La modélisation Monte-Carlo cinétique :
un outil pour comprendre la corrosion des verres

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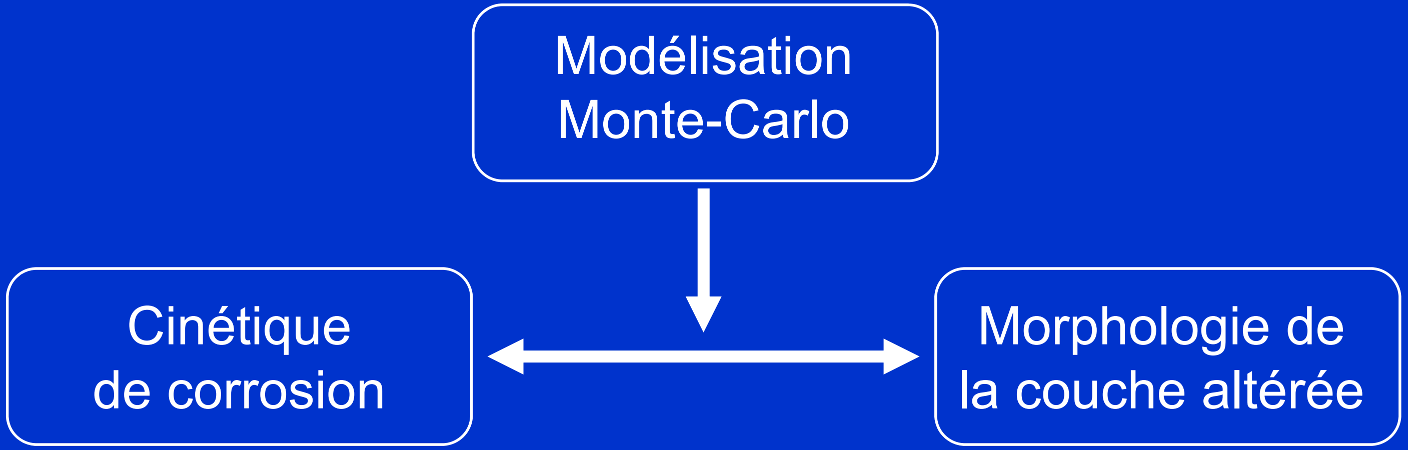
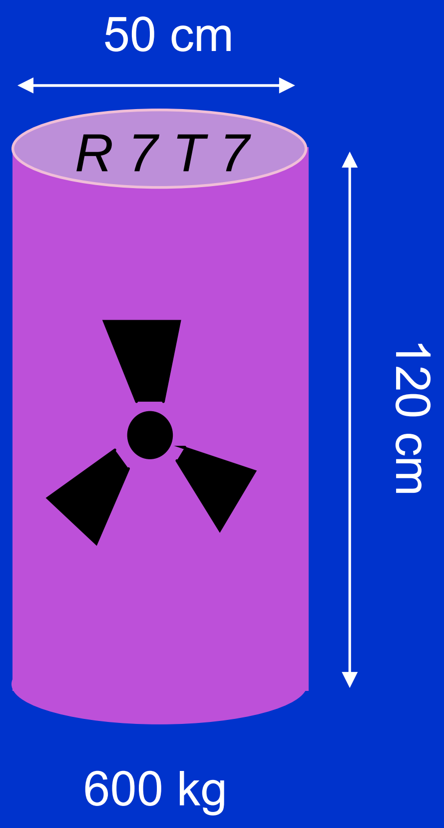


Modélisation
Monte-Carlo

Cinétique
de corrosion

Morphologie de
la couche altérée

Nuclear waste confinement glasses



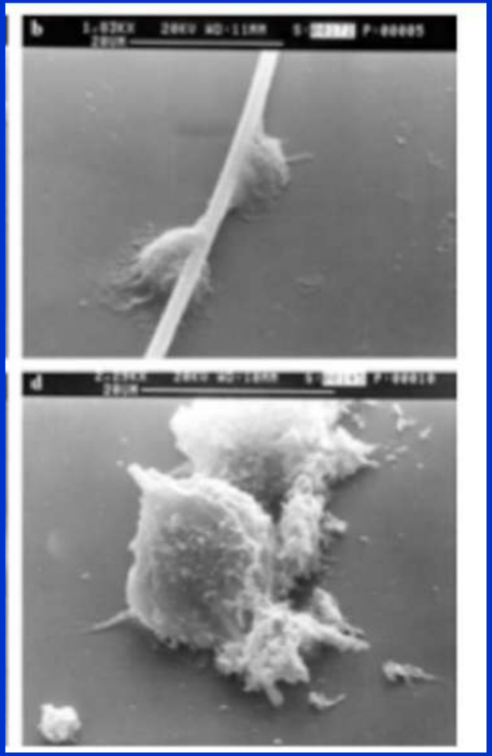
Among more than 30 oxides :

Silica	45%
Boron oxide	14%
Alkali oxide	14%
Earth-alkali oxide	5%
Alumina	4%
Zirconia	2%
Fission products	12%
Minor Actinides	1%

Long term geological storage

Need for understanding and modeling the dissolution mechanisms for safety assessment

Biosolubility of insulation and reinforcement fibers



Nguea *et al.*, Arch. Toxicol. **79**, 487 (2005)

Lung clearance mechanisms

- short fibers (< 20 μm)
  - transport by macrophages
- long fibers (> 20 μm)
  - dissolution in extra celullar fluid (pH 7)
  - breaking after partial dissolution in macrophage phagolysosomes (pH 4.5)

↓

Fibers with high alumina content

Is there a threshold for biosolubility?

F. Devreux *et al.* J. Mater. Sci. **45**, 1154-1159 (2010)

Work guidelines

- ♣ to associate Monte-Carlo simulations and experiments on the same glasses

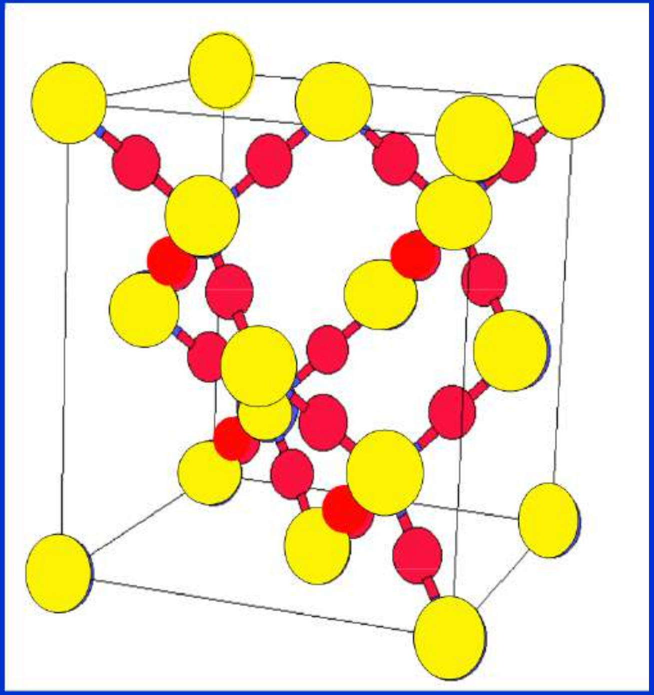
- ♣ to study series of glasses with simplified composition
  - ♦ influence of oxides more soluble than silica
    - ♠ $(100\text{-}2x)\ SiO_2 - x\ B_2O_3 - x\ Na_2O$
    - ♠ $(64\text{-}x)\ SiO_2 - x\ Al_2O_3 - 36\ Na_2O$ / CaO

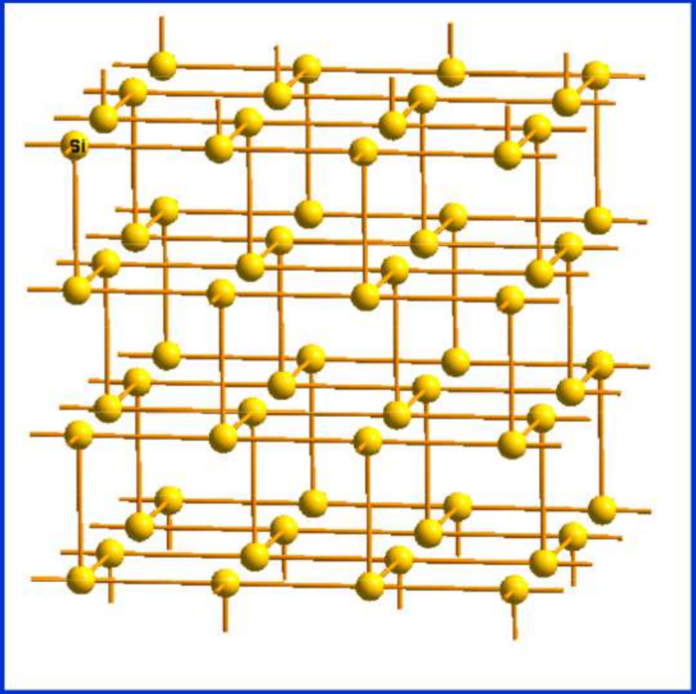
$$R = \frac{[B/Al]}{[Si] + [B/Al]}$$

  - ♦ influence of oxides less soluble than silica
    - ♠ $(61\text{-}x)\ SiO_2 - x\ ZrO_2 - 17\ B_2O_3 - 18\ Na_2O - 4\ CaO$
  - ♦ effect of substituting earth-alkali for alkali
    - ♠ $62\ SiO_2 - 2\ ZrO_2 - 17\ B_2O_3 - (19\text{-}x)\ Na_2O - x\ CaO$

- ♣ to use controlled corrosion conditions
  - ⅄ Calibrated powders + monoliths
  - ⅄ Initial dissolution (low SA/V) and saturation regime (high SA/V)
  - ⅄ Fixed temperature and pH : T = 90°C, pH 7 and 8 / T = 37°C, pH 4.5

The simulated "glass"

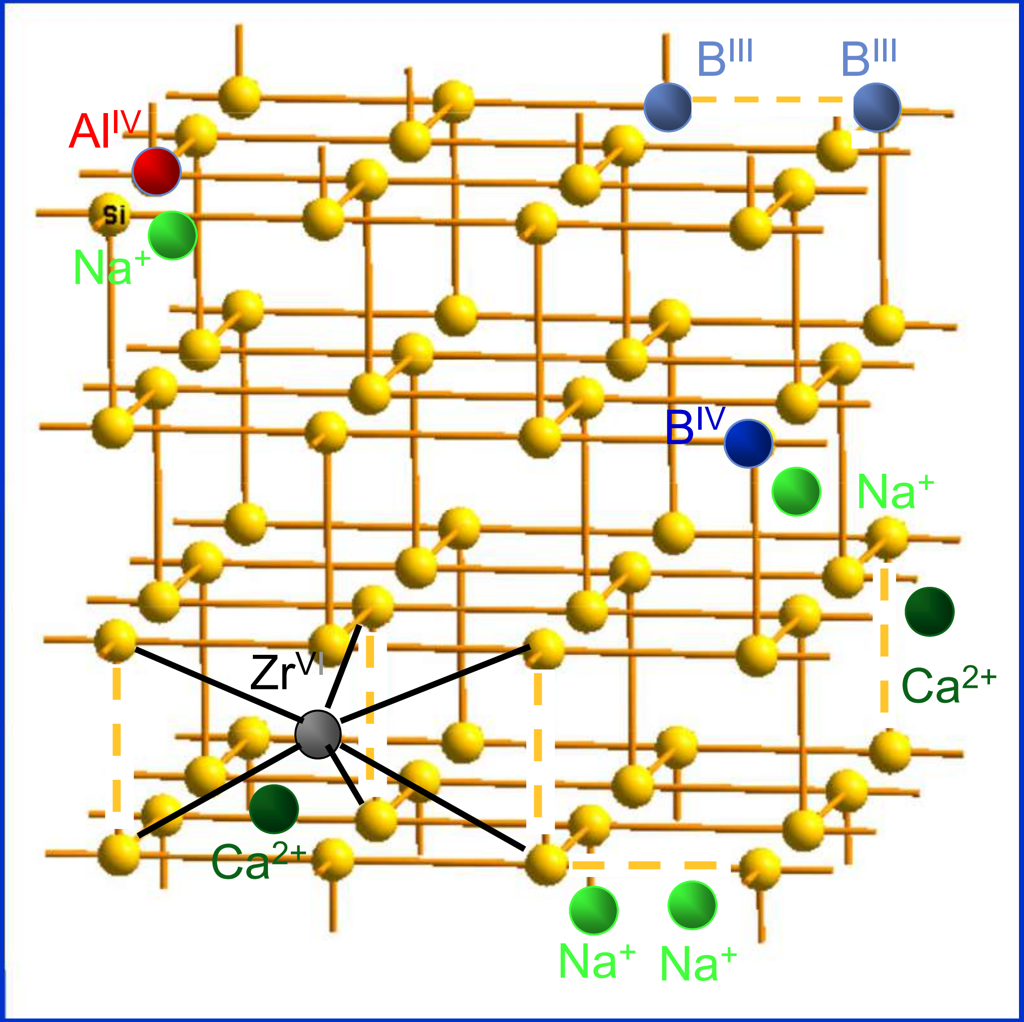




β-cristobalit structure

Mapped on a cube

Simulation of samples of 10^8 sites in a few hours to a few days
The local environment of cations is preserved



M. Arab *et al.* J. Non-Cryst. Solids **354**, 155-161 (2008)

Reactivity model

✓ All the reactions take place at the solid-water interface

✓ Soluble cations (boron, alkali, earth-alkali, Al in acidic medium) are dissolved immediately and never condense again

✓ Si dissolution probability depends on Si neighboring :

w_1, w_2, w_3 for 1, 2, 3 bonds Si-O-X

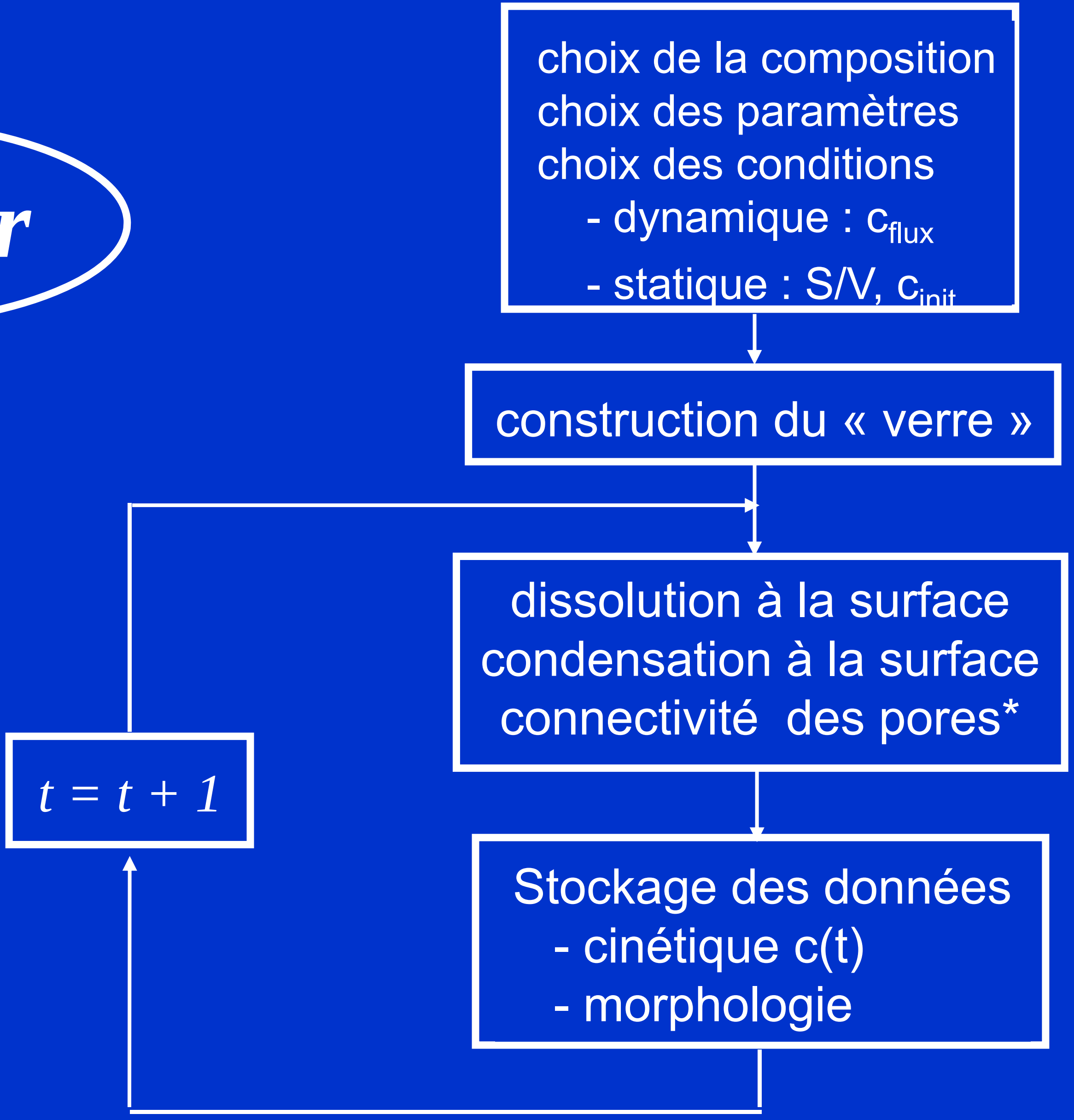
$P_{\mathrm{diss}} = f * w_n$ with $f = 1$ (Si), $f > 1$ (B, Ca) ou $f < 1$ (Zr)

✓ Si condensation probability is proportional to the concentration

in solution : $P_{\mathrm{cond}} = w_{\mathrm{c}}$ 🗄 c_{Si}

✓ Insoluble cations (Zr, RN) are only dissolved as colloidal particles

Simuliver



choix de la composition
choix des paramètres
choix des conditions
- dynamique : c_{flux}
- statique : S/V, c_{init}

construction du « verre »

dissolution à la surface
condensation à la surface
connectivité des pores*

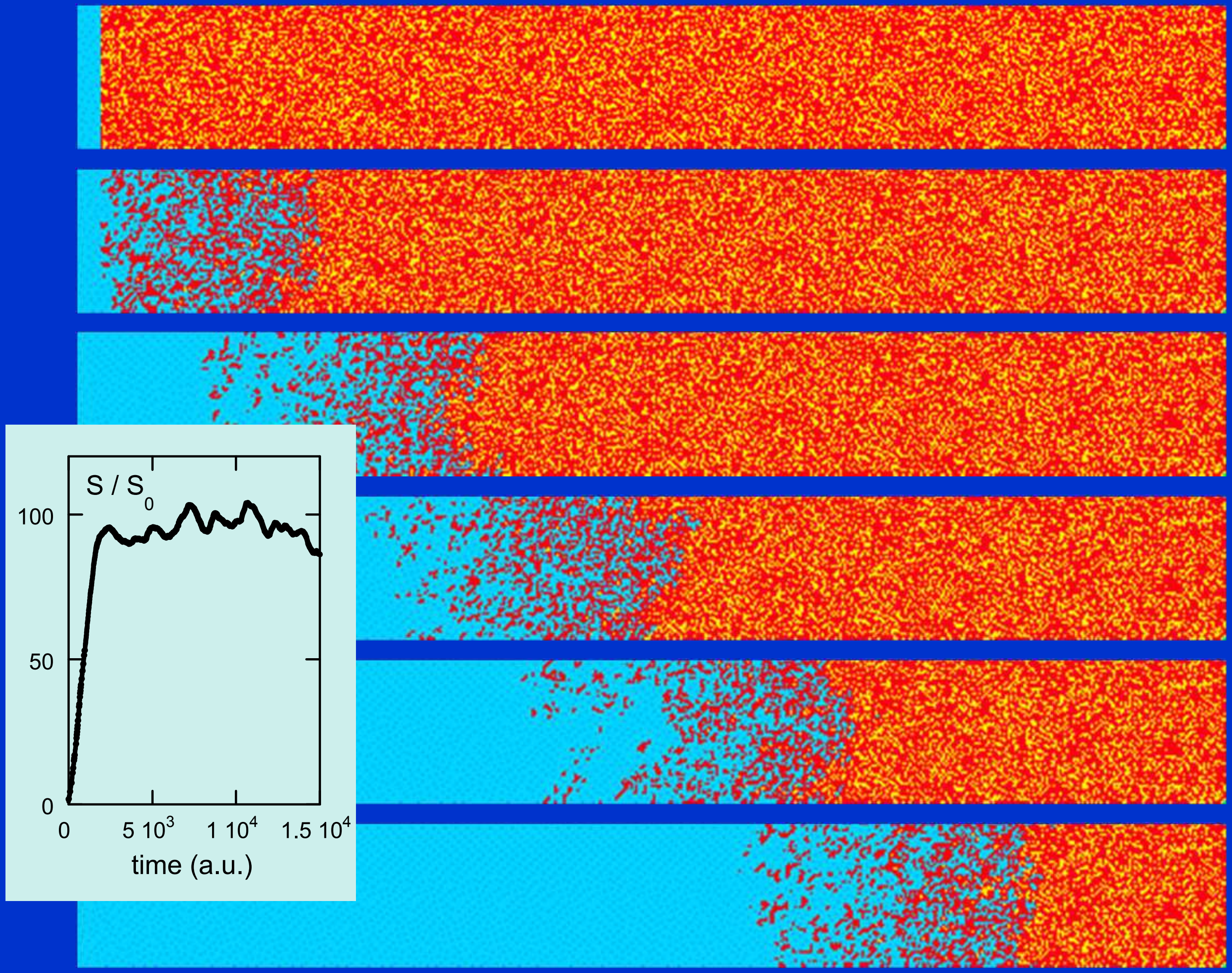
Stockage des données
- cinétique c(t)
- morphologie

t = *t* + *1*

* Algorithme de Hoschen-Kopelman

Initial dissolution regime (far from saturation)

R = 0.30



Effect of composition on the initial dissolution rate

(t = 5000)

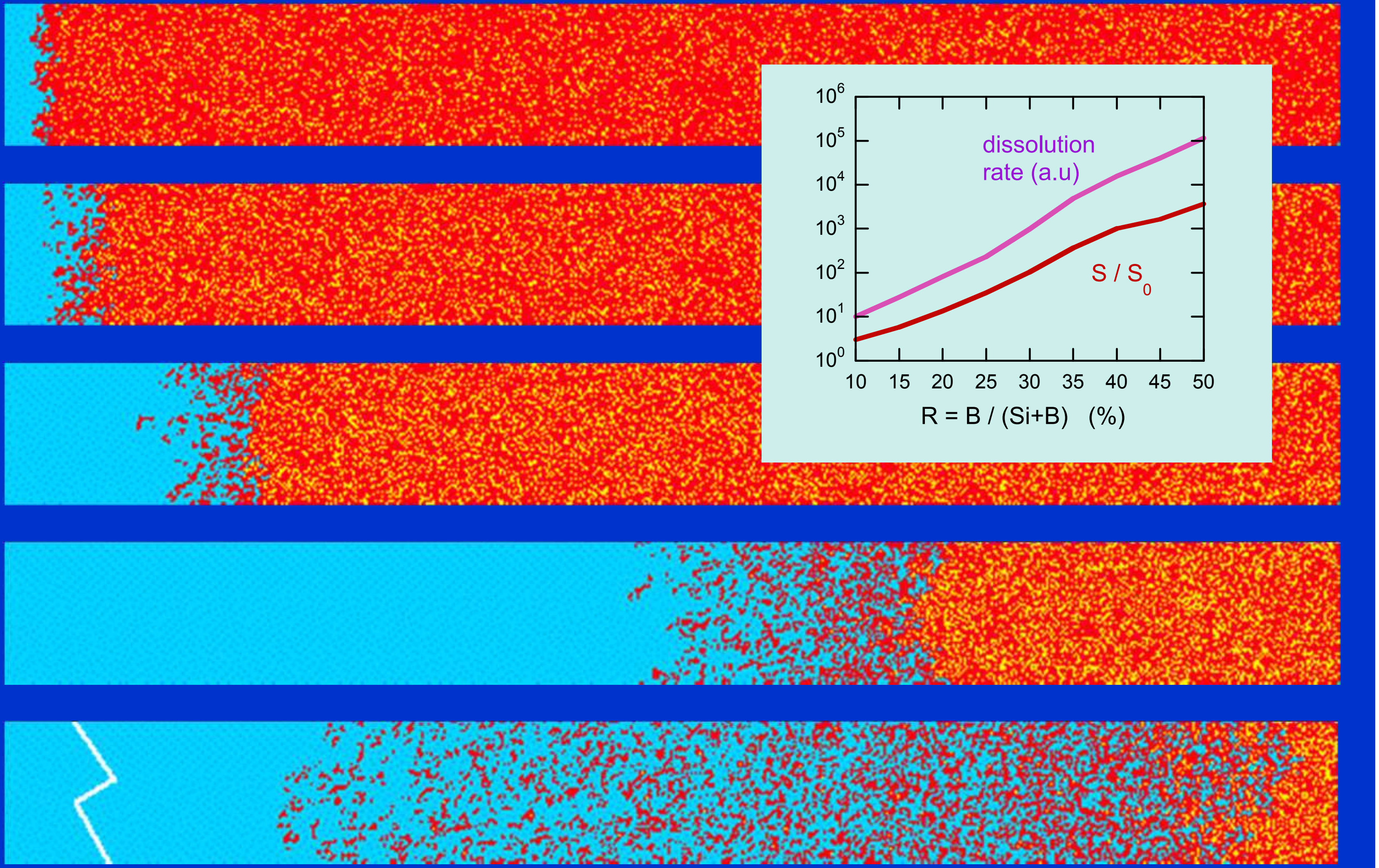
***R* = 0.15**

***R* = 0.20**

***R* = 0.25**

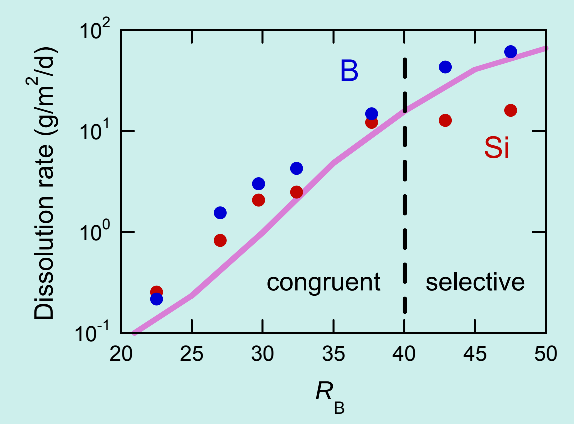
***R* = 0.30**

***R* = 0.35**



Variation of the initial dissolution rate with glass composition

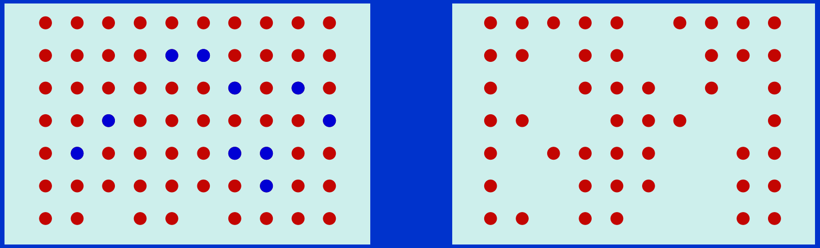
(100-2x) SiO_2 - x B_2O_3 - x Na_2O



Percolation of the boron sublattice

$R_B < p_c$

$R_B > p_c$



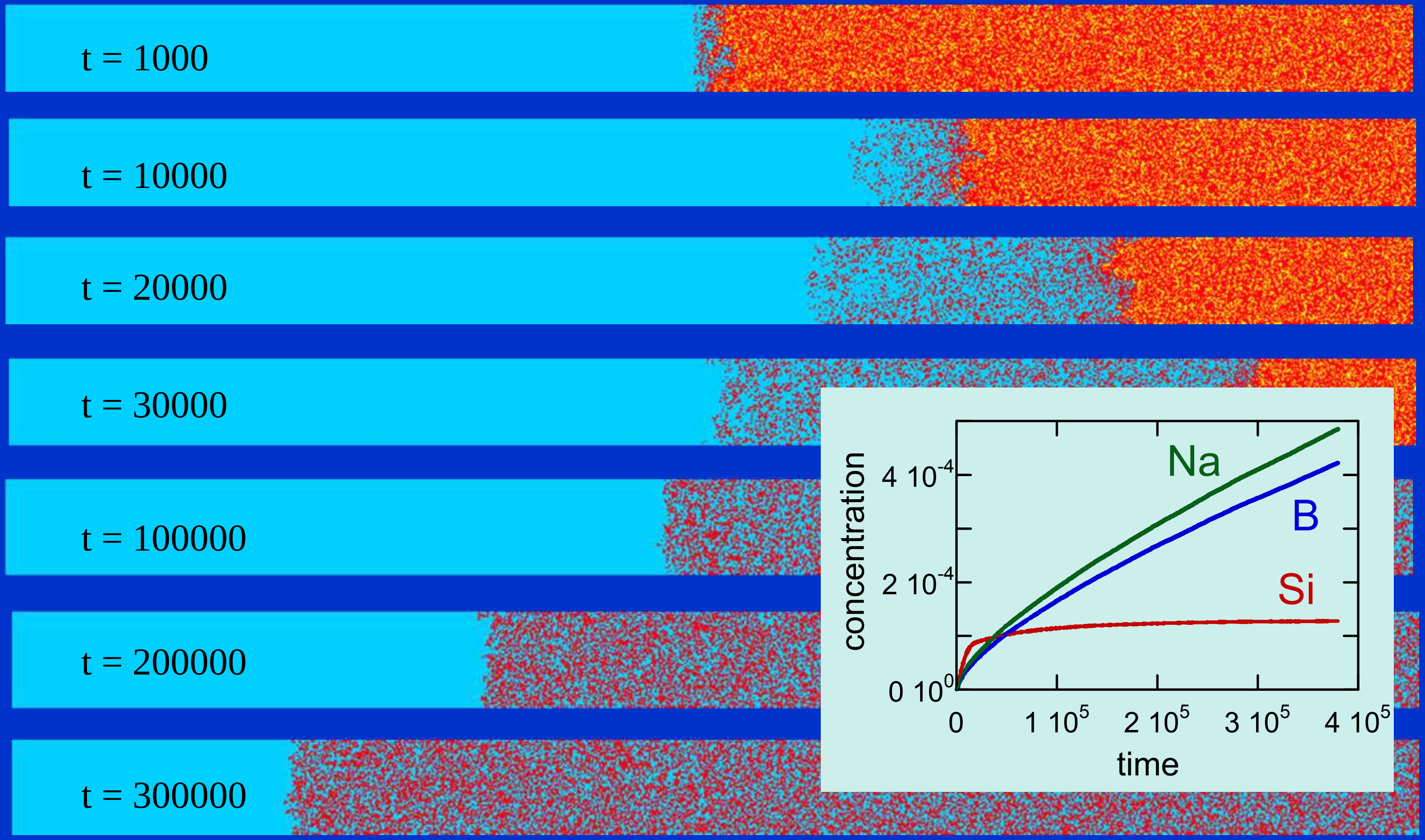
Si limited congruent dissolution

Selective dissolution

percolation threshold on diamond lattice

- site: $p_c = 0.42$
- bond: $p_c = 0.39$

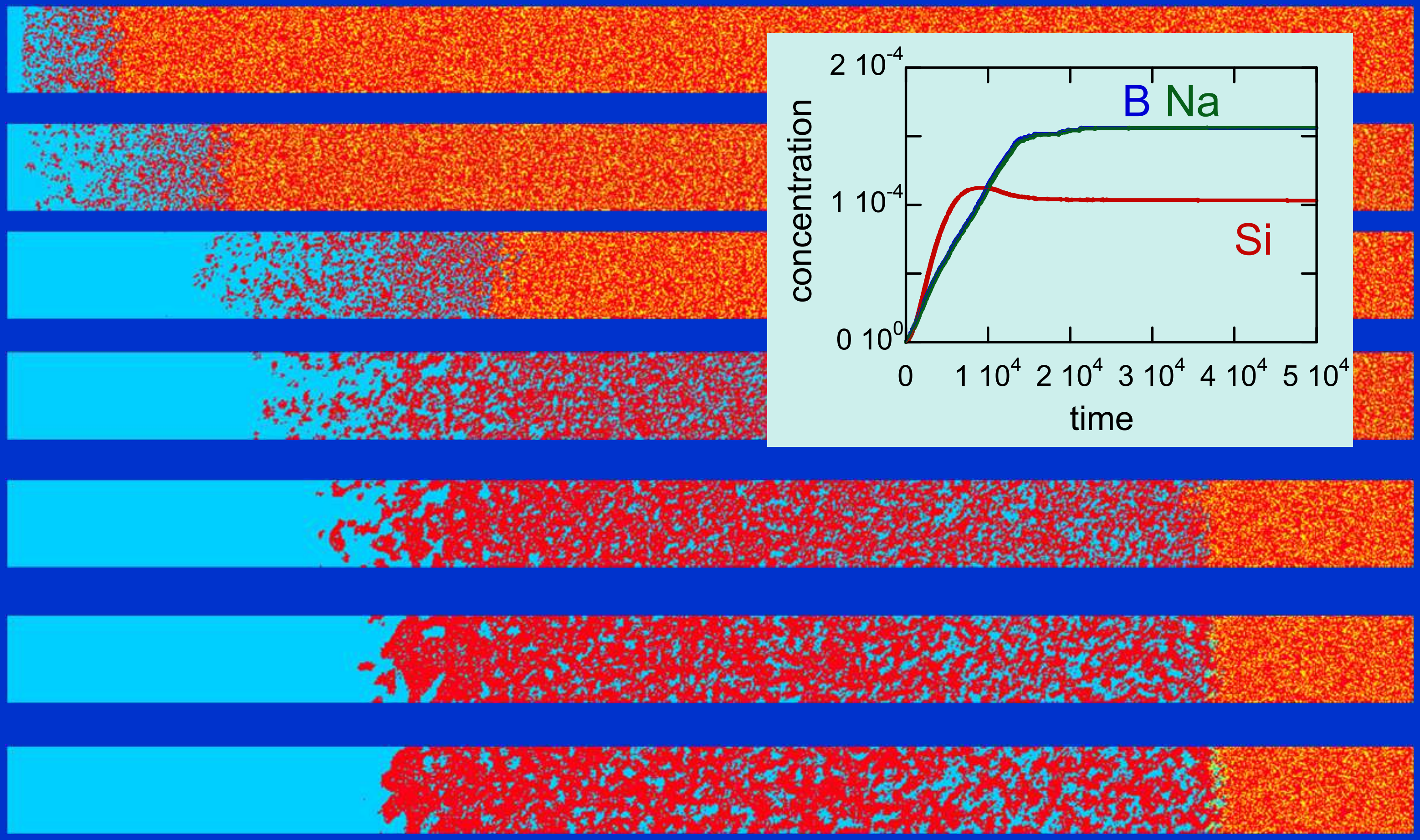
Saturation regime 1) $w_1 = w_2 = w_3$



formation of a swelling foam

F. Devreux *et al.* J. Mater. Sci. **36**, 1331-1341 (2001)

Saturation regime 2) $w_1 > w_2 > w_3$

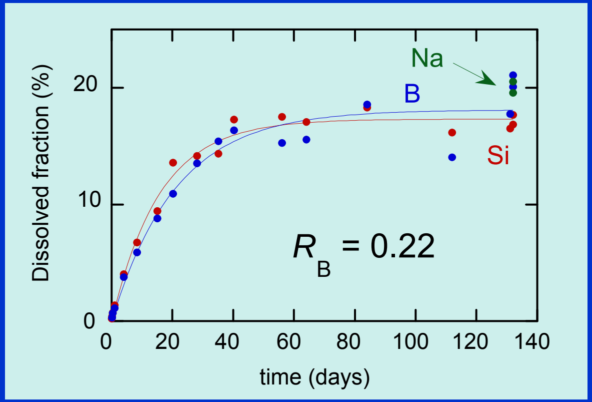


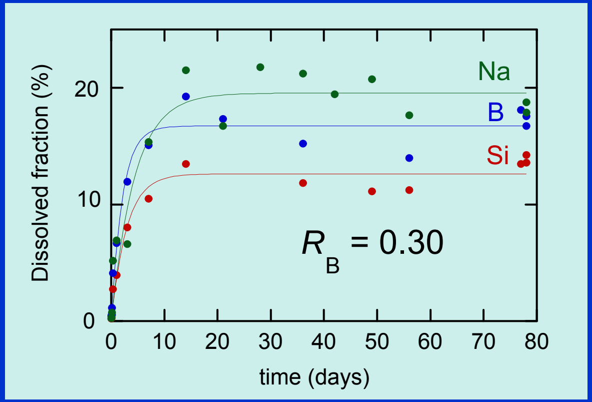
formation of a passivating layer

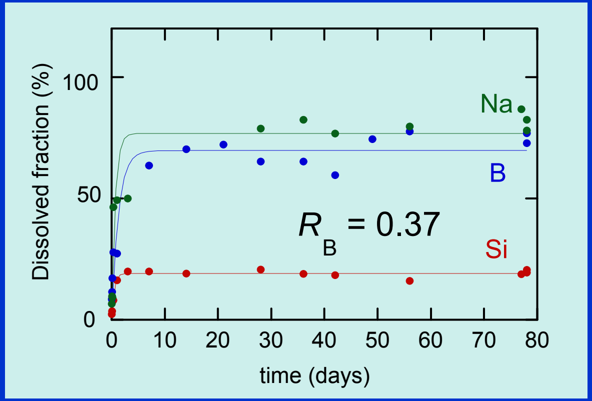
F. Devreux *et al.* J. Mater. Sci. **36**, 1331-1341 (2001)

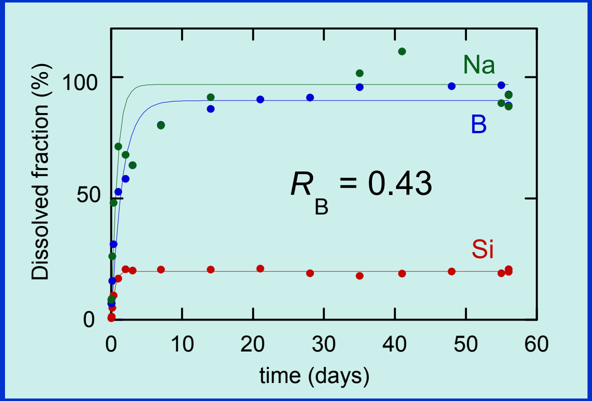
Long term corrosion kinetics

$(100\text{-}2x)\ SiO_2 - x\ B_2O_3 - x\ Na_2O$ T = 90°C pH 8.5 100 μm SA/V=1 cm^{-1}



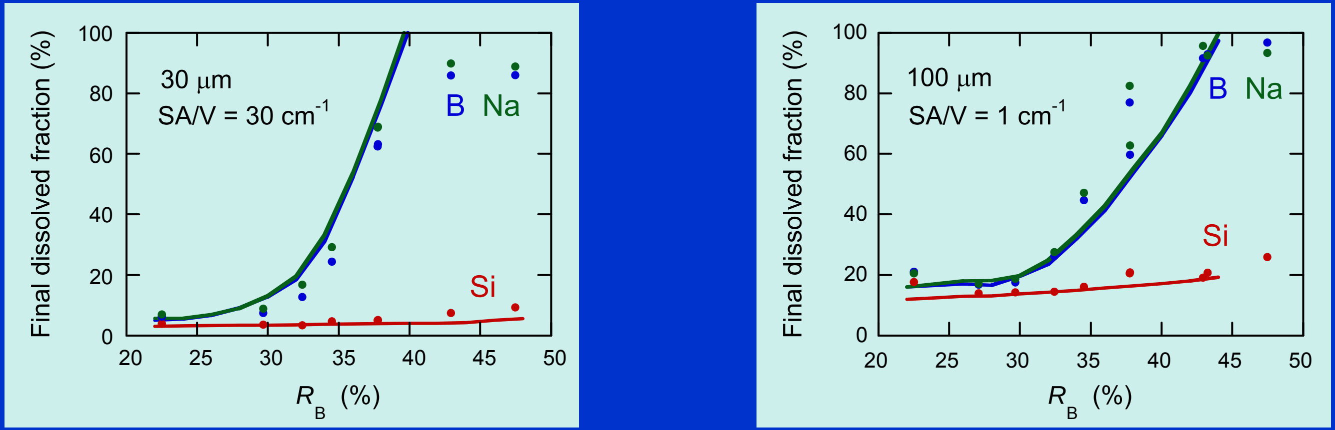






A. Ledieu *et al.* J. Non-Cryst. Solids **343**, 3-12 (2004)

Variation of the final degree of corrosion with glass composition



Si: chemical equilibrium (c ≈ c* ≈ 150 mg/L)

B and Na: controlled by the formation of the passivating barrier

The degree of corrosion results from a competition between:

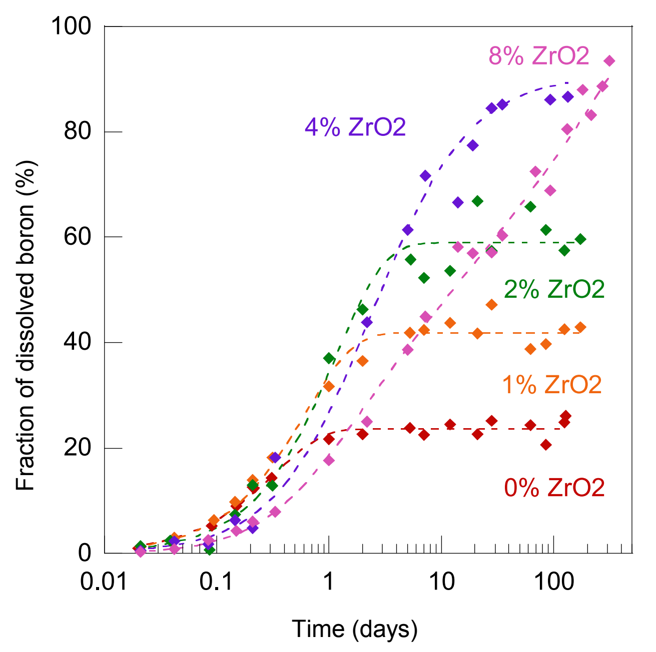
- the formation of the porous structure, whose thickness increases with *R*
- the restructuring due to Si dissolution-condensation kinetics

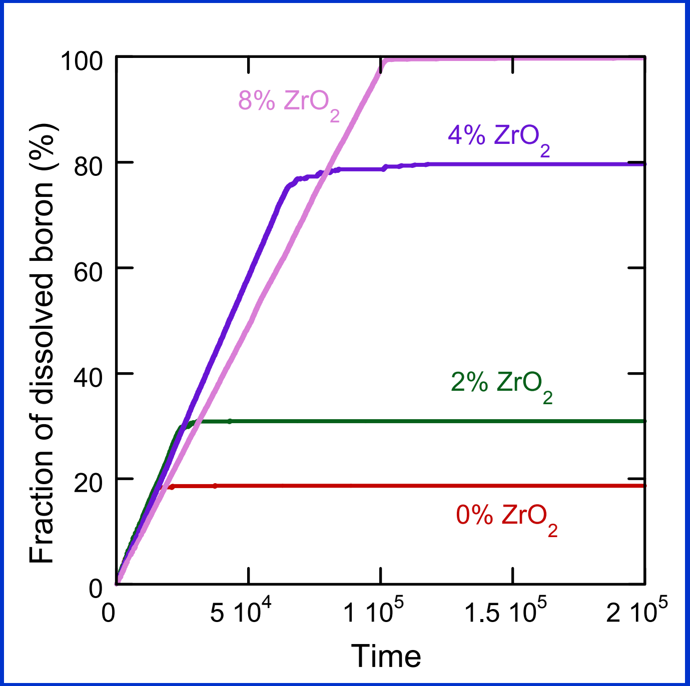
F. Devreux *et al.* J. Non-Cryst. Solids **343**, 13-25 (2004)

Influence of insoluble oxides: replacing SiO_2 by ZrO_2

(61-x) SiO_2 - x ZrO_2 - 17 B_2O_3 - 18 Na_2O - 4 CaO

90°C, pH 7, 30 μm, SA/V = 15 cm^{-1}

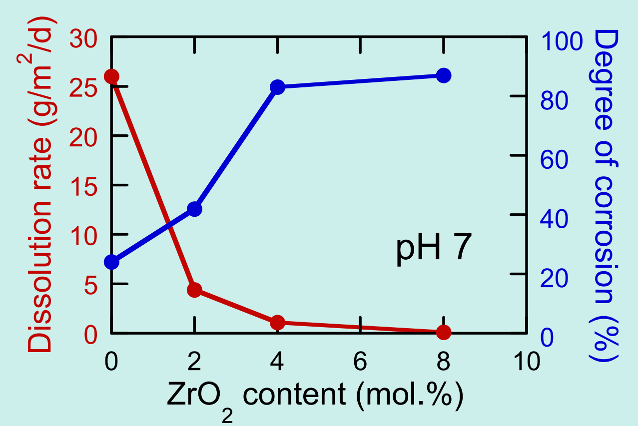


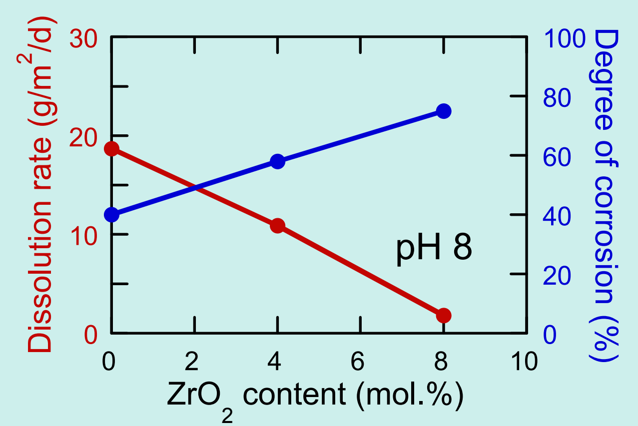


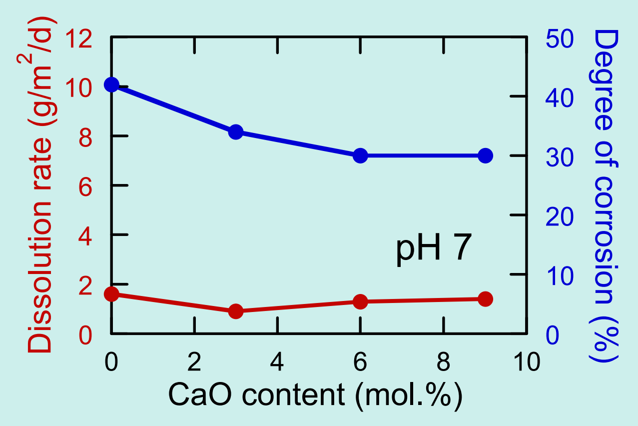
The corrosion is slowed down, but the final degree of corrosion is higher.

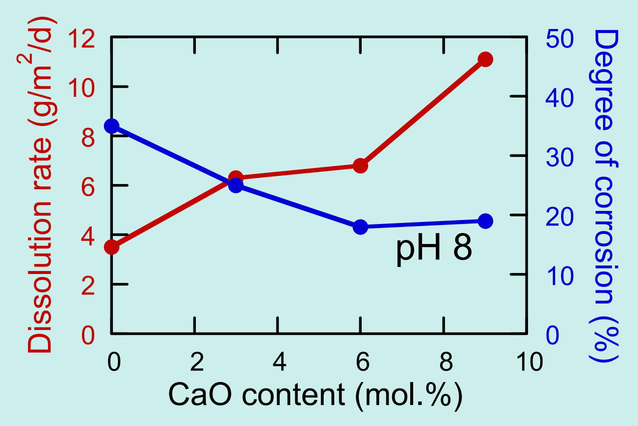
C. Cailleteau, PhD Thesis, Ecole Polytechnique (2008)

Initial dissolution rate versus final degree of corrosion







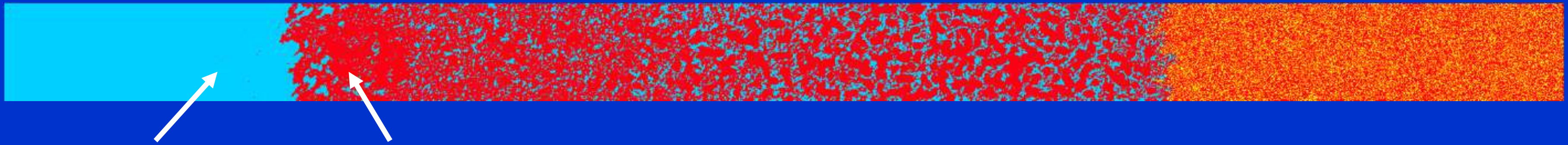


Why do the glasses with a low dissolution rate undergo a high degree of corrosion?

C. Cailleteau *et al.* J. Phys. Chem. C **115**, 5846-5855 (2011)

The Monte-Carlo answer: gel restructuring !

- Without insoluble oxides: the restructuring induces a corrosion blocking

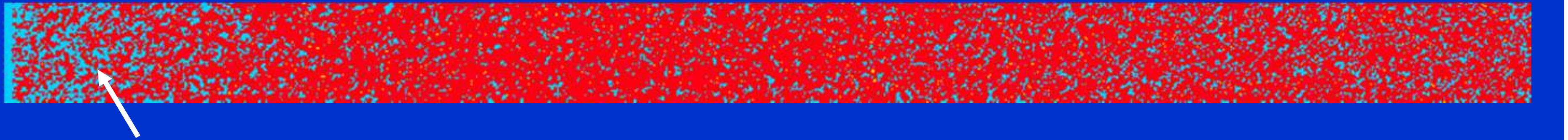


shrinkage

densification and porosity closure

✓ The pore network gets non-percolating and the corrosion stops

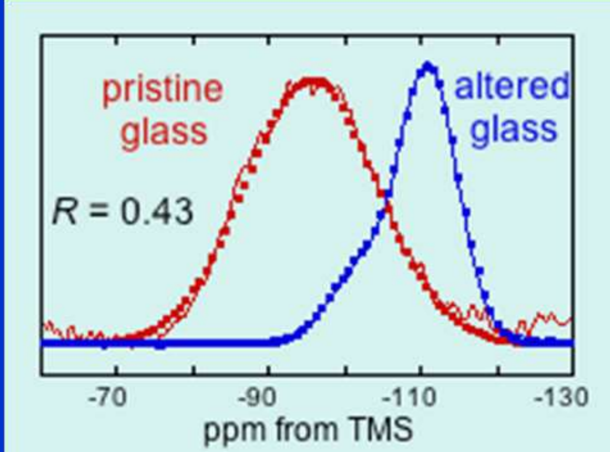
- With insoluble oxides: the restructuring is slowed or inhibited owing to the strengthening of the glass network.

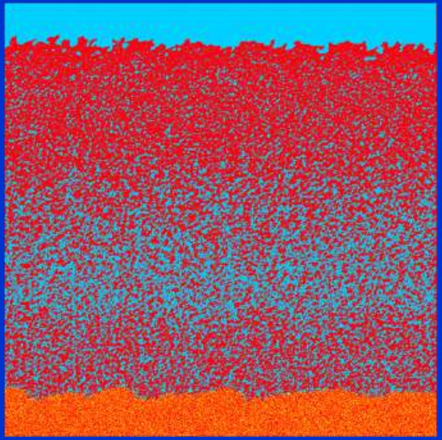


no shrinkage, no densification

✓ The pore network remains percolating and the corrosion goes on

The gel restructuring at the atomic scale (^{29}Si NMR)





Pristine glass:

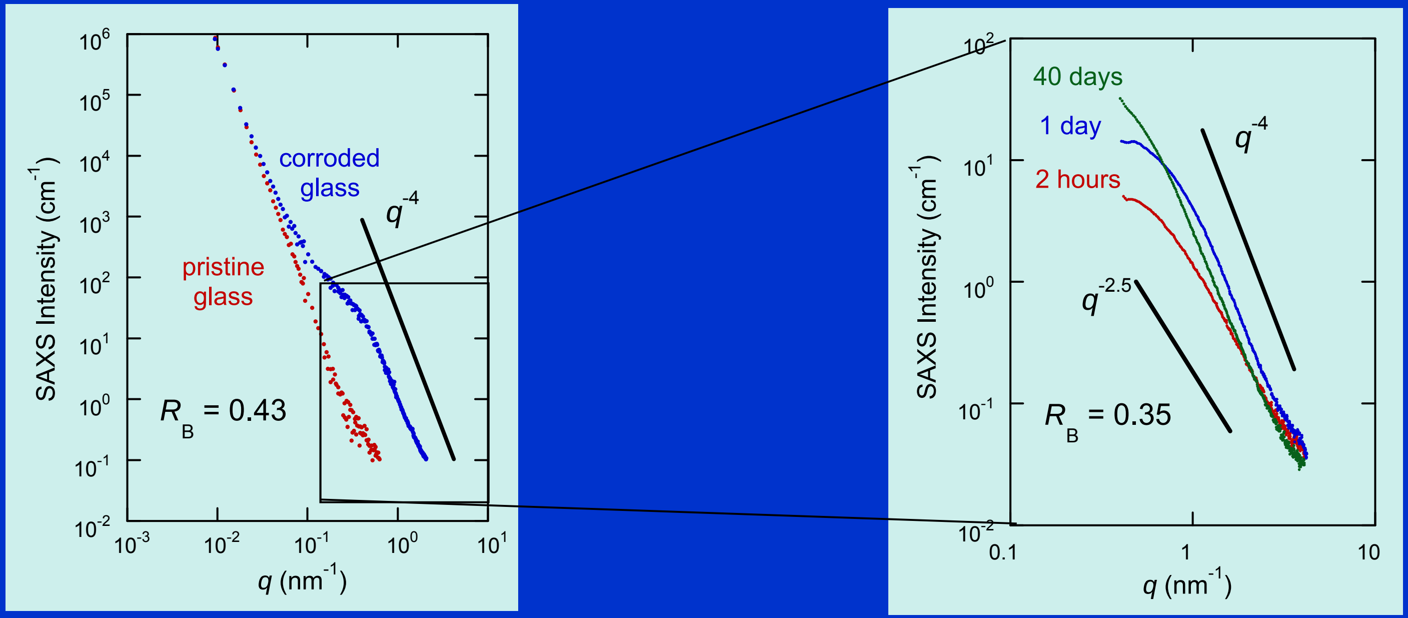
broad line, $T_1 \approx 5000$s

100% corroded glass:

	Q^1	Q^2	Q^3	Q^4
ppm	- 80	- 90	- 100	- 110
Exp	-	-	20 %	80 %
T_1	-	-	30 s	70 s

MC	2 %	7 %	20 %	71 %

The gel restructuring at the mesoscopic scale (SAXS)



Porod law : $I(q) \sim \Sigma q^{-4}$

$I(q) \sim q^{-h}$

Pristine glass: $\Sigma = 0.43$ m^2/g

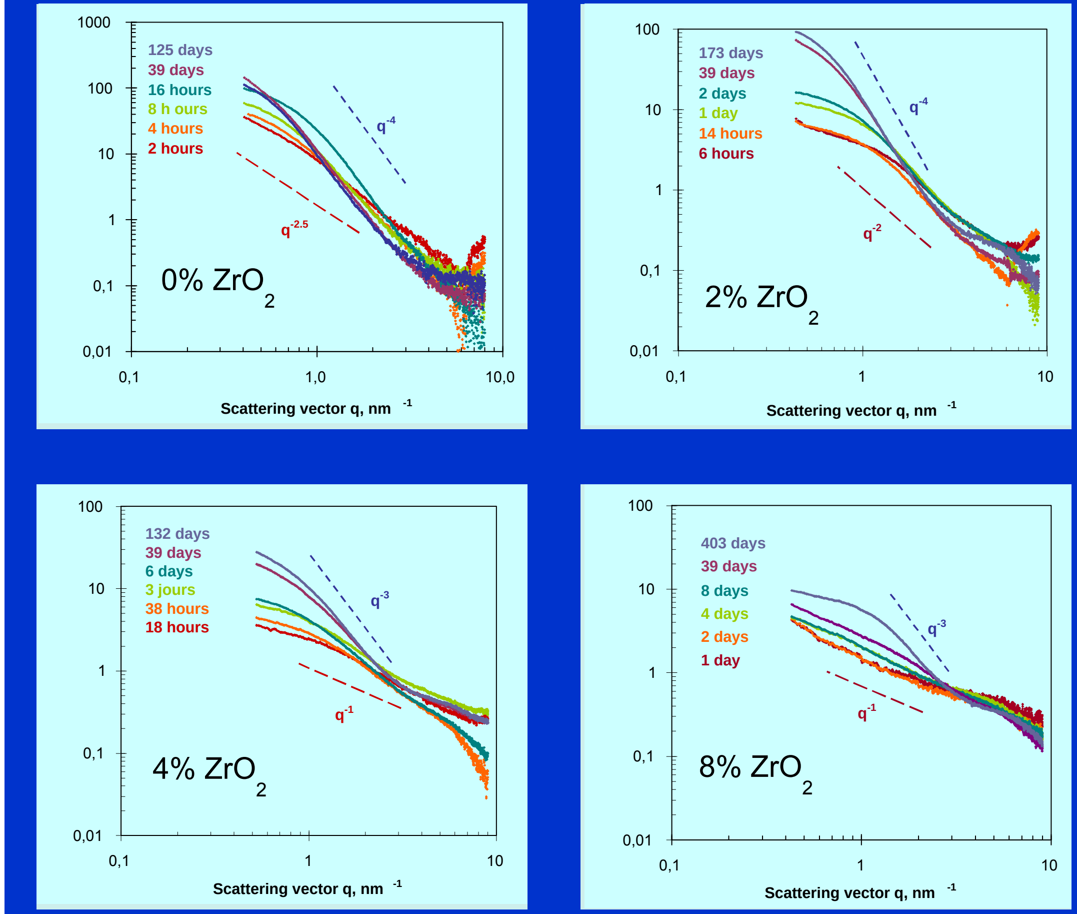
Corroded glass: $\Sigma = 108$ m^2/g

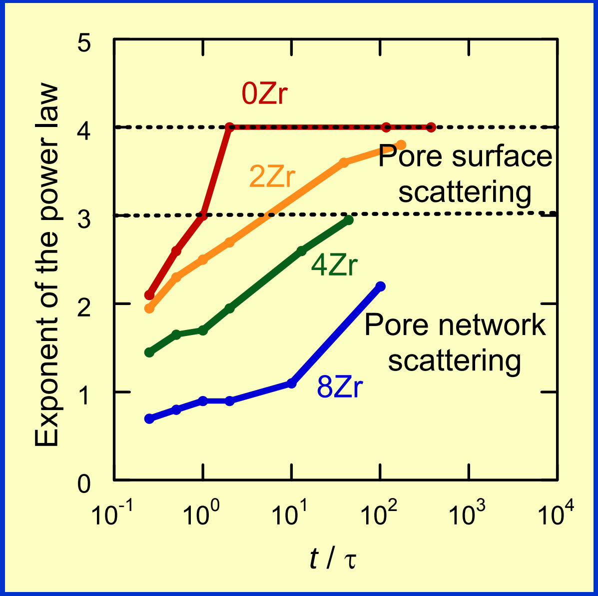
$h < 3$ network scattering $h = D_F$

$3 < h \leq 4$ surface scattering $h = 6 - D_S$

Glass restructuring as studied by SAXS

SAXS measurements after $\tau_K/4$, $\tau_K/2$, τ_K, $2\tau_K$, 40 days and long term corrosion





Without Zr: fast restructuring

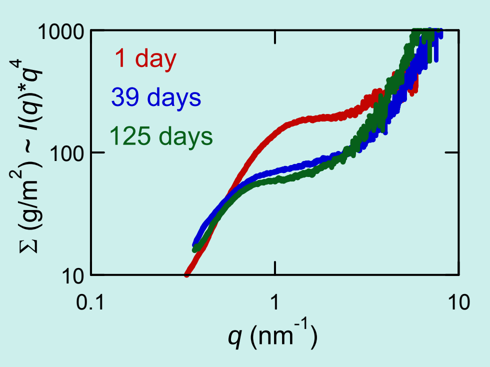
With Zr: slow restructuring

C. Cailleteau *et al.* J. Phys. Chem. C **115**, 5846-5855 (2011)

Evolution of the surface area of the porous network in 0Zr

SAXS

$$\Sigma = \frac{I(q)\, q^4}{2\pi\, d\, b^2\, \Delta\rho^2}$$



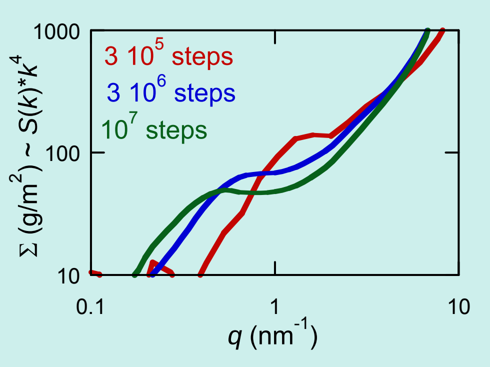
time	Σ (m^2/g)	size (nm)
1 day	202	2.5
39 days	84	3.6
125 days	69	4.2

BET
2.2 m^2/g

MC simulations

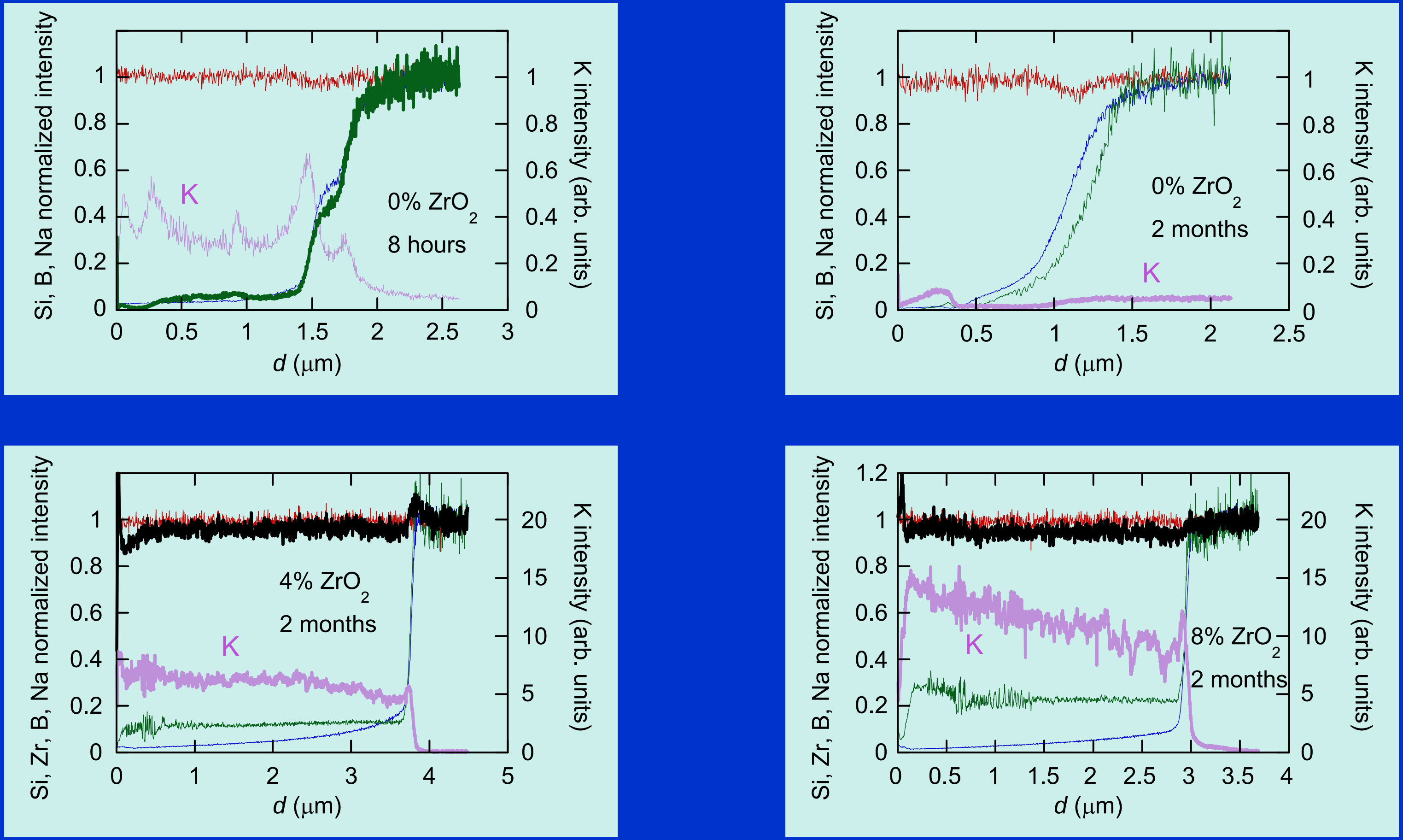
$$\Sigma = \frac{S(k)\, k^4}{2\pi\, d\, a}$$

($k = q\,a$ $a = 0.32$ nm)



time	Σ (m^2/g)
3 10^5	140
3 10^6	71
10^7	49

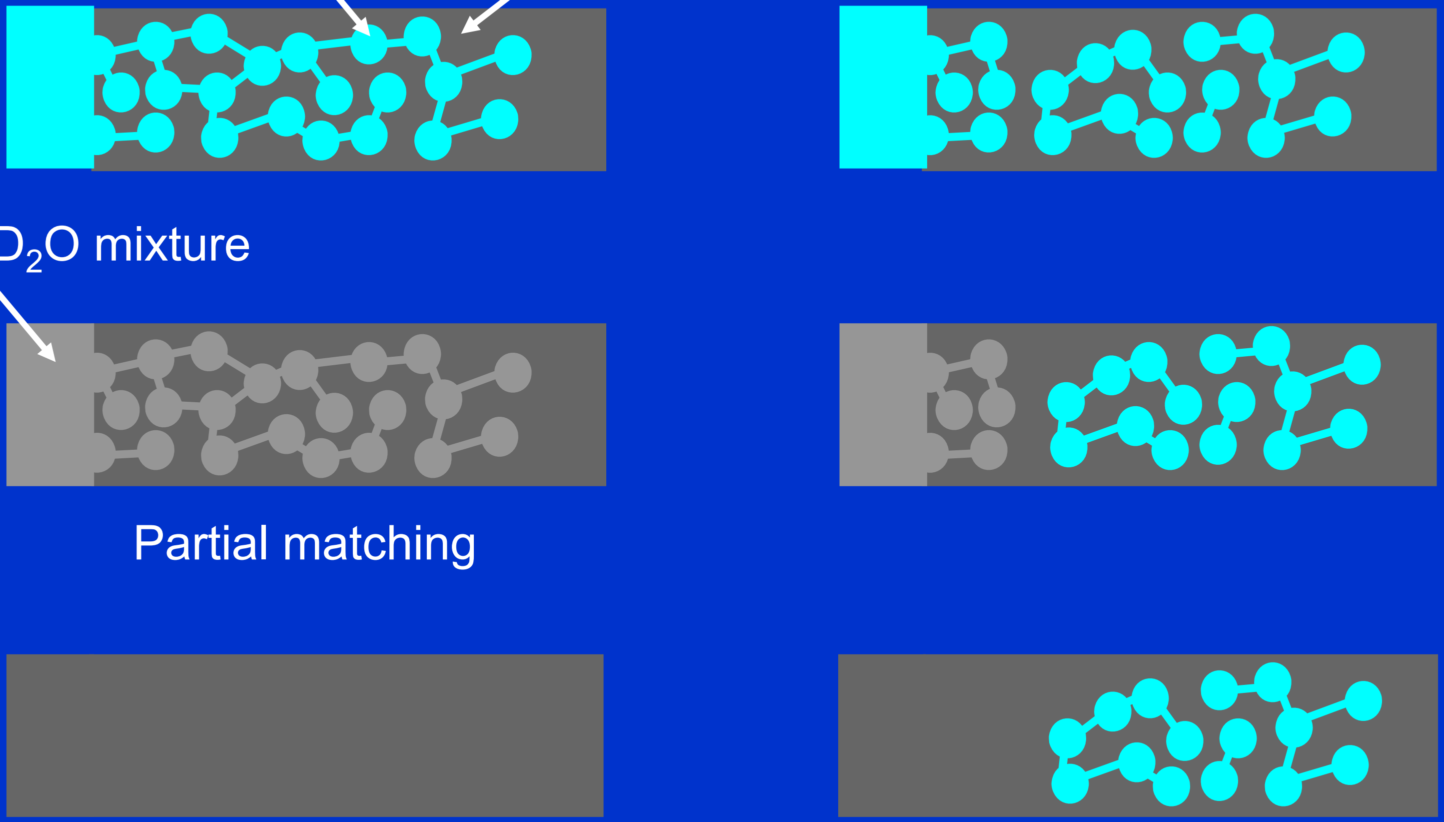
The porosity closure tested by ToF-SIMS after solvent exchange with a K^+ labeled solution



The porosity closes at long time in the glass without ZrO_2, not in the others

C. Cailleteau *et al*. J. Phys. Chem C **115**, 5846-5855 (2011)

The porosity closure tested by small angle neutron scattering with index matching



H_2O

Glass

Close porosity

H_2O-D_2O mixture

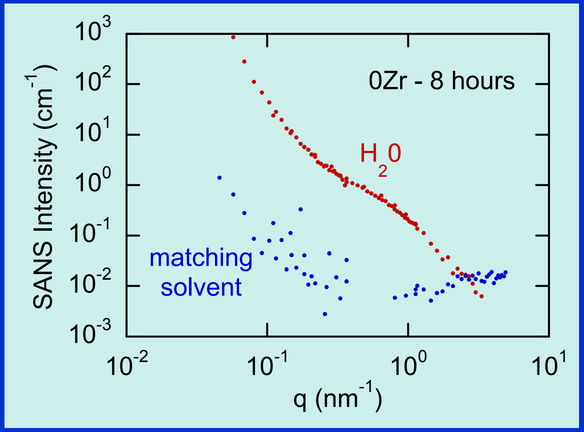
Partial matching

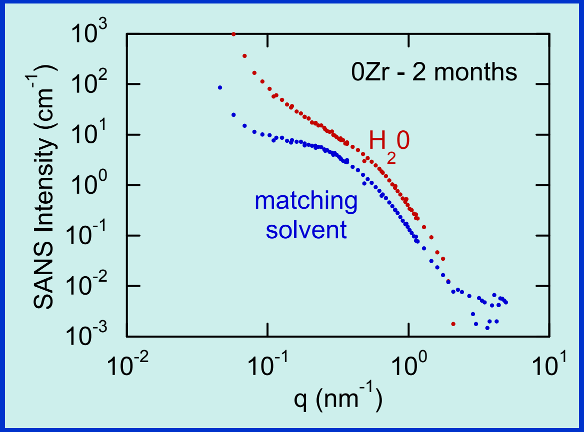
Perfect matching (~ 65 % D_2O)

Signal extinction

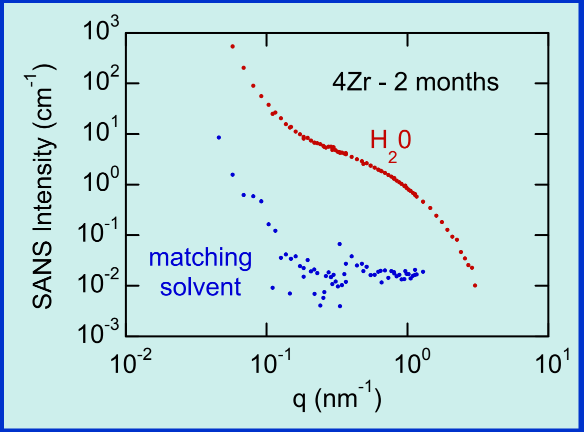
No extinction

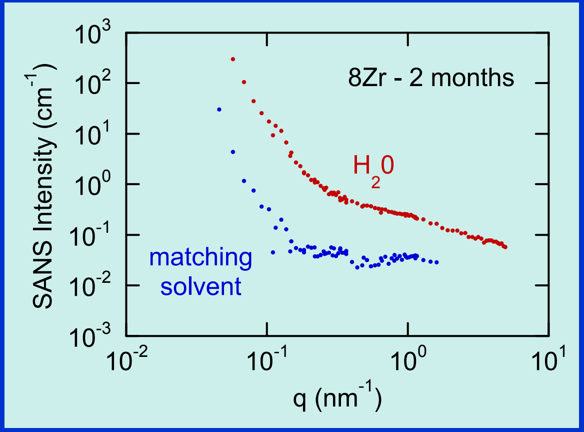
Small angle neutron scattering with index matching





The porosity closes at long time in glass 0Zr





It remains open in glasses 4Zr and 8 Zr

C. Cailleteau *et al*. Nature Mater. **7**, 978-983 (2008)

Principales conclusions

1. L'augmentation de la vitesse de dissolution avec la proportion de cations solubles (B, Al) est due à l'augmentation de la surface active en relation avec des effets de percolation

2. Dans certaines conditions, il se forme une couche passivante qui conduit à un (quasi) blocage de la corrosion. Cette passivation est due à la restructuration de la couche poreuse altérée, qui entraîne retrait, densification et fermeture de la porosité.

3. La présence d'oxydes insolubles ralentit l'altération, mais elle ralentit aussi la restructuration, ce qui conduit à une augmentation du degré de corrosion.

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PhD 2004

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Implicit hypotheses

✓ Si first order kinetics :

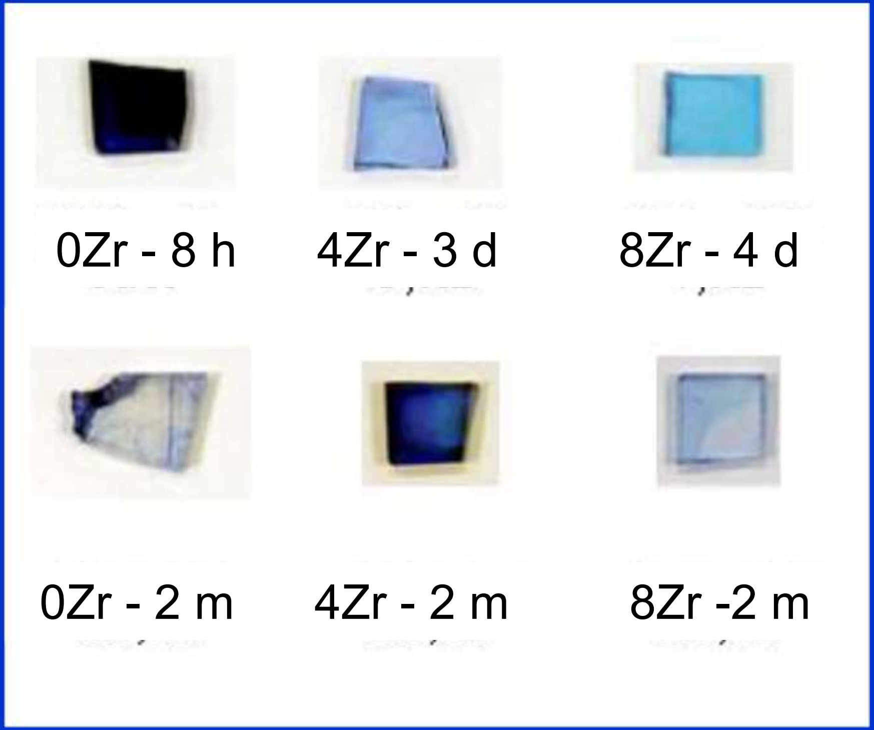
$$\frac{dN_{Si}}{dt} = \sum\nolimits_{i \in S} \left\{ P_{diss}(i) - w_c \times c_{Si} \right\} \;\rightarrow\; c^*_{Si} = \frac{\langle P_{diss}(i) \rangle_{i \in S}}{w_c}$$

✓ Diffusion in solution is very fast

✓ Solid-state diffusion is neglected

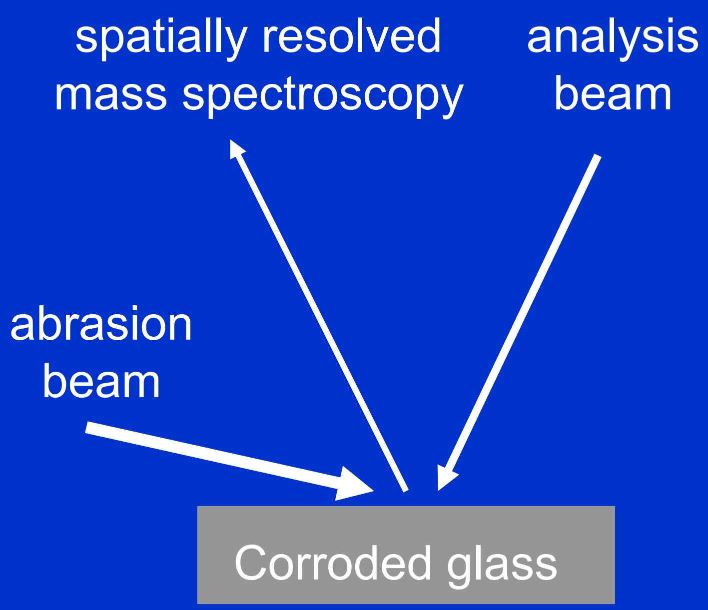
Porosity closure tested by solvent exchange

methylene blue permeation



ToF-SIMS

K$^+$ labeled solution



spatially resolved mass spectroscopy

analysis beam

abrasion beam

Corroded glass

C. Cailleteau, PhD thesis, Ecole Polytechnique (2008)

Main conclusions

1. The increase of the dissolution rate with the proportion of soluble network forming cations is mainly due to the increase of the glass-water interface area in relation with percolation properties.

2. In certain conditions, a passivating layer is formed, which causes a corrosion blocking after saturation of the solution with respect of silica.

3. The passivation is due to the restructuring of the porous surface layer which leads to sample shrinkage, densification of the layer and closure of the porosity.

4. The presence of insoluble oxides slows down the kinetics, but increases the degree of corrosion by inhibiting the porous layer restructuring.

5. The glasses with a high dissolution rate undergo fast restructuring and corrode slightly; the glasses with a low dissolution rate undergo slow restructuring and corrode deeply.