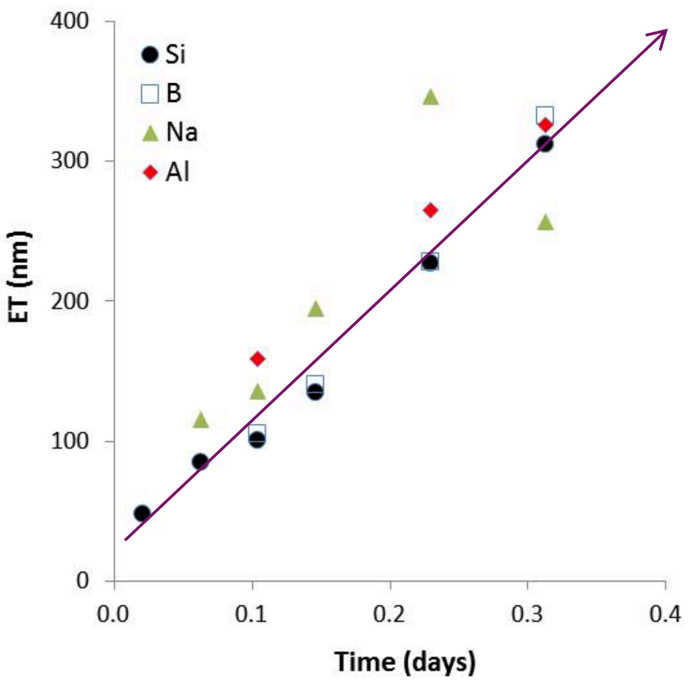
Hydrolysis: -> stress relaxation
-> decrease of local disorder

(Geneste, unpublished data)

R_0 measurments at pH 9, 90°C

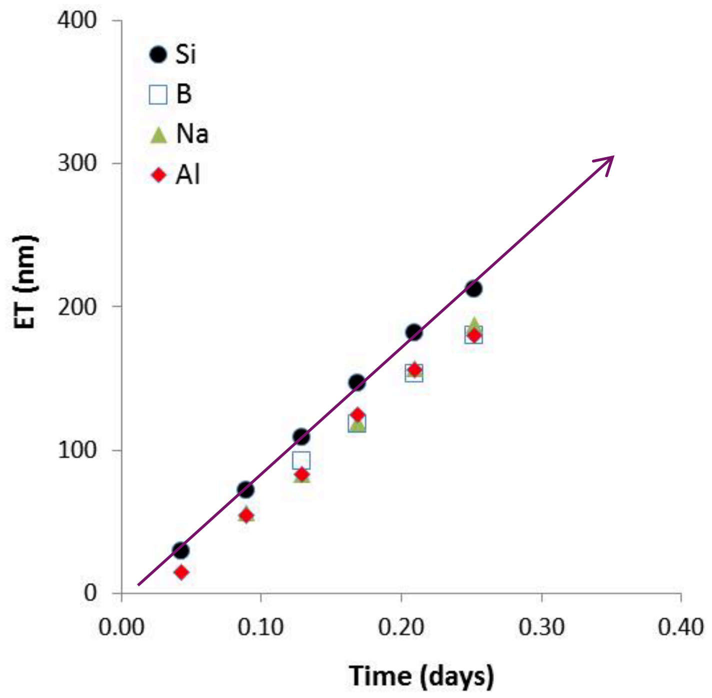
(wt%)	SiO2	B203	Na20	Al203	CaO	La203	Zr02
La-glass	53	19	10	5	7	6	
Zr-glass	56	17	12	6	5	-	3

La-glass **pH 9**



$R_0(Si) = 2.3\ g.m^{-2}.d^{-1}$

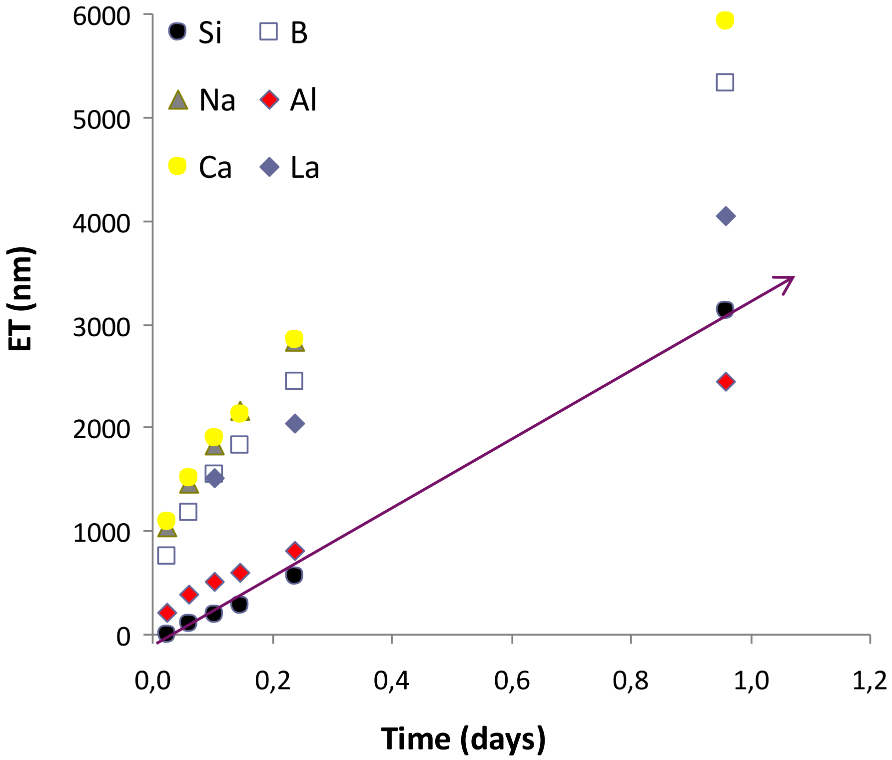
Zr-glass **pH 9**



$R_0(Si) = 2.2\ g.m^{-2}.d^{-1}$

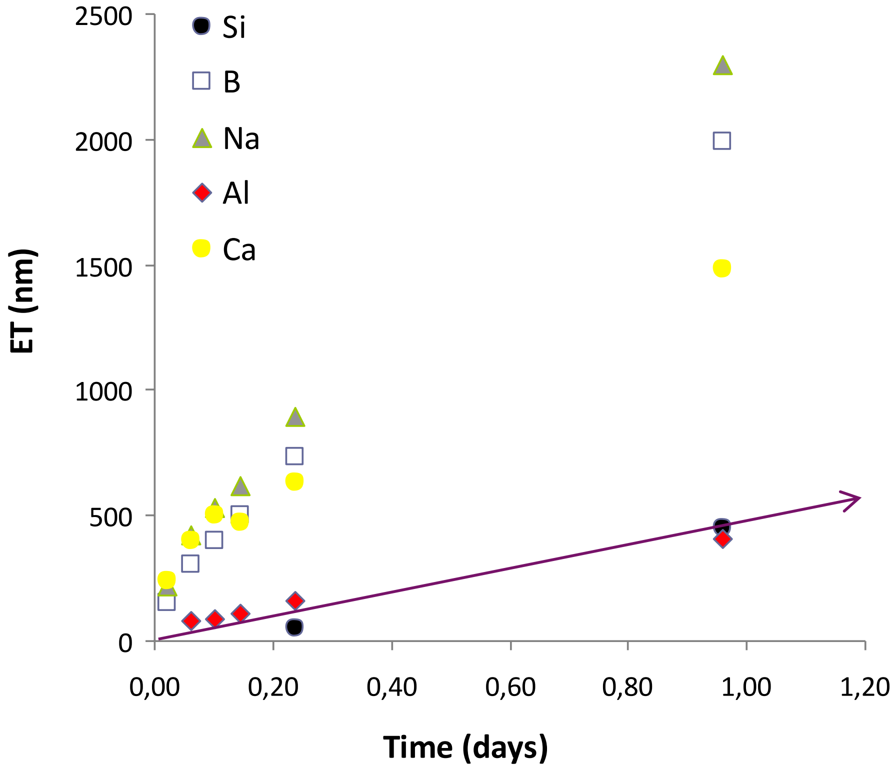
R_0 measurments at pH 3, 90°C

La-glass **pH 3**



$R_0(Si) = 6.6\ g.m^{-2}.d^{-1}$

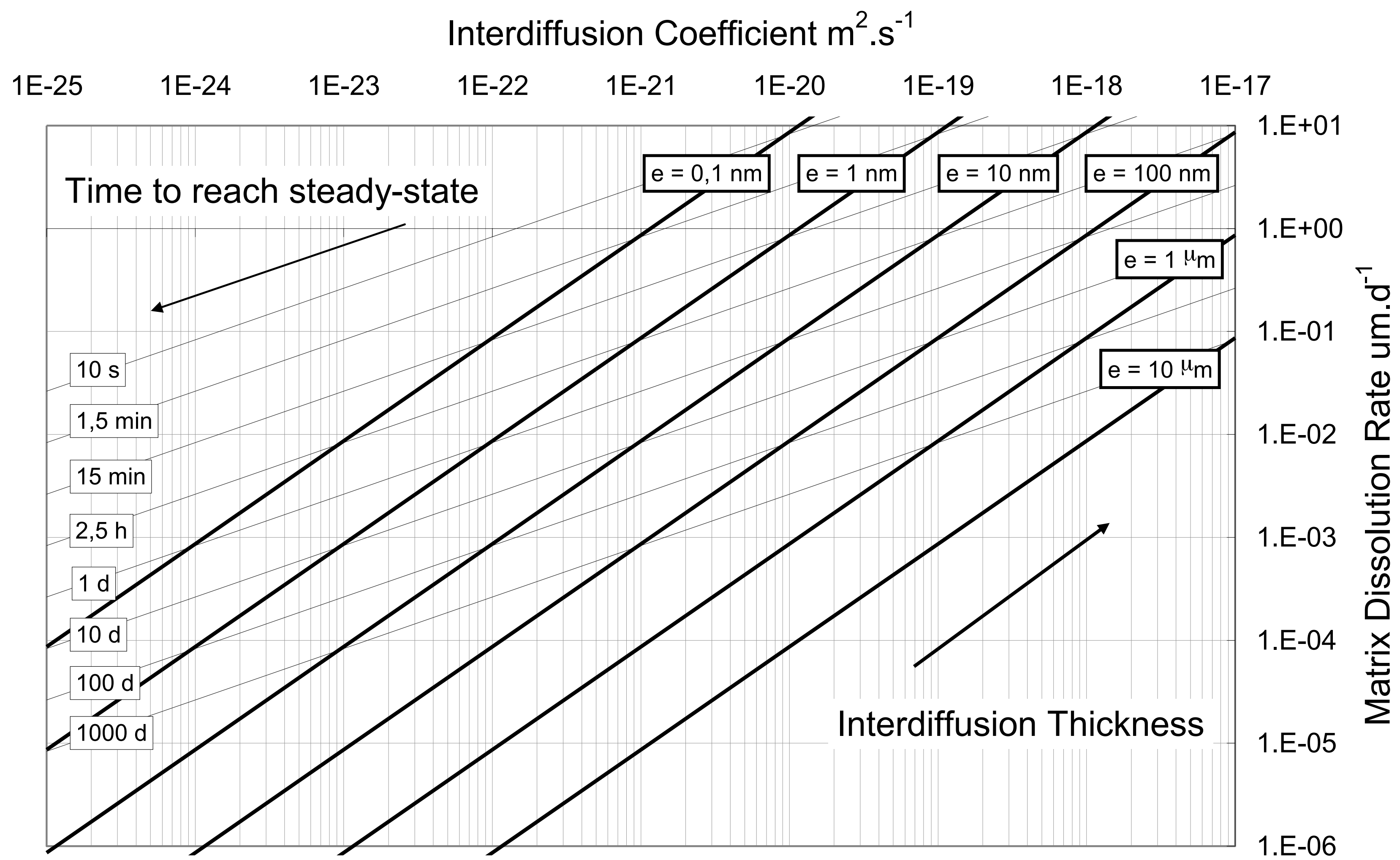
Zr-glass **pH 3**



$R_0(Si) = 0.9\ g.m^{-2}.d^{-1}$

Transition Interdiffusion/Hydrolysis

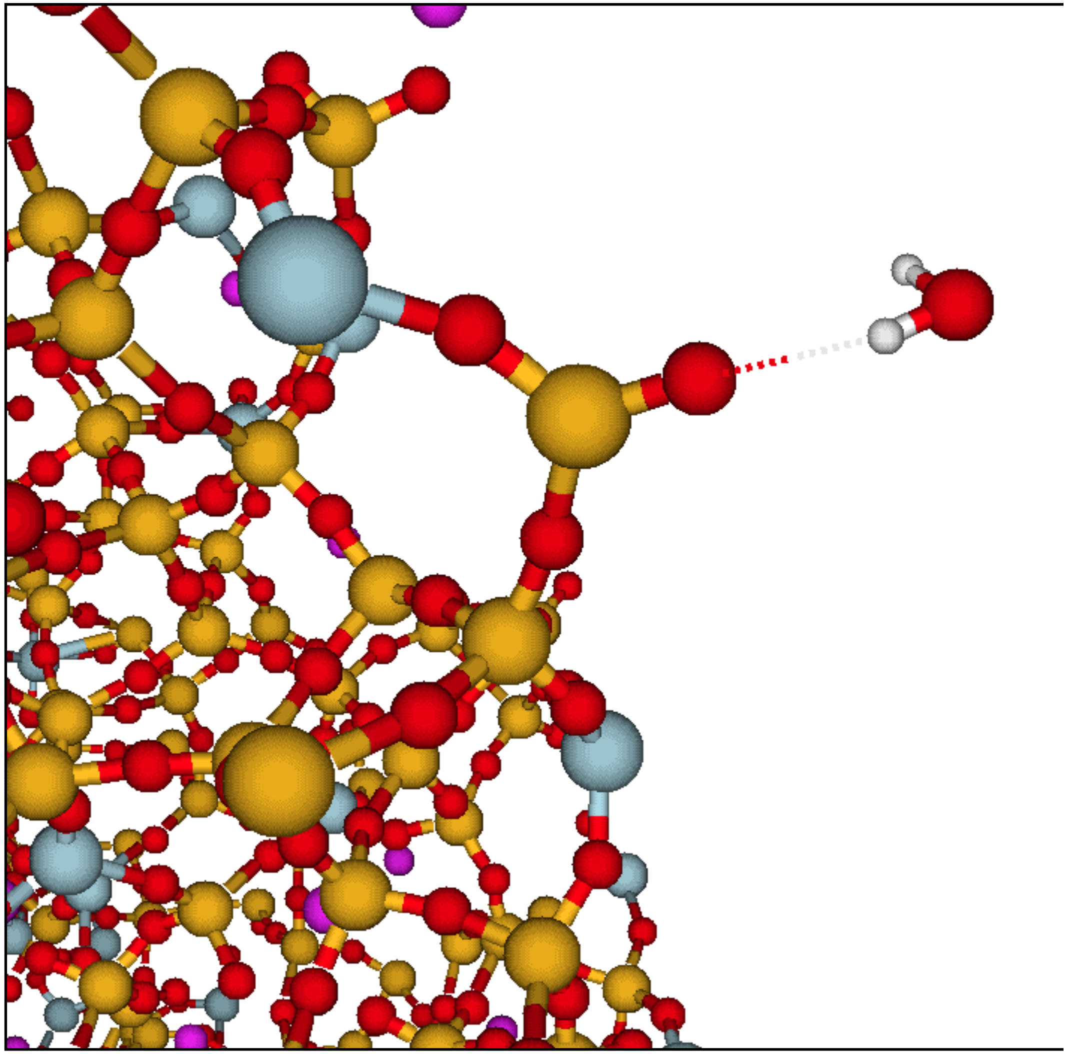
(Frugier et al., *JNM*, 2008)



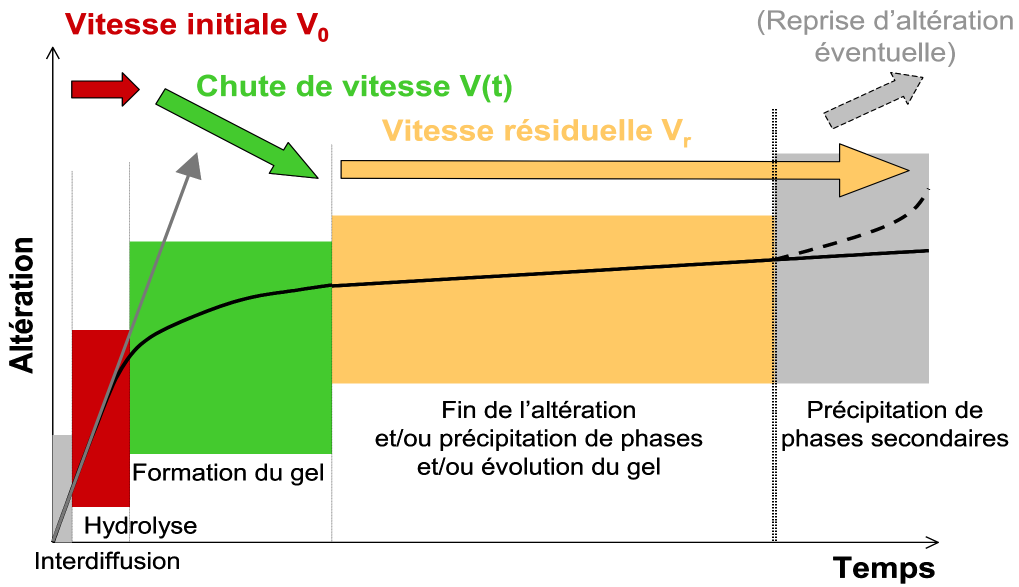
Ex: a glass, with $r_0 = 10^{-2}$ µm·d^{-1} and D = 10^{-21} m^2·s^{-1}, will reach steady-state conditions in about 10 days and the Na depleted layer will be 10 nm thick

Basic Mechanisms

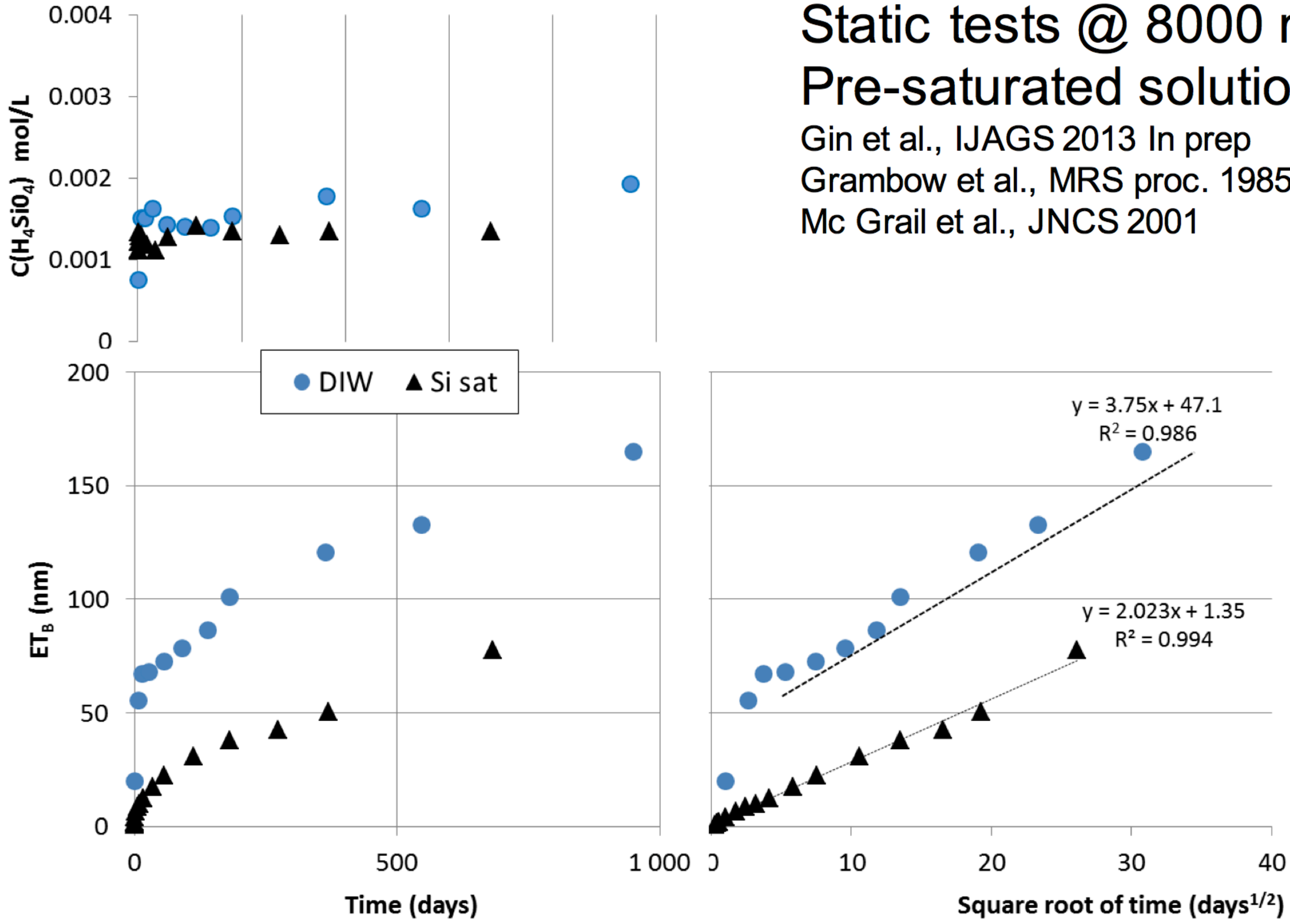
- Hydration / Interdiffusion
- Hydrolysis of glass formers
- **Condensation** of some hydrolyzed species (Si, Al, Ca…)
- Precipitation of secondary phases



Reasons why the rate drops by several orders of magnitude



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

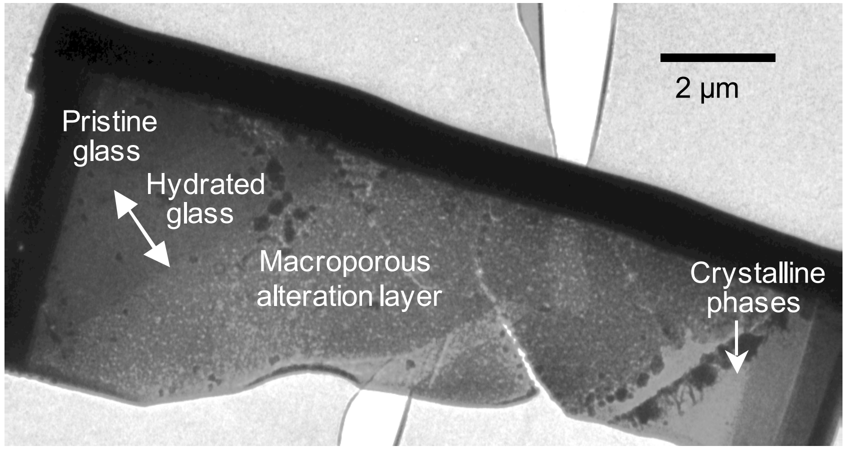
Gin et al., IJAGS 2013 In prep

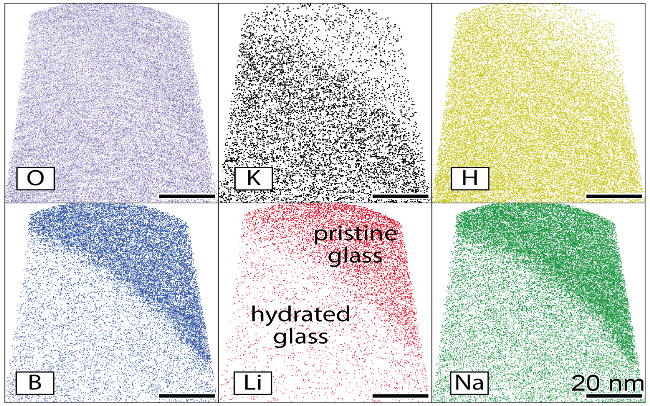
Grambow et al., MRS proc. 1985

Mc Grail et al., JNCS 2001

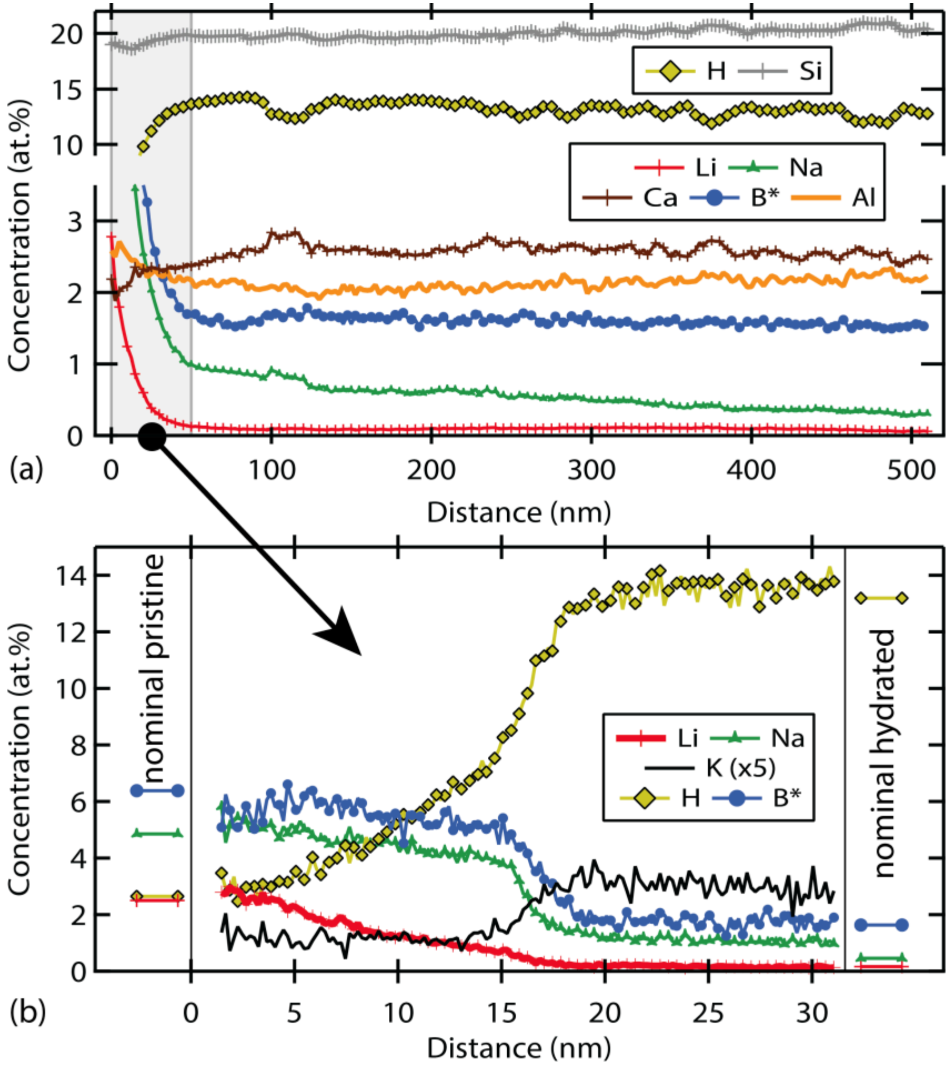
Pre-sat solution makes the RD stage much shorter but does not impact the RR regime. The first hundreds of days are dominated by interdiffusion

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

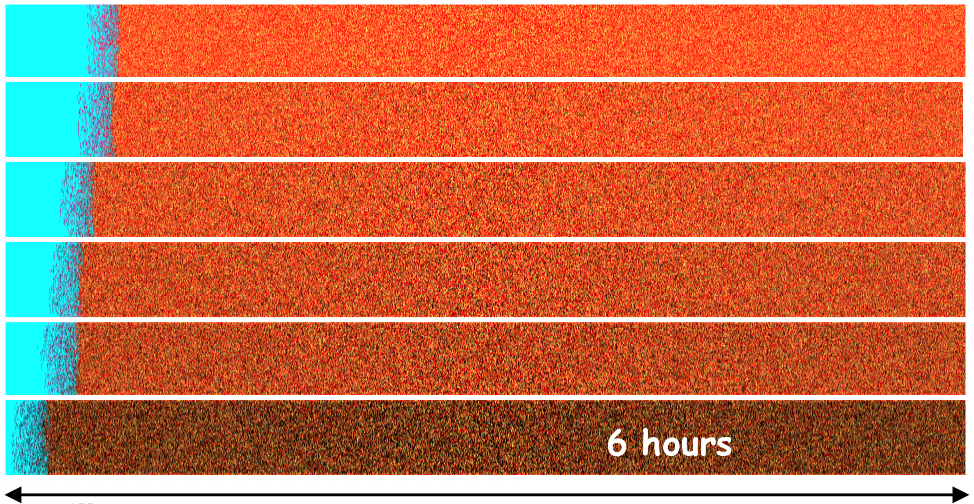
3 processes causing the drop of the rate
3 : Effect of porosity clogging

ZrO_2

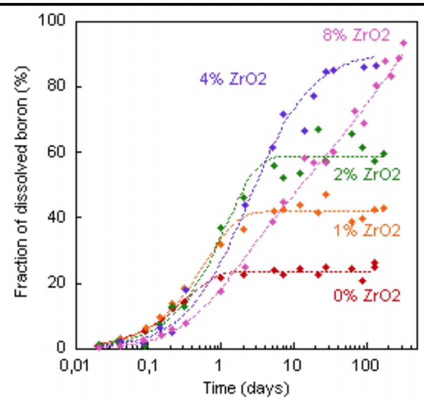
Water Glass

Forward rate of alteration

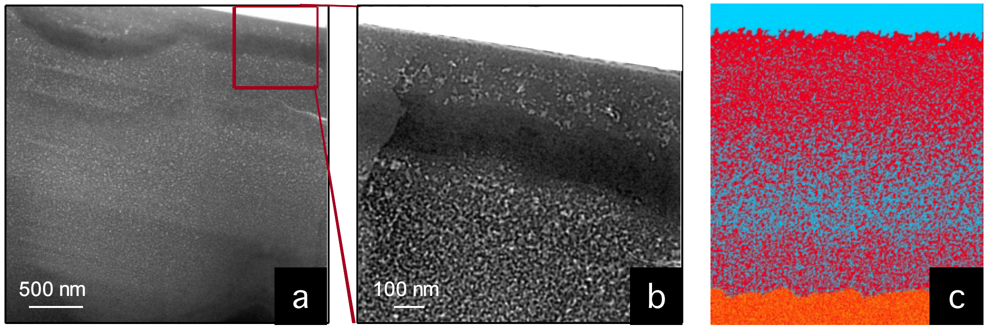
0%
1%
2%
3%
4%
8%



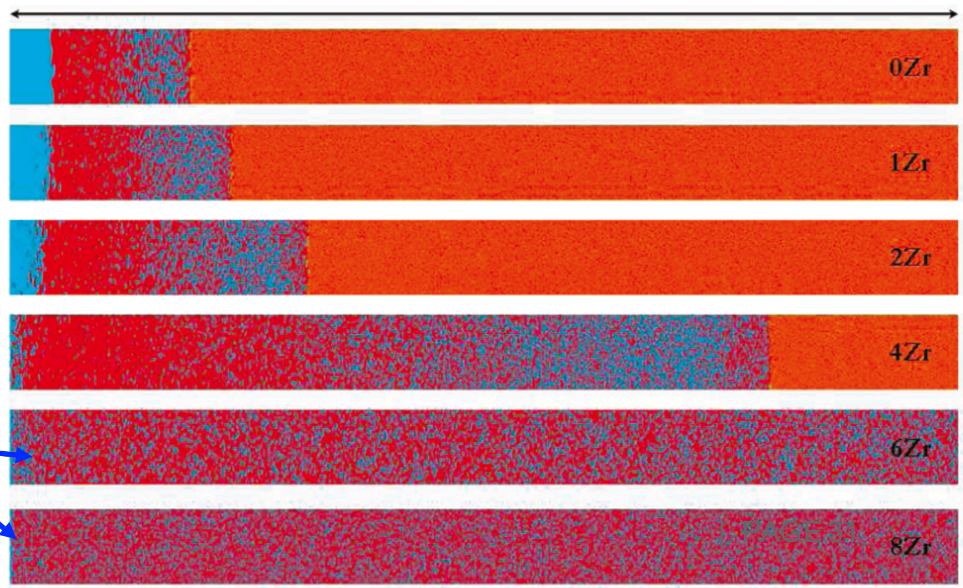
2.5 microns



Cailleteau et al. Nature Materials 2008



Porosity clogging: up to 4% of ZrO_2



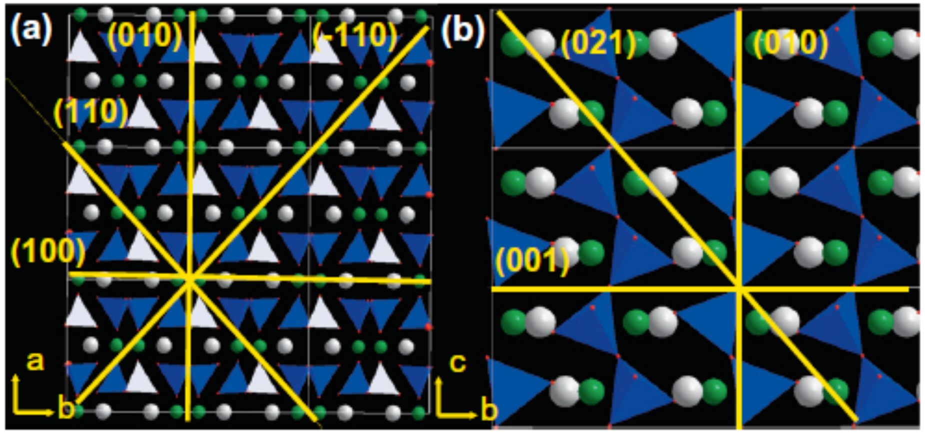
Zr at.: immobilize increasing numbers of Si

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

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

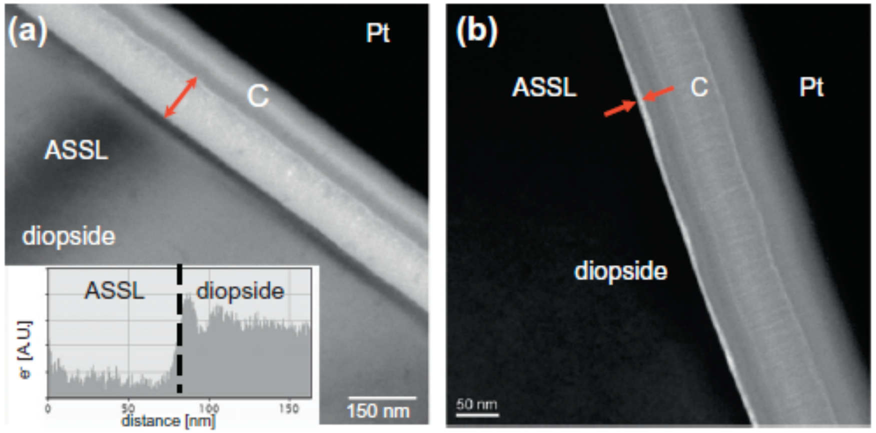
What happens on silicate minerals?

- Dissolution tests in Si-rich solutions
- ASSL: amorphous Si-rich surface layer



Diopside (inosilicate (Q_2), $CaMgSi_2O_6$)

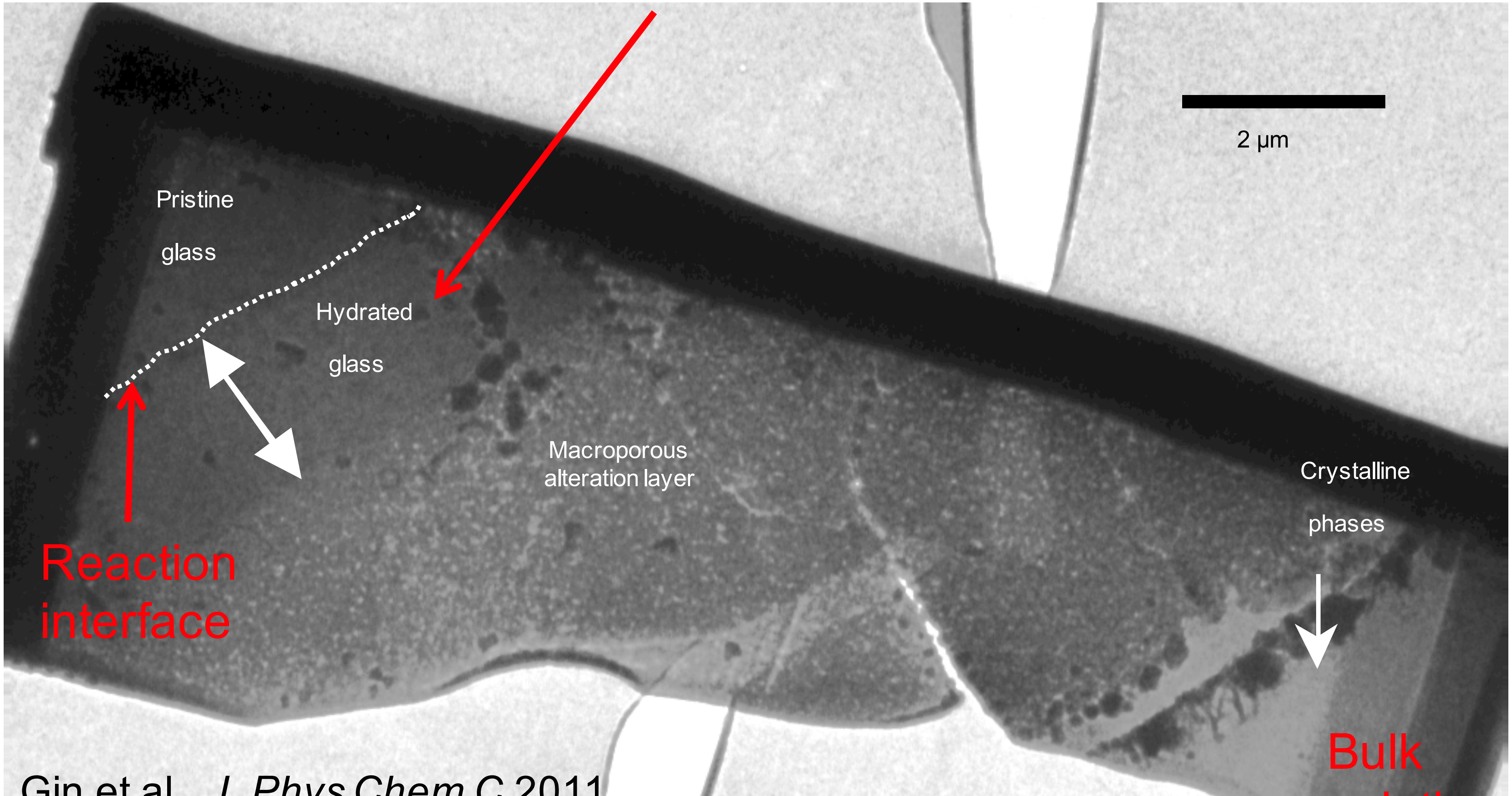
(021) (110)



Face	$R^{(hkl)}_{\text{low-Si}}$ (mol m^{-2} s^{-1})
(100)	9.30E-10
(010)	2.39E-09
(001)	3.20E-08
(110)	3.69E-09
(1$\bar{1}$0)	2.91E-09
(021)	2.28E-08

- Dissolution rate/mechanisms is face-dependent
- ASSL development is face-dependent
- When ASSL is passivating dissolution rate decreases far from equilibrium

Daval et al., GCA 2013



Gin et al., *J. Phys Chem C* 2011

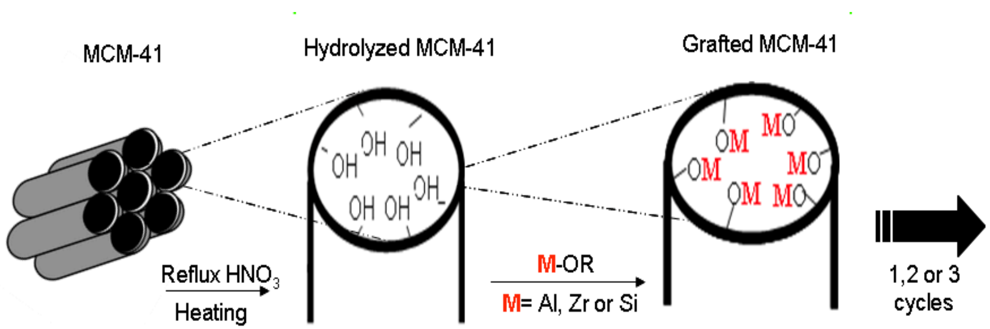
No free water in pores of 1 nm: e.g. Bourg et al., *J. Phys Chem C* 2012

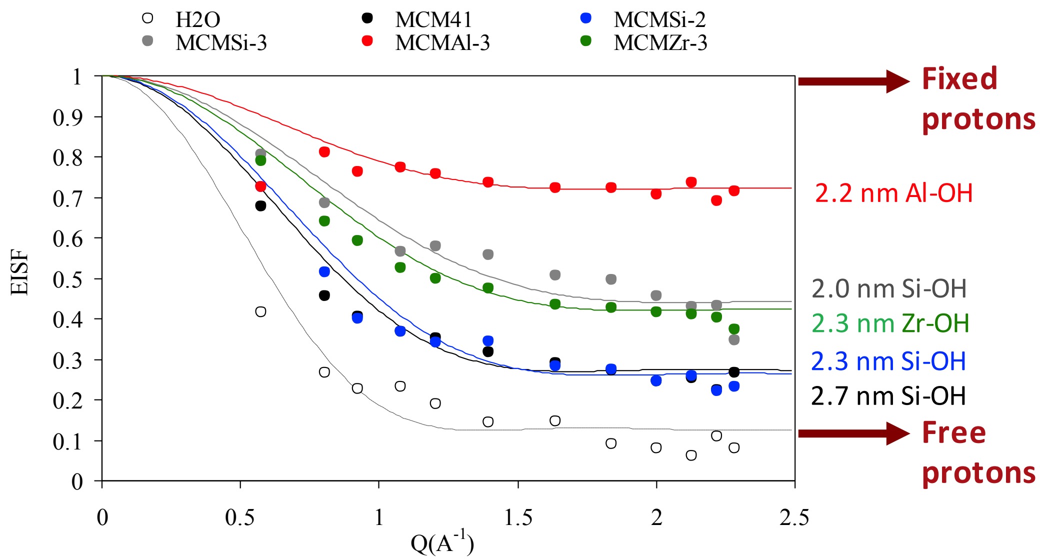
Water dynamics and reactivity in confined media

Does **pore size** and/or **surface chemistry** impact the species mobility?

-> mesoporous silica with various pore sizes, and pore wall surfaces (Si-OH, Zr-OH or Al-OH terminations)

Schematic concept of the hydrolytic sol-gel grafting method





Quasi-elastic neutron scattering
(correlation times in the picosecond range)

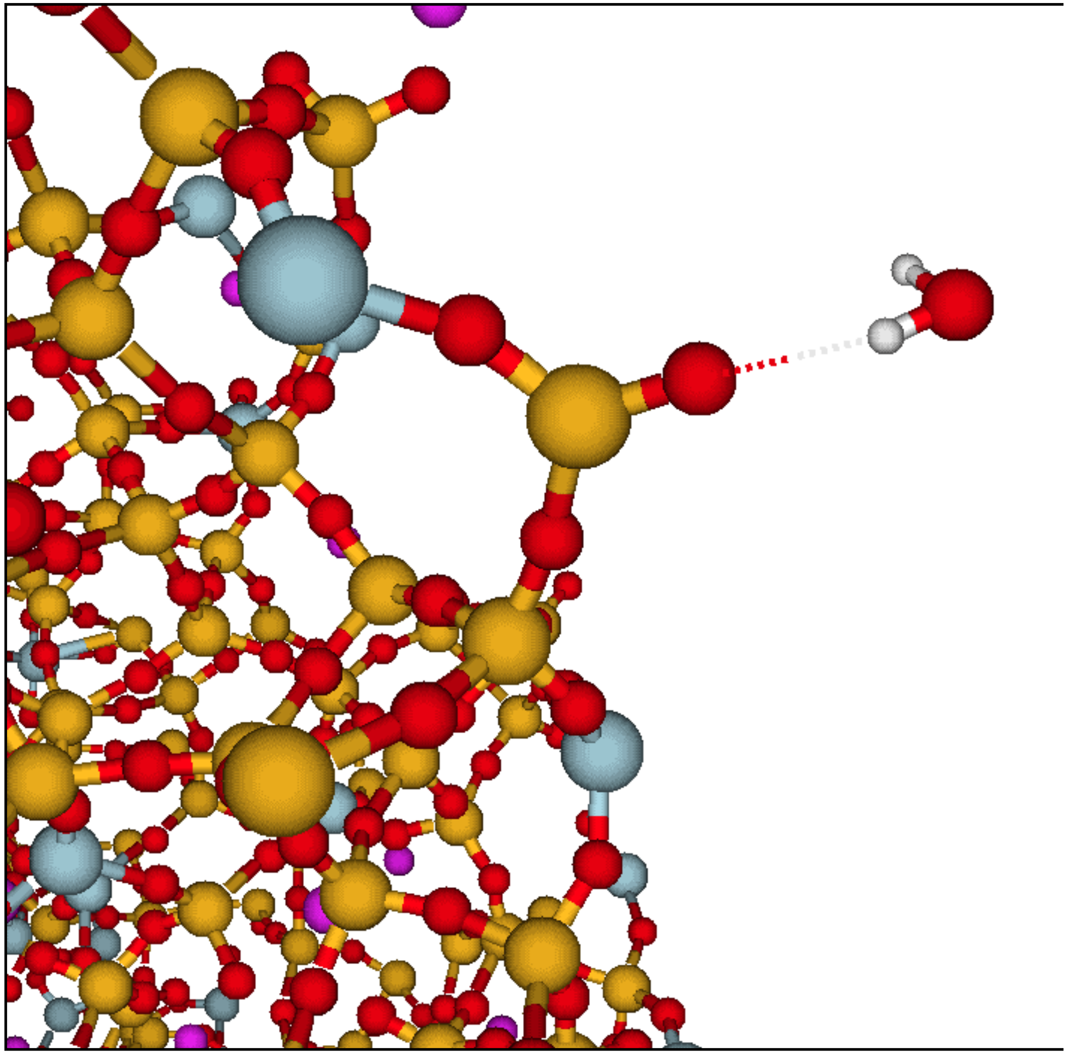
Water diffusion is strongly influenced by :

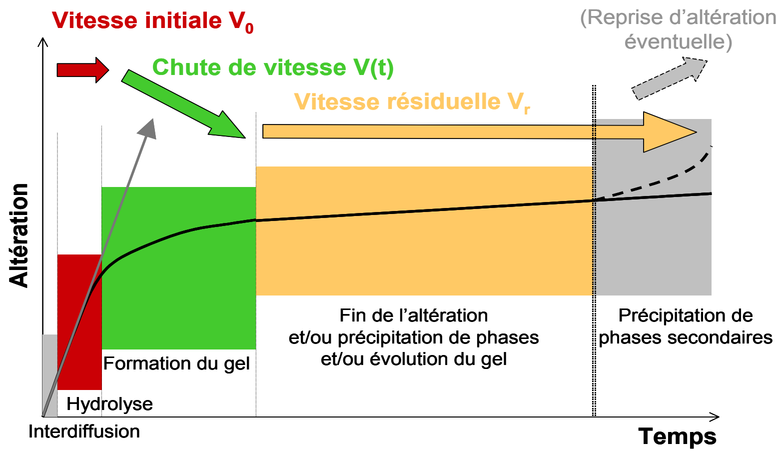
- pores surface composition
- pores size

-> predominant effect of pores surface composition on the water mobility (ability of Al to immobilize more water molecules than Zr then than Si)

Matar Briman et al. (2012) J. Phys. Chem. C

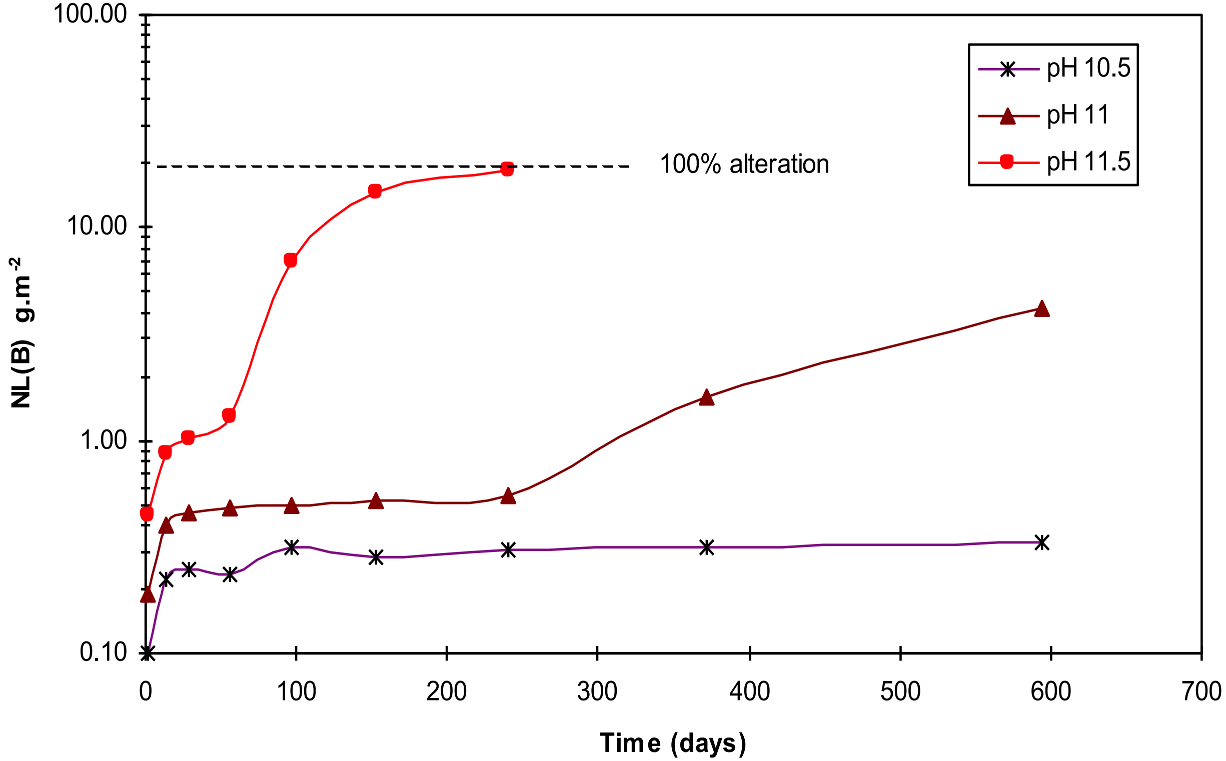
- Hydration / Interdiffusion
- Hydrolysis of glass formers
- Condensation of some hydrolyzed species (Si, Al, Ca…)
- **Precipitation** of secondary phases

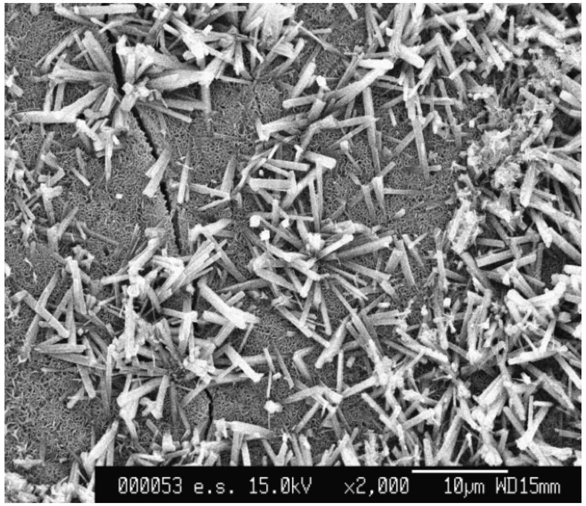


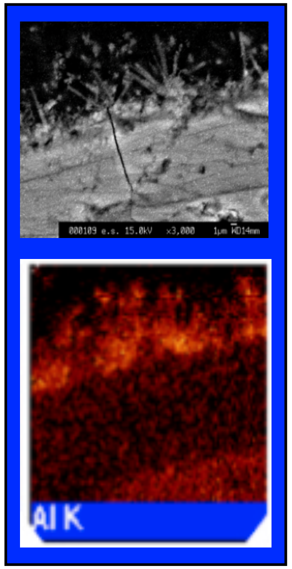


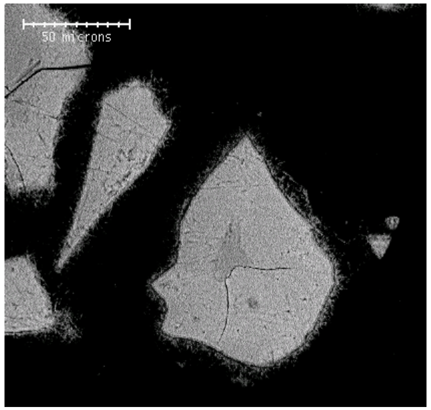
Alteration Resumption

SON68 glass alteration at 90°C, imposed pH







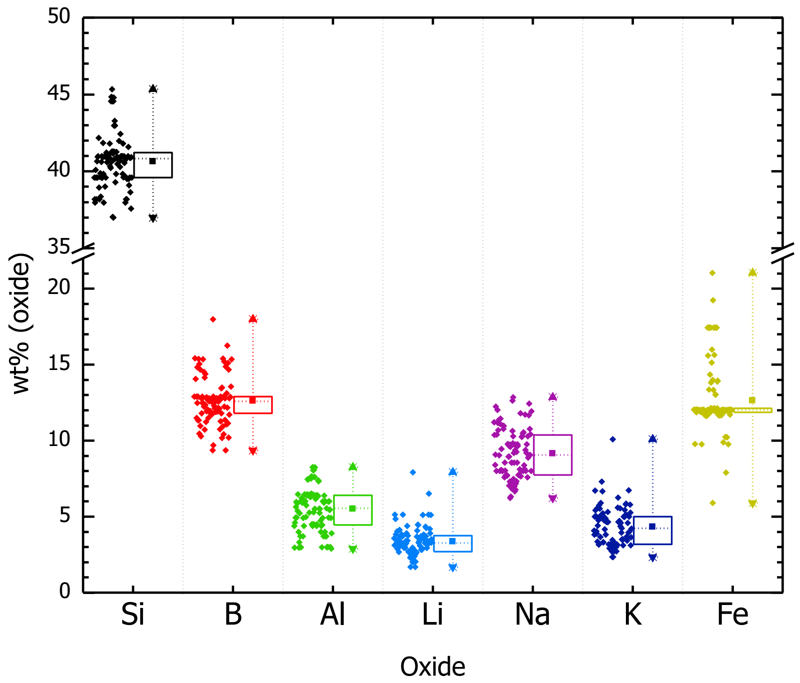


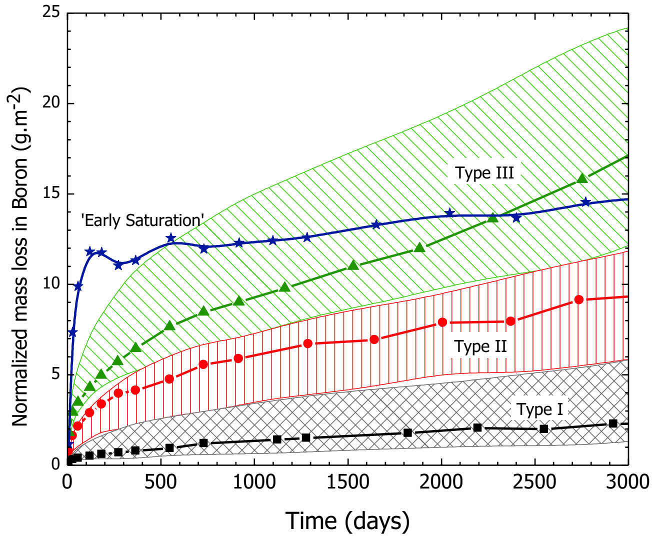
The protective gel is dissolved when zeolites precipitates

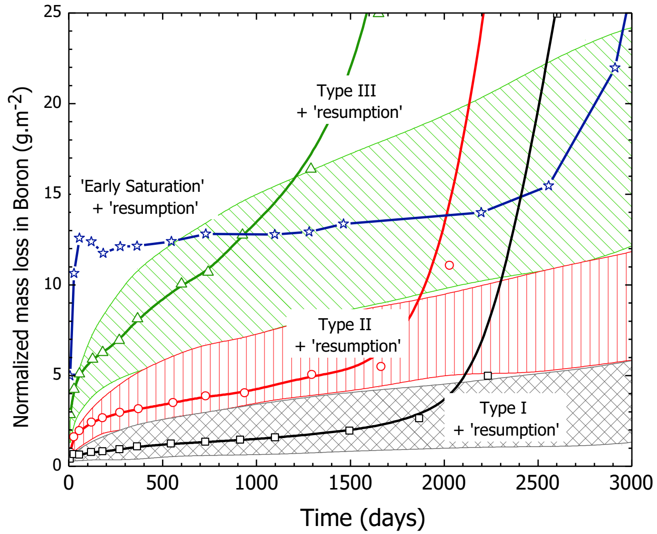
Ebert, *Nucl. Tech.* 1993
Ribet et al., J*NM* 2004

Alteration Resumption

98 glasses « West Valley »



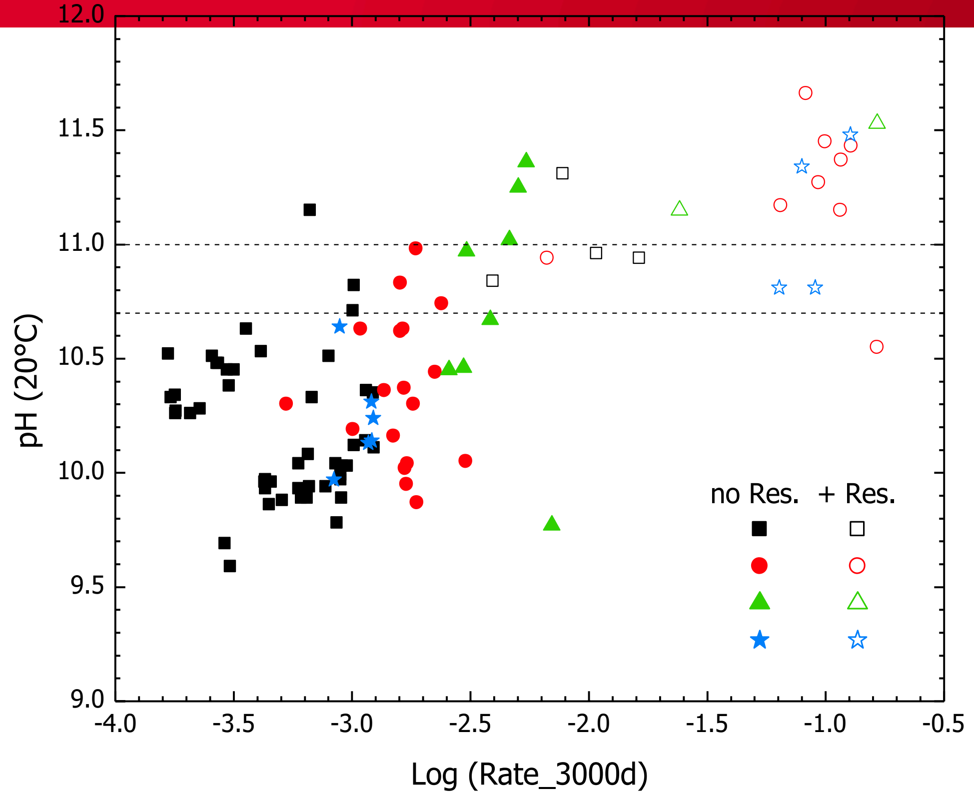


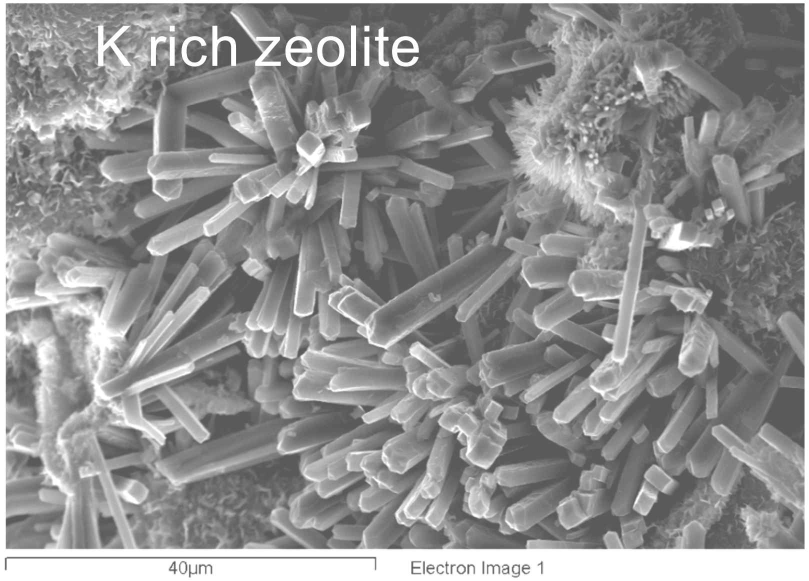


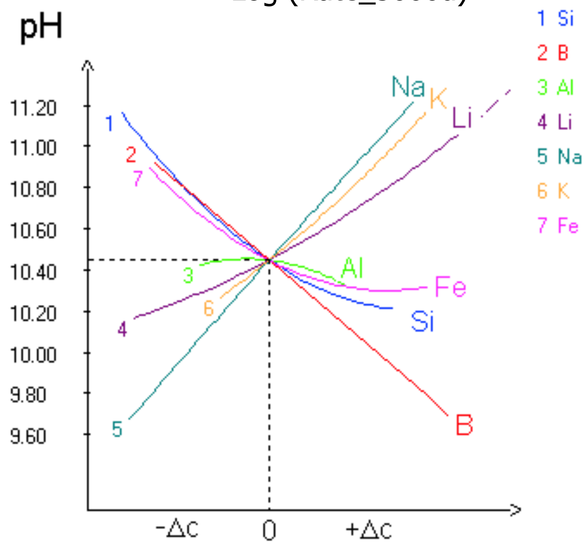
Ribet et al., *MRS proc.*, 2004
Collaboration with I.Muller, CUA

Leaching from 6 to 14y at 90°C

Alteration Resumption







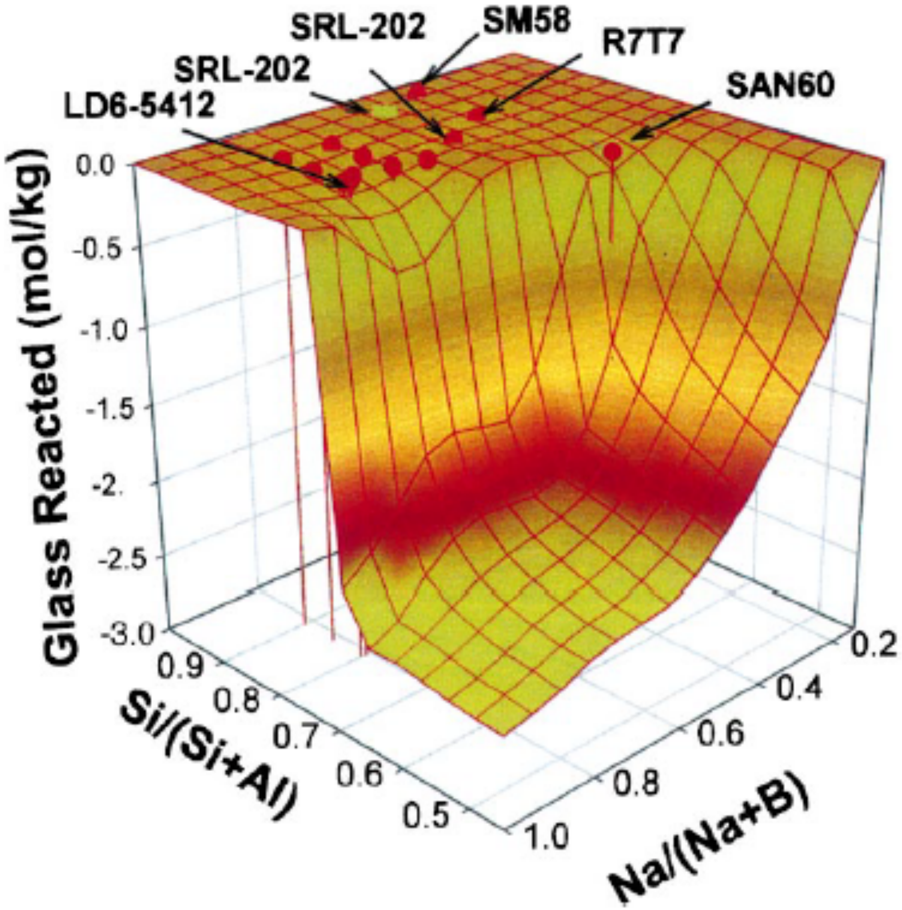
pH (20°C) used as indicator for resumption:

- pH < 10.7 => NO resumption is expected
- pH > 11.0 => Resumption most likely to happen

This behaviour depend on the glass composition

Alteration Resumption

Even unable to predict the rate, geochemical calculation at thermodynamic equilibrium can help compare glasses in terms of ability to form analcime during alteration



Competition between SiO2am and analcime

How to model glass dissolution rate?

Rate laws over time

1935 *Transtion state theory (Eyring)*

1982 TST applied to silicate minerals (Aagaard & Helgeson)

1985 First order law applied to nuclear glasses $r = r_0[1\text{-}C/C_{sat}]$ (Grambow)

1995 General rate law applicable to minerals and glasses (Lasaga)

2001 GM2001 model: coupling affinity and D_{H2O} and D_{si} (Grambow)

2006 European Glamor project (including USA): importance of the residual rate

2008 GRAAL model: introduces the notion of PRI (Frugier)

2012 µContinuum model (Steefel)

TST-based Rate Laws (used for PA)

$$\text{rate } (g/m^2 \bullet d) = k_0 \bullet 10^{\eta \bullet pH} \bullet \exp(-E_a/RT) \bullet (1 - Q/K)$$

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

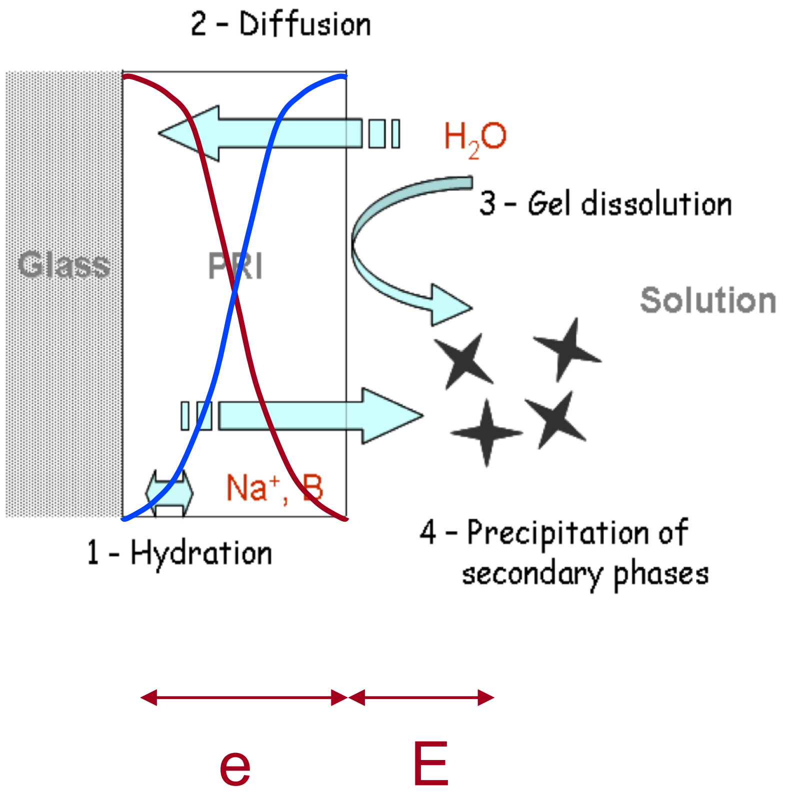
Q is activity of orthosilicic acid

K is activity of orthosilicic acid at “equilibrium”

Limitations: interdiffusion/passivation not taken into account (several implications for the residual rate regime and stage III)

The GRAAL model

Frugier et al., *J. Nucl. Mat.* (2008; 2009)
Minet et al., *J. Nucl. Mat* (2010)
Rajmohan et al., *Chem. Geol.* (2010)



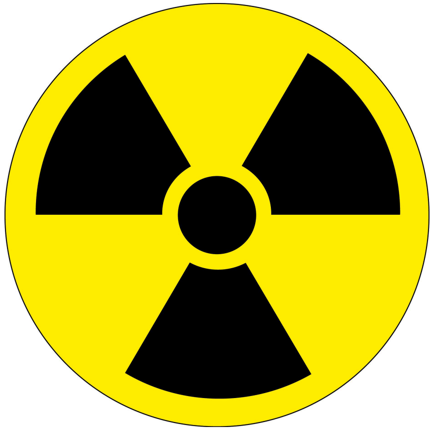
E(t) : Thickness of the dissolved PRI
e(t) : Thickness of the PRI

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

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

Equations are implemented either in a reactive transport code (HYTEC) or solved analytically (by adding mass conservation equations)

Applications: decipher coupled phenomena, design experiments, make predictions



What other phenomenon could affect the rate?

From lab experiments to long-term predictions

Experimental Studies
(short tem)

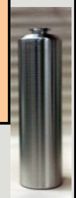
Characterization of old natural samples *(long term)*

Does it match ?

Parameters
thermo & kinetics

Long-term
simulation

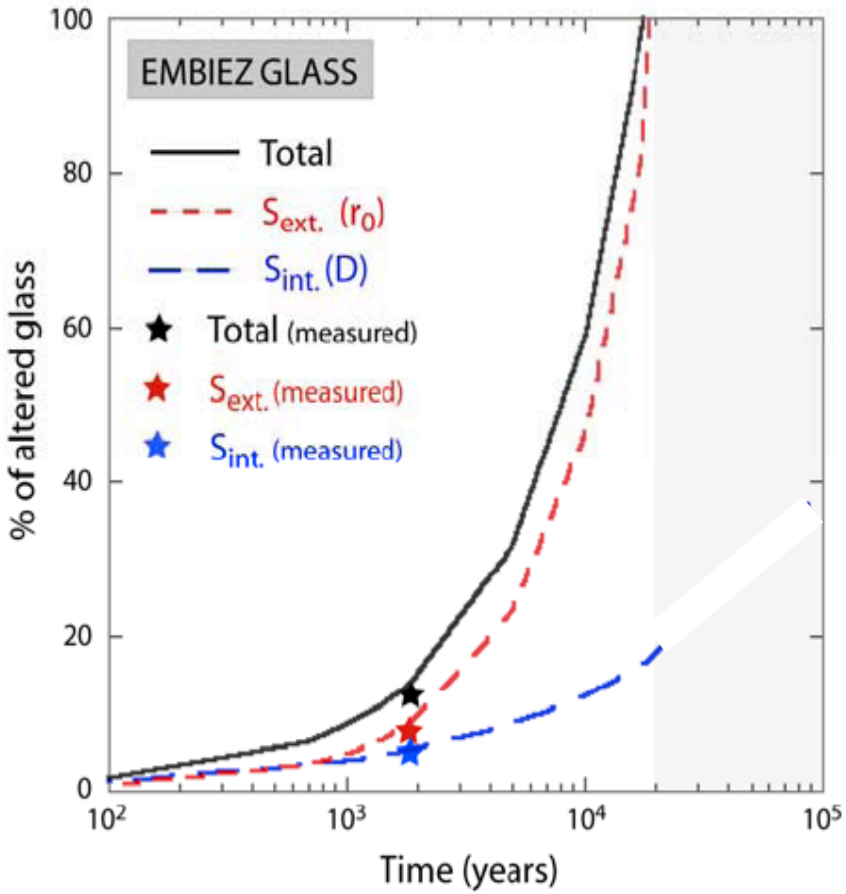
Mechanistic Model
Natural & Archeo Glasses

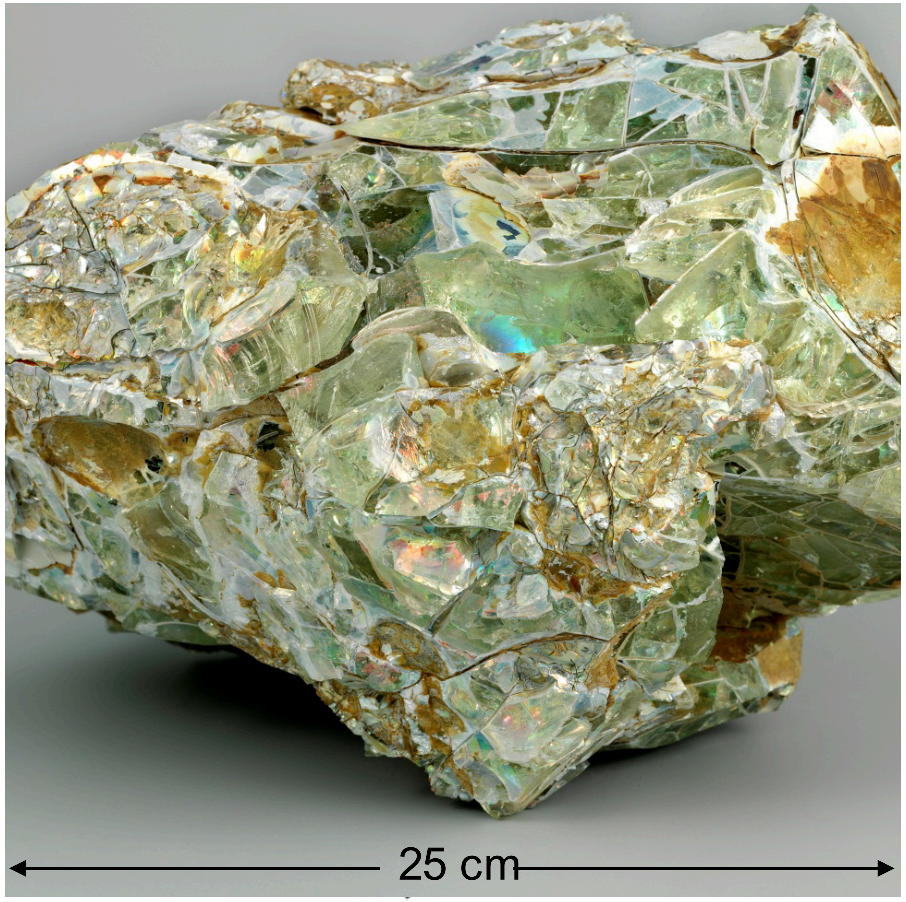


Nuclear Glasses

Model validation: Contribution of archaeological analogs

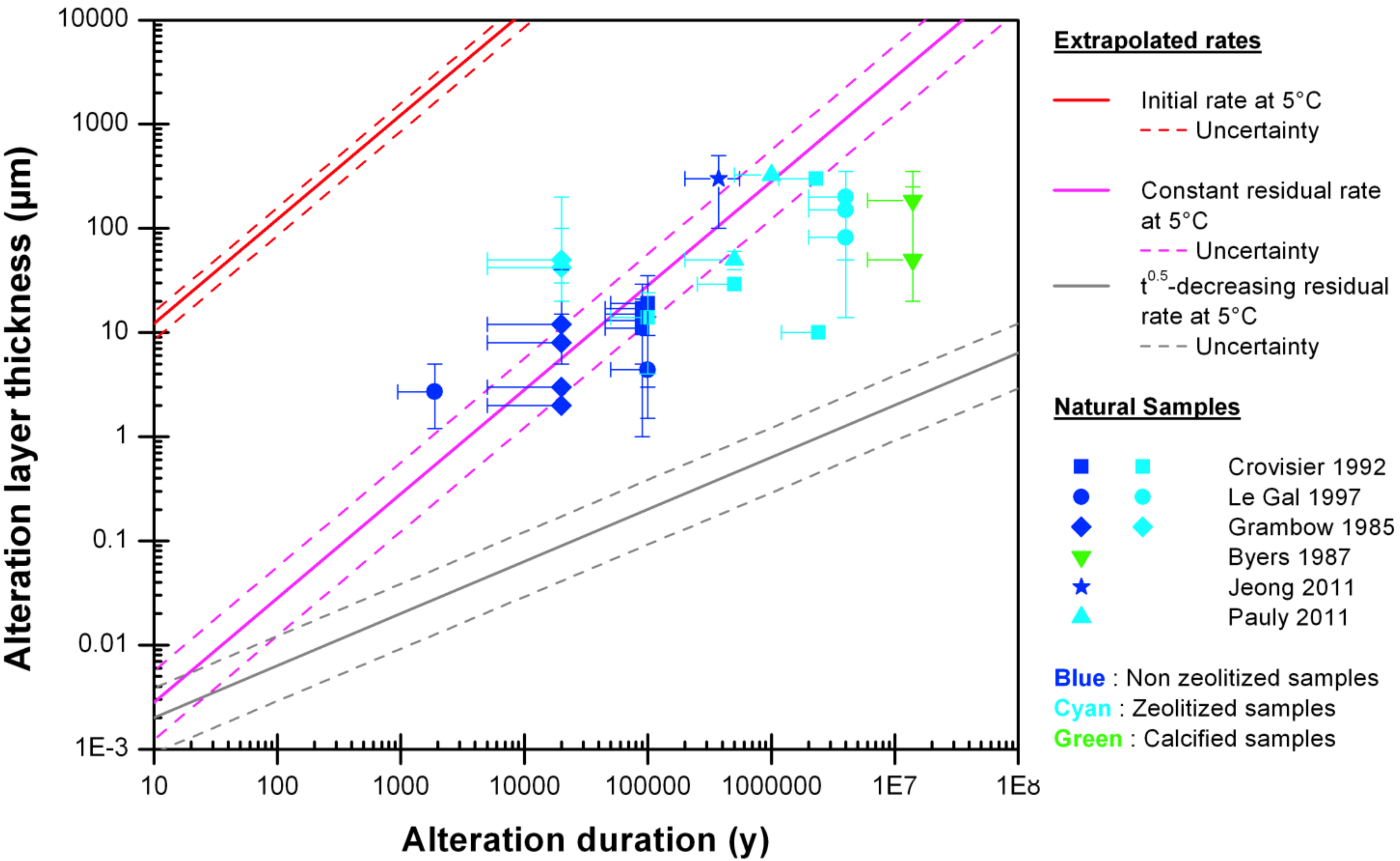
Verney-Carron et al., *Geochim. Cosmochim. Acta* 2008 ; 2010
Verney-Carron et al., *J. Nucl. Mat.*, 2010





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

Natural analogues: Residual rate of basaltic glass



First time that correlation is made between lab data and long-term rate from field samples

Parruzot et al., Subm. GCA

Acknowledgement: CEA (LCLT, P. Dillmann, T. Charpentier, O. Bildstein), Univ Paris VI (G. Calas, L. Galoisy), IEM Monptellier (A. Ayral), Ecole Polytechnique (F. Devreux), ENSCP (P. Barboux, O. Majérus), CRPG (G. Libourel), Subatech (A. Abdelouas), ENSMP (L. De Windt)

International Collaboration on Glass Corrosion