Studies on natural and archeological glasses

Opportunities to learn about long-term nuclear waste glass corrosion

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Since 2010: Assistant Professor at LISA, France
2009-2010: Post-doc at CRPG on Li isotopes to trace basaltic glass alteration
2005-2008: PhD at CEA on the Study of archaeological analog for the validation of nuclear glass long-term behavior models

Summer Board Meeting of the U.S. Nuclear Waste Technical Review Board
June 21, 2017 - Richland

Studies of ancient glasses

Natural glass Nuclear glass **Archaeological glass**

Basaltic glass

Ewing (1979, 2001)
Allen (1983)
Birchard (1984)
Lutze et al. (1985)
Grambow et al. (1986)
Ewing and Jercinovic (1987); Jercinovic and Ewing (1988)
Cowan and Ewing (1989)
Crovisier et al. (1989)
Murakami et al. (1989)
Arai et al. (1989)
Werme et al. (1990)
Techer et al. (2001, 2001a,b)
Parruzot et al. (2015)

Obsidian

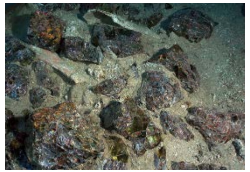
Magonthier et al. (1992)
Rani et al. (2013)

Tektites

Chondrites

Morlok and Libourel (2013)
Libourel et al. (2011)

Roman glass (shipwreck)



Embiez

Iulia Felix

Verney-Carron et al. (2008, 2010a,b)
Ryan et al. (in prep)
Strachan et al. (2014)

Stained glass windows

Sterpenich and Libourel (2001, 2006)

Buried archaeological glass

Macquet and Thomassin (1992) Saint-Denis
Sterpenich and Libourel (2001, 2006)

Vitreous slags

Michelin et al. (2015)

Vitrified forts

Sjöblom et al. (2013)

Reviews ★★★★★

Strachan & Pierce (2010) PNNL-19752 Report
Weaver et al. (2016)

Objectives of analogs study

A Ancient glass
(short-term alteration)

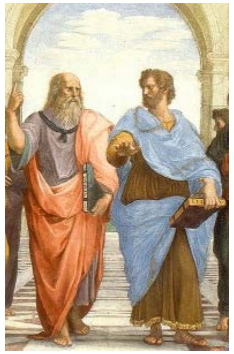
C Nuclear glass
(short-term alteration)

B Ancient glass
(long-term alteration)

?
Nuclear glass
(long-term alteration)

REASONING BY ANALOGY

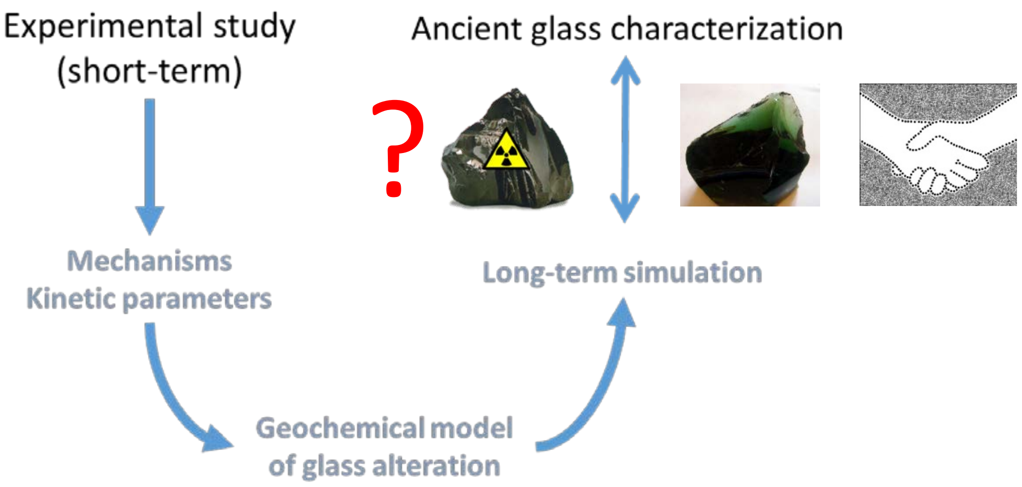
- A is similar to C in certain known respects.
- A has some further feature B.
- Therefore, probably, C also has the feature B.



✓ Features: long-term durability, retention of elements, low contribution of cracks, …

✓ Similarities between ancient and nuclear glasses

✓ Demonstration of the predictive capacity of the models


Experimental study
(short-term)

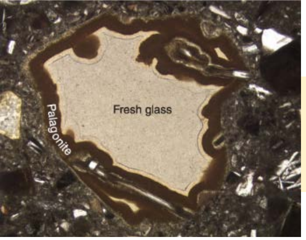
Ancient glass characterization

?

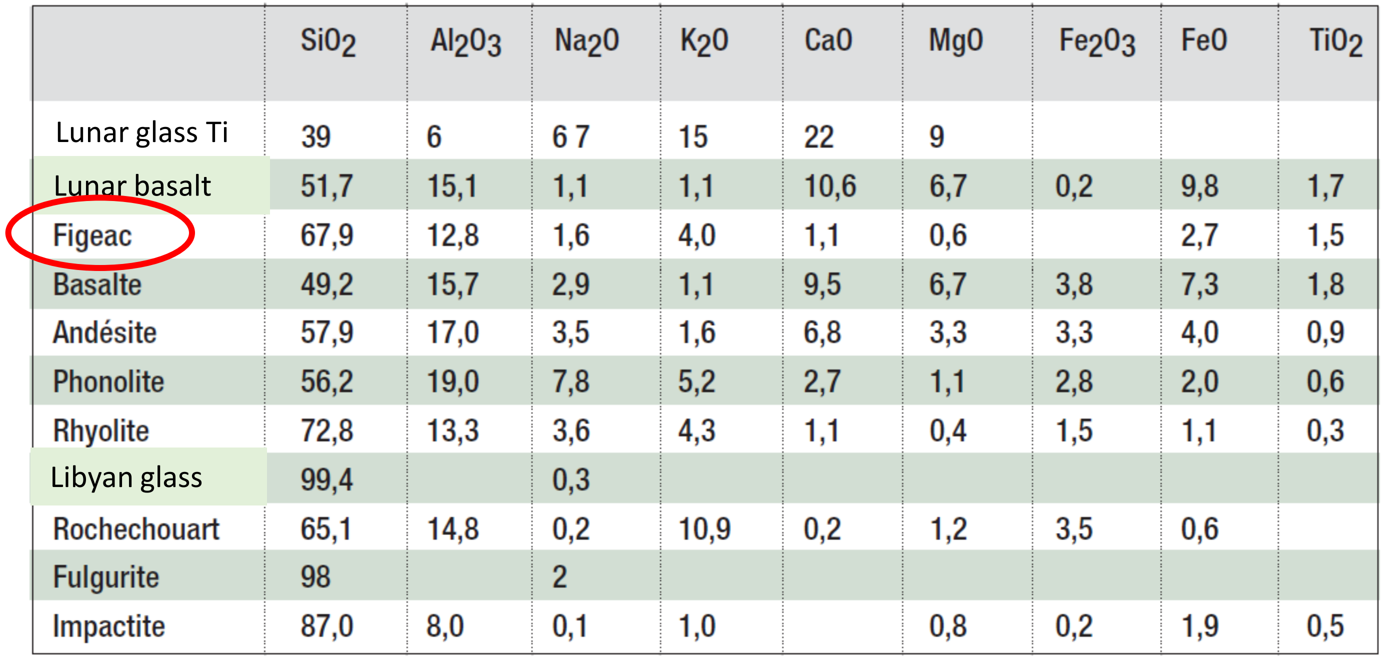
Mechanisms
Kinetic parameters

Long-term simulation

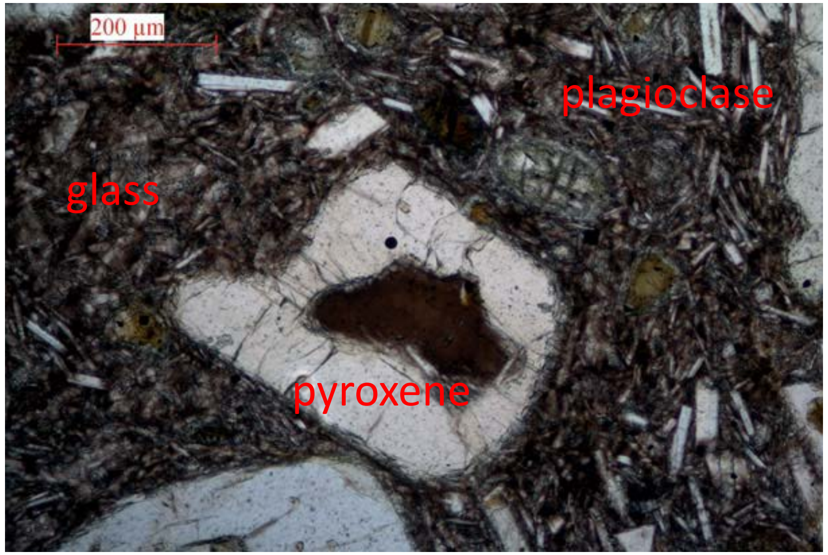
Geochemical model
of glass alteration



I.A. Properties : long-term durability of natural glass



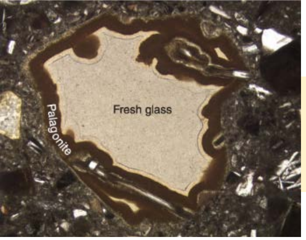
	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	FeO	TiO_2
Lunar glass Ti	39	6	6 7	15	22	9			
Lunar basalt	51,7	15,1	1,1	1,1	10,6	6,7	0,2	9,8	1,7
Figeac	67,9	12,8	1,6	4,0	1,1	0,6		2,7	1,5
Basalte	49,2	15,7	2,9	1,1	9,5	6,7	3,8	7,3	1,8
Andésite	57,9	17,0	3,5	1,6	6,8	3,3	3,3	4,0	0,9
Phonolite	56,2	19,0	7,8	5,2	2,7	1,1	2,8	2,0	0,6
Rhyolite	72,8	13,3	3,6	4,3	1,1	0,4	1,5	1,1	0,3
Libyan glass	99,4		0,3						
Rochechouart	65,1	14,8	0,2	10,9	0,2	1,2	3,5	0,6	
Fulgurite	98		2						
Impactite	87,0	8,0	0,1	1,0		0,8	0,2	1,9	0,5



Rocks from Figeac (Lot, France) – 280 My

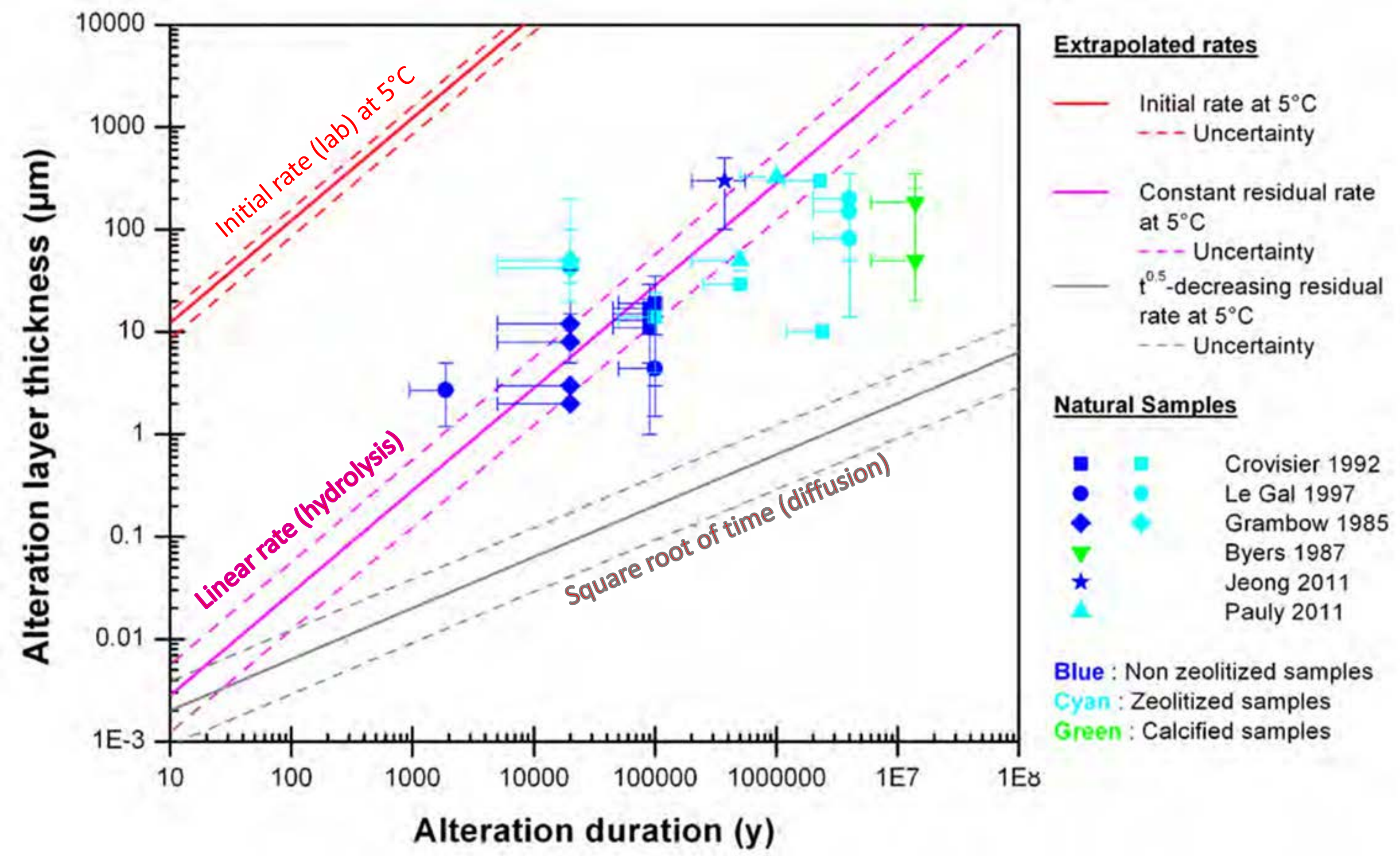
⇒ Old basaltic glasses despite tectonic and erosion

Richet (2009) Verre



I.A. Properties : long-term durability of natural glass

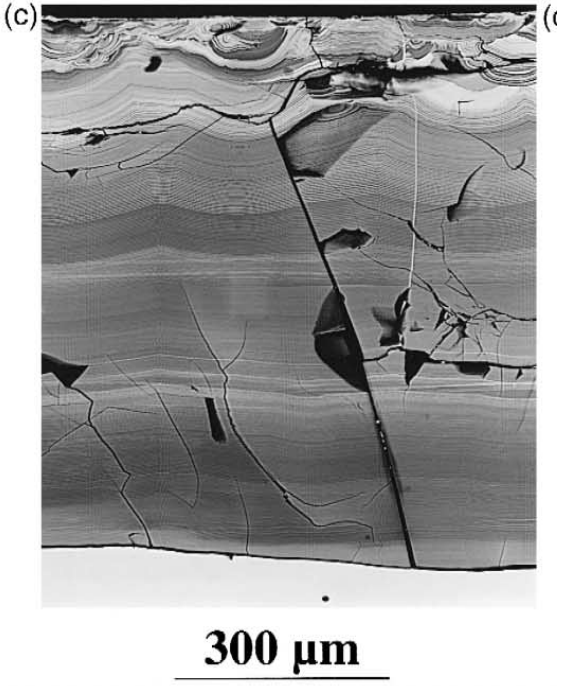
Parruzot (2015)



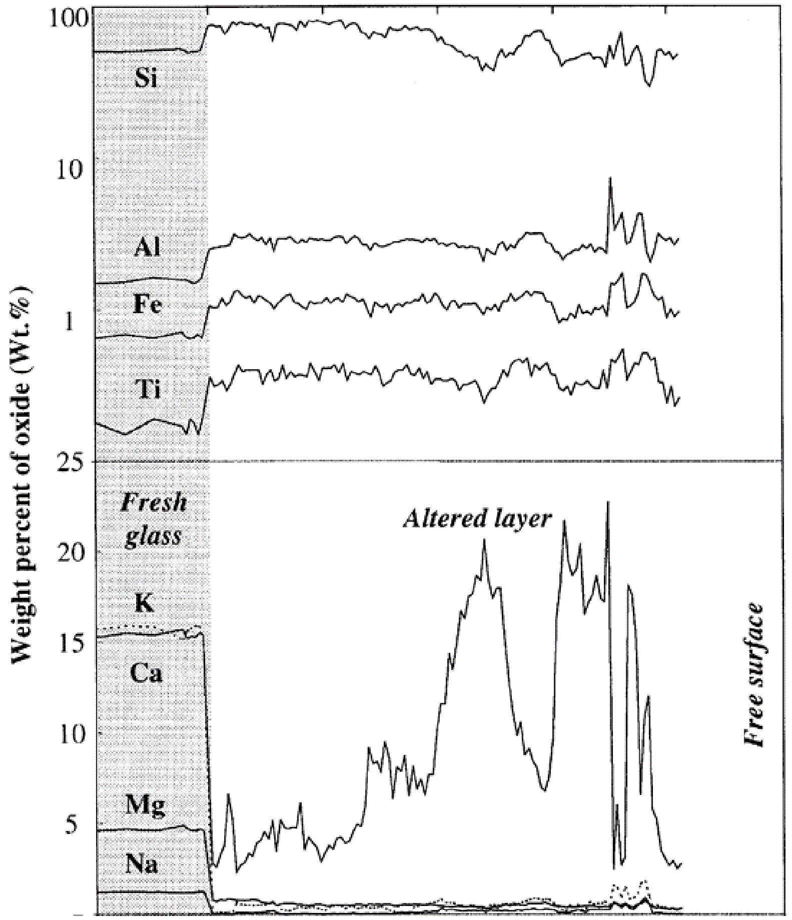
⇒ Decrease of the apparent dissolution rate with time

⇒ Extrapolation of a linear residual rate measured at the laboratory consistent with ancient samples

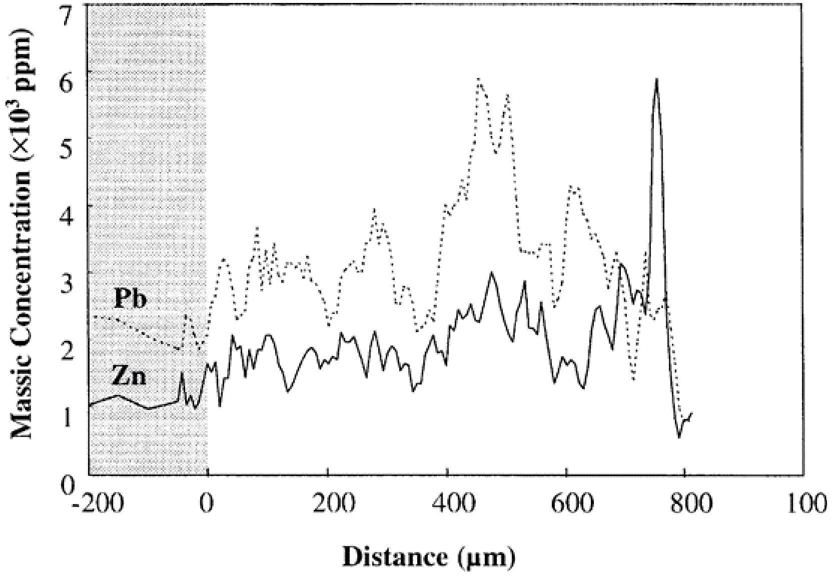
I.B. Partition of elements altered glass / solution



Stained glass excavated from the site of Notre-Dame-de Bourg (Digne), 12th century



Sterpenich and Libourel (2001)

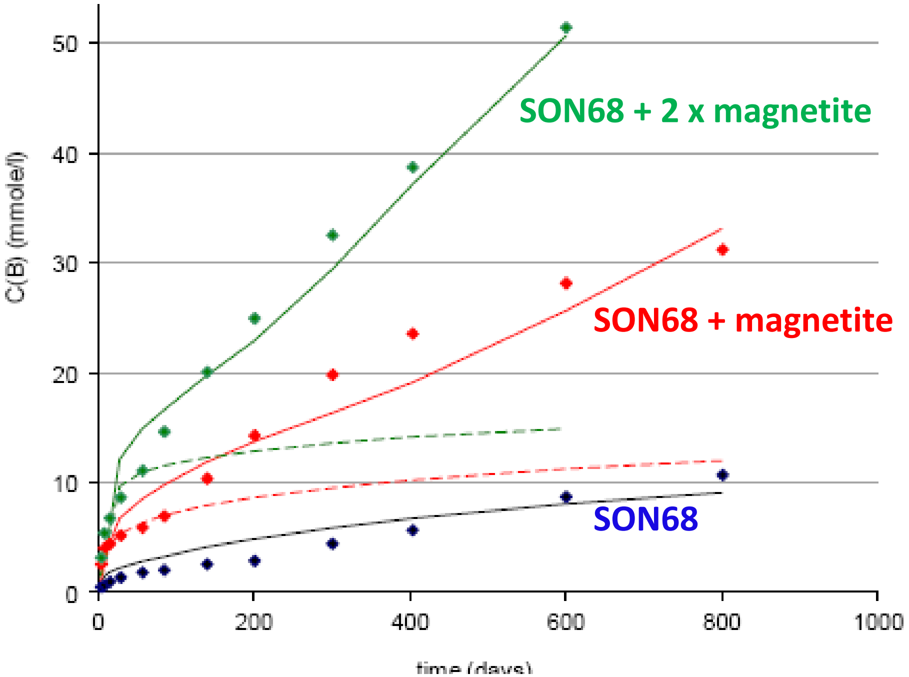


⇒ Retention of transition elements and heavy metals

I.C. Interactions between glass and iron

De Combarieu et al. (2011)

EXPERIMENT
T = 50°C
Synthetic clay-based groundwater

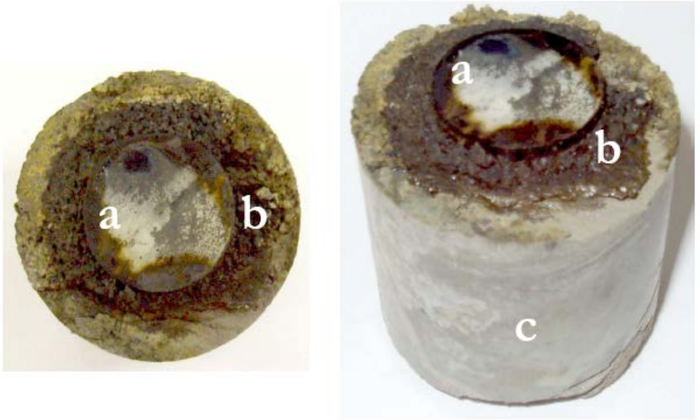


Comparison between experimental results (diamonds), modelling with sorption of Si (dashed lines) and sorption of Si + precipitation of iron silicates.

Godon et al. (2013)

⇒ Iron increases glass alteration rate due to the precipitation of Fe-silicates

EXPERIMENT
SON68 + iron (10 µm) + Bure argilite + water
T = 90°C for 18 months



⇒ Formation of Fe-silicates
⇒ Alteration thickness = $r_0/2$
⇒ Iron sustains a high alteration rate

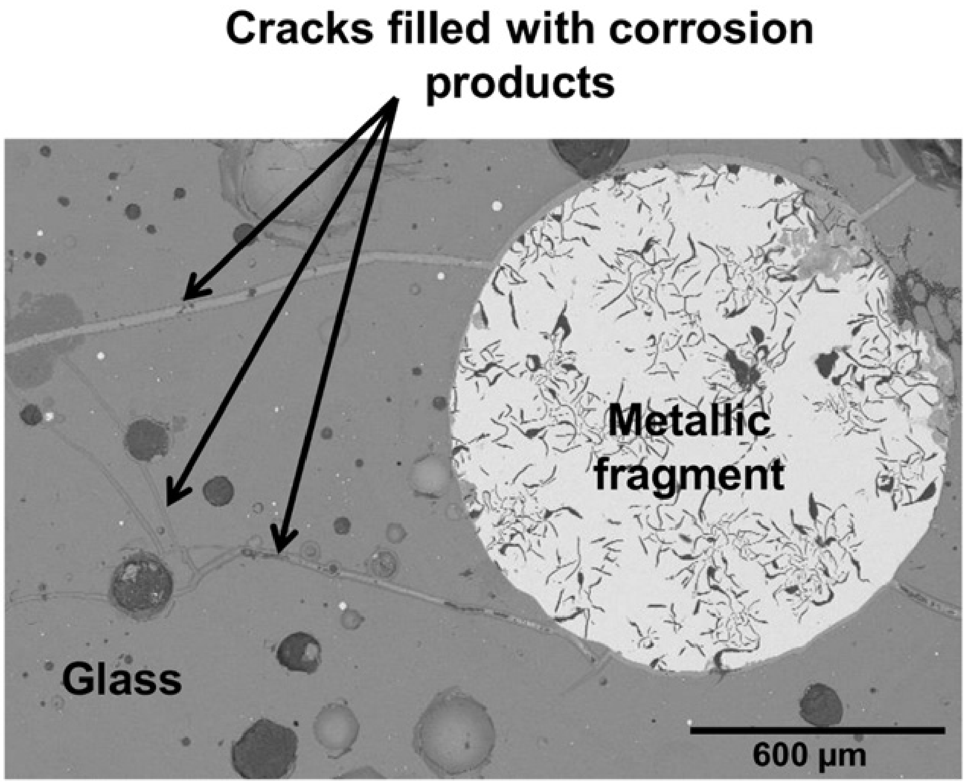
I.C. Interactions between glass and iron

Michelin et al. (2013, 2015)

VITREOUS SLAGS

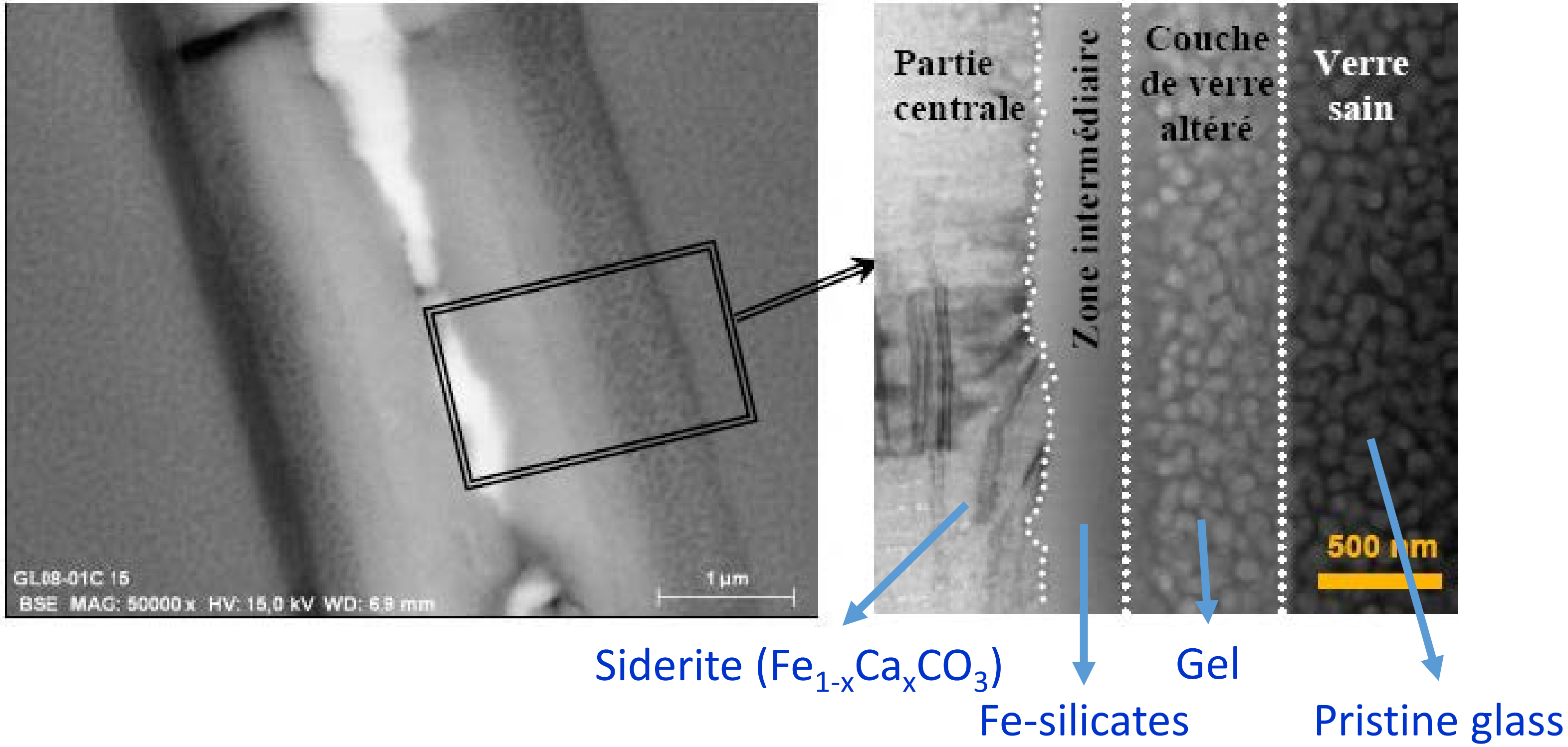
Site of Glinet (Normandy)
16th c.
Soil saturated with anoxic water

SiO_2 : 62 à 77 %, Al_2O_3 : 5 à 9 %,
CaO : 16 à 25 %



⇒ Analogy: vitreous slag / glass package and steel container

I.C. Interactions between glass and iron



Siderite ($Fe_{1-x}Ca_xCO_3$)

Fe-silicates

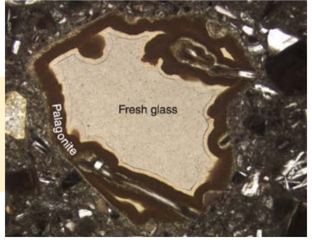
Gel

Pristine glass

Alteration thickness: ~ 20 µm (external cracks) / 2-6 µm (internal cracks)

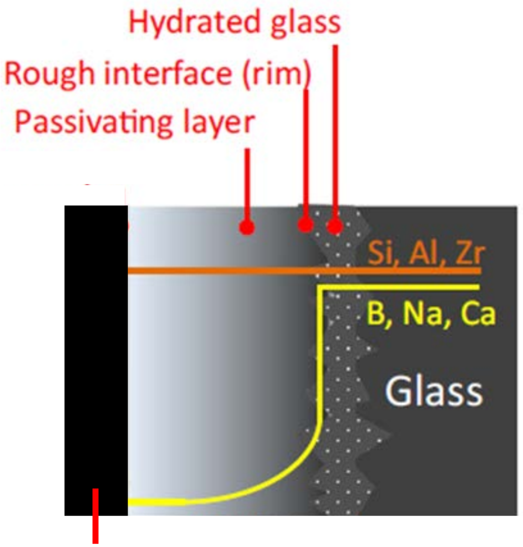
⇒ Fe-silicates precipitation is a long-term mechanism but there is a drop in the alteration rate in cracks

II. Similarities ?

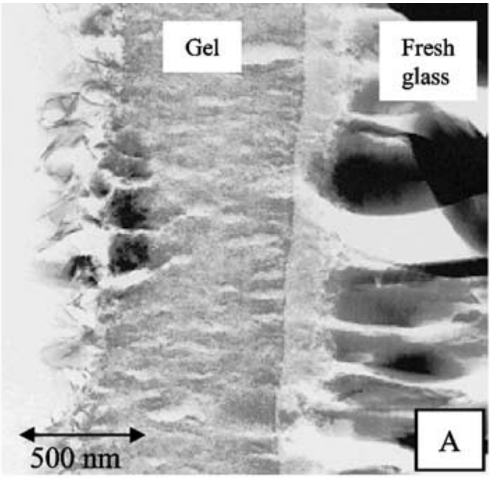


- Composition
- Phenomenology

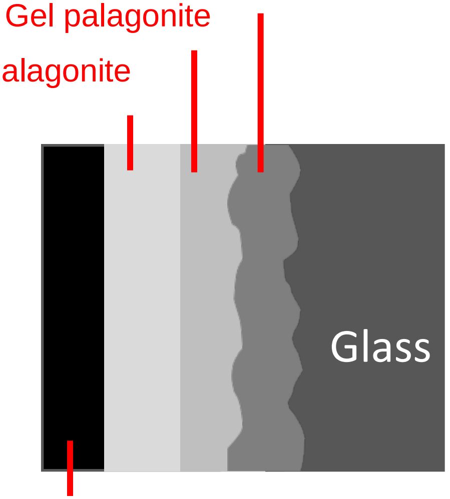
NUCLEAR GLASS


Hydrated glass
Rough interface (rim)
Passivating layer

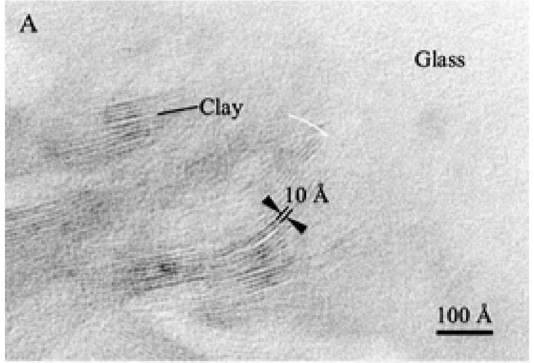
Smectites, zeolites



BASALTIC GLASS


Alteration front
Gel palagonite
Fibrous palagonite

Smectites, calcite, oxides, zeolites)



From Gin et al. (2017)
Gin et al. (2001)

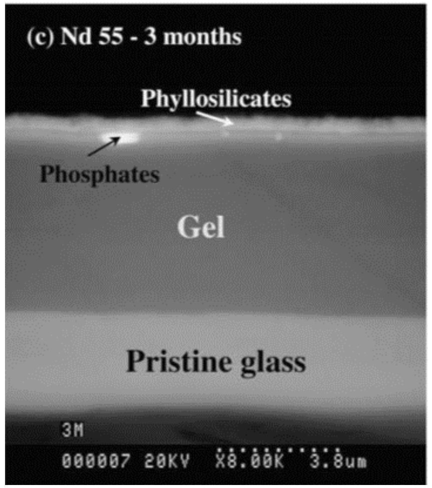
From Zhou & Fyfe (1989)
Zhou et al. (2001)

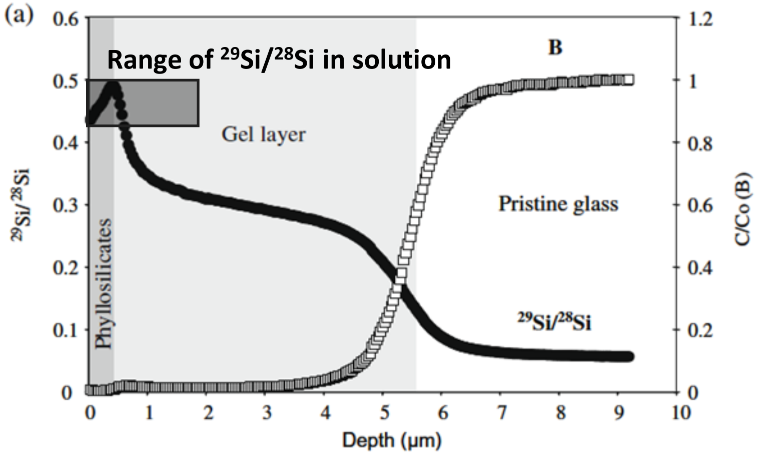
⇒ Similar alteration facies

II. Similarities ?

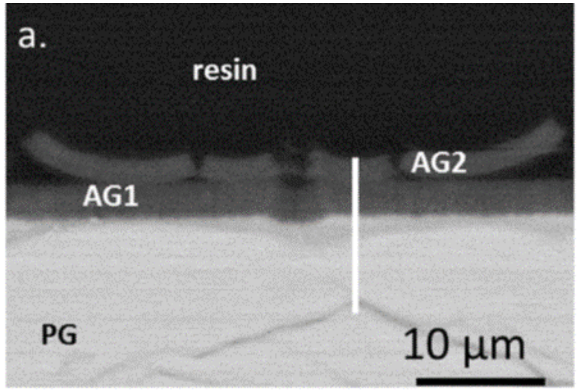
- Mechanisms: ^{29}Si tracing in solution

NUCLEAR GLASS
T = 90°C

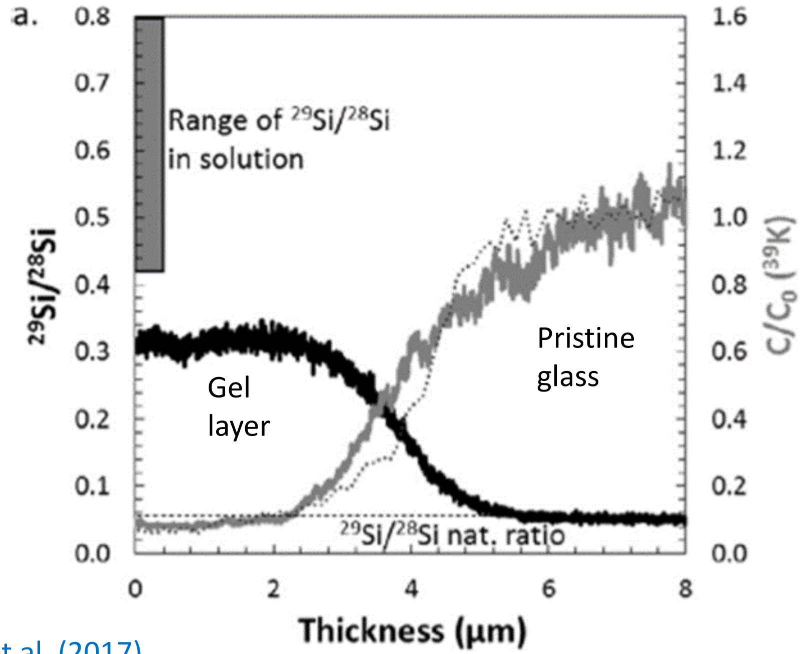




Valle et al. (2010)



STAINED GLASS
T = 30°C



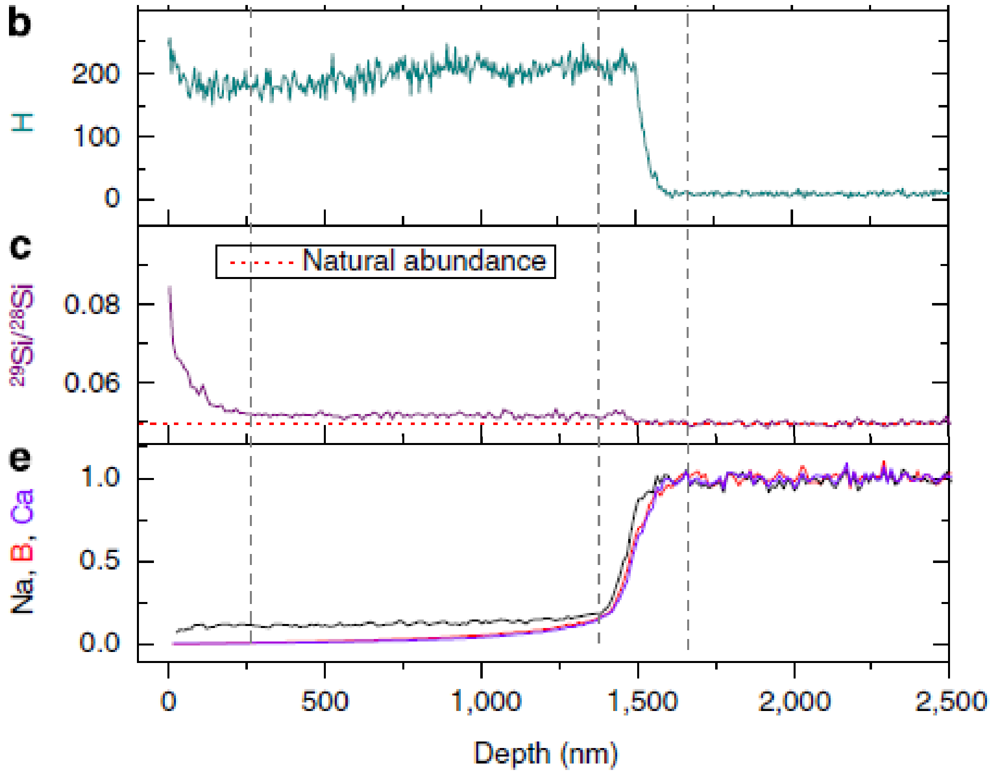
Verney-Carron et al. (2017)

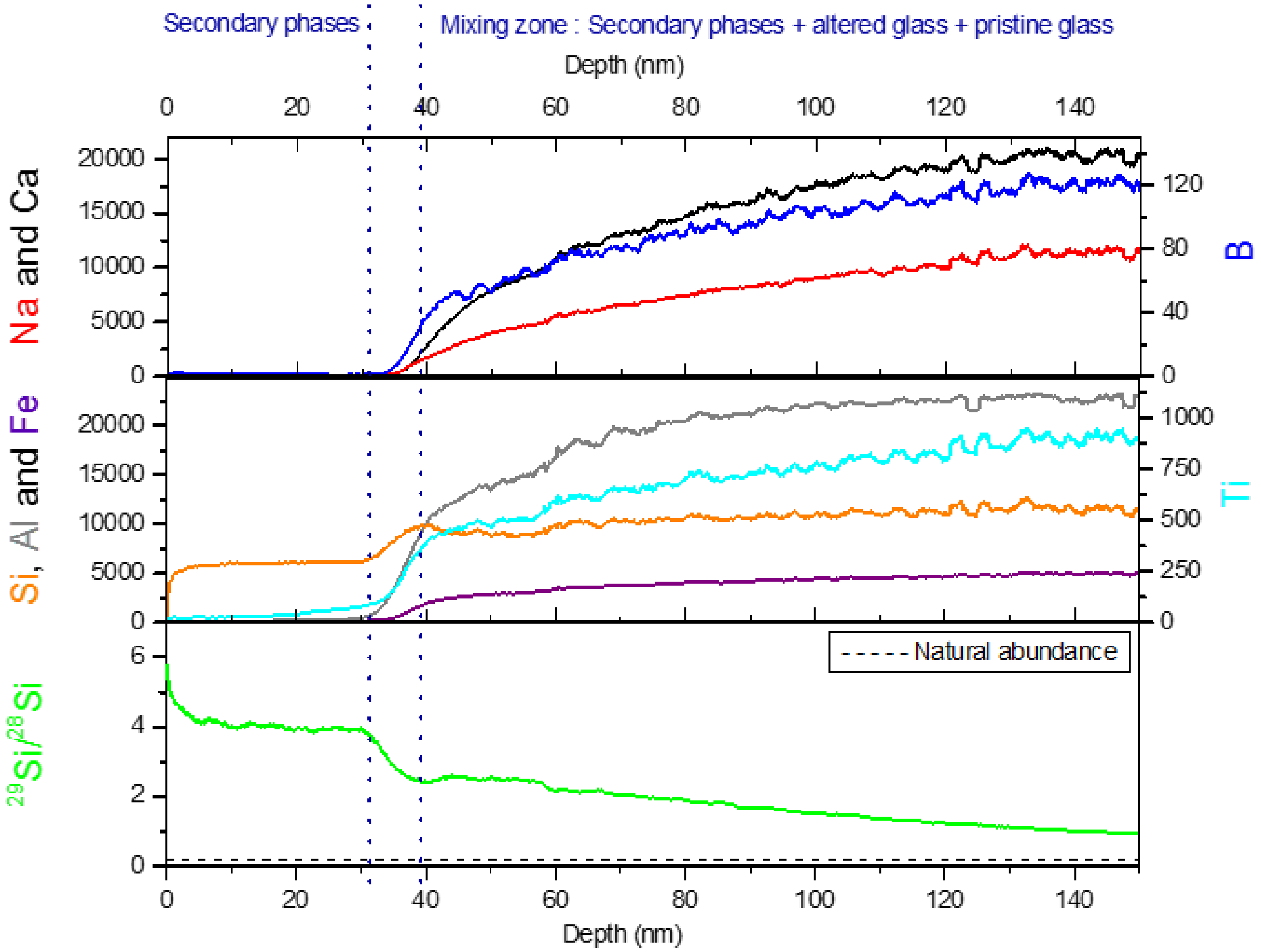
⇒ Similar mechanisms far from saturation

ISG GLASS
T = 90°C,
pH 7 and 9
Si saturated solution
t = 209 d

BASATIC GLASS
T = 90°C, pH 7 (at 90°C)
Si saturated solution
t = 600 d

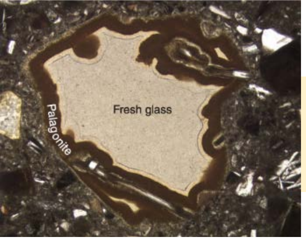
Ducasse et al. (in prep)
ISG : Gin et al. (2015,2017)



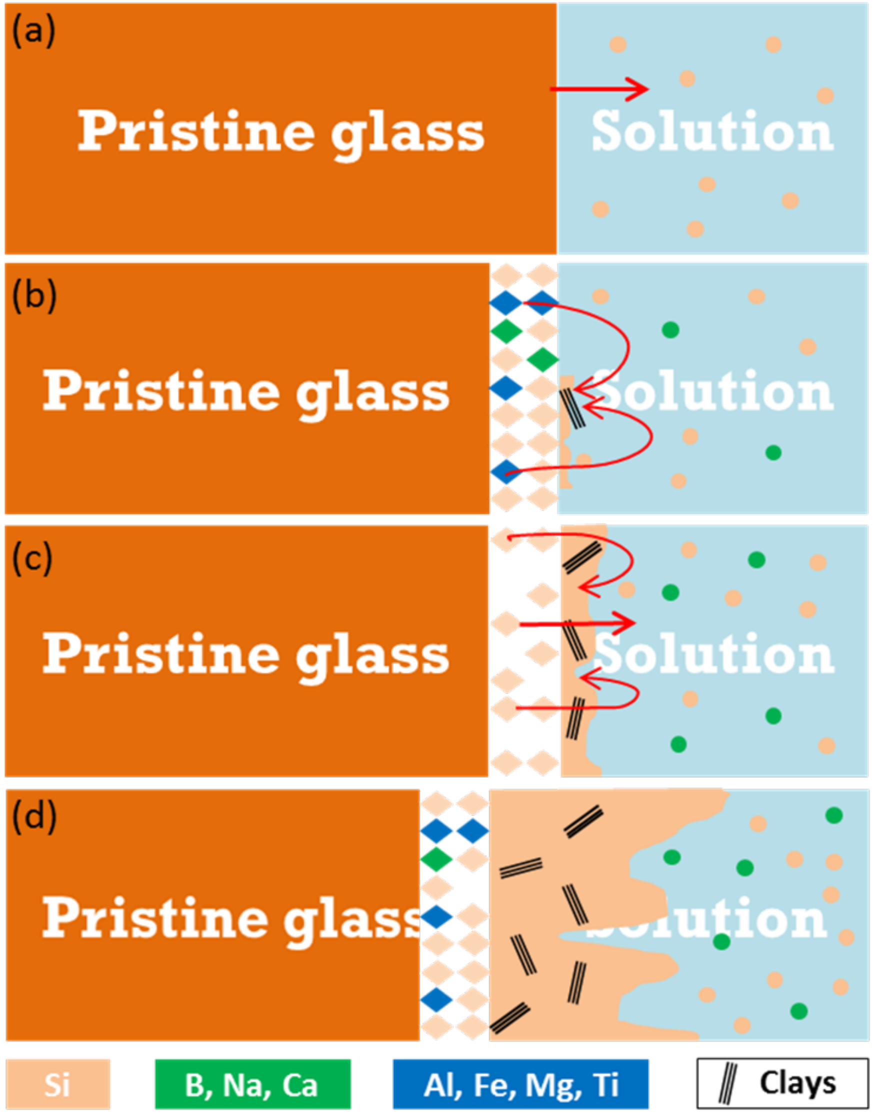


⇒ Weak interaction of ^{29}Si with gel

⇒ Enrichment in ^{29}Si in the mixing zone



II. Similarities ?



BASATIC GLASS

(a) Quick interdiffusion and hydrolysis → release of Na and Ca and B
(b) Precipitation of clays (Si, Al, Fe, Mg, Ti) and SiO_2(am)
(c) The remaining silicate network dissolves and SiO_2(am) precipitates
(d) The layer of secondary phases grows up, sustaining glass dissolution

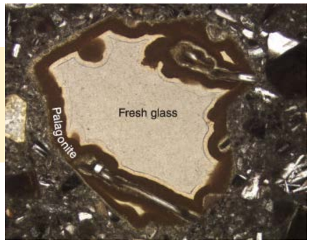
COMPARISON WITH NUCLEAR GLASS

⇒ Differences with ISG Glass
ISG: selective dissolution → passivating layer (glass alteration is limited by water diffusion)

BG: congruent dissolution → clays (equilibrium)
The dissolution is controlled by the hydrolysis of the glass network and is sustained by the precipitation of secondary phases.

Ducasse et al. (in prep)
ISG : Gin et al. (2015,2017)

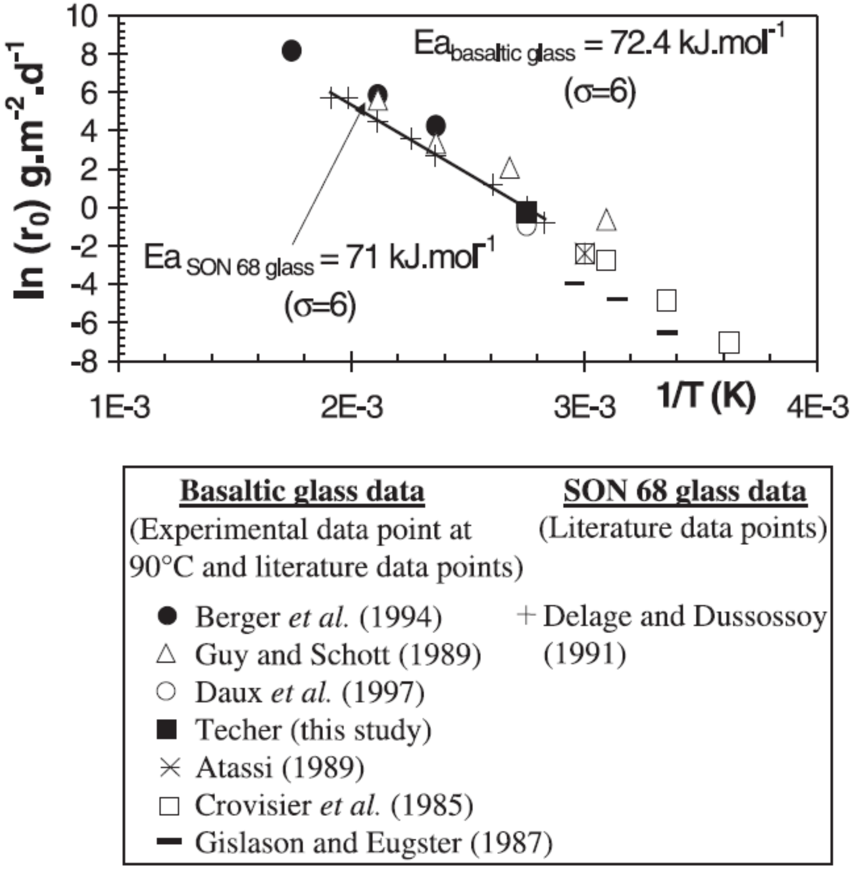
II. Similarities ?



- Kinetics

NUCLEAR / BASALTIC GLASS

Forward dissolution rate



Techer et al. (2000)

Residual rate

Parruzot et al. (2015)

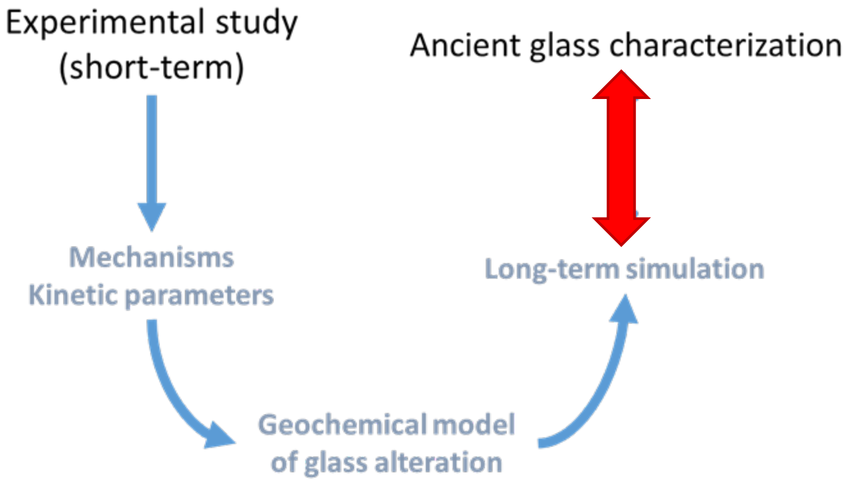
- r_r (BG) = $9.6 \cdot 10^{-6}$ g/m²/d (90°C)
- r_r (NG) = $2 \cdot 10^{-4}$ g/m²/d (90°C)

⇒ Similar alteration rates

Summary

- To a unified understanding of glass alteration
- Similar alteration facies
- Similar mechanisms with a different contribution as a function of glass composition and environmental conditions (kinetics)
- Kinetics dependent of the glass composition and structure

III. Glass alteration modelling


Experimental study (short-term)

Mechanisms
Kinetic parameters

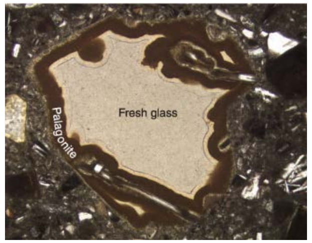
Geochemical model of glass alteration

Long-term simulation

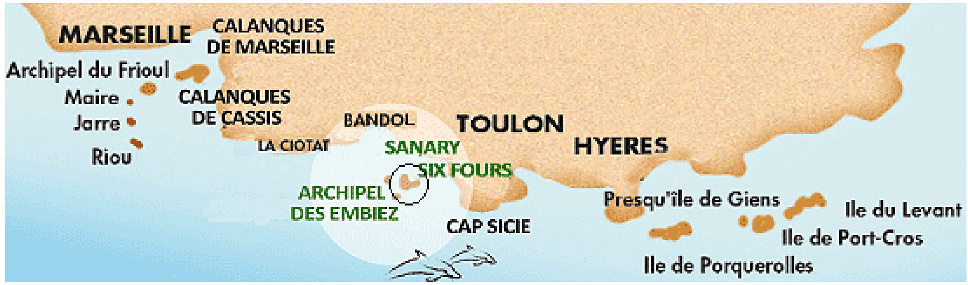
Ancient glass characterization

Simple geochemical model applied to Roman glass
(Verney-Carron et al., 2008, 2010a,b)

GRAAL model applied to basaltic glass
(PhD Ducasse in progress)

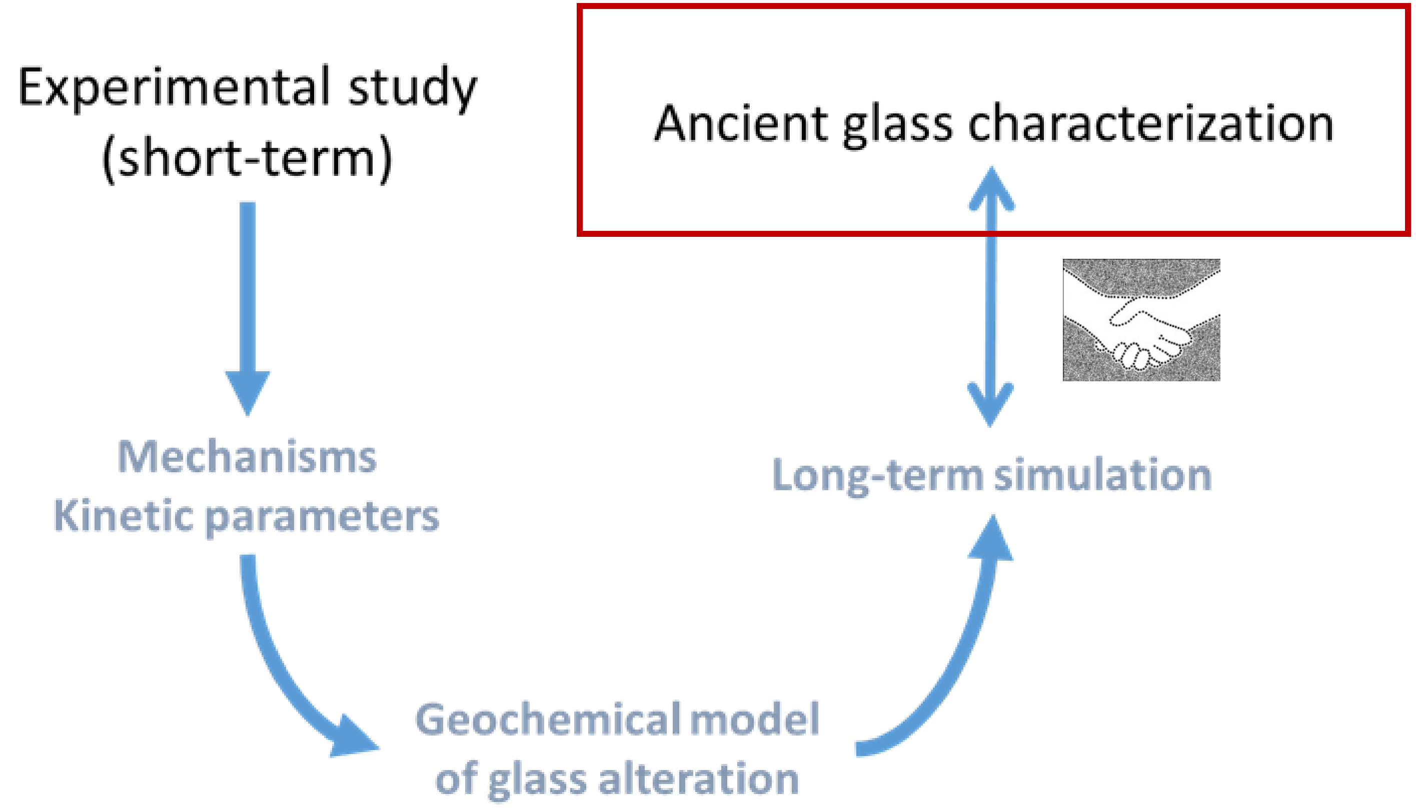


III.A. Roman glass alteration modeling



Alteration for 1800 years
In a stable environment
(seawater at 15°C)

Morphological analogy



Experimental study
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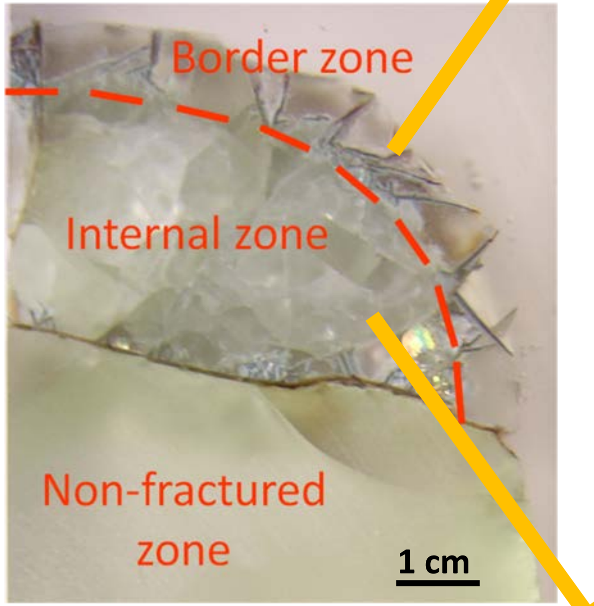
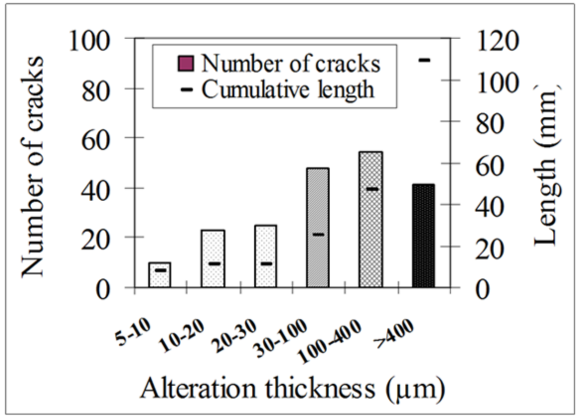
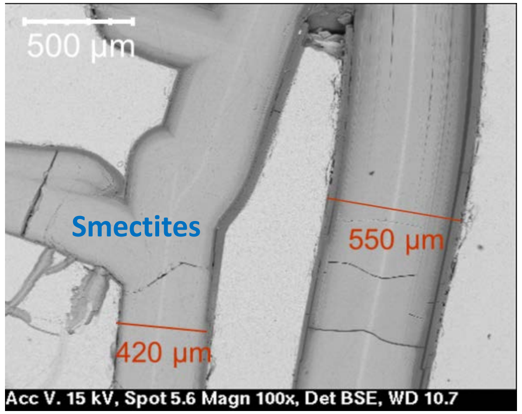
ALTERATION PHENOMENOLOGY

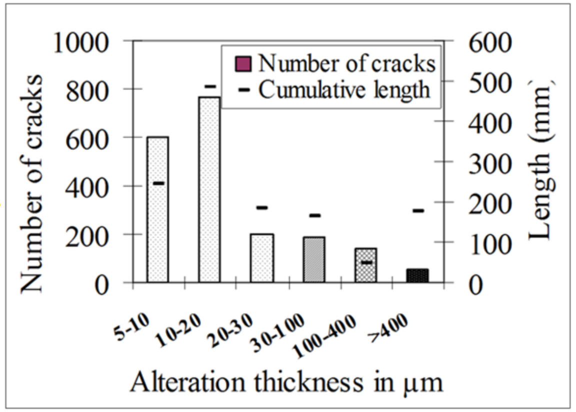


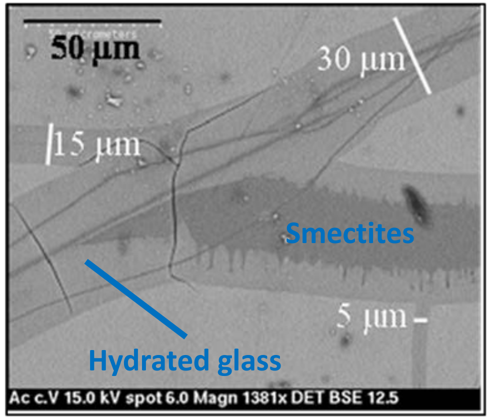




Border zone (BZ)

- Thick altered cracks
- Smectites
- 84 % of total alteration

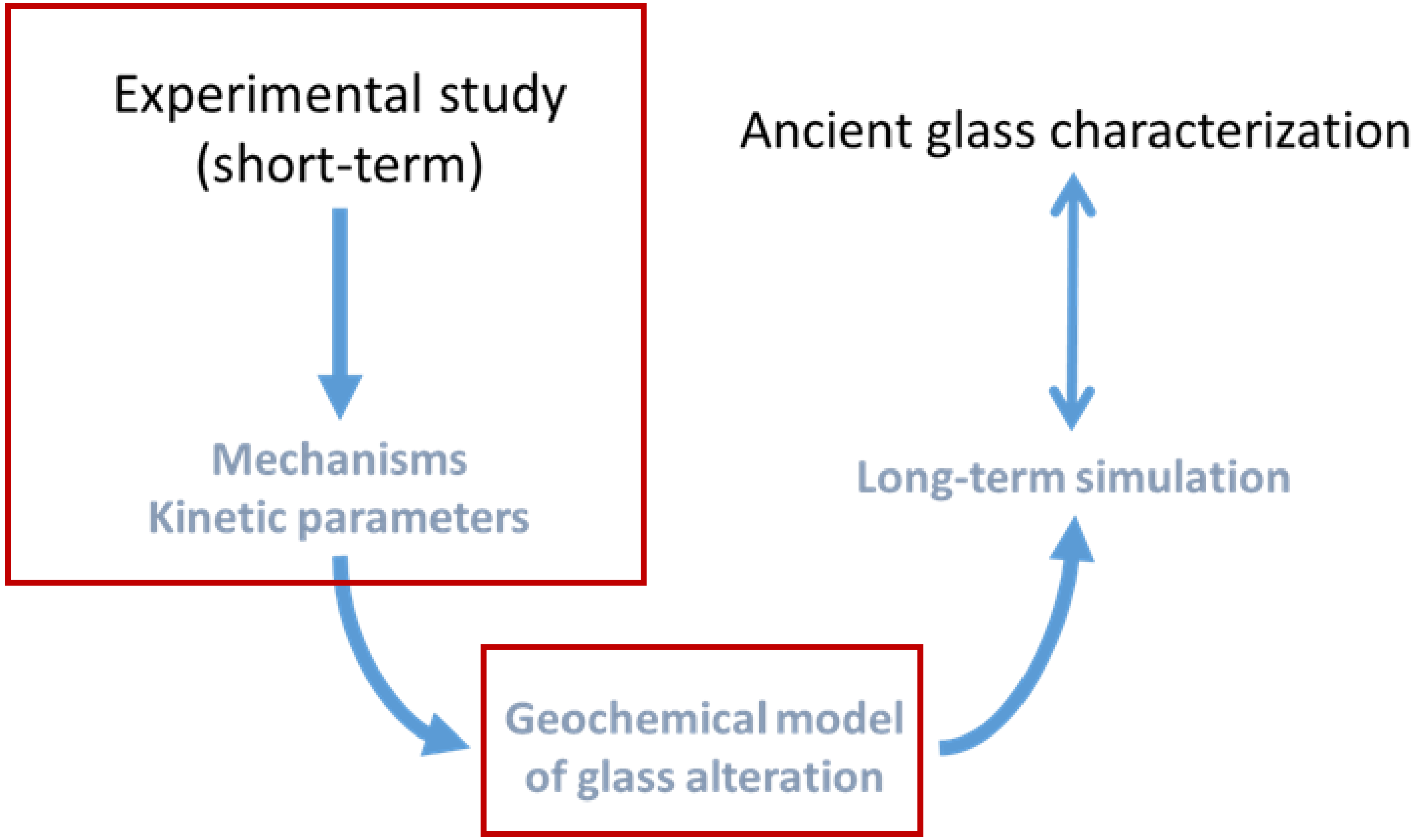




Internal zone (IZ)

- Thin altered cracks (5-20 µm)
- Hydrated glass (and smectites)
- Cracks density 6x higher
- 16 % of total alteration

⇒ Low contribution of internal cracks to global alteration (+ sealing)



Experimental study
(short-term)

Mechanisms
Kinetic parameters

Geochemical model
of glass alteration

Long-term simulation

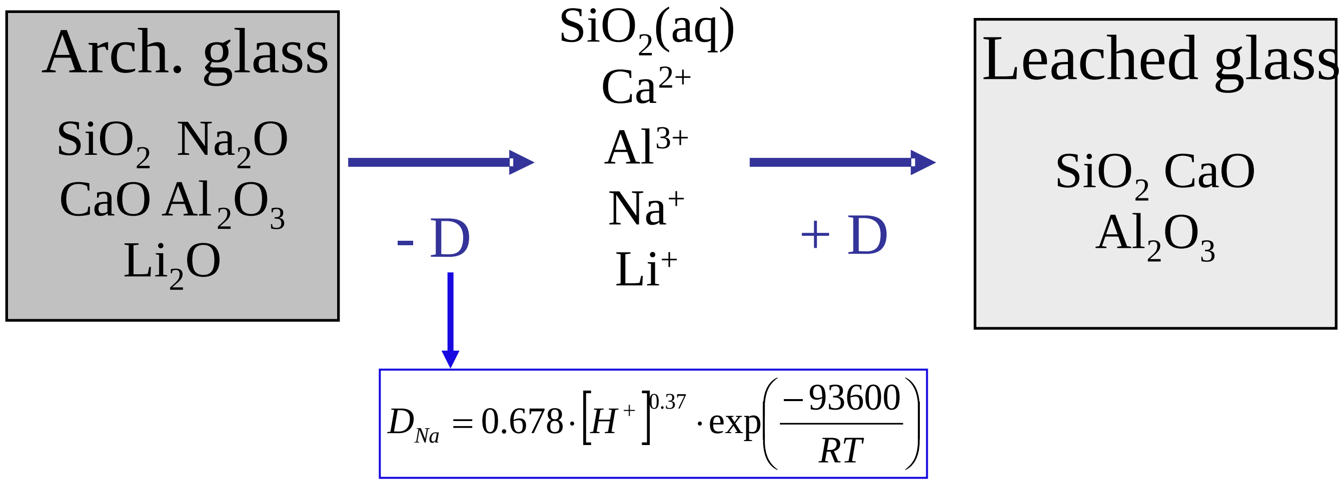
Ancient glass characterization

GEOCHEMICAL MODEL

van der Lee (2005) ; van der Lee et De Windt (2002) ; Lagneau (2005)

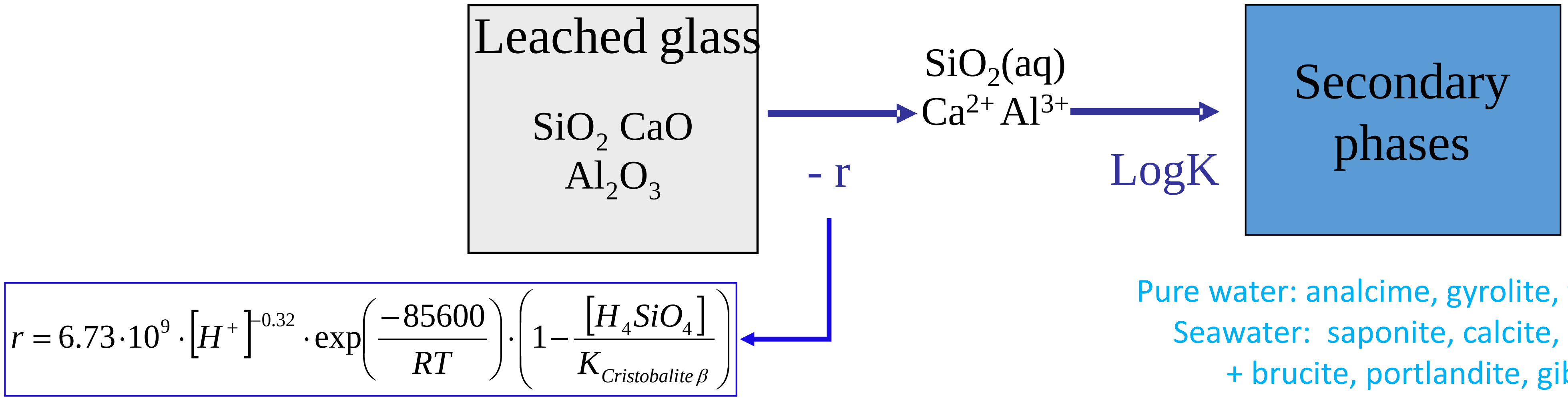
HYTEC software
Thermodynamic database (Chess – EQ3/6)

1st step: interdiffusion

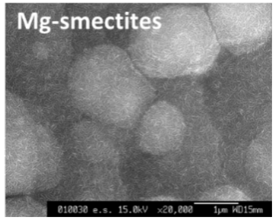


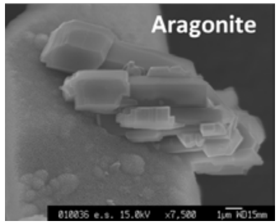
$$D_{Na} = 0.678 \cdot \left[H^+\right]^{0.37} \cdot \exp\left(\frac{-93600}{RT}\right)$$

2nd step: dissolution/precipitation



$$r = 6.73 \cdot 10^9 \cdot \left[H^+\right]^{-0.32} \cdot \exp\left(\frac{-85600}{RT}\right) \cdot \left(1 - \frac{\left[H_4SiO_4\right]}{K_{Cristobalite\,\beta}}\right)$$

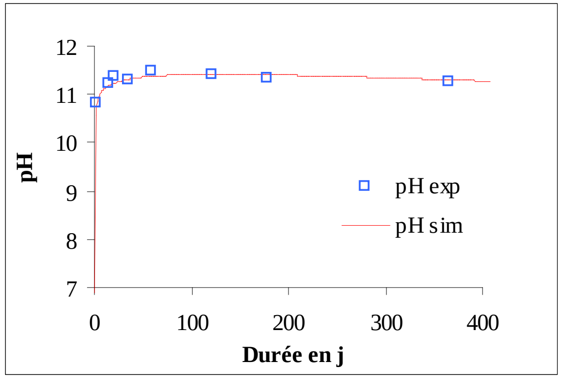


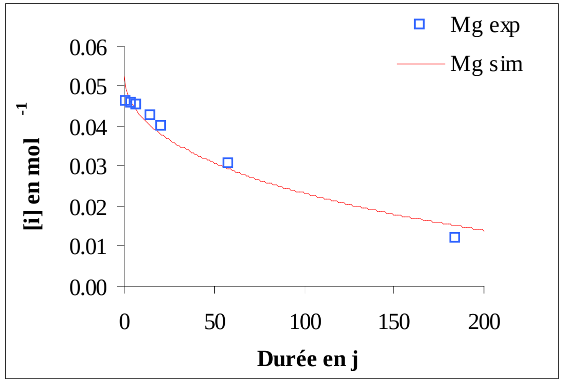


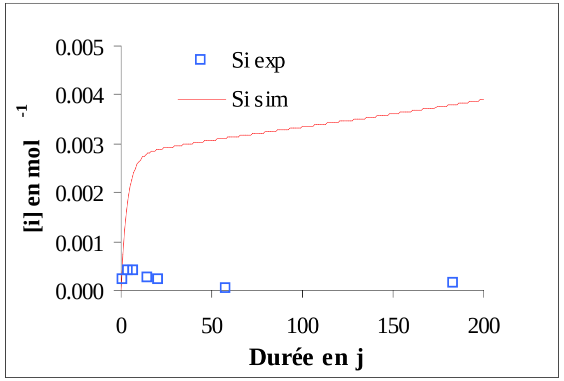
Pure water: analcime, gyrolite, tobermorite
Seawater: saponite, calcite, aragonite
+ brucite, portlandite, gibbsite

EXPERIMENTAL VALIDATION

Experiment in seawater at 50°C and SA/V = 20 cm^{-1}







SUMMARY

- ✓ Alkalis and pH: good simulation

  pH is an important parameter of the coupling between chemistry and transport

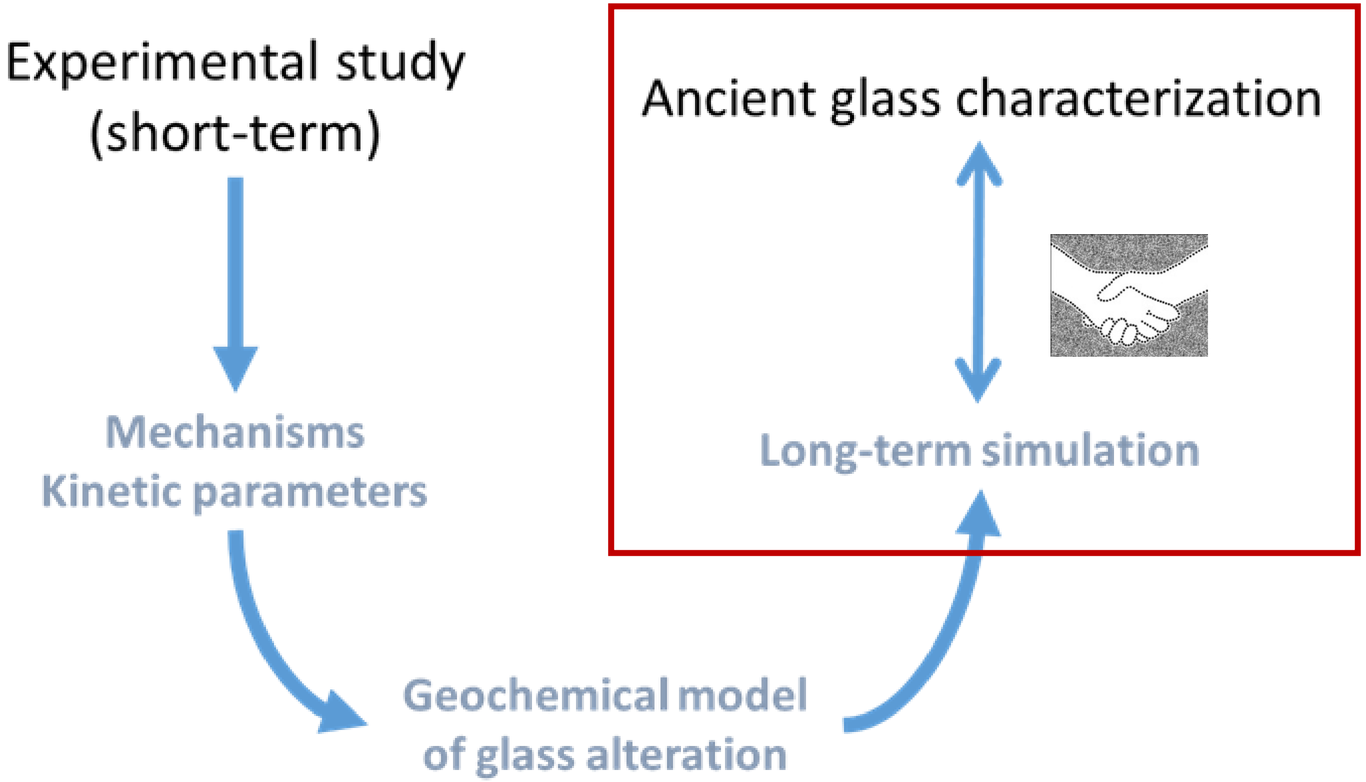
- ✓ Ca: underestimated at low pH due to its release by interdiffusion

  However, Ca is highly concentrated in seawater

- ✓ Si: overestimated at high pH (interactions with Ca) and in seawater (stoichiometry)

  Change of the database (smectites)

⇒ The chemical model can be coupled with transport and tested on long-term



Experimental study (short-term)

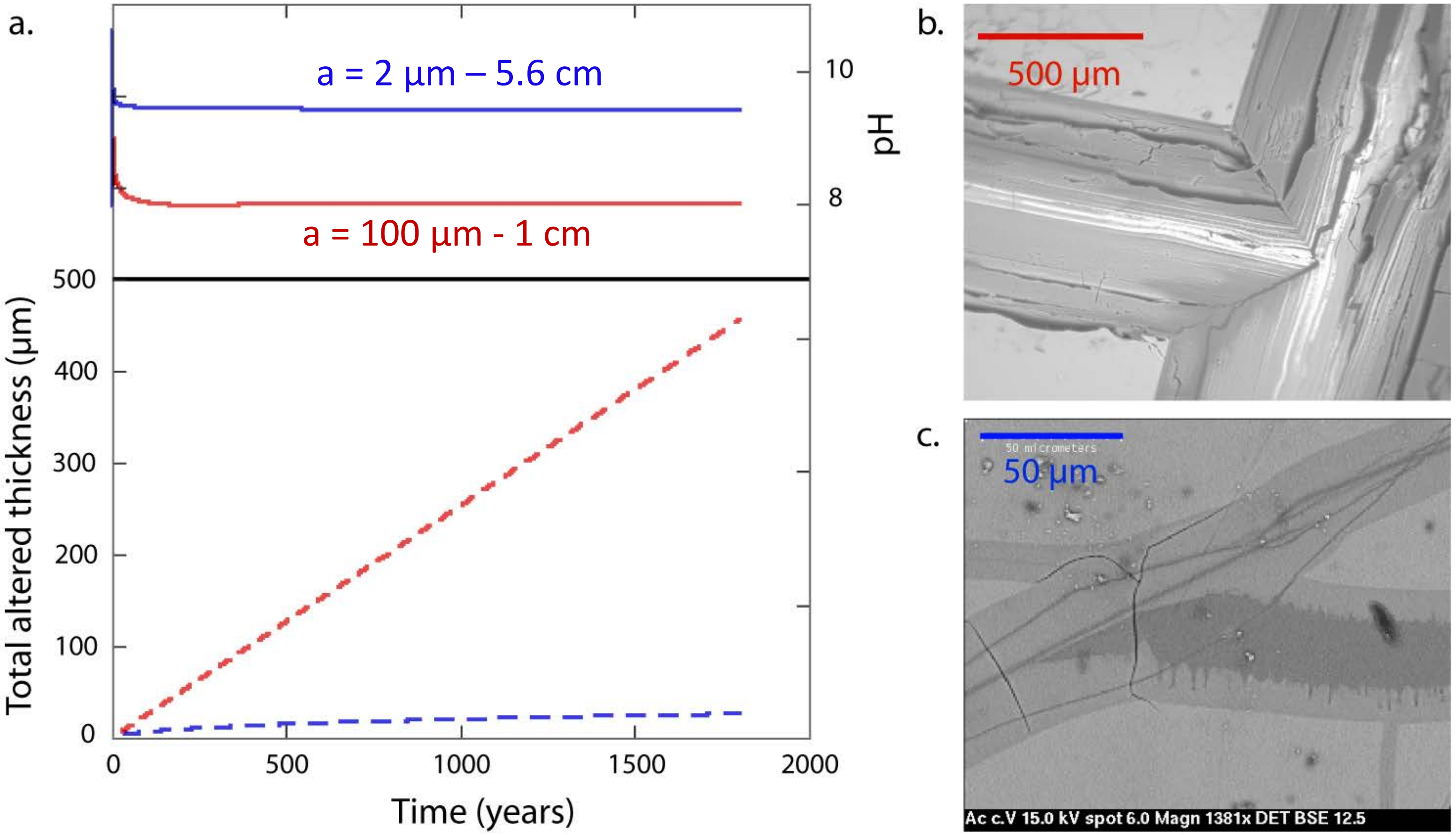
Mechanisms
Kinetic parameters

Geochemical model of glass alteration

Long-term simulation

Ancient glass characterization

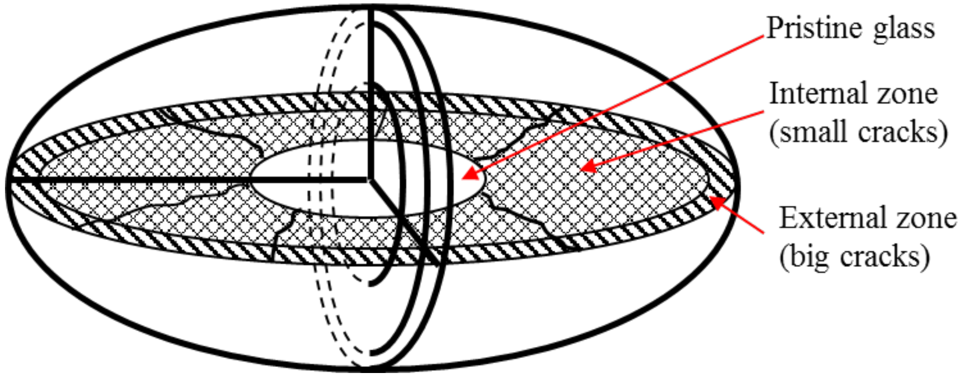
Simulation results of 2 cracks (≠ apertures a and ≠ distance from the external surface)



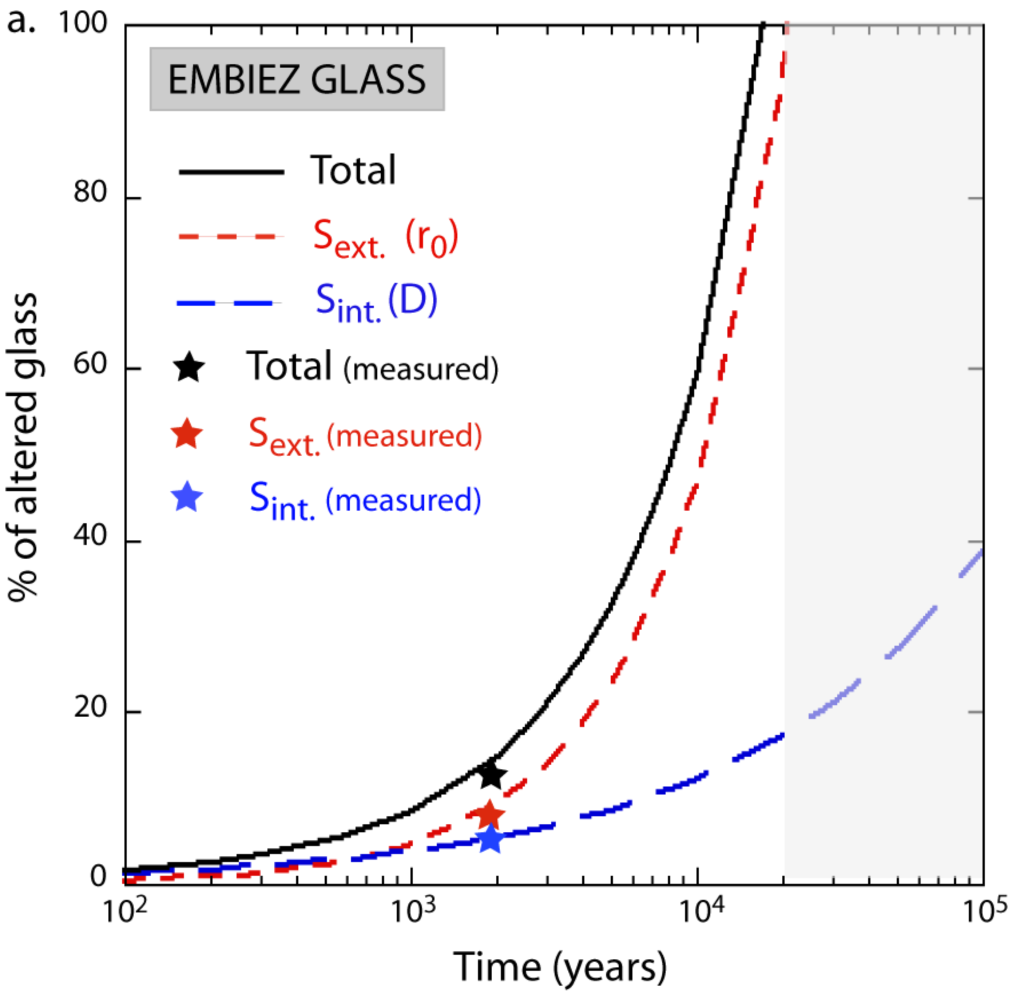
⇒ The external cracks are in contact with a diluted medium → r_0

⇒ Strong coupling between chemistry and transport

⇒ Good agreement between simulations and observations
⇒ Validation of the predictive capacity of the geochemical model



$S_{ext} = 7 \times S_{geo}$
$S_{int} = 79 \times S_{geo}$

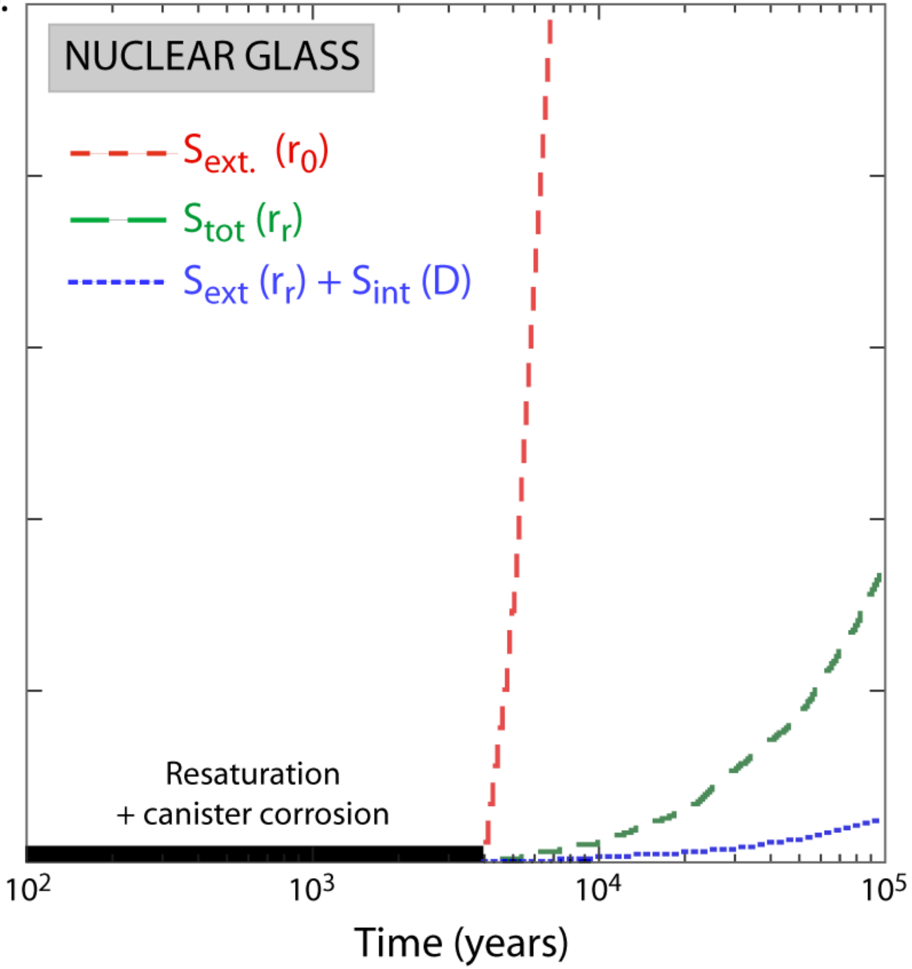


⇒ If only the internal surfaces were leached, more than 650,000 years would be necessary for complete alteration of the Roman glass blocks, but external surfaces alteration would limit the lifetime to about 20,000 years.

Transposition to nuclear glass alteration

S_{geo} = 1.7 m²
S_{ext} = 5 x S_{geo}
S_{int} = 40 x S_{geo}
T = 50°C (after 4000 years)
r_0 = 5.1 µm/y
r_r = 0.008 µm/y
D (50°C, pH 7) = $6.8 \cdot 10^{-23}$ m²/s

b.



⇒ If like for Roman glass, internal surfaces are controlled by diffusion, 5% of alteration after 100 000 years.

Outcomes

- Important to study other kinds of glasses
  → General understanding of glass alteration (even minerals)
  → Questions raised by the differences

- Important to continue the modeling work
  → To demonstrate the feasibility and the predictive capacity
  → To extend the range of applications of nuclear glass models

Skylights in Seattle