Alteration of Nuclear Glasses

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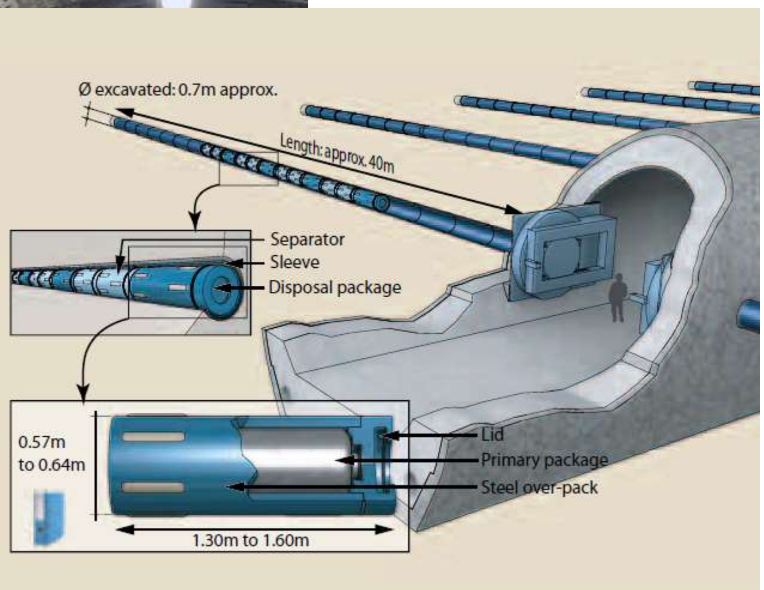
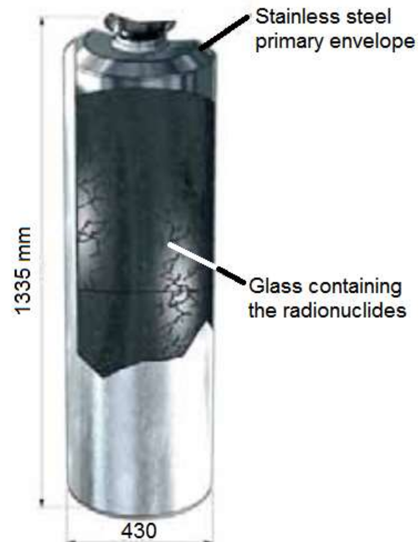
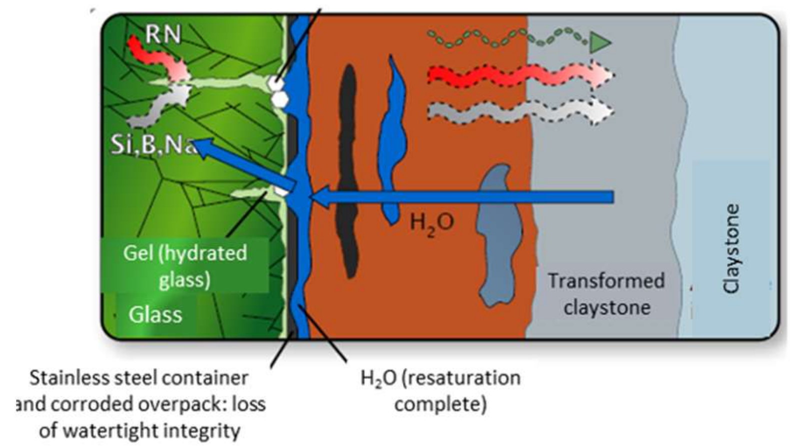
A complex material in a complex environment





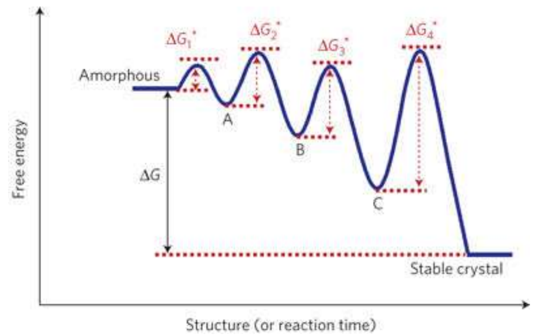


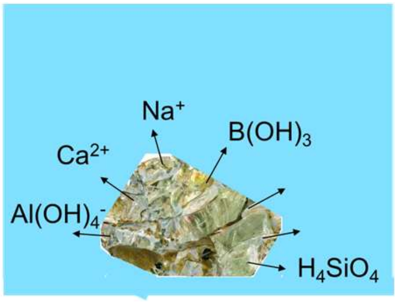
RN release from the glass over 10^5-10^6 years?

Why glass corrodes in water?

- **Why: For thermodynamic and chemical reasons**
  - $\mu_{i,glass} \neq \mu_{i,solution} \rightarrow \Delta G_{reaction} < 0$ + glass and water react
  - K_{eq} (glass) >> K_{eq} (crystal) due to structural disorder
  - Secondary phases with low solubility AND fast precipitation kinetics control the solution chemistry
- **How?** Glass + $H_2O \rightarrow$ Aq. Species + Hydrated materials

  $\hookrightarrow$ Gels $\rightarrow$ Crystalline Phases

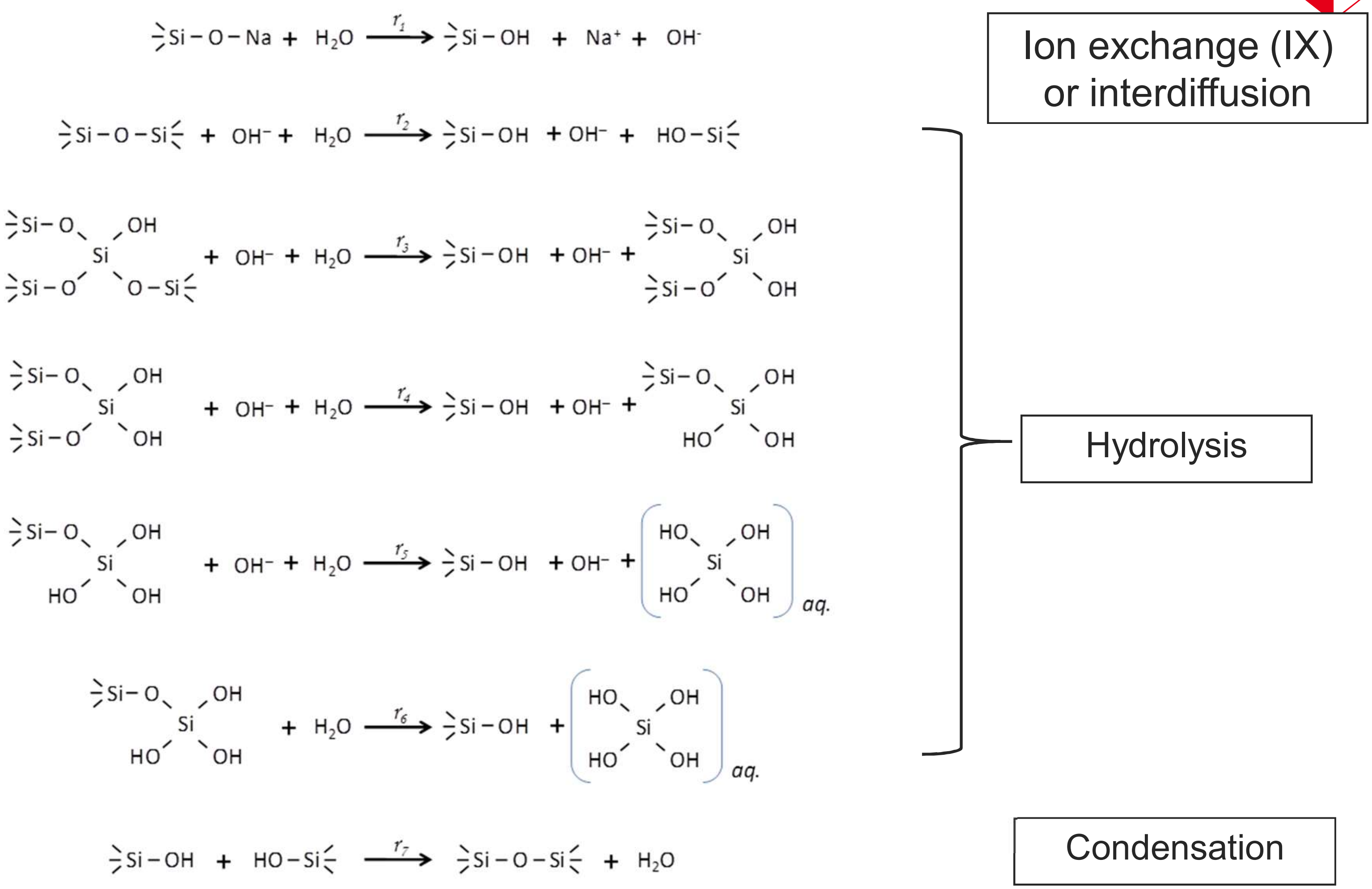




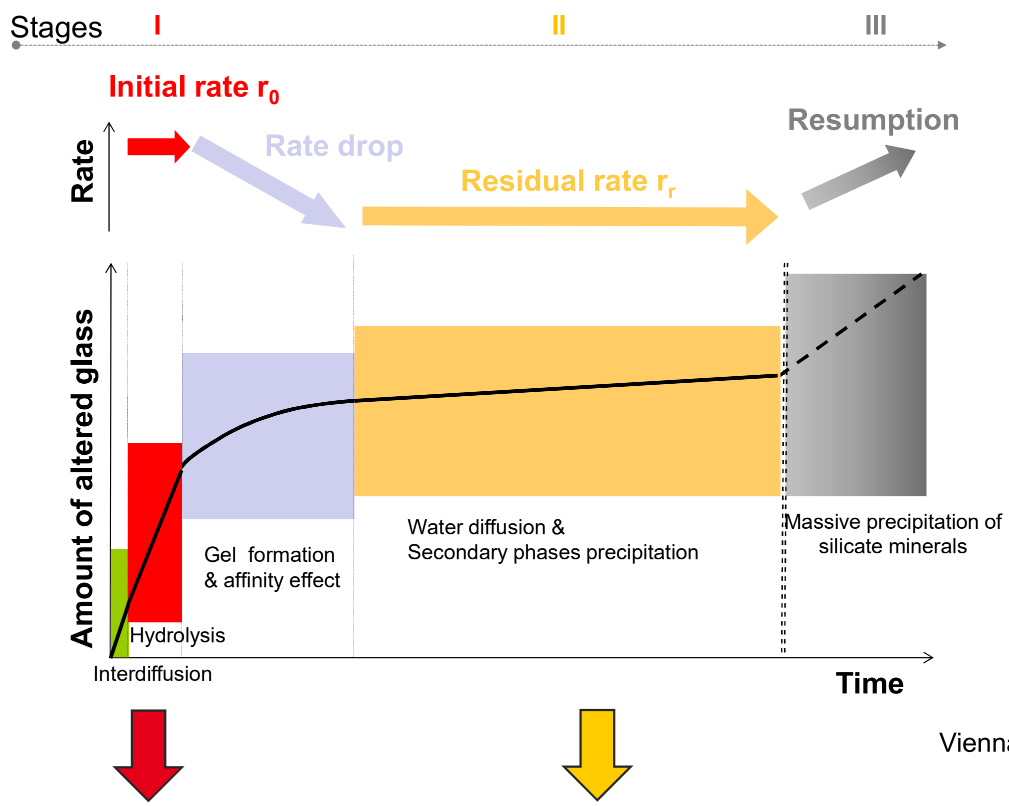
- **4 main mechanisms: Ion-exchange, hydrolysis, condensation, precipitation**

Grambow, *J. Nucl. Mater.* 2001
Frugier, *J. Nucl. Mater.* 2008
Vienna et al. *Inter. J. Applied. Glass Sci.* (2013)
Gin, *npj-Mater. Degrad.* 2021

How glass corrodes?



Glass dissolution kinetics

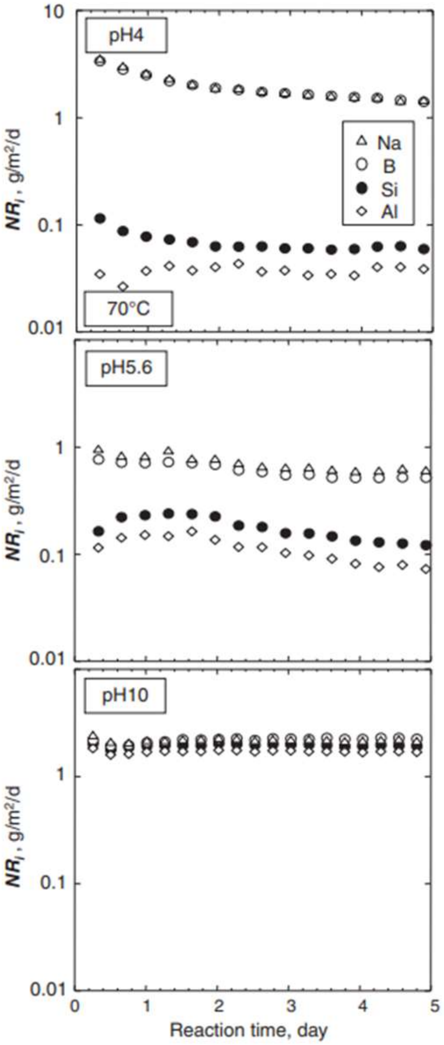


Vienna et al., *Int. J. Appl. Glass Sci.* 4 (2013)

Rate ~µm/d
Canister lifetime ~$10^{2\text{-}3}$ yr

Rate ~nm/yr
Canister lifetime ~$10^{5\text{-}6}$ yr

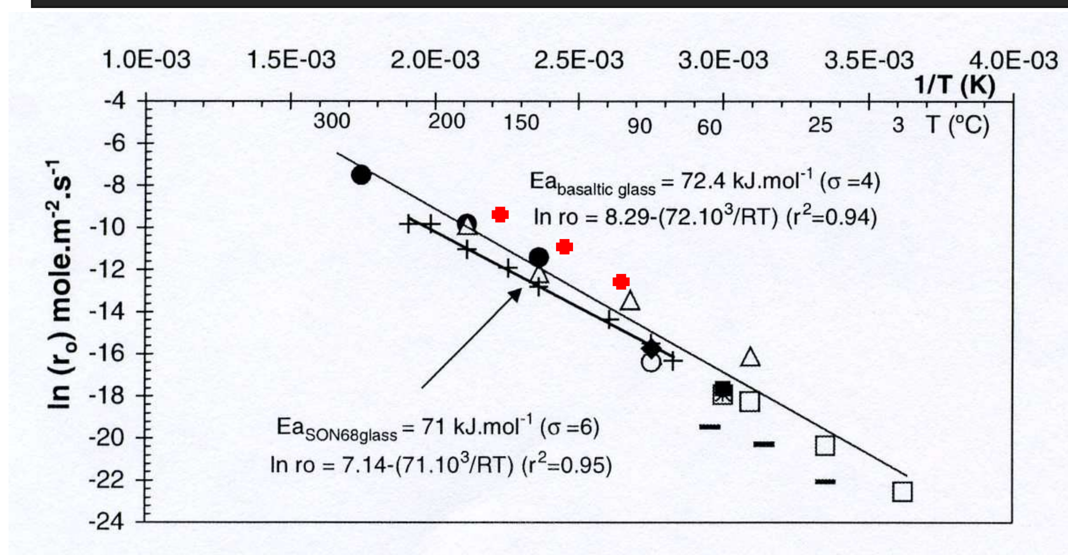
Initial dissolution rate



ISG
70°C @ pH 4, 5.6 or 10

Inagaki et al., *Int. J. Appl. Glass Sci.* (2013)

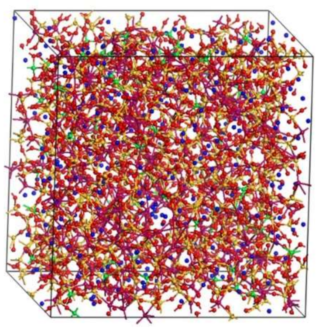
- Easy to measure
- Only dependent on T and pH
- Rate limiting step: hydrolysis of Si-O-M linkages

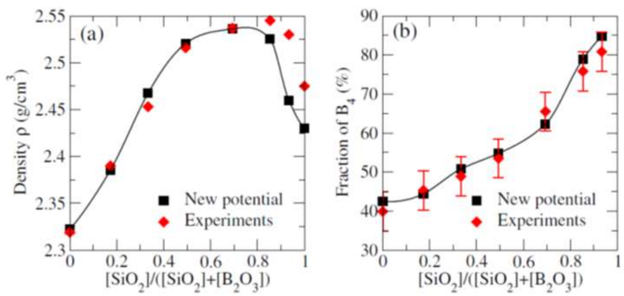


Can we predict the initial dissolution rate?

Quantitative Structure Properties Relationship (QSPR) approaches relying on accurate MD simulations

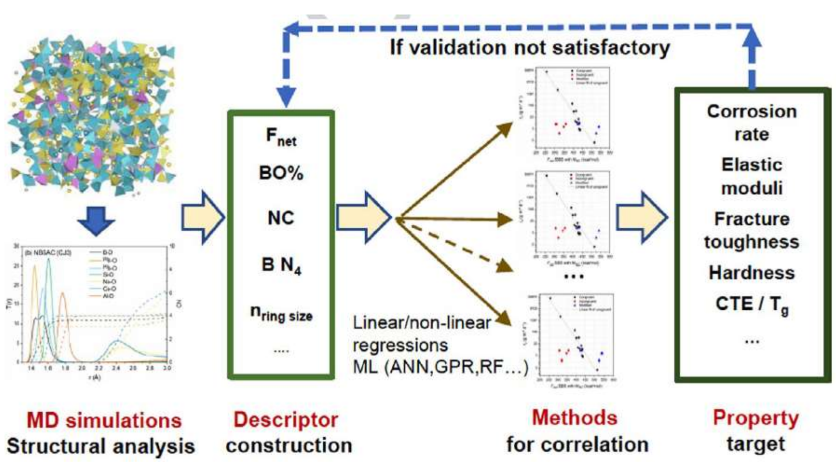
a).





- Ring size distribution
- n_c (nb of constraints/ atom)
- BO%
- Network connectivity
- F_{net} (bond strengh)

$$F_{\mathrm{net}} = \frac{1}{N}\sum_{X}^{\mathrm{cations}} n_X \cdot CN_{\mathrm{XO}} \cdot SBS_{\mathrm{XO}} \cdot m_X$$



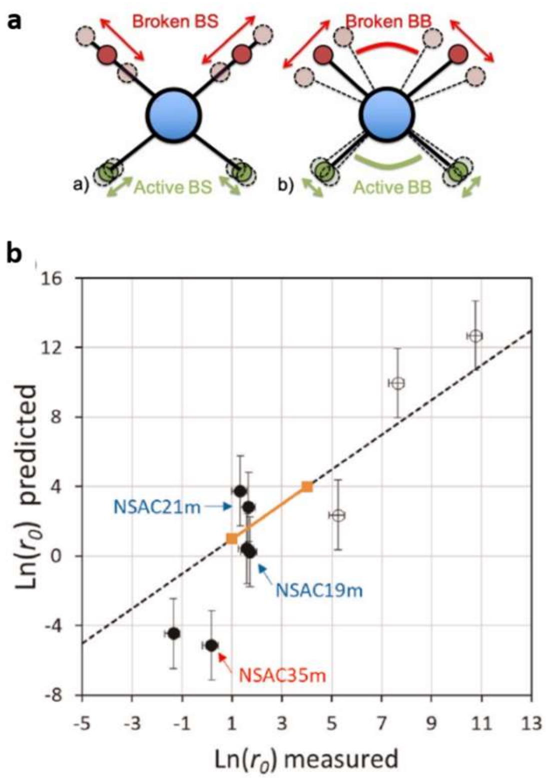
Du et al. *J. Amer. Cer. Soc.* (2021)

Initial dissolution rate

	ISG	SON68	Albite glass	Basaltic Glass	Obsidian	Roman Glass	Soda-lime	Pyrex	Bioglass 45S5	E
Glass composition in mol%										
SiO_2	60.1	52.7	75	61.6	**83**	72.4	72.9	81.0	**46.1**	57.0
B_2O_3	16.0	14.0						13.0		6.1
Al_2O_3	3.8	3.4	12.5	10.9	8.2	1.1	1.0	2.0		8.8
P_2O_5		0.1							2.6	
Fe_2O_3		3.0		5.1	0.6	0.1				
Na_2O	12.6	11.4	12.5	3.2	**3.9**	19.4	12.3	4.0	**24.4**	0.6
Li_2O		4.6		2.5						
K_2O					**2.9**					
CaO	5.7	5.0		14.6	1.0	5.4	7.2		26.9	19.6
MgO					0.3		6.6			6.5
BaO		0.3								
ZrO_2	1.7	1.5								
$\sum RE_2O_3$		0.9								
Other		2.0		2.0		1.5	<1			<1
Initial dissolution rate r_0 in $g \cdot m^{-2} \cdot d^{-1}$ @ at 90°C pH 9										
	8.2	0.3	0.26	1.4	**$2\ 10^{-3}$**	2.5	23	3	**>8000**	4.6

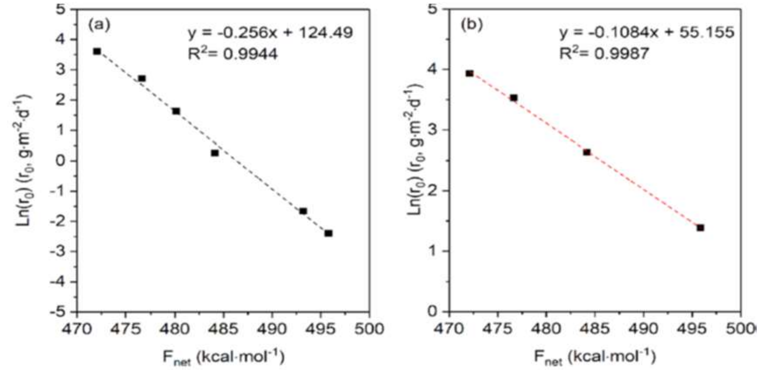
Gin et al., *npj Mat. Deg.* (2021)

Initial dissolution rate

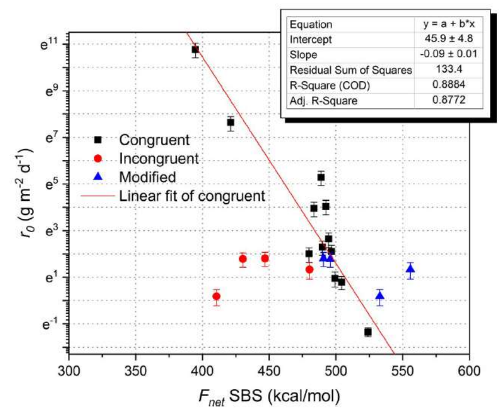


$$r_0 = r_{n_c=0} \exp\left(-\frac{n_c E_0}{RT}\right)$$

Gin et al. *npj-Mater. Degrad.* (2020) 6



Lu *J. Phys. Chem. B* 123 (2019)



$$F_{\text{net}} = \frac{1}{N} \sum_{X}^{\text{cations}} n_X \cdot CN_{\text{XO}} \cdot SBS_{\text{XO}} \cdot m_X$$

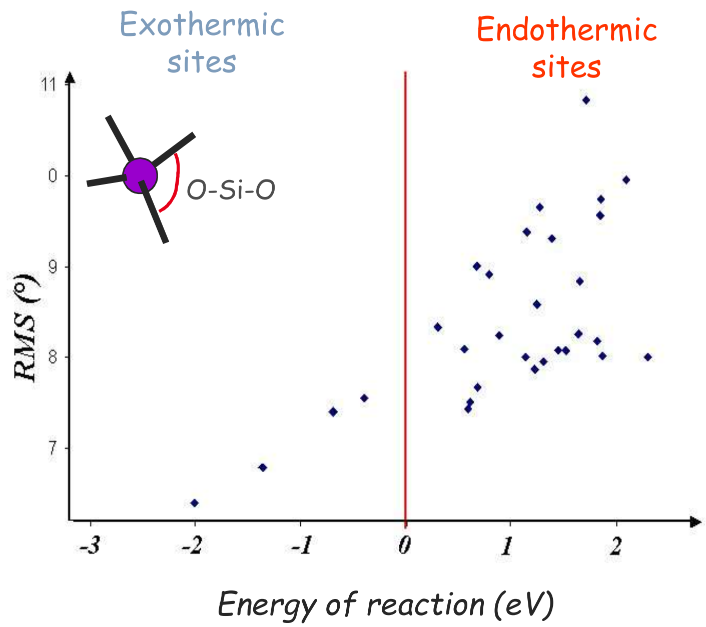
Du et al. *J. Amer. Cer. Soc.* (2021)

Disorder makes things complicated

Is there a unique value of E_{barr} for a given type of bond?

Favorable/Unfavorable sites for hydrolysis reaction

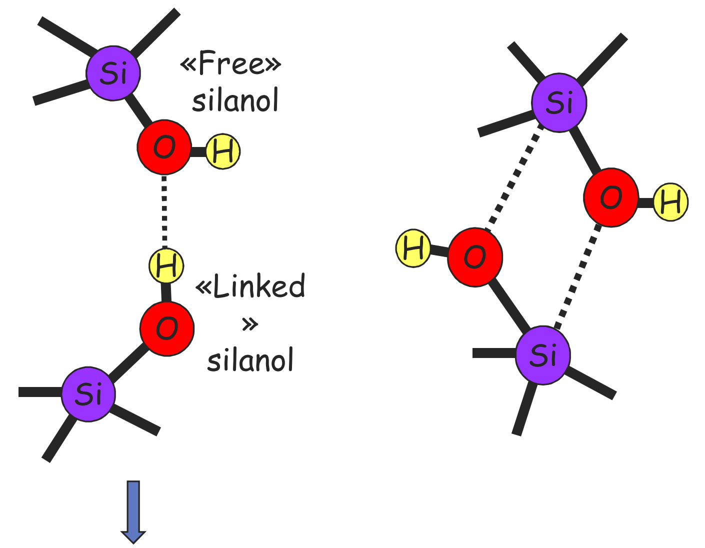
Distribution of the final O—Si—O angles (after hydrolysis)



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

Exothermic sites
stretched Si—O—Si

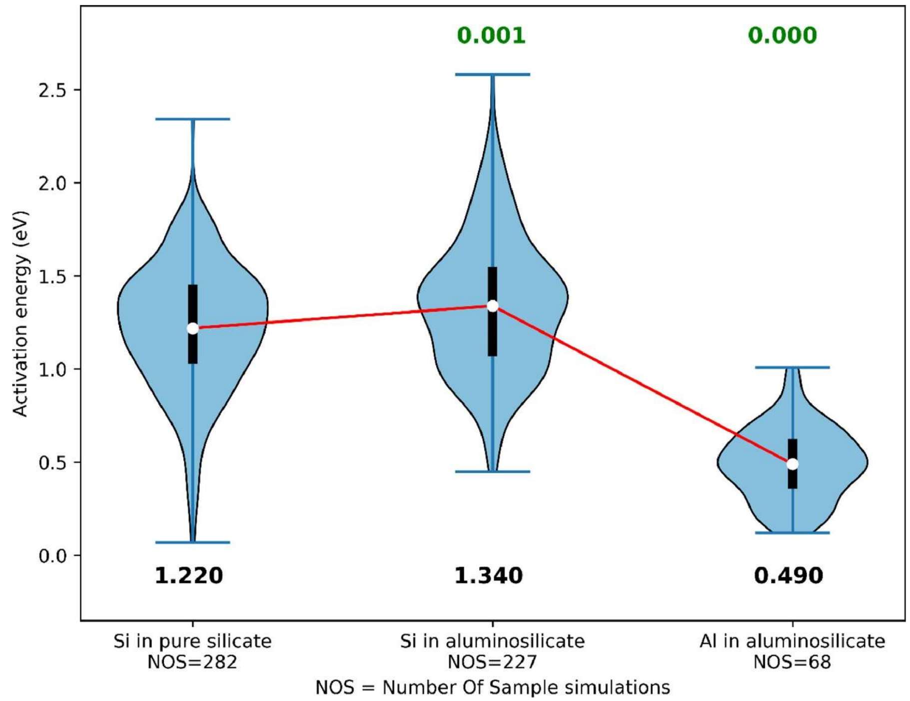
Endothermic sites
compressed Si—O—Si



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

Bouyer et al., *J.Sol.State Chem.* (2010)

Disorder makes things complicated



A huge statistics was necessary to understand the role of Al in silicate glasses

Damodaran et al. *Acta Mater.* (2022)

Little focus on International Simple Glass

Materials Today • Volume 16, Number 6 • June 2013 RESEARCH

ELSEVIER

An international initiative on long-term behavior of high-level nuclear waste glass

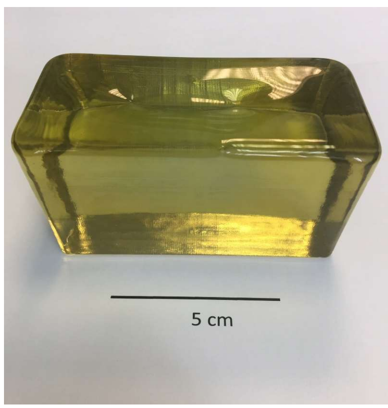
RESEARCH: Review

S. Gin[1,*], A. Abdelouas[2], L.J. Criscenti[3], W.L. Ebert[4], K. Ferrand[5], T. Geisler[6], M.T. Harrison[7], Y. Inagaki[8], S. Mitsui[9], K.T. Mueller[10], J.C. Marra[11], C.G. Pantano[12], E.M. Pierce[13], J.V. Ryan[14], J.M. Schofield[15], C.I. Steefel[16] and J.D. Vienna[14]

Acknowledgement to
MoSci Corp, USA
Corning Corp, USA

Create a common knowledge base on the alteration mechanisms of silicate glasses

→ 86 papers published since 2014



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

ISG – 2 is born and available!

npj | materials degradation www.nature.com/npjmatdeg

ARTICLE OPEN Check for updates

ISG-2: properties of the second International Simple Glass

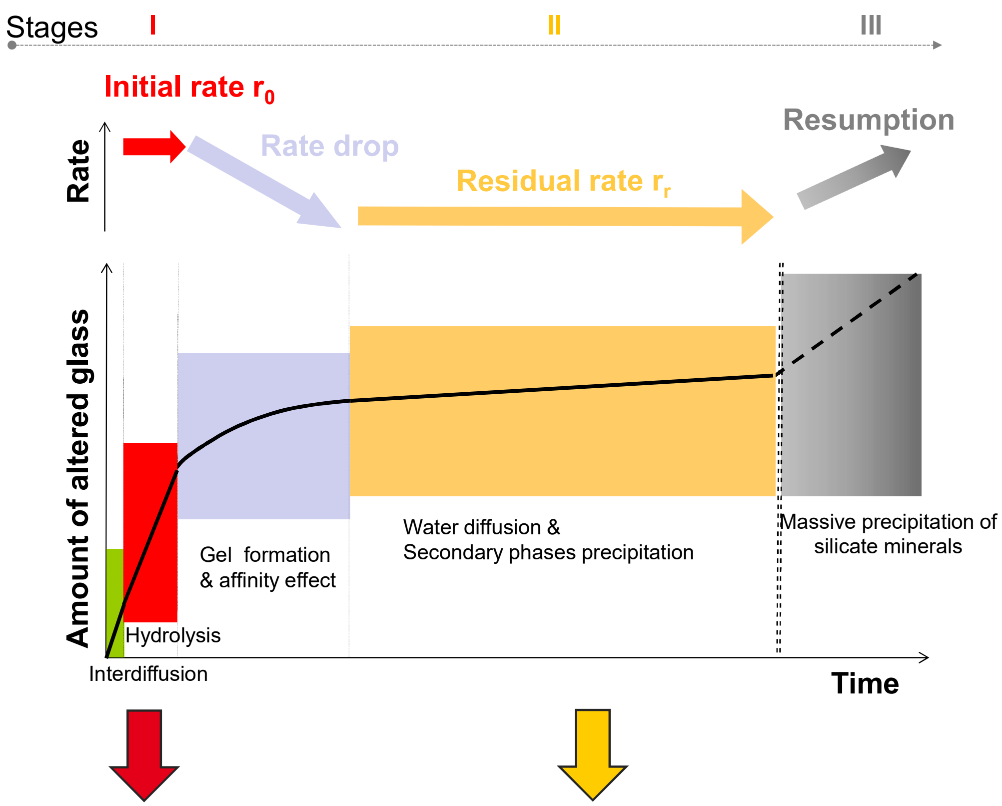
Joseph V. Ryan[1], Nicholas J. Smith[2], James J. Neeway[1], Joelle T. Reiser[1], Benjamin Parruzot[1], Steve Tietje[2], Elzbieta Bakowska[2], Jarrod V. Crum[1] and Robert A. Schaut[2]

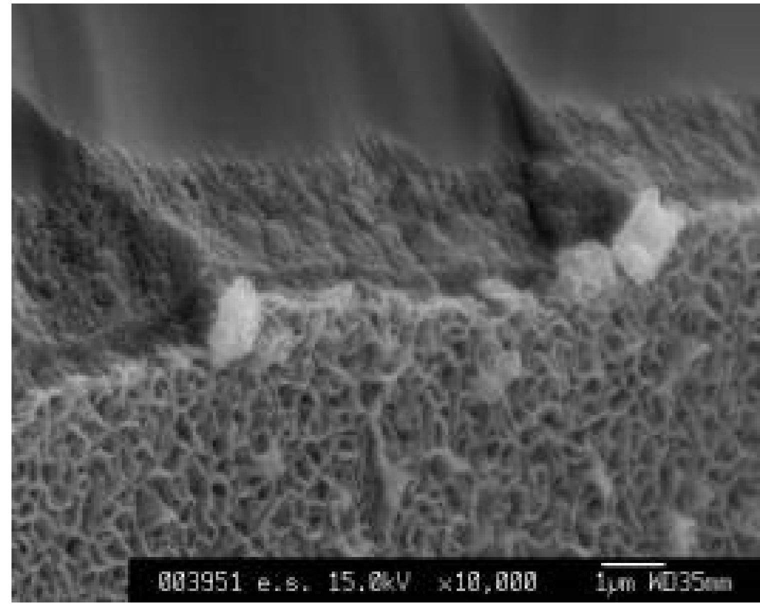
Given the importance of glass materials to society, their durability when exposed to aqueous solutions is a critical area for research, particularly for vitrified radioactive wastes. This spurred an international team to fabricate a standardized composition based on waste immobilization glass called the International Simple Glass (ISG), which has been the subject of numerous experimental and computational studies focused on aqueous corrosion resistance.

With the original batch of ISG nearly depleted, the international team designed and fabricated a standard glass material, ISG-2, where half the Ca in the original composition was replaced with Mg by mole. This paper presents information on both the ISG-2 composition and a new batch with the same nominal composition as the original ISG, designated ISG-1, including their homogeneity, their physical and thermal properties. The results of static alteration experiments are presented as well to provide a baseline for future aqueous corrosion performance investigations.

npj Materials Degradation (2023)7:47 ; https://doi.org/10.1038/s41529-023-00352-7

Glass dissolution kinetics





Rate ~μm/d
Canister lifetime ~10^{2-3} yr

Rate ~nm/yr
Canister lifetime ~10^{5-6} yr

Rate laws/kinetic model over time

1935 **T**ranstion State Theory (Eyring)

1982 **T**ST applied to silicate minerals (Aagaard & Helgeson)

1985 **F**irst order law applied to nuclear glasses (Grambow)

$r_{disso} = r_0[1\text{-}C(Si)/C(Si)_{sat}]$

1995 **G**eneral rate law applicable to mineral and glass (Lasaga)

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

1996 **M**onte Carlo (1^{st} version) (Aertsens)

2001 **G**M2001 model: coupling affinity and D_{H2O} and D_{si} (Grambow)

2006 **E**uropean project Glamor : importance of the residual rate

2008 **G**RAAL model: introduces the notion of PRI (Frugier)

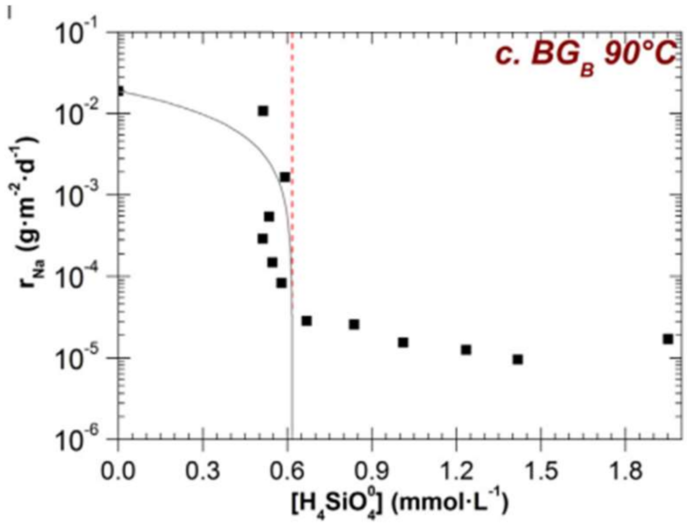
2014 **M**onte Carlo including diffusion (Kerisit)

2020 **P**atchy particles model (Kerisit & Du)

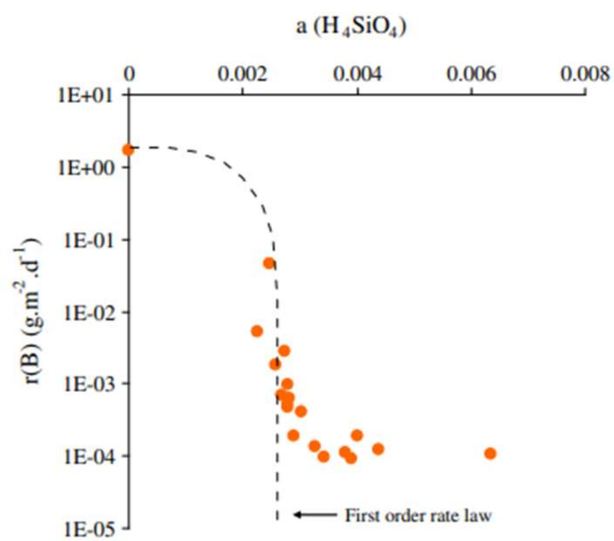
2023 ***M****onte Carlo including water diffusion (Delaye),* ***P****hase field model (Cartalade)*

Limitations of the 1st order rate law

$$r = r_0\left(1 - \frac{a_{Si}}{a_{Si}^{sat}}\right)$$



Case of Basaltic glass altered at 90°C pH 9
Parruzot et al., *Geochim. Cosmochim. Acta.* (2012)

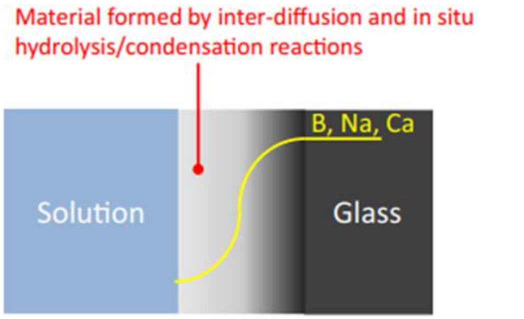


Case of ISG altered at 90°C pH 9
Gin et al., *J. Non-Cryst. Sol.* (2012)

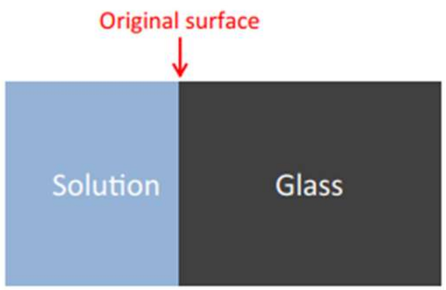
Something continues or something new happens beyond C(Si)sat

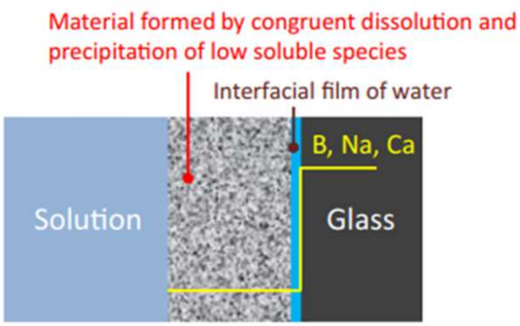
Controversy on how gels form

Classical theory
involving inter-diffusion

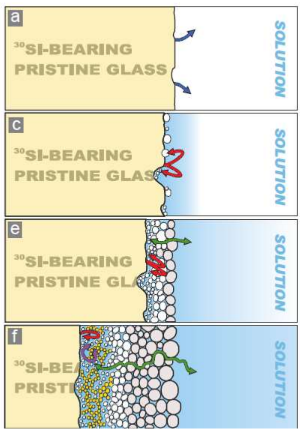


Frugier et al., *J. Nucl. Mater.* (2008)
Gin et al., *Nat. Comm.* (2015)



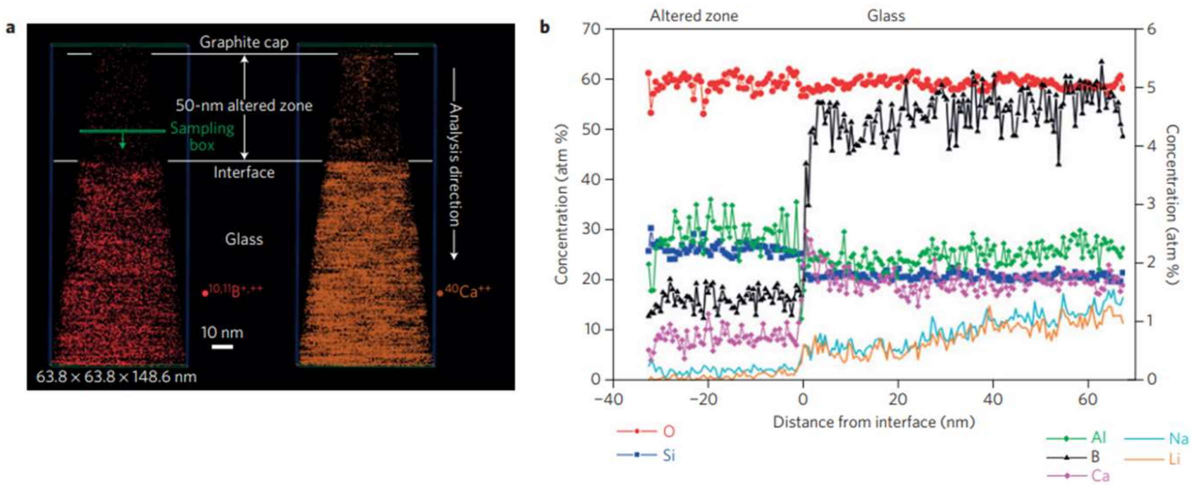


Interfacial
Dissolution/precipitation
theory

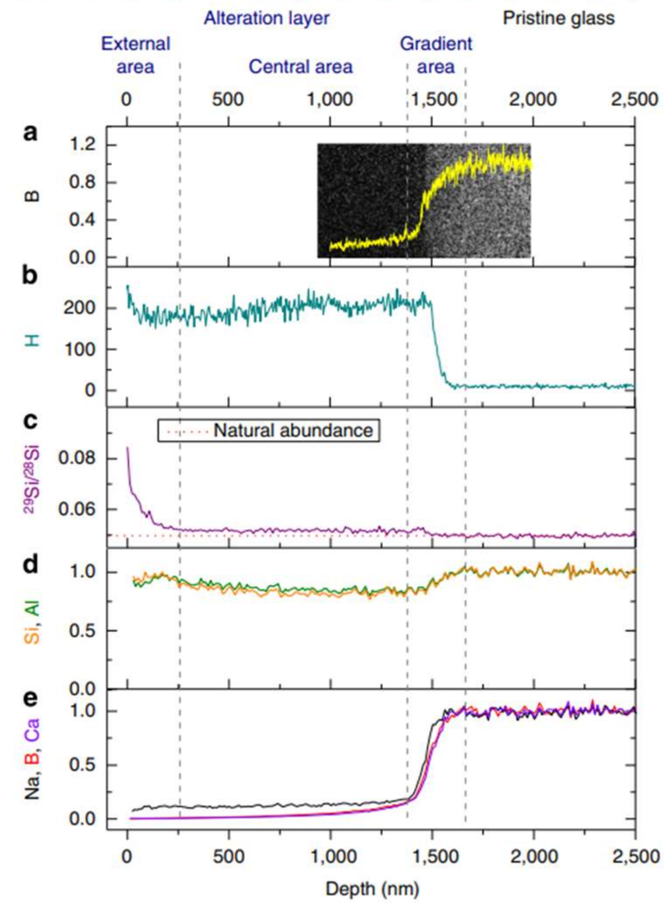


Geisler et al., *J. non-Cryst. Solids* 356 (2010)
Hellmann et al., *Nat. Mater,* (2015)

Searching evidences

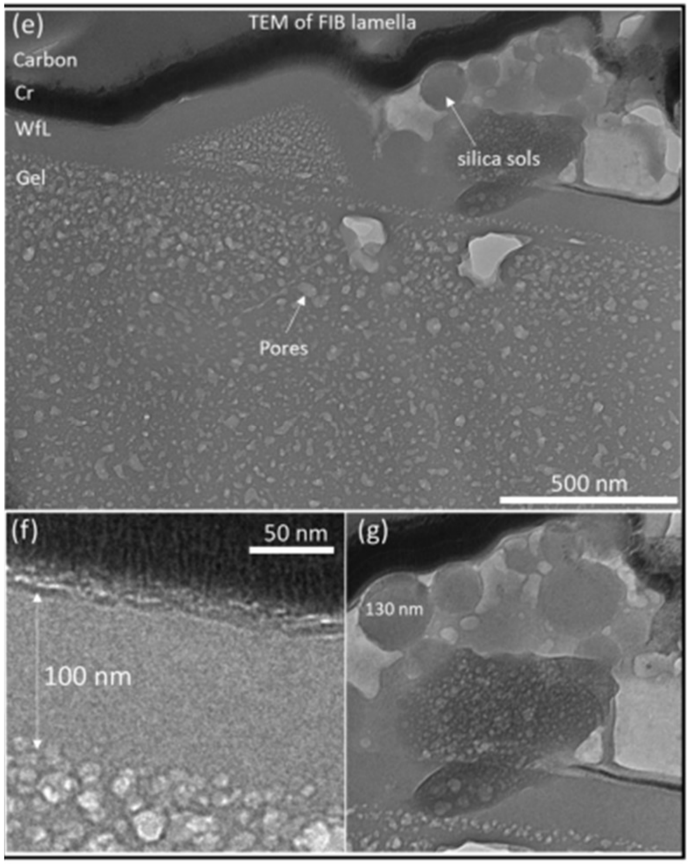


Sharp interface ➔ dissolution/precipitation mechanism
Hellmann et al., *Nat. Mater.* (2015)



Isotopic signature ➔ in situ reorganization mechanism
Gin et al., *Nat. Comms.* (2015)

Searching evidences



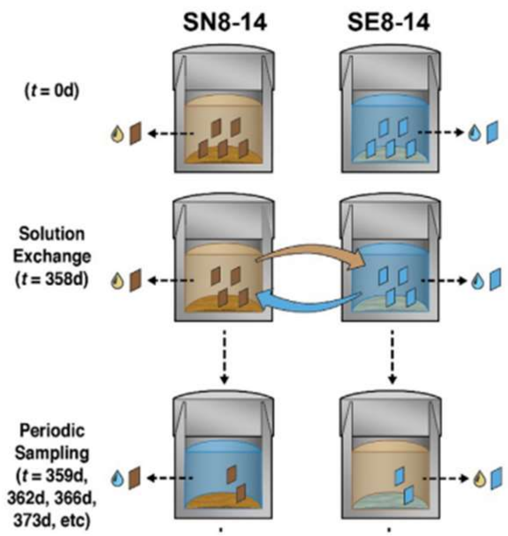
SNB glass experienced both mechanisms during the course of a single experiment ➔ no universal mechanism exists!

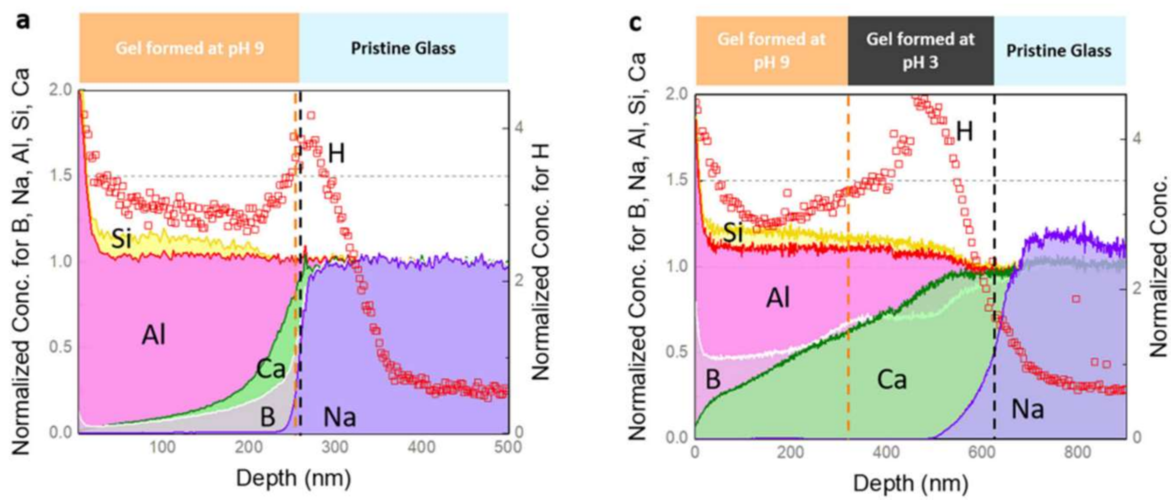
Gin et al., *J. Phys. Chem. C* (2020)

How the gel becomes passivating?

Can passivation control the long-term behavior of silicate glasses?

What mechanism controls the residual rate?

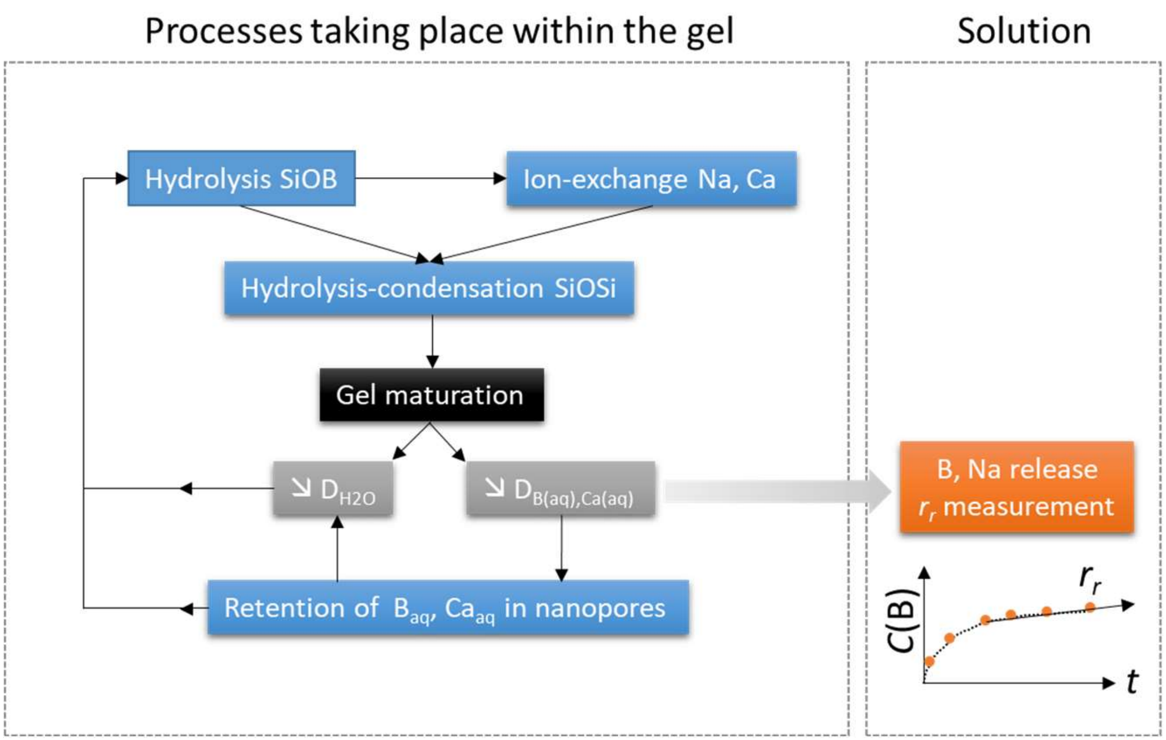




ToF-SIMS profiles of gels formed on SON68 glass ➔ the gel has no effect, ion-exchange controls the long-term rate
Strachan et al., *Geochim. Cosmochim. Acta* (2022)

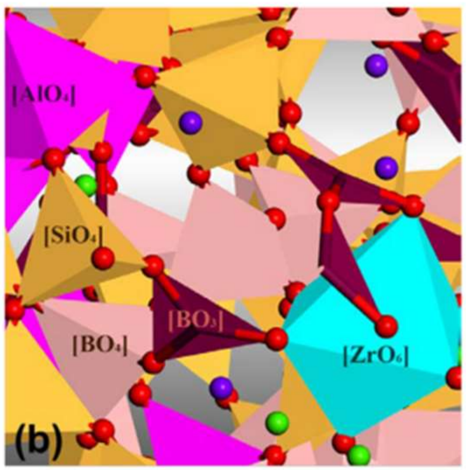
ToF-SIMS profiles after 6 yr at 90° pH 9 (left) and followed by 1 month at pH 3 ➔ in this particular case B diffusion in gel controls the long-term rate
Gin et al., *npj Mat. Deg*. (2022)

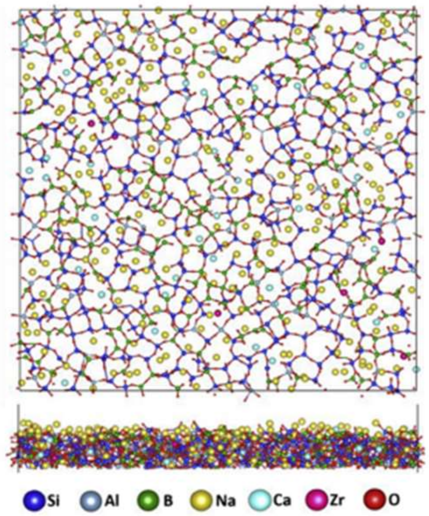
What mechanism controls the residual rate?
Case of ISG

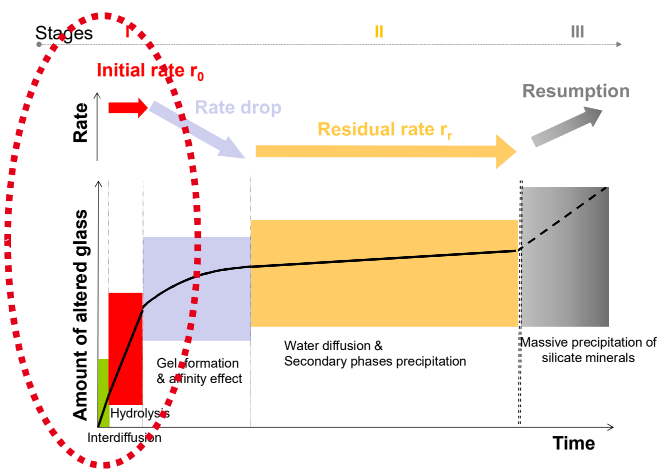


A complex set of reactions must be considered and implemented in models
Gin et al., *npj Mat. Deg.* (2022)

Summary: case of ISG

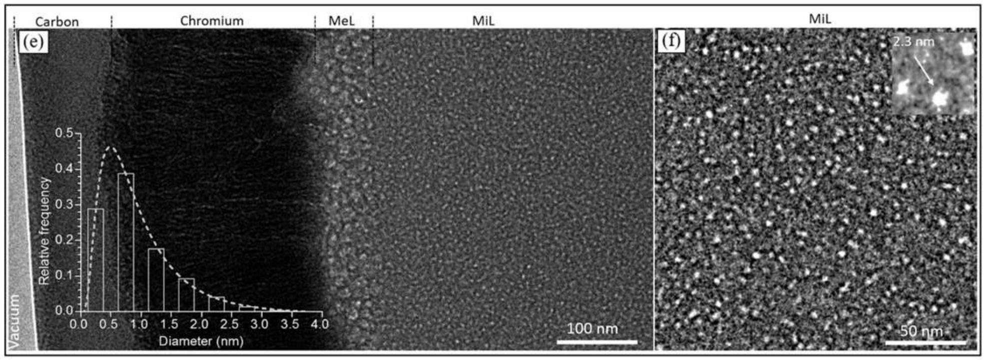




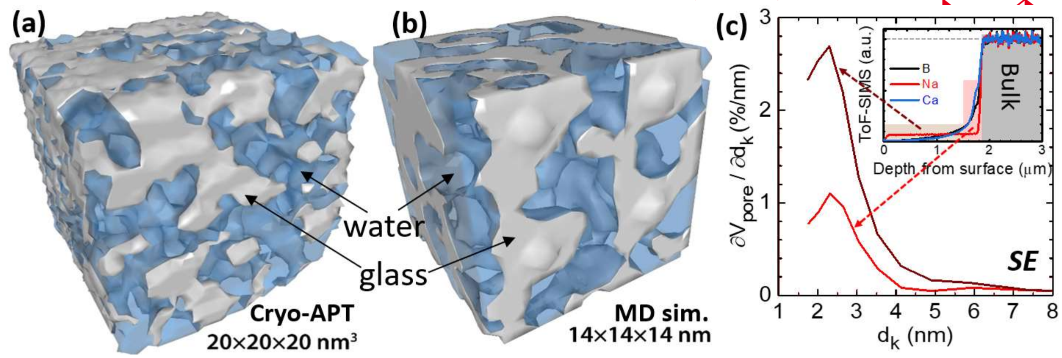


- **Let us start the reaction in deionized water**
- Low impact of IX: Almost no NBO
- The pH increases up to 9 (buffer effect of B)
- r_0 is controlled by hydrolysis of Si–O–Si bonds
- Dissolution is congruent in basic pH (preferential release of B and Na in acidic pH)
- r decreases as Si_{aq} increases

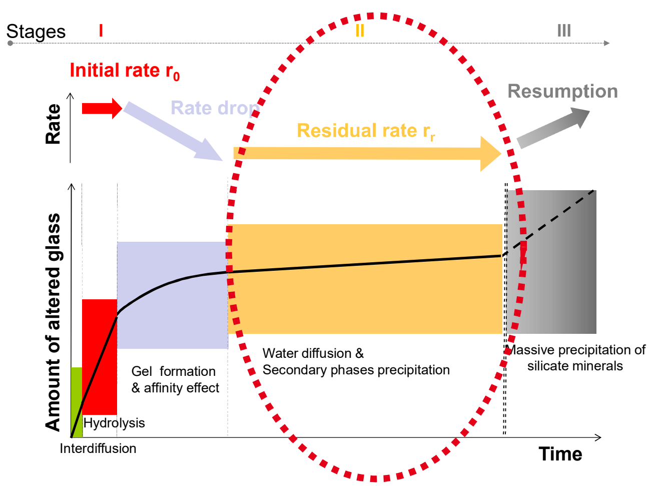
Summary: case of ISG



Mir et al., *npj Mat. Deg.* (2020)

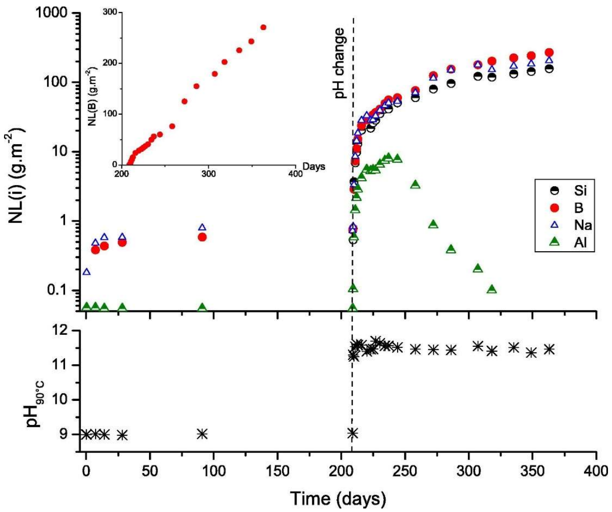


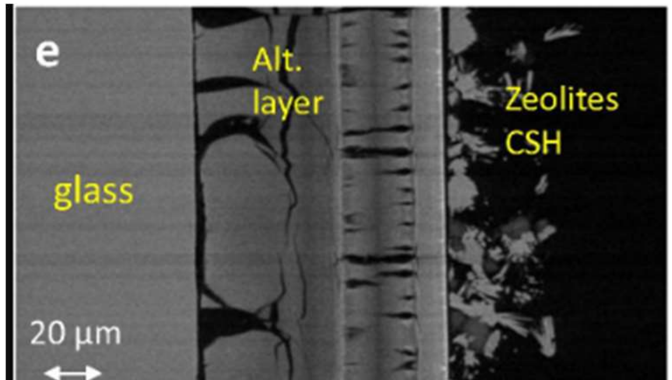
Perea et al., *npj Mat. Deg.* (2020) ; Ngo et al., *npj Mat. Deg.* (2018)



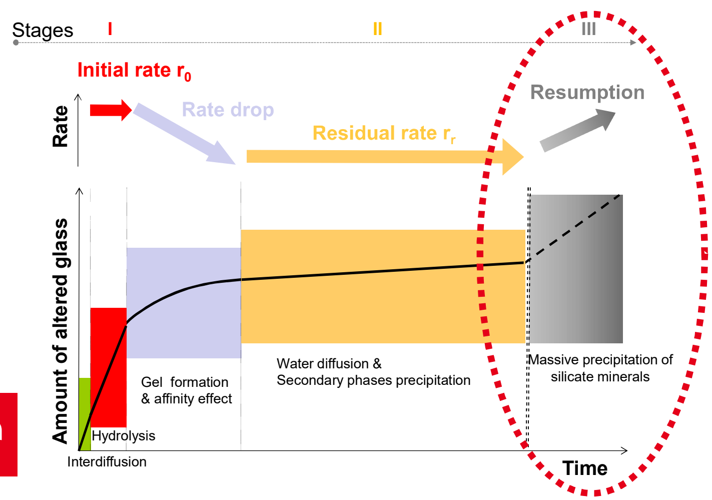
- Si_{aq} becomes saturated
- Gel forms by in situ hydrolysis of Si–O–B/condensation of Si–OH
- First gel inherits from the glass structure (low mobility of Si)
- Gel reorganizes and densifies: it becomes passivating for B, B is partly retained at the glass/gel interphase.
- The residual rate is ~10^4 times lower than r_0
- Gel is not a diffusion barrier for water, it remains extremely sensitive to external conditions

Summary: case of ISG





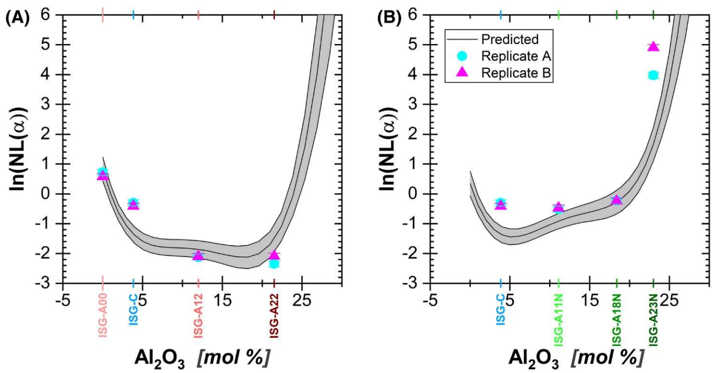
Gin et al., *Geochim. Cosmochim. Acta* (2015)



- **Let us rise the pH to 10.5 (at 90°C)**
- The gel dissolves at the expense of secondary phases (CSH, Zeolites).
- The mechanism is highly favoured in superalkaline solutions
- $r_{\nearrow} < r_0$
- Zeo precipitation decreases the pH, a new passivating gel can form

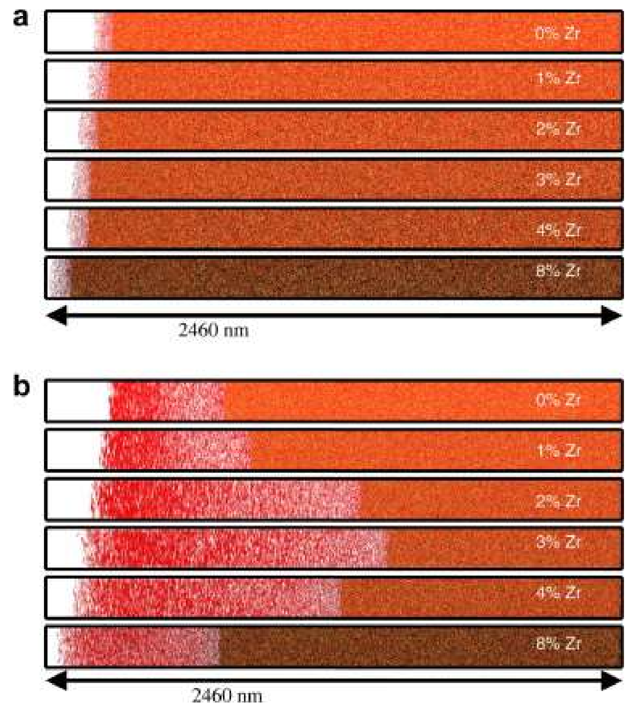
Glass composition effects

Role of Al in ISG on PCT glass response



Reiser et al., *Int. J. Appl. Glass Sci.* (2021)

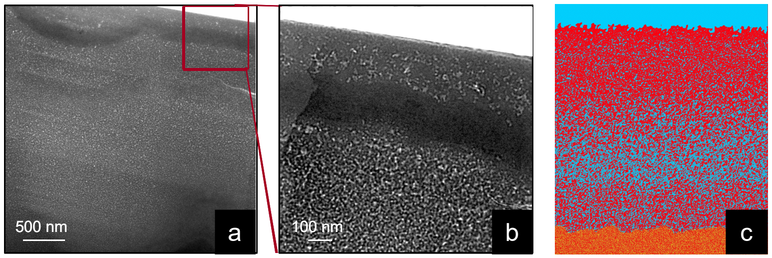
Role of Zr in borosilicate glass on r_0 and r_r



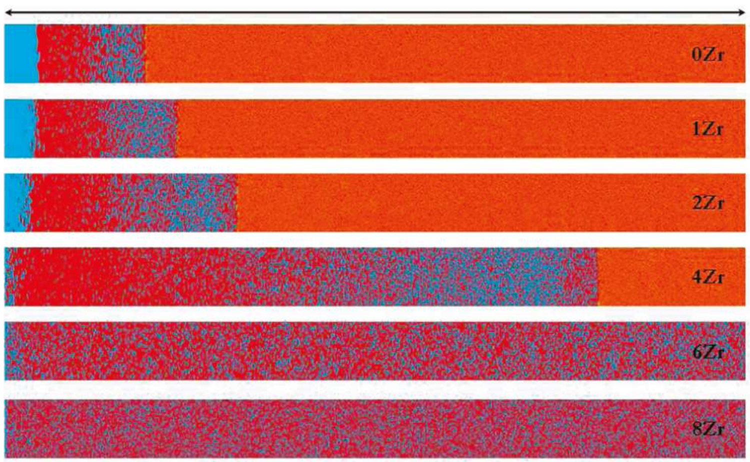
Arab et al., *J. Non-Cryst. Sol.* (2008)

Models partly capture the complexity

Monte Carlo model deciphered the role of Zr

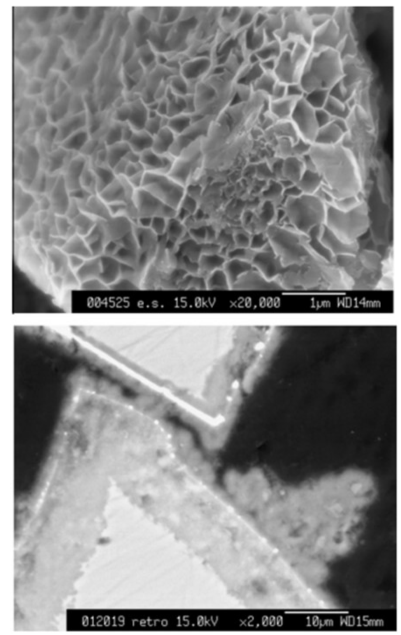


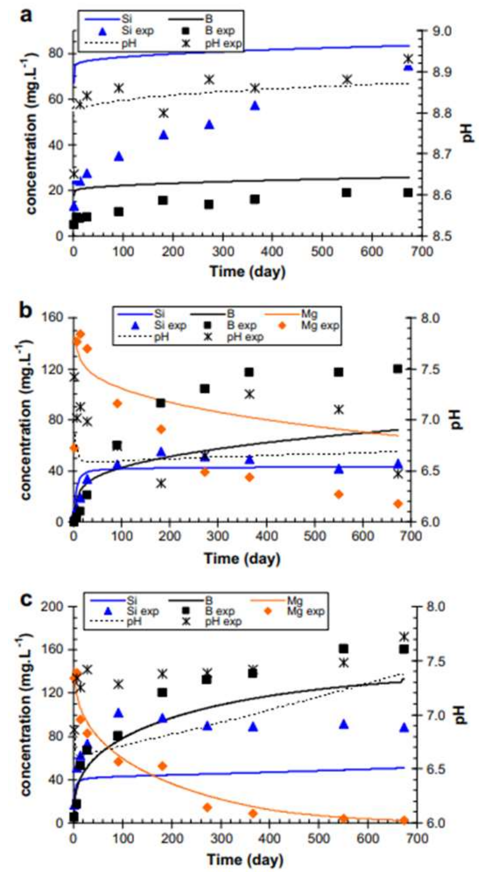
Porosity clogging: up to 4% of ZrO_2



Cailleteau et al., *Nat. Mater.* (2008)

GRAAL model explained the effect of ground water



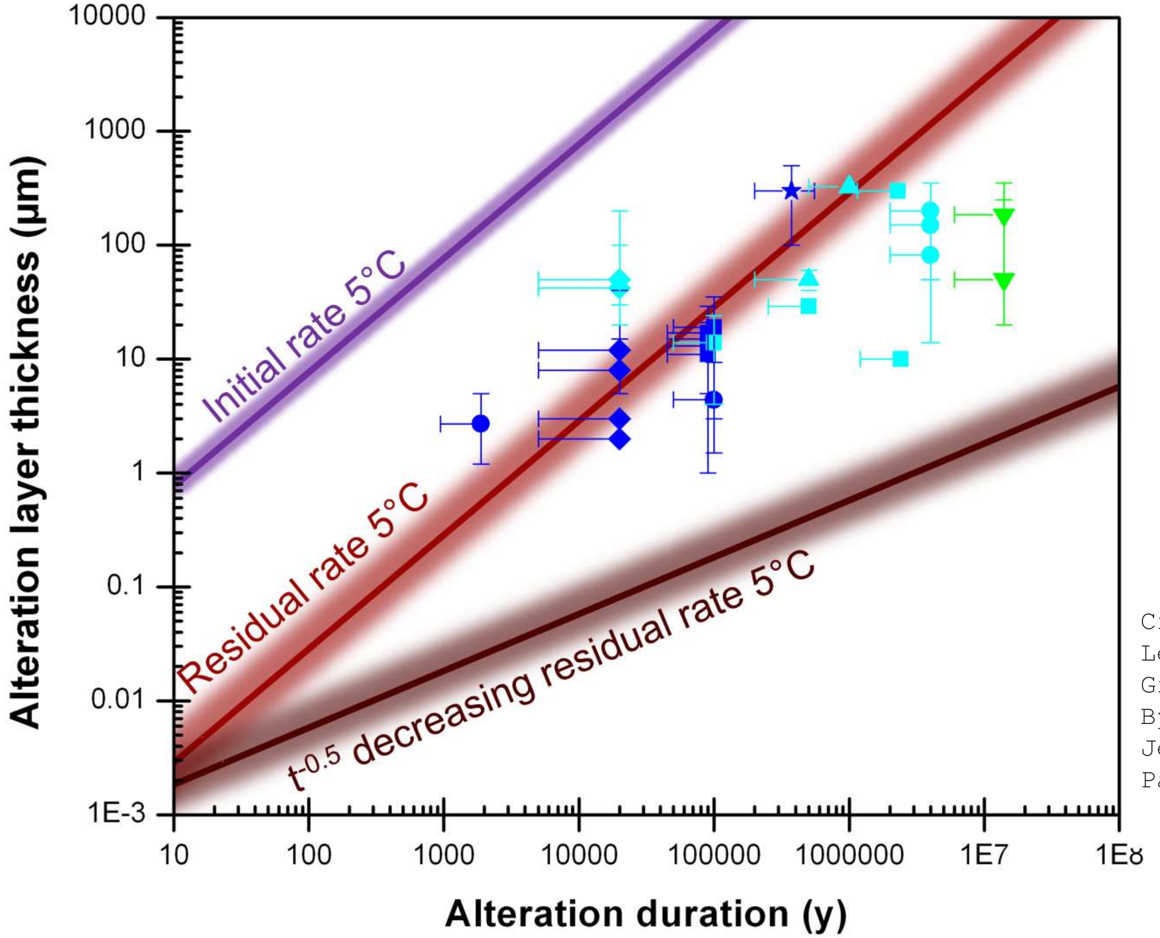


Jollivet et al., *J. Nucl. Mater.* (2012)

Looking beyond the boundaries of the lab

Long term extrapolation: what do we learn from Nature?

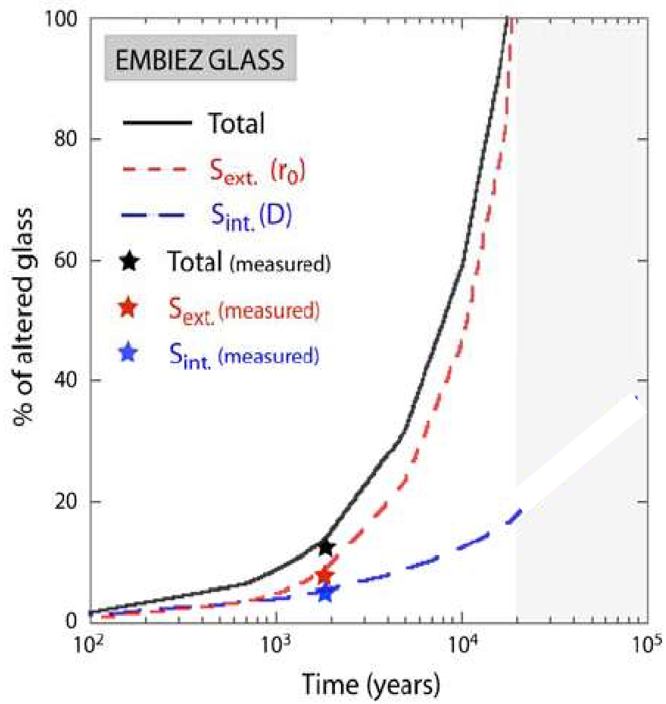
Dark blue: Non zeolitized natural samples || **Light blue** and **green:** Zeolitized or calcified samples

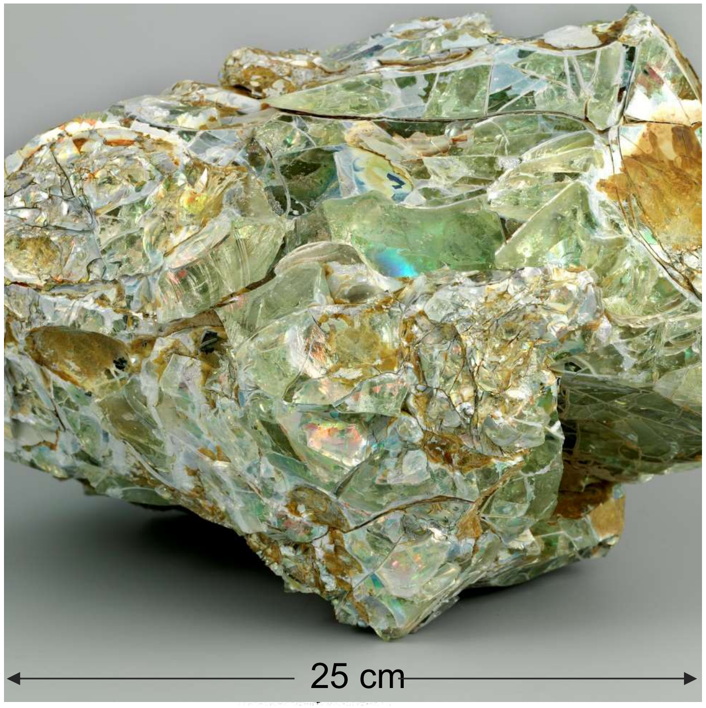


Crovisier 1992
Le Gal 1997
Grambow 1985
Byers 1987
Jeong 2011
Pauly 2011

Long term extrapolation: what do we learn from Aercheology?

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



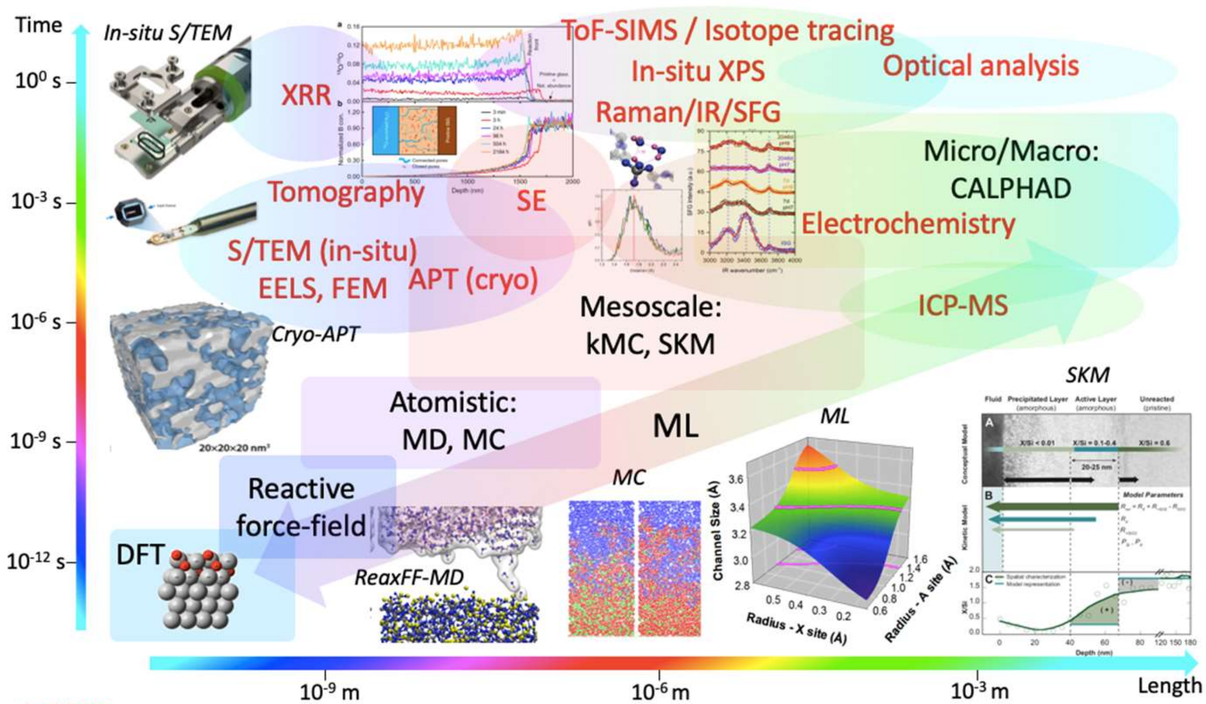


Quantitative validation of a mechanistic model over 1800 years – Applicable to other glasses by the analogy of the mechanisms involved

And Now?

The key question has not yet been solved but some progress has been made!

❶ It seems now possible to design highly durable glass that could meet the 1 Ma criterion by playing both on the glass composition and the environmental conditions



❷ **Both experimental and simulation powerful tools exist at various scales. The main challenge is to link the various scales**

❸ **Reinforce international and cross cutting collaborations** (Example of EFRC WastePD)

Acknowledgements

Warm thanks to SOPHIE

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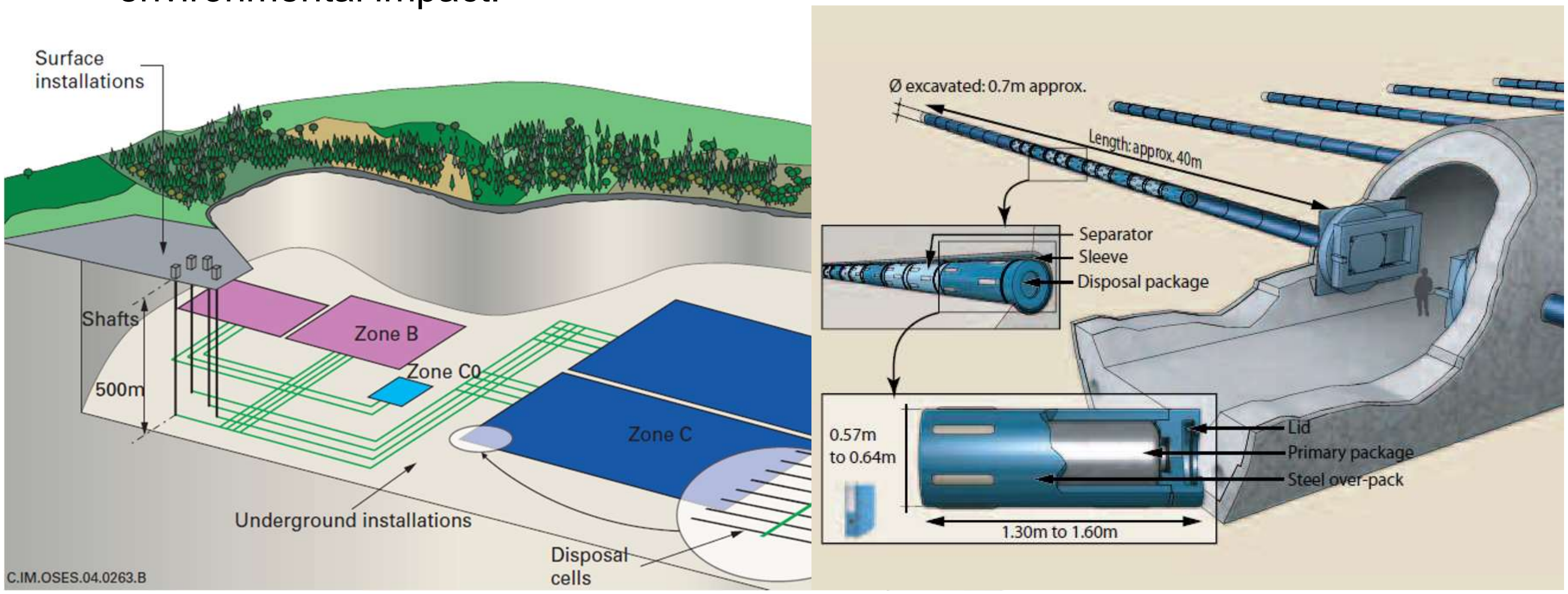
Context

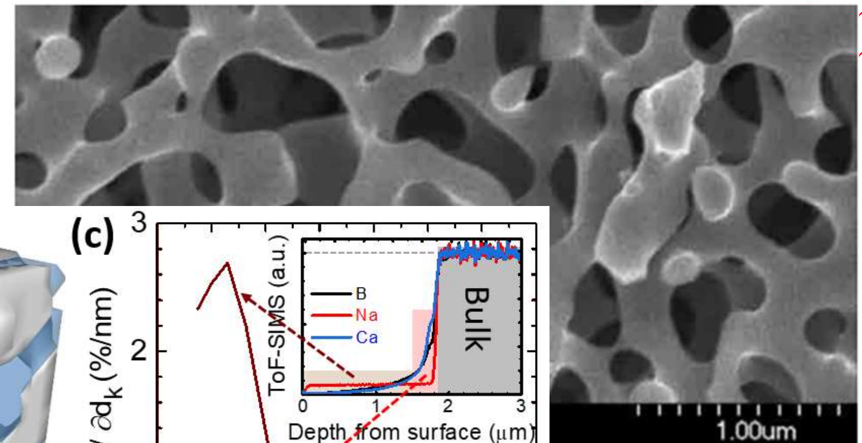
- Minor actinides and fission products arising from spent fuel reprocessing in France are confined in **borosilicate glasses, made of >30 oxides**
- Deep geological disposal—currently the most consensual solution for these wasteforms—requires a study of their **long-term behavior** to assess their environmental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

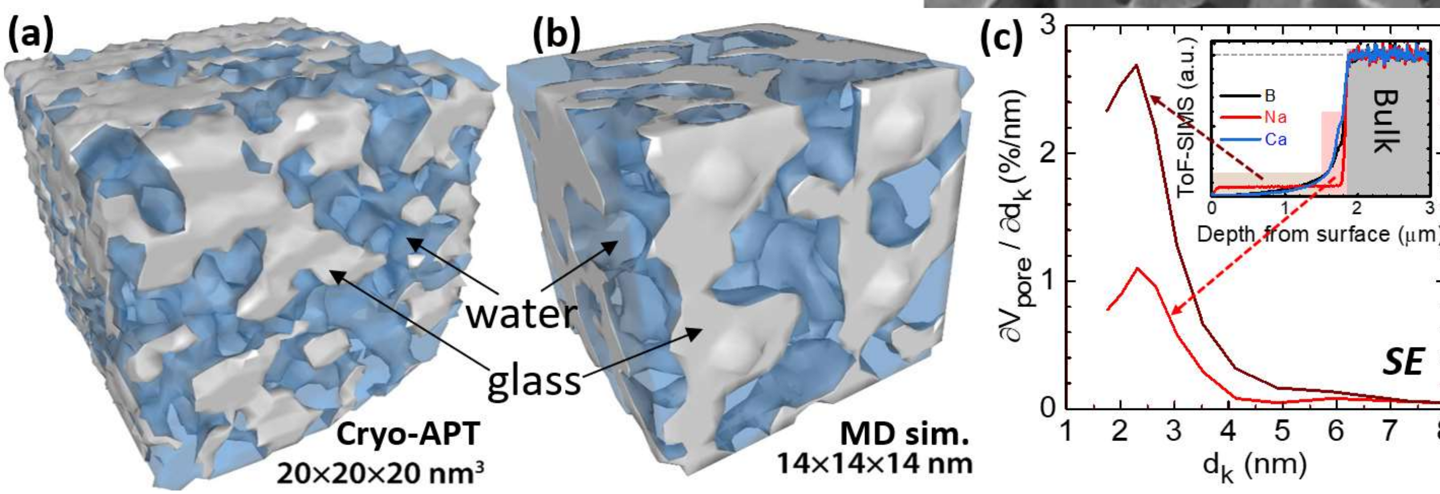


French high-level waste package and disposal cell [1]

[1] Andra 265 VA, 2006

What mechanism controls the residual rate?
Case of ISG



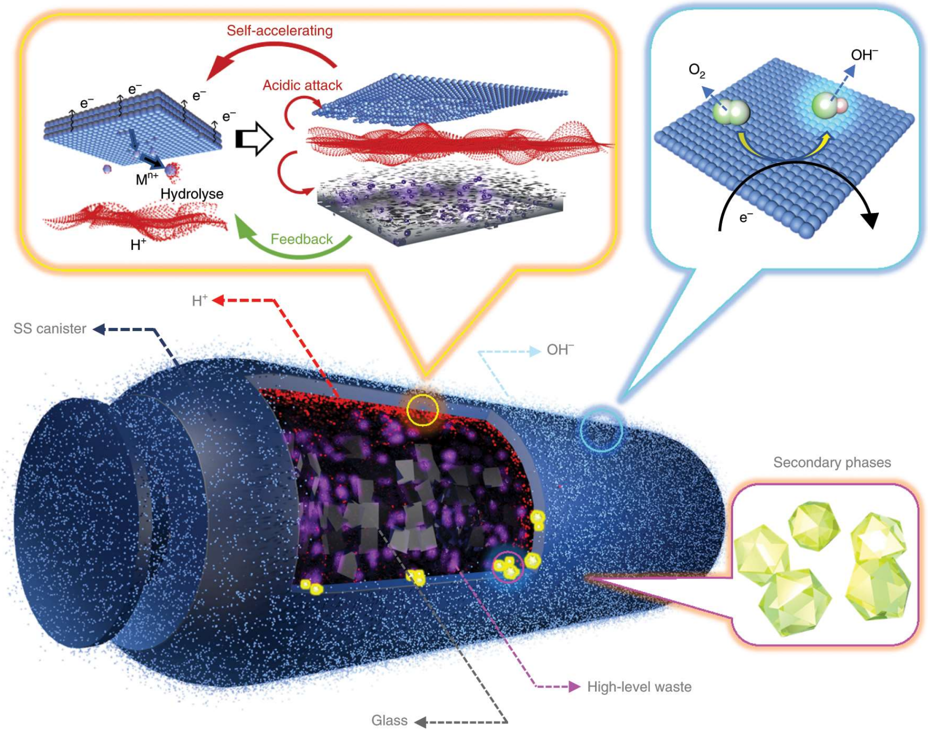


A complex set of reactions must be considered and implemented in models

Gin et al., npj Mat. Deg. (2022)

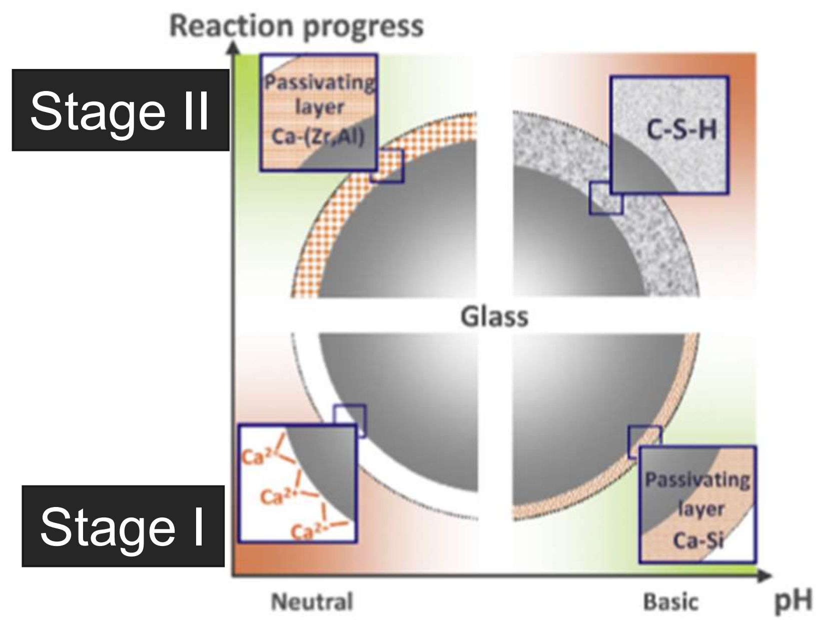
Glass behavior in complex environments

Self-accelerating alteration at SS/glass interface



Guo et al., *Nat. Mater.* (2021)

Role of Ca on glass dissolution



Mercado-Depierre et al., *J. Nucl. Mater.* (2013)