Aging of nuclear glass analogues

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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

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Objectives of analogs study

❑ To know the long-term alteration

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

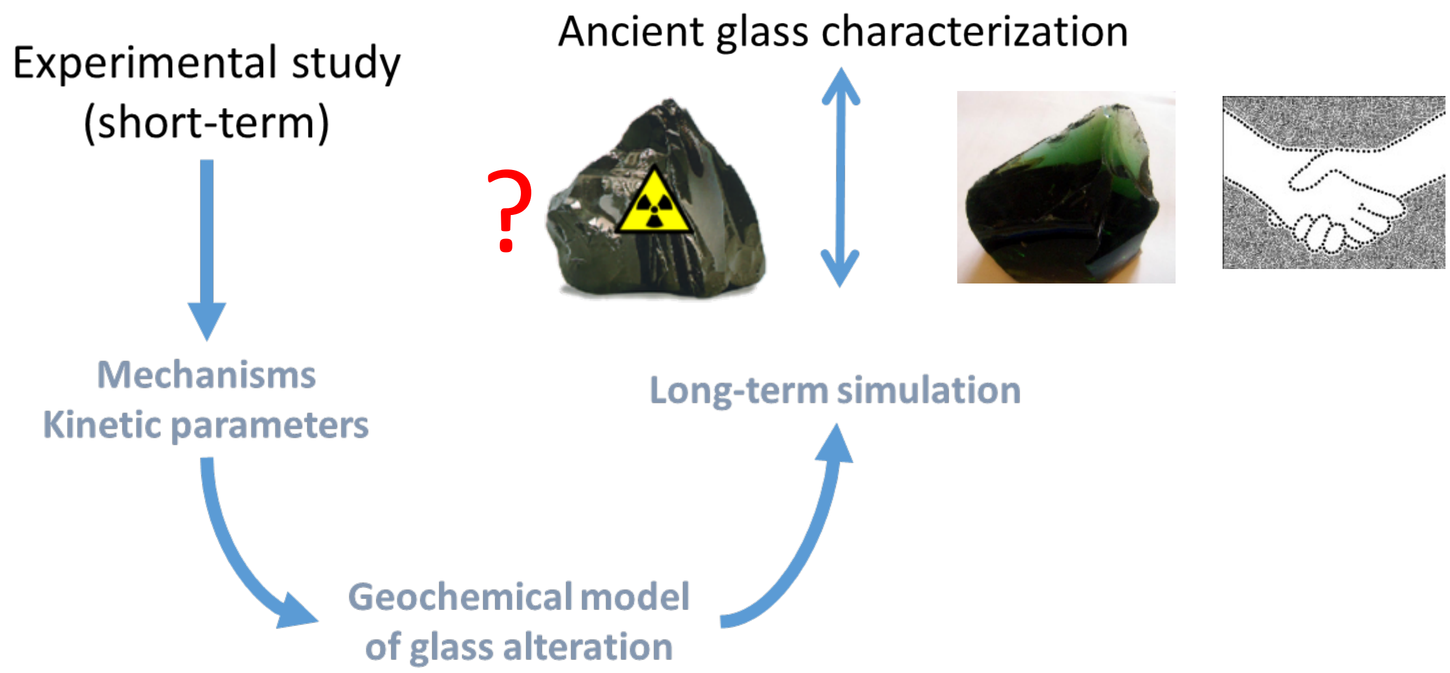
- A is similar to C in certain known respects.
- A has some further feature B.
- Therefore, probably, C also has the feature B.

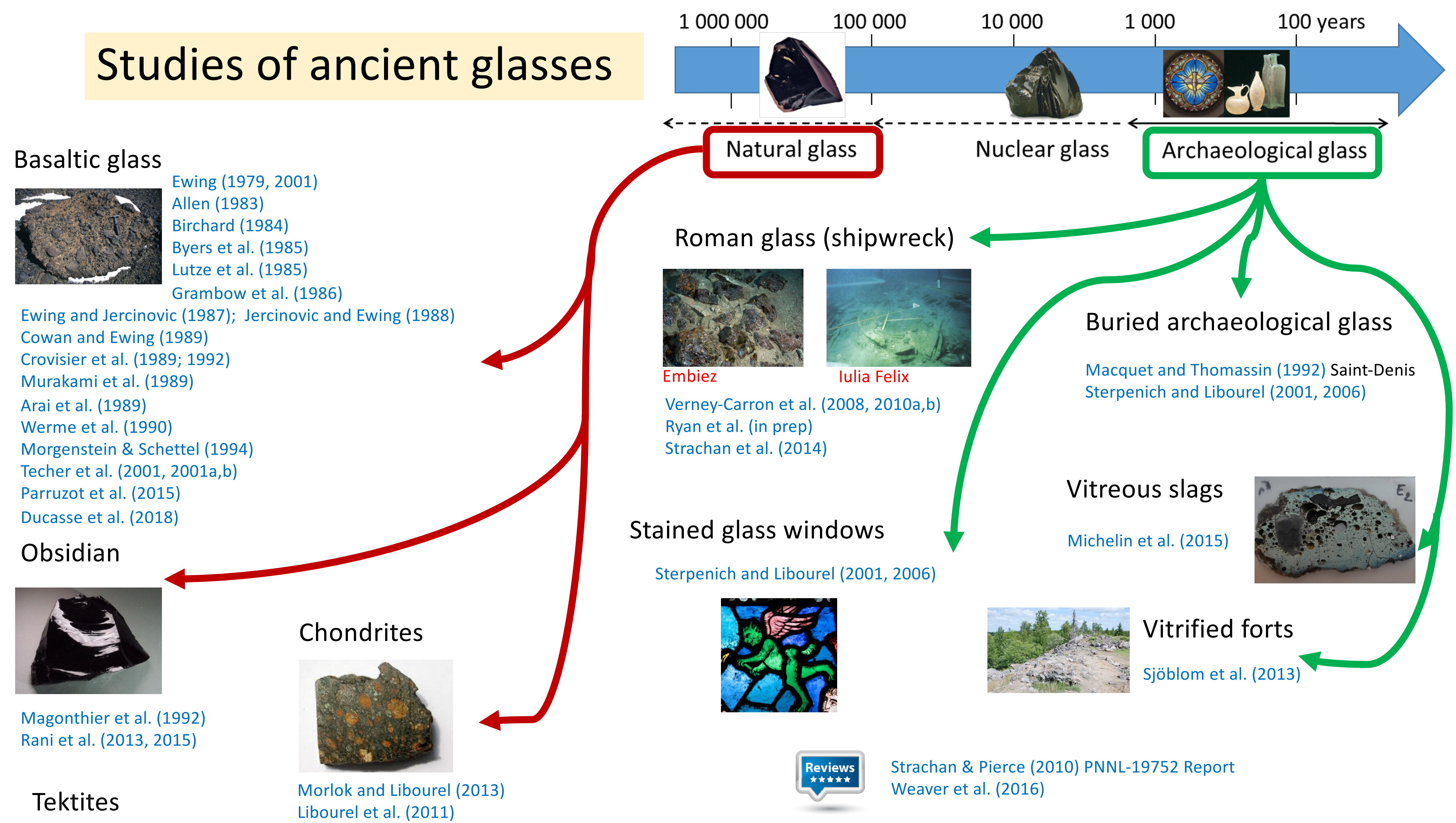
✓ Different examples : long-term durability of natural glasses, retention of transition elements used as colorants in stained glass windows, contribution of cracks of Roman glass blocks, …

✓ It requires to demonstrate the analogy between the different glasses

Objectives of analogs study

- To validate the predictive capacity of alteration models





Studies of ancient glasses
1 000 000
100 000
10 000
1 000
100 years
Natural glass
Nuclear glass
Archaeological glass
Basaltic glass
Ewing (1979, 2001)
Allen (1983)
Birchard (1984)
Byers et al. (1985)
Lutze et al. (1985)
Grambow et al. (1986)
Ewing and Jercinovic (1987); Jercinovic and Ewing (1988)
Cowan and Ewing (1989)
Crovisier et al. (1989; 1992)
Murakami et al. (1989)
Arai et al. (1989)
Werme et al. (1990)
Morgenstein & Schettel (1994)
Techer et al. (2001, 2001a,b)
Parruzot et al. (2015)
Ducasse et al. (2018)
Obsidian
Magonthier et al. (1992)
Rani et al. (2013, 2015)
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)

Order

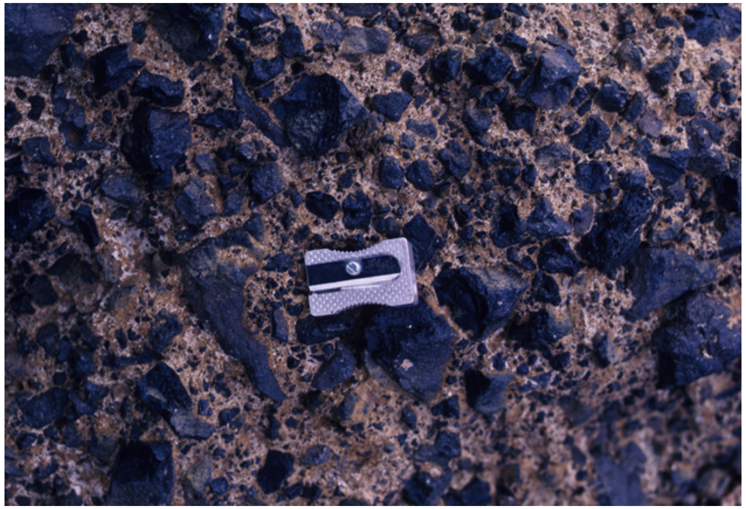
A- NATURAL GLASSES

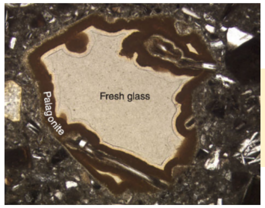
- I. Volcanic glasses
- II. Properties: long-term durability
- III. Analogy between basaltic glass and nuclear glass
- IV. Analogy between obsidian and nuclear glass
- V. Primitive meteorites (chondrites)

B- HUMAN-MADE GLASSES

- I. The stained glass windows
- II. Vitreous slags : interactions glass / iron
- III. Roman glass alteration modeling
- IV. Pre-viking Swedish hillfort glass / LAW glasses

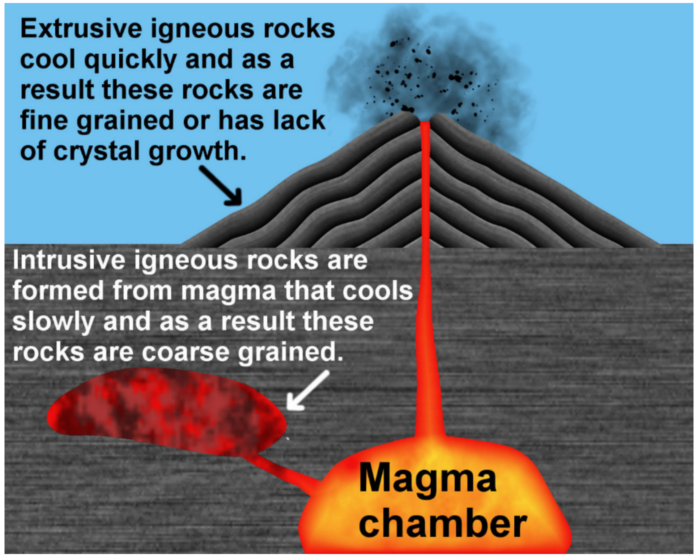
A- Natural glasses

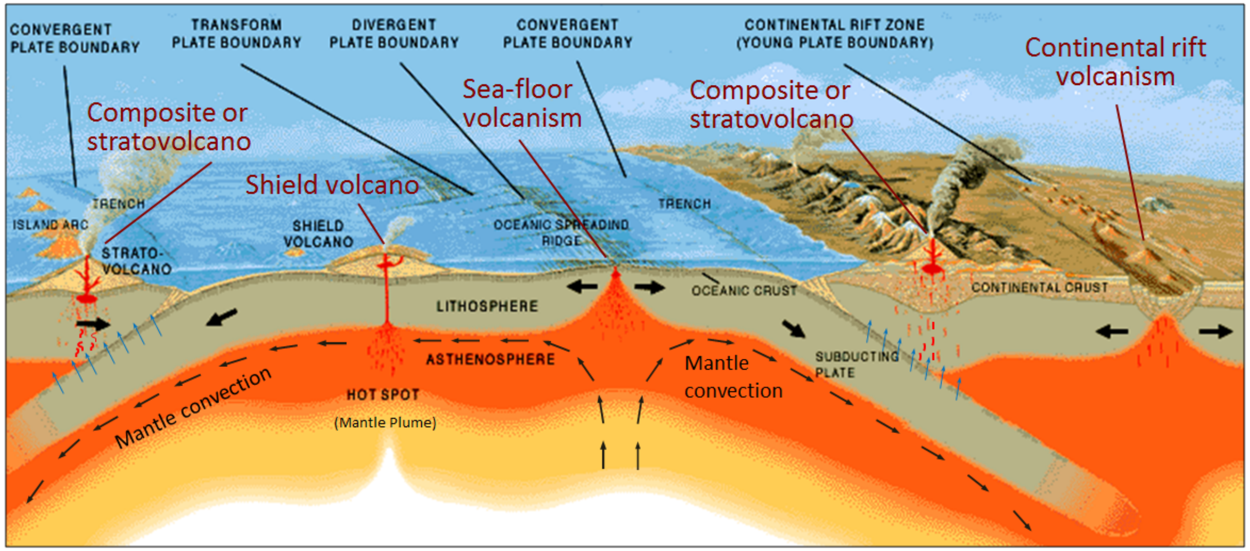




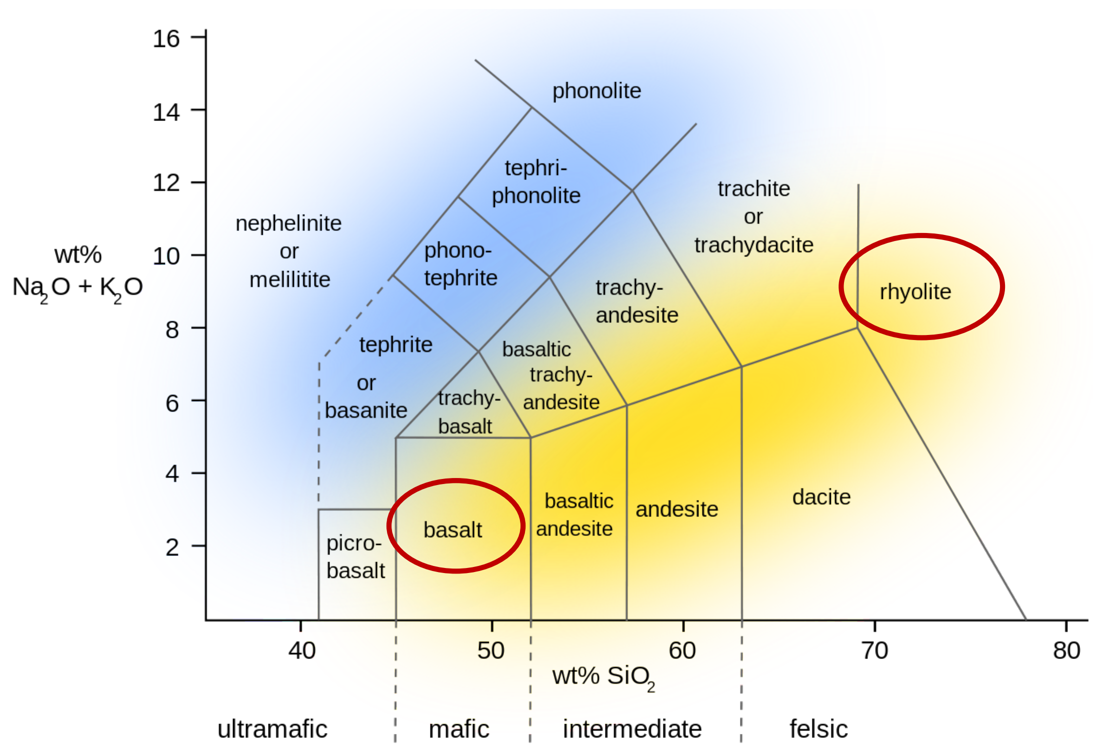
I. Volcanic glasses

Volcanic rocks are formed by the fast cooling of magma (lava) at the Earth surface in different geodynamic contexts.





The composition influences the viscosity and the vitrification.



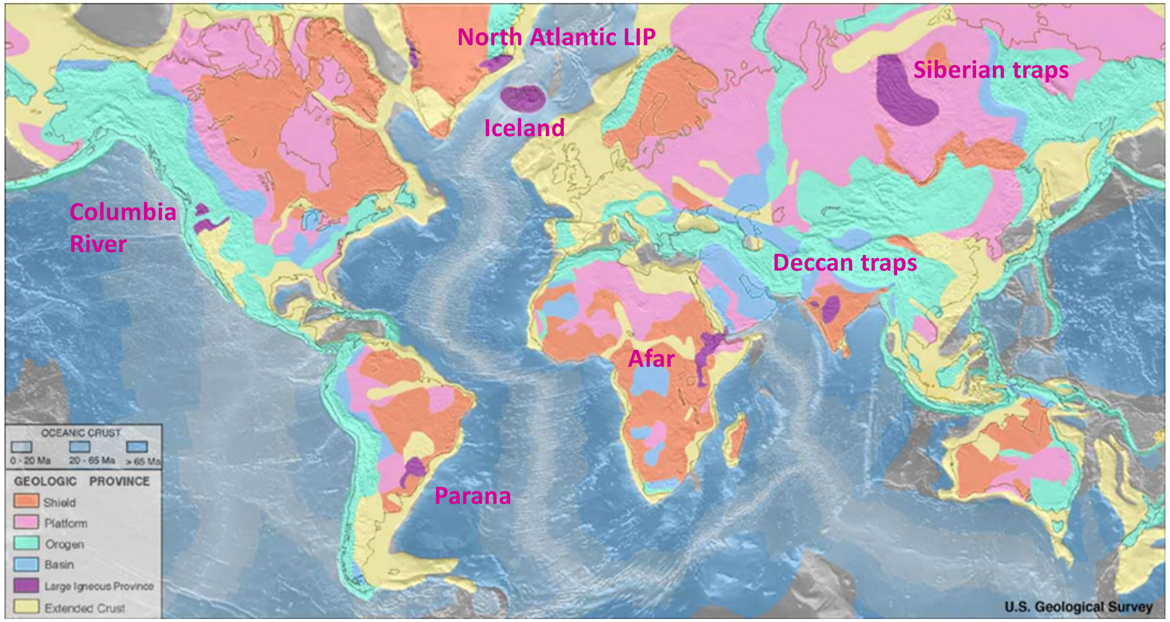
Glass < high viscosity (to inhibit the crystallization) + sudden cooling to chill the material to a glass

BASALTIC GLASS

Low viscosity → high cooling rate (oceanic seafloor, subglacial volcanoes)

Pillow lavas in Iceland (vitreous crust)

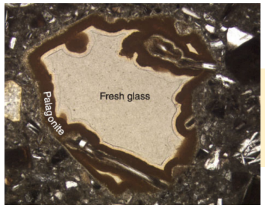
Hyaloclastites



Main locations of natural glasses: oceanic seafloor and Large Igneous Provinces (LIP)

OBSIDIAN

high viscosity but rare



II. Properties : long-term durability

J.-L. Crovisier et al. / Journal of Nuclear Materials 321 (2003) 91–109

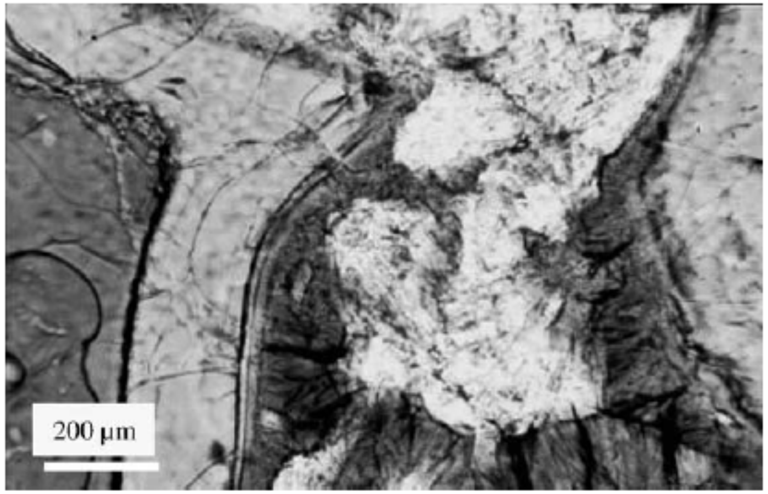
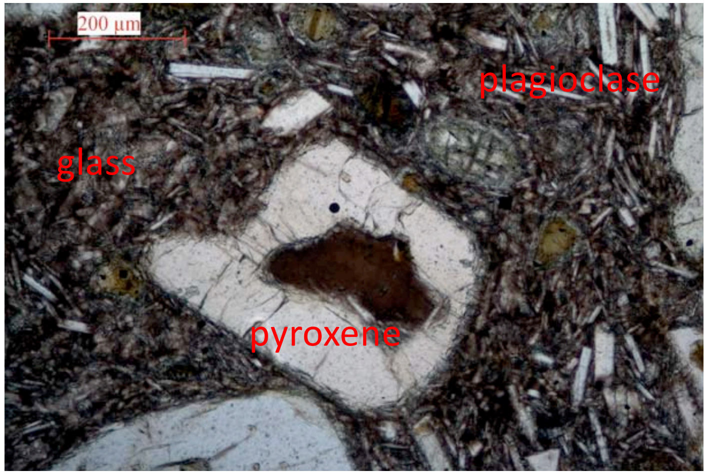


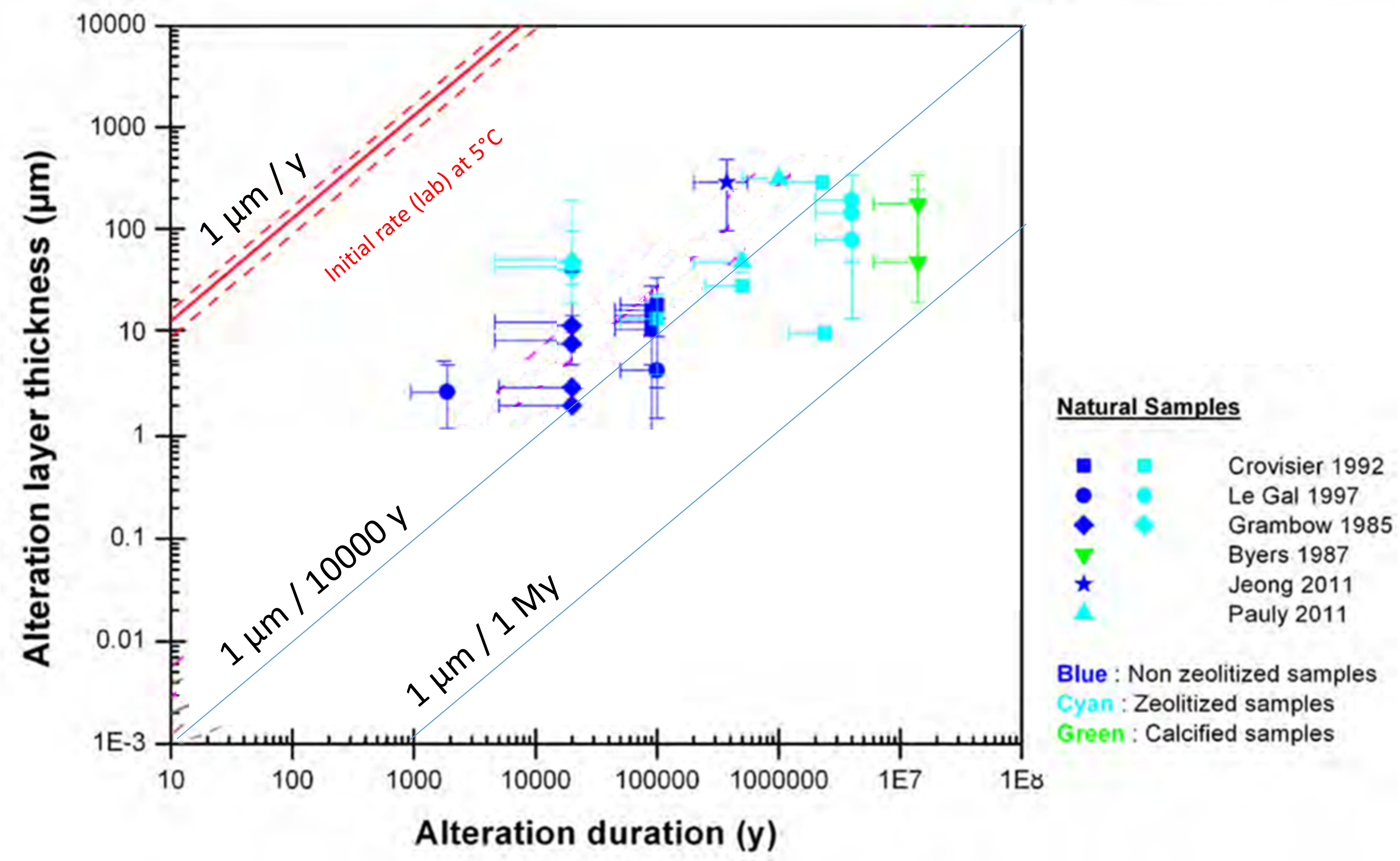
Fig. 7. Optical micrograph of subglacial Icelandic glass sample (3–4 My). Vatnajökull Region [43].

Richet (2009) Verre



Rocks from Figeac (Lot, France) – 280 My

⇒ **Old** natural glasses despite tectonic and erosion



Parruzot (2015)

⇒ **The apparent alteration rate decreases with time.**

⇒ **The field alteration rate (confined medium) is lower than the lab alteration rate.**

Parruzot et al. (2015)

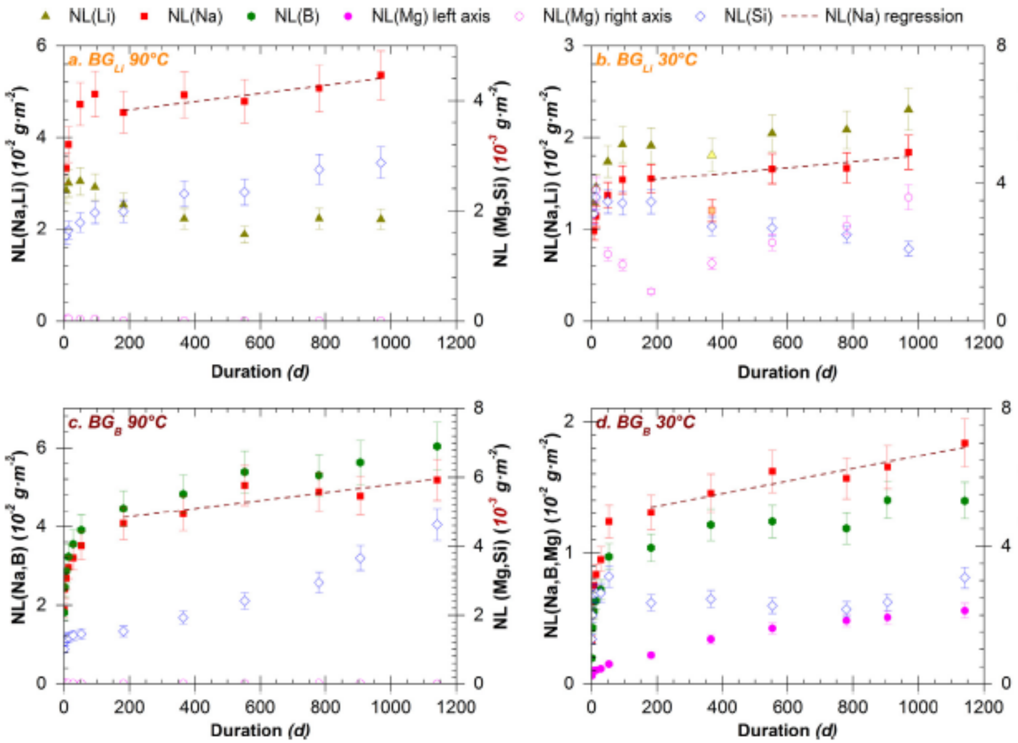
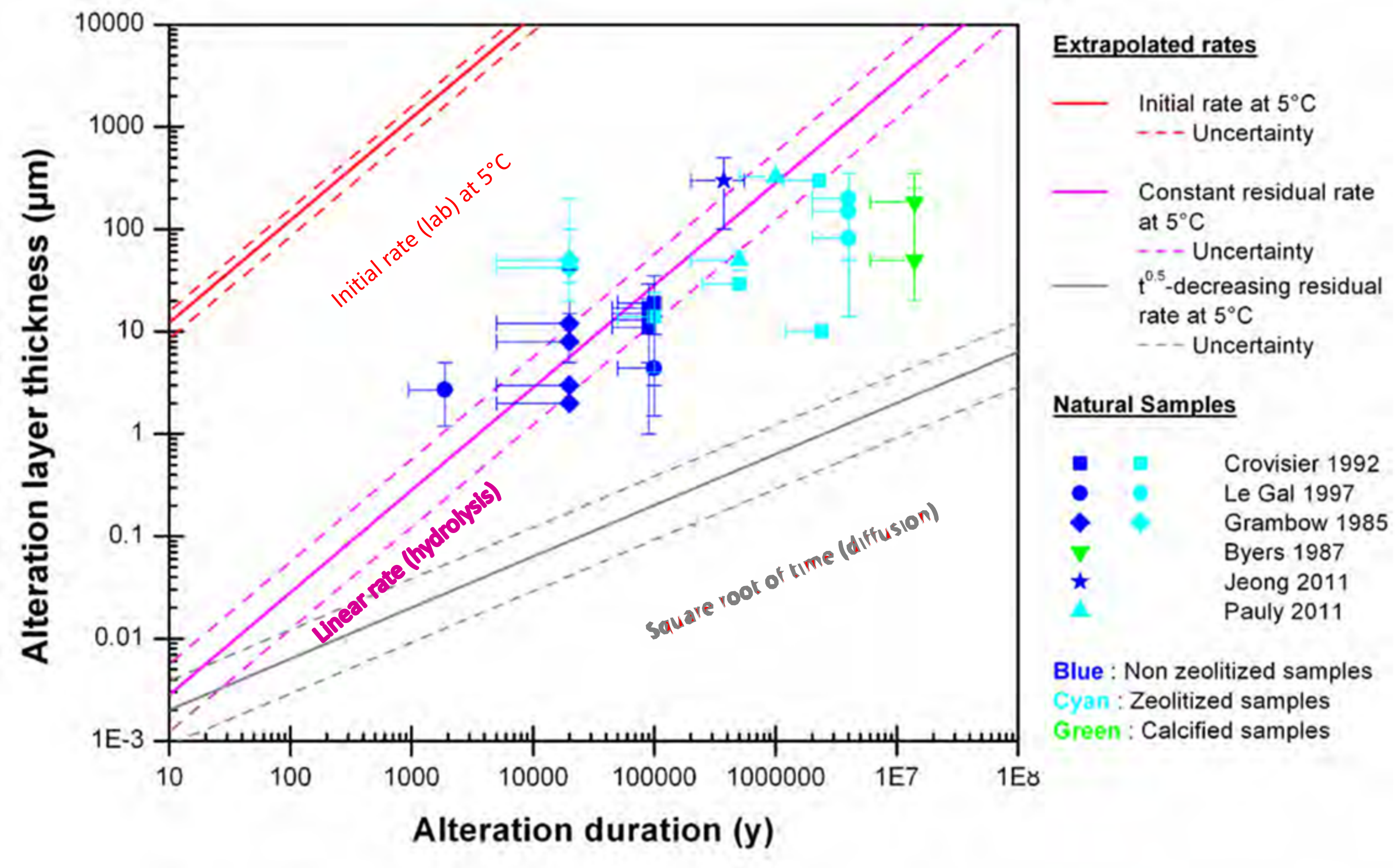


Fig. 3. Normalized mass losses versus time for BG$_{Li}$ and BG$_B$ main leaching experiments. Left axis, filled symbols: NL(Na), red squares; NL(Li), green triangles; NL(B), green hexagons and NL(Mg), magenta circles (BG$_B$ 30 °C only) Right axis, empty symbols: NL(Si), blue diamonds and NL(Mg), magenta circles (all experiments except BG$_B$ 30 °C only) Brown dashed line represents NL(Na) regression versus time on the residual rate domain. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$r_r = 9.6 \cdot 10^{-6}$ g/m²/d at 90°C
$r_r = 4.0 \cdot 10^{-6}$ g/m²/d at 30°C

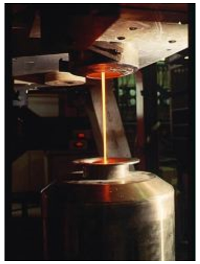
$D = 2.5 \cdot 10^{-25}$ g/m²/d at 90°C
$D = 4.7 \cdot 10^{-26}$ g/m²/d at 30°C

⇒ Measurement of the residual rate using a t-dependent law and Na diffusion coefficients using a √t law

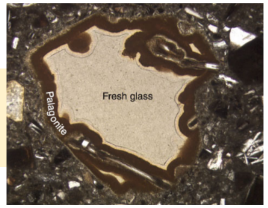


Parruzot (2015)

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

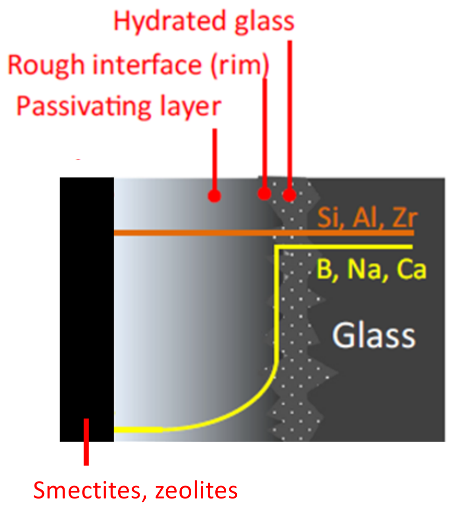


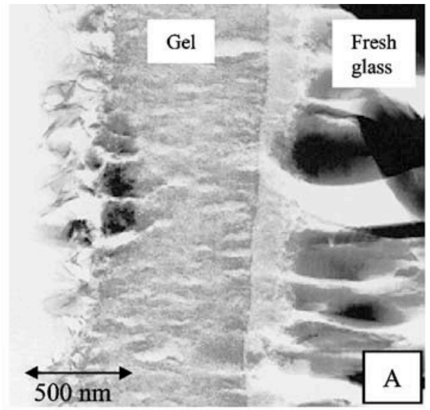
III. Analogy between BG and NG



- Phenomenology

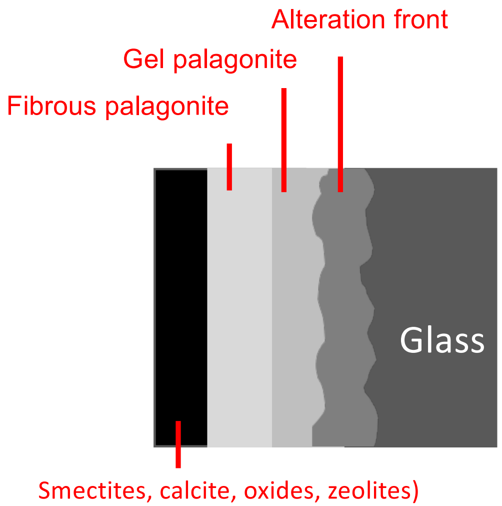
NUCLEAR GLASS



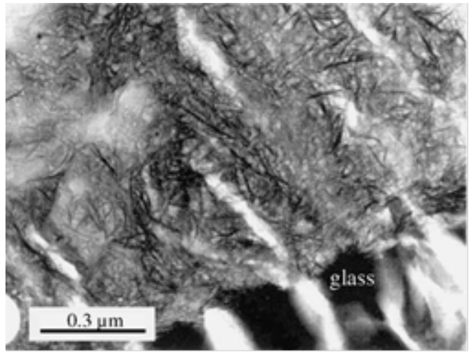


From Gin et al. (2017)
Gin et al. (2001)

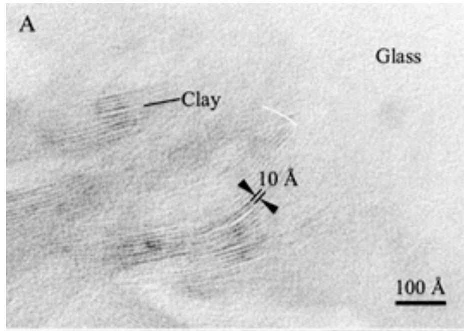
BASALTIC GLASS



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



TEM image of an Icelandic basaltic glass (0,1 My) [Crovisier et al., 2003]



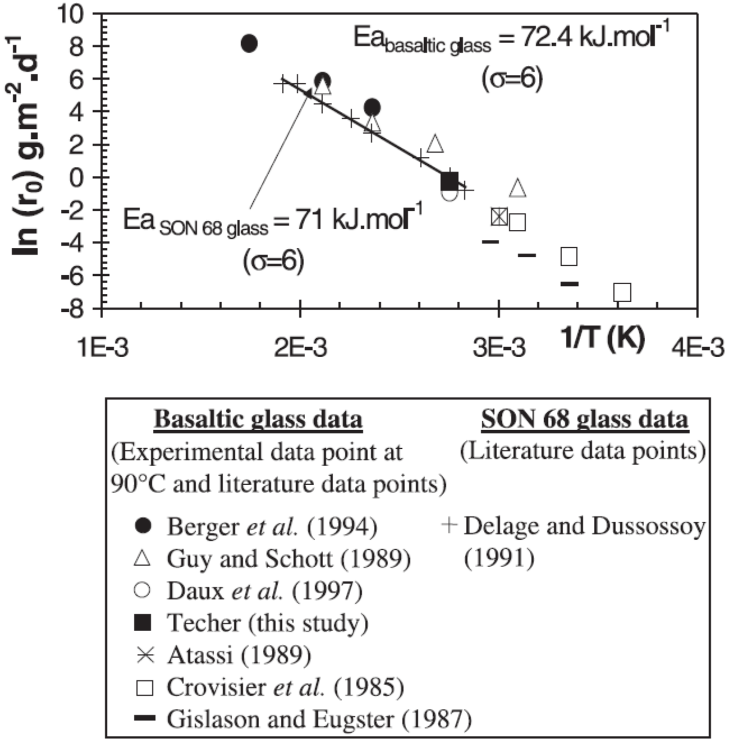
TEM image of an oceanic basaltic glass (10,1 Ma): saponite at 10 Å [Zhou et al., 2001].

⇒ Similar alteration facies

- Kinetics

NUCLEAR / BASALTIC GLASS

Forward dissolution rate



Techer et al. (2000)

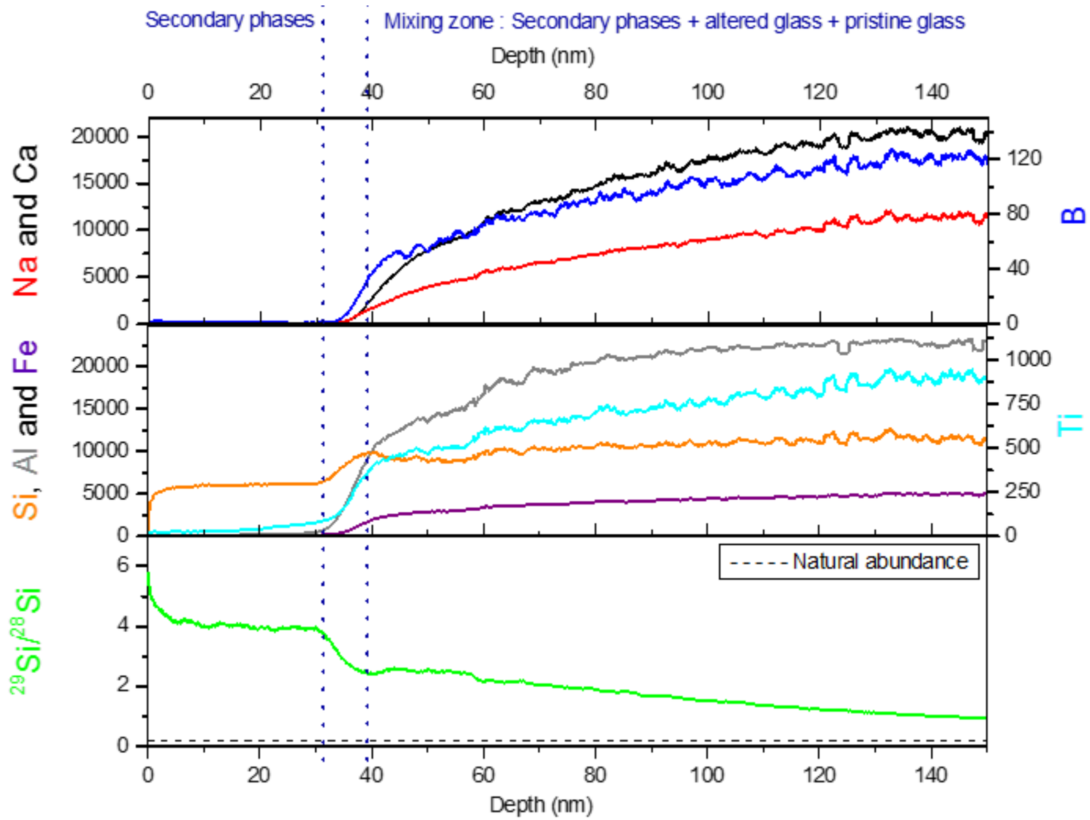
Residual rate

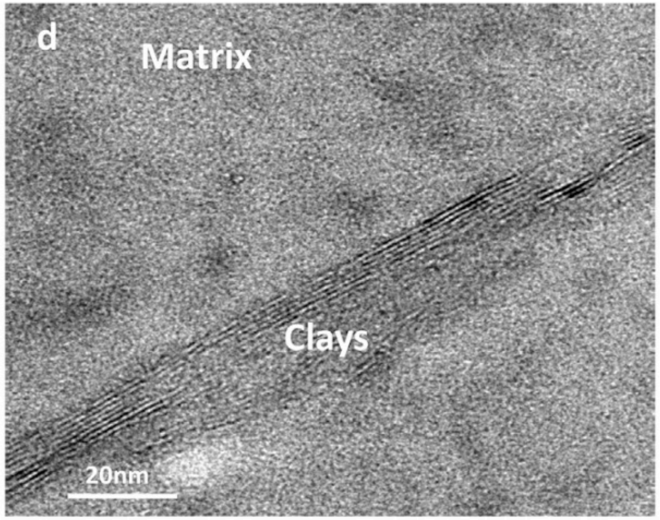
- r_r (ISG) = $2{\cdot}10^{-4}$ g/m²/d (90°C)
- r_r (BG) = $9.6{\cdot}10^{-6}$ g/m²/d (90°C) at pH 7 Parruzot et al. (2015)
- r_r (BG) = $4{\cdot}10^{-3}$ g/m²/d (90°C) at pH 9,3 Ducasse et al. (2018)

⇒ Similar alteration rates

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

Ducasse et al. (2018)

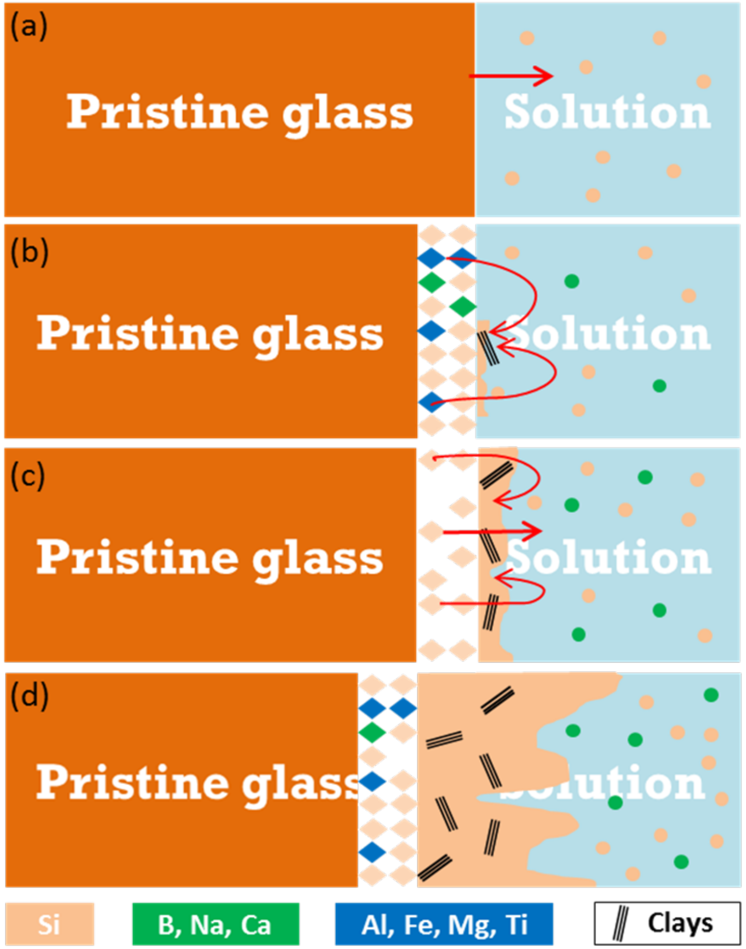




⇒ Complete depletion in Na, Ca, B
⇒ Si (~ Al, Ti) in the alteration layer (clays and amorphous silica)
⇒ Enrichment in ^{29}Si (// solution)

BASATIC GLASS

Ducasse et al. (2018)
ISG : Gin et al. (2015,2017)



(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.

⇒ A similar phenomenology but different mechanisms controlling the long-term alteration rate (due to composition)

IV. Analogy between obsidian and NG

- Composition

SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3 tot	TiO_2	LOI
69.50	12.00	3.50	3.71	1.00	0.07	2.63	0.182	7.11

- Phenomenology: dioctahedral smectite

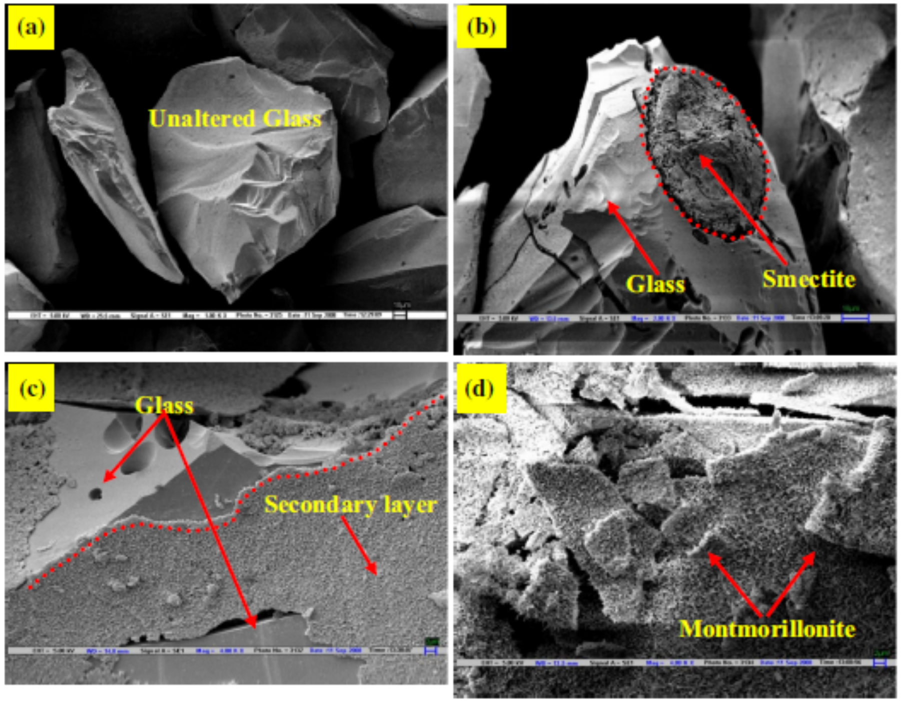


Fig. 6 SEM–EDS of obsidian glass (after Rani et al. 2013) at different temperatures and time **a** untreated glass specimen, **b** showing boundary where amount of dissolution is noticed in the middle of the glass particles, **c** two distinct morphology of glass is identified and **d** complete transformation of glass into neo-formed mineral

Rani et al. (2013, 2015)

V. Primitive meteorites (chondrites)

- Fe and Mg minerals, Si-Al glass, Fe-Ni metal and clays → glass / iron / clays (storage)
- Different alteration stages between 50 and 150°C

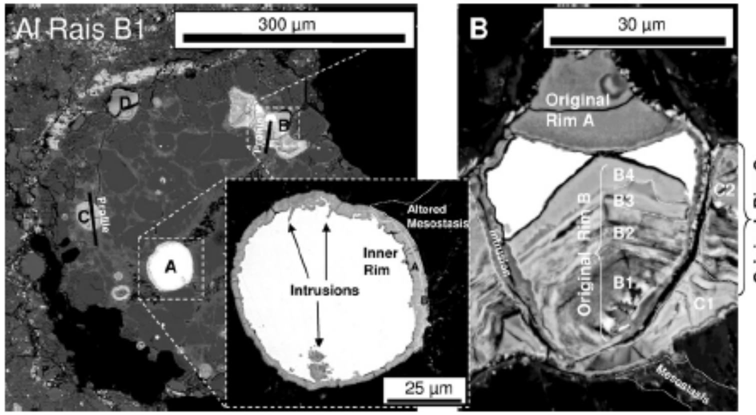


Fig. 3b. (SEM/BSE image) Altered chondrule Al Rais A1 represents the advanced state of Renazzo B4, with the mesostasis is completely hydrated. Metal grain (A) has a thin, already layered rim A/B. Small intrusions penetrate into the metal grain. Grain (B) shows a more advanced alteration, several inner rims with varying composition surround a core of remaining unaltered metal. The alteration features of grains (A) and (B) are reminiscent of metal grain Al Rais A1 in the same sample. The other metal grains (C), (D), and (E, not visible) have been altered completely.

78 A. Morlok, G. Libourel / Geochimica et Cosmochimica Acta 103 (2013) 76–103

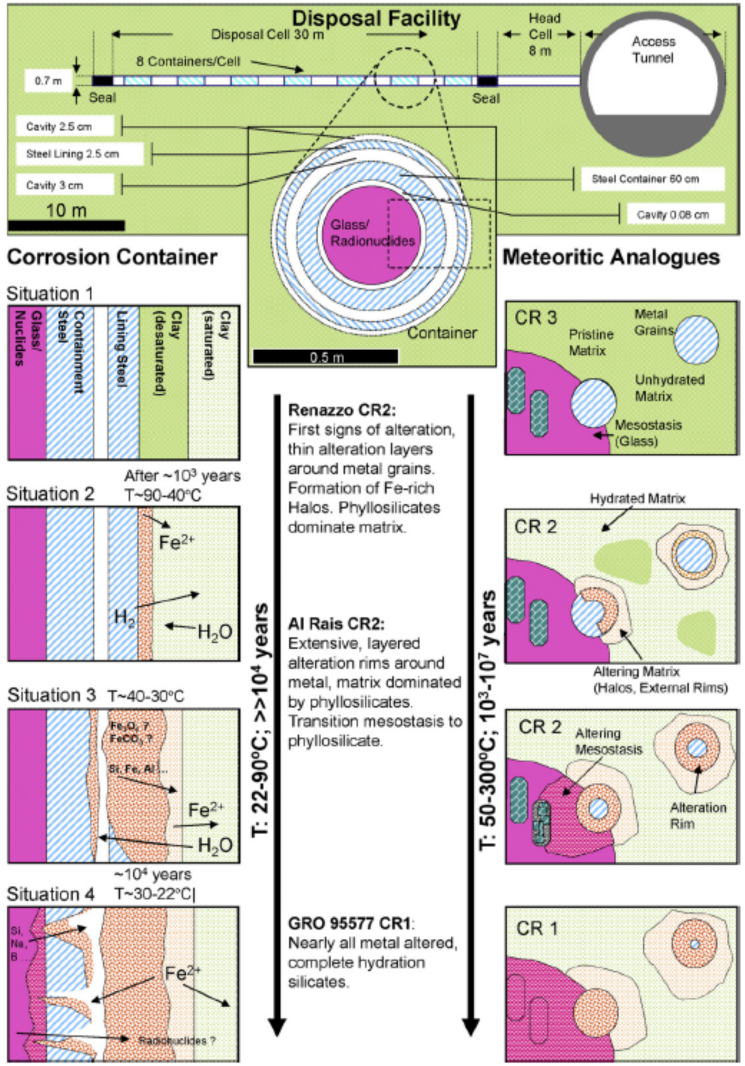


Fig. 1. (Top) Overview of the planned disposal facility, with crosscut of a typical storage container. The schema on the left shows the changes of the container, the nuclide glass, and the surrounding clay with increasing alteration (Situations 1–4) (*Source:* ANDRA, 2005). The analogous processes for the alteration of the CR chondrites are on the right (Weisberg and Huber, 2007; Libourel et al., 2011).

Morlok et al. (2013)

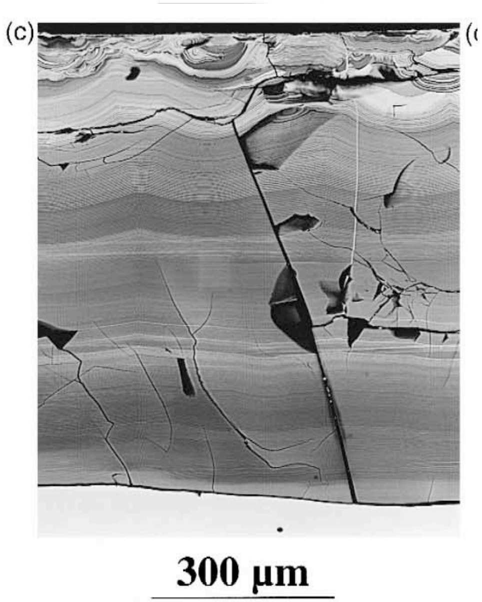
Paris, musée du Louvre.
Inv. BJ652
© Photo RMN - Hervé Lewandowski

B- Human-made glasses

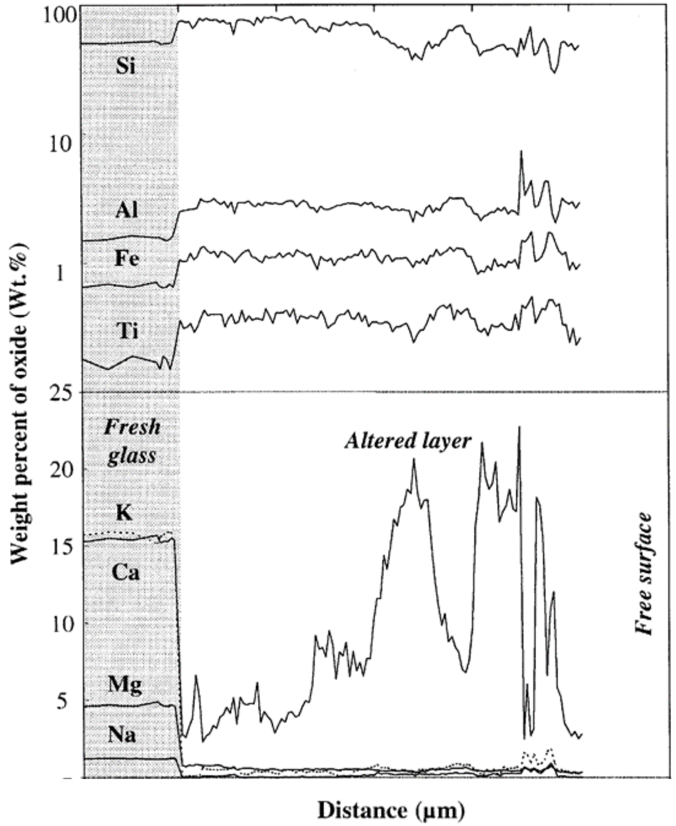
Paris, musée du Louvre.
Inv. AM1715
© Photo RMN - Franck Raux

I. The stained glass windows

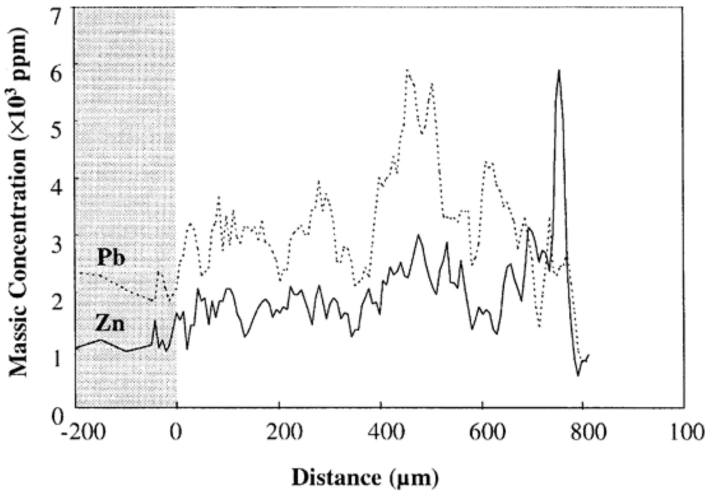
- Archaeological stained glass (buried in soils)



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



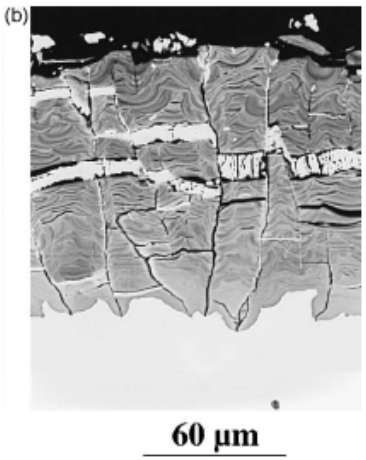
Sterpenich and Libourel (2001)

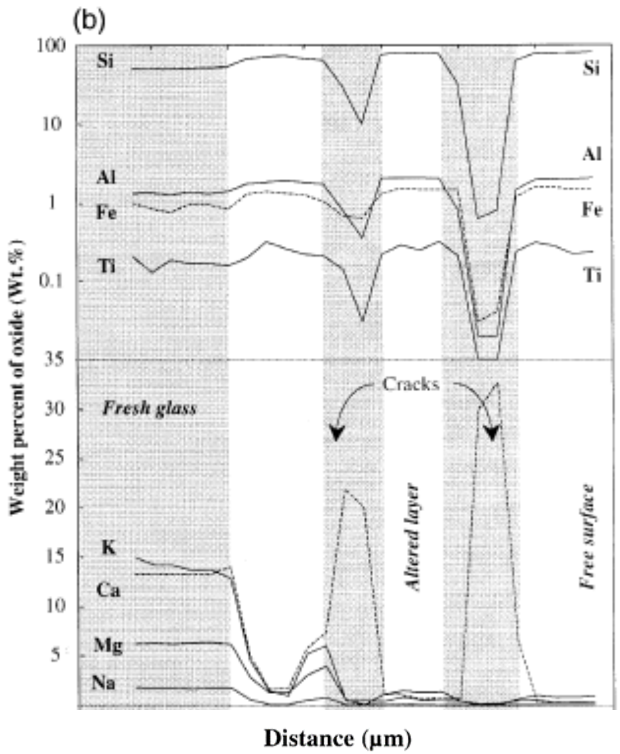


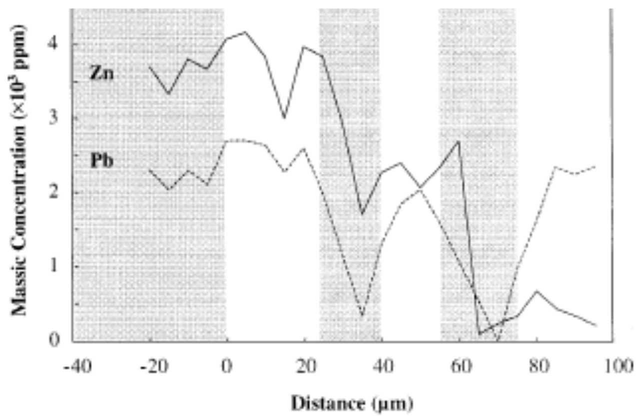
⇒ High retention of transition elements and heavy metals

- Stained glass weathered in atmosphere

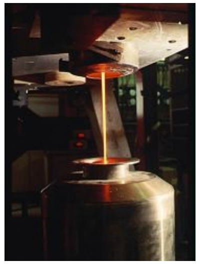
Sterpenich and Libourel (2001)

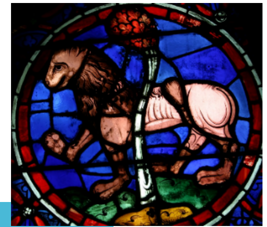






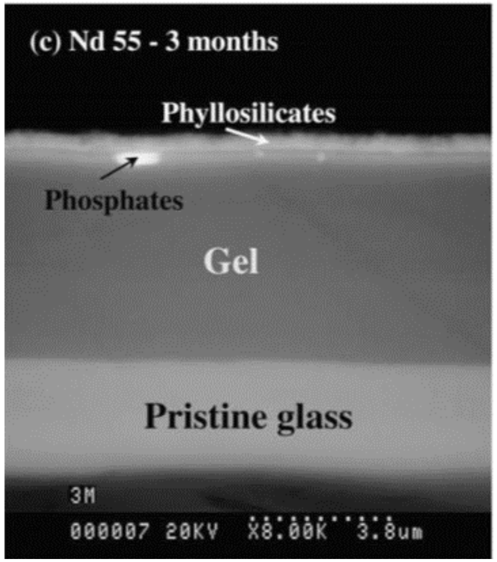
⇒ Partial retention of transition elements and heavy metals

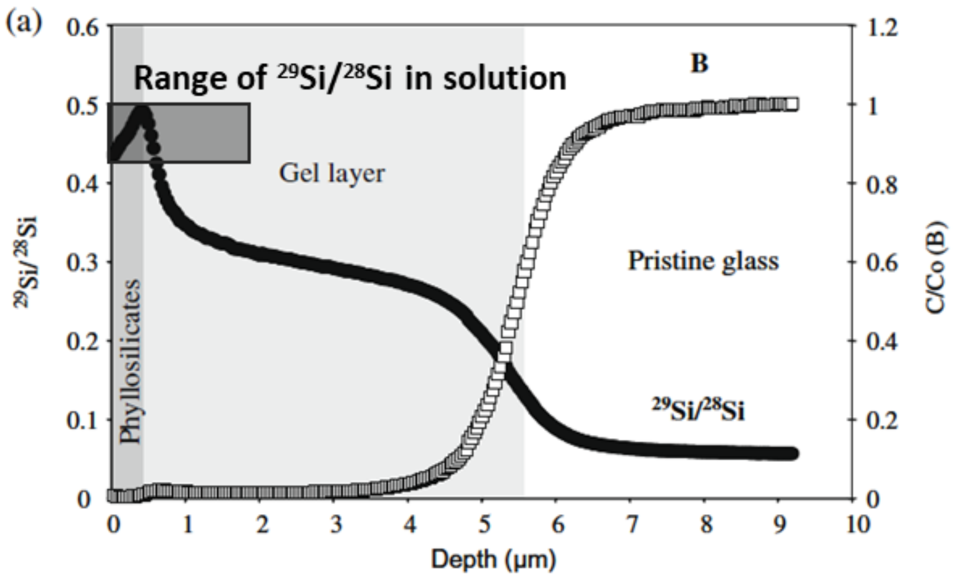




- Analogy

NUCLEAR GLASS
T = 90°C

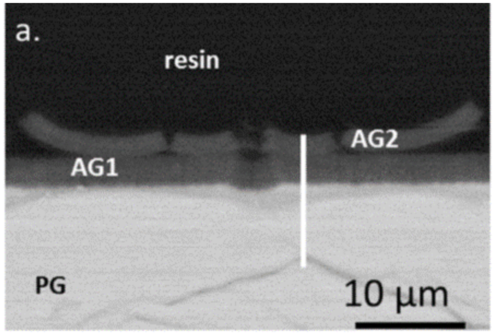


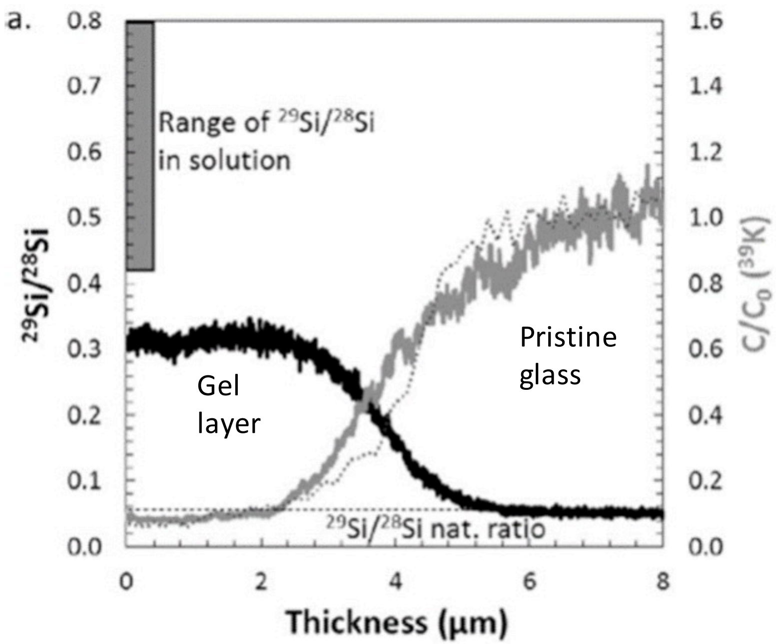


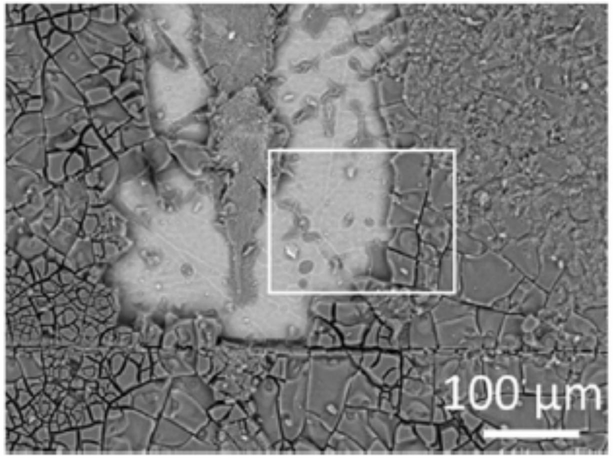
Valle et al. (2010)

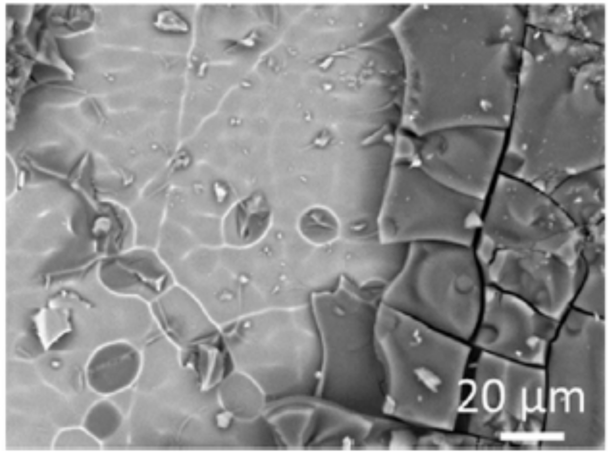
Verney-Carron et al. (2017)

STAINED GLASS
T = 30°C
1 month
Dynamic
conditions

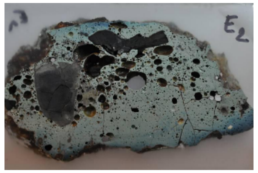




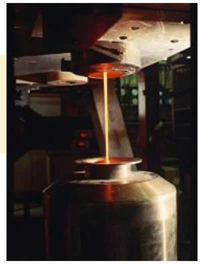




⇒ Indication on the long-term partition of transition elements and similar mechanisms far from saturation



II. Vitreous slags : interactions glass / iron

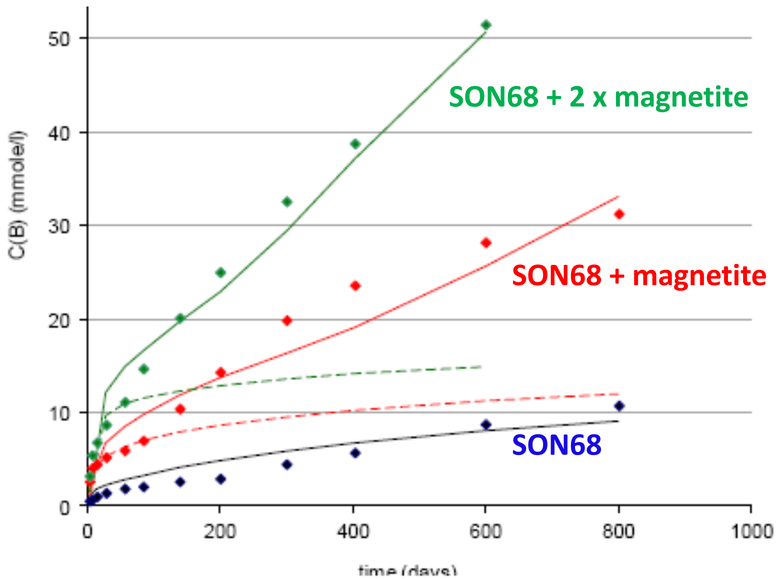


De Combarieu et al. (2011)

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.

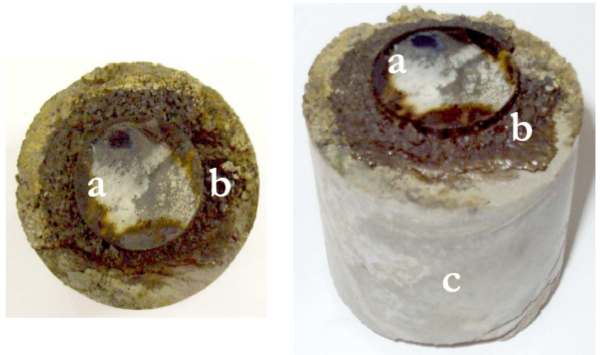
Godon et al. (2013)

⇒ 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



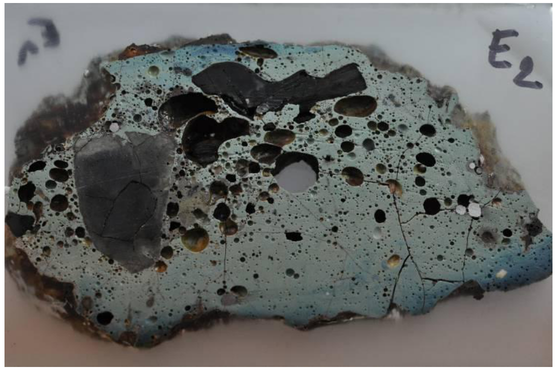
⇒ Formation of Fe-silicates

⇒ Alteration thickness = $r_0/2$

⇒ Iron sustains a high alteration rate

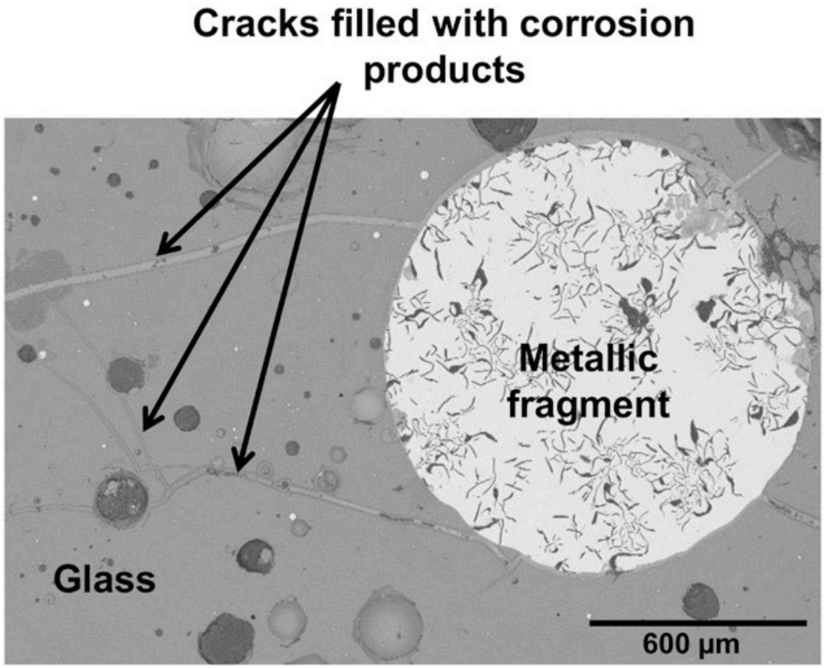
Michelin et al. (2013, 2015)

VITREOUS SLAGS

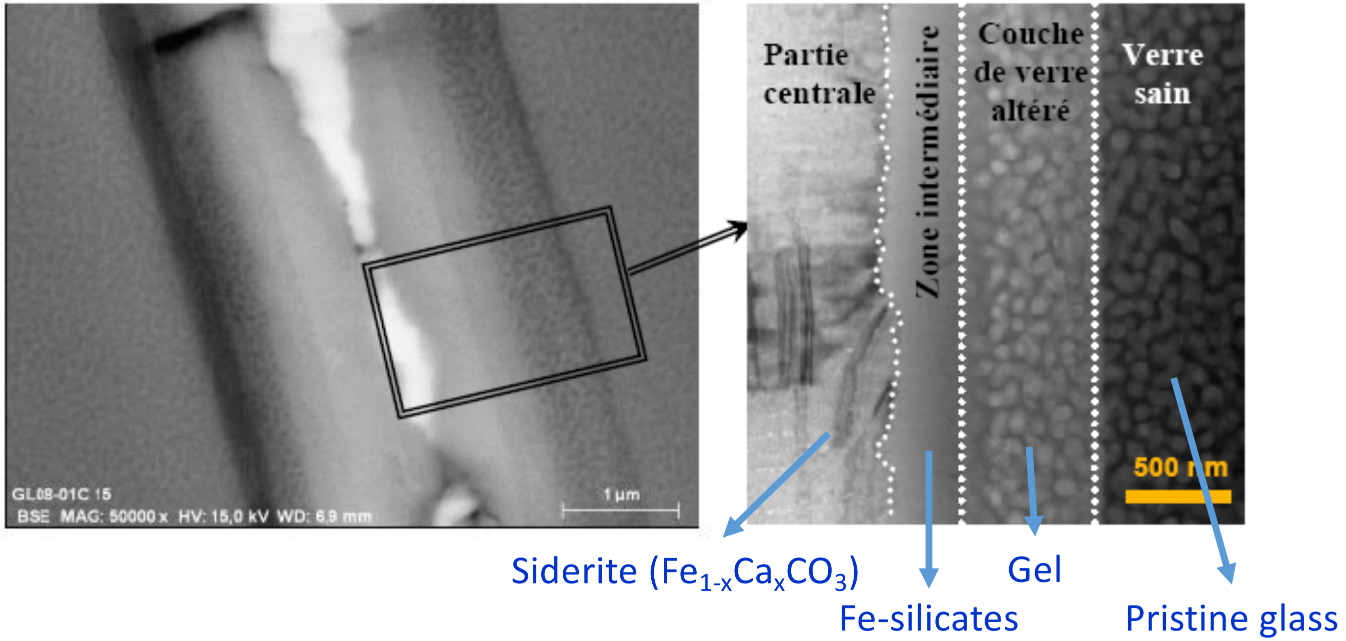


Site of Glinet (Normandy)
Blast furnace
16th c.
Soil saturated with anoxic water

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



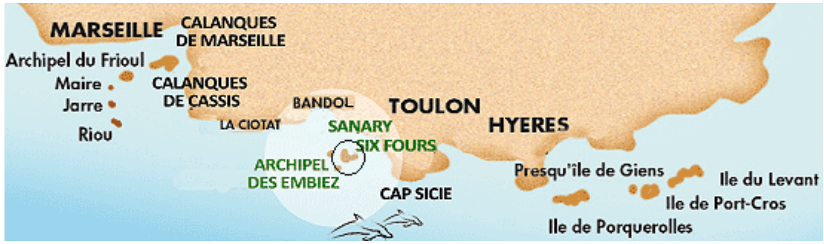
⇒ Analogy: vitreous slag / glass package and steel container



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

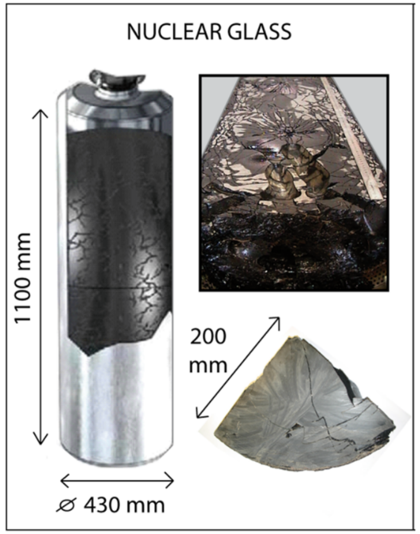
⇒ Fe-silicates precipitation is a long-term mechanism but there is a drop in the alteration rate in cracks

III. Roman glass alteration modeling



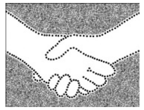
Alteration for 1800 years
In a stable environment
(seawater at 15°C)

Morphological analogy



Experimental study
(short-term)

Ancient glass characterization

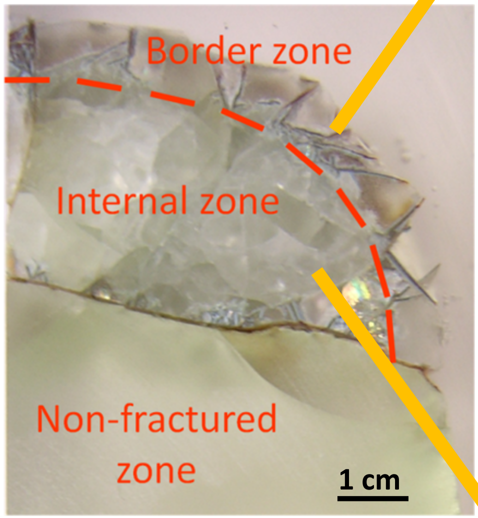


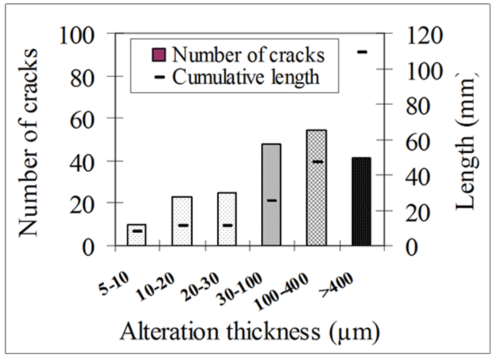
Mechanisms
Kinetic parameters

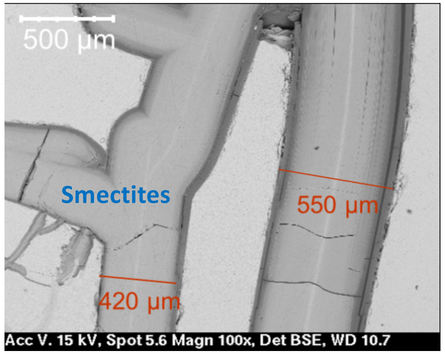
Long-term simulation

Geochemical model
of glass alteration

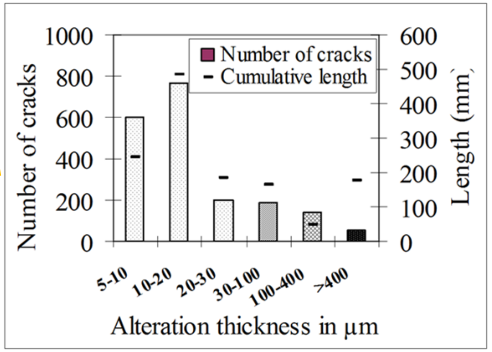
ALTERATION PHENOMENOLOGY

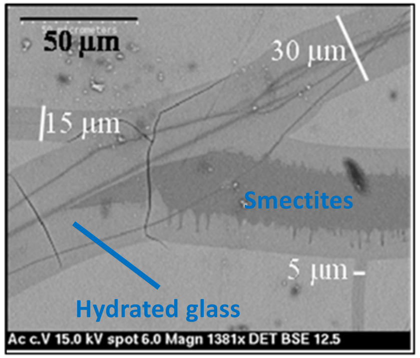






Border zone (BZ)
- Thick altered cracks
- Smectites
- 84 % of total alteration

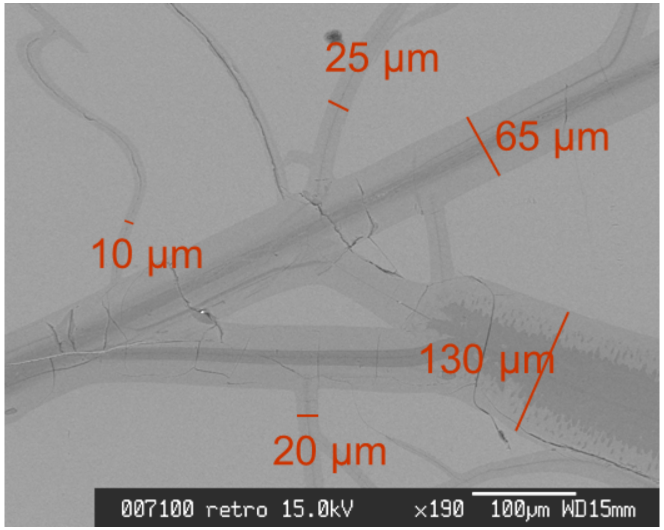




Internal zone (IZ)
- Thin altered cracks (5-20 µm)
- Hydrated glass (and smectites)
- Cracks density 6x higher
- 16 % of total alteration

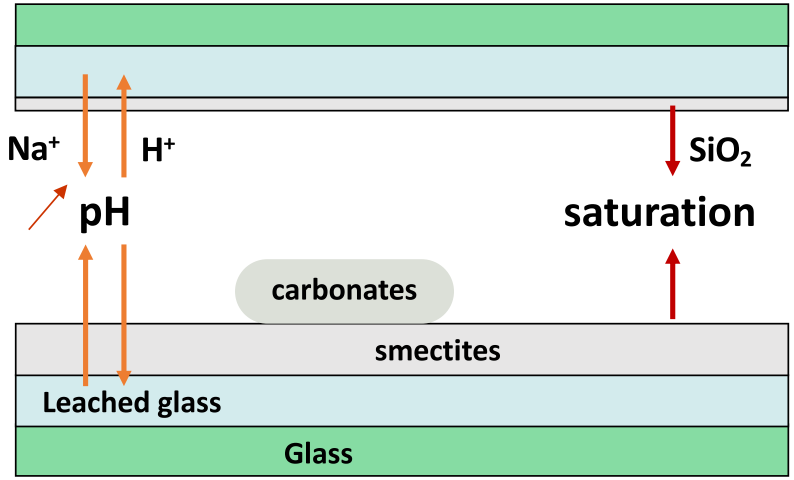
⇒ Low contribution of internal cracks to global alteration (+ sealing)

Verney-Carron et al. (2008)

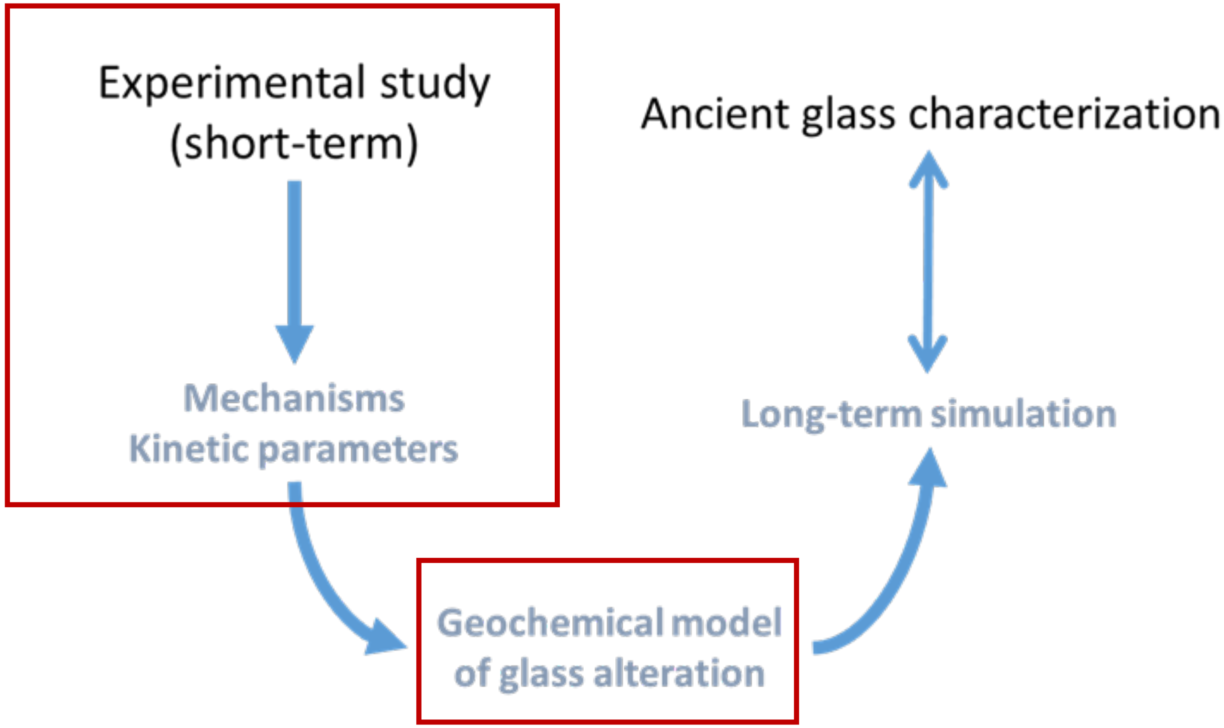


diffusion

pH, Mg, CO_3^{2-}



⇒ Need to model the coupling between chemistry and transport


Experimental study
(short-term)
Mechanisms
Kinetic parameters
Ancient glass characterization
Long-term simulation
Geochemical model
of glass alteration

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

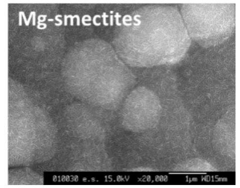
Arch. glass: SiO_2 Na_2O CaO Al_2O_3 Li_2O → (- D) → $SiO_2(aq)$, Ca^{2+}, Al^{3+}, Na^{+}, Li^{+} → (+ D) → **Leached glass**: SiO_2 CaO Al_2O_3

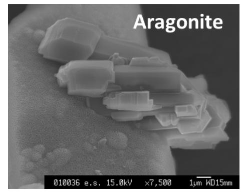
$$D_{Na} = 0.678 \cdot \left[H^+\right]^{0.37} \cdot \exp\left(\frac{-93600}{RT}\right)$$

2nd step: dissolution/precipitation

Leached glass: SiO_2 CaO Al_2O_3 → (- r) → $SiO_2(aq)$, Ca^{2+} Al^{3+} → (LogK) → **Secondary phases**

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



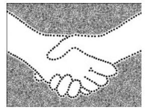


Pure water: analcime, gyrolite, tobermorite
Seawater: saponite, calcite, aragonite
+ brucite, portlandite, gibbsite

Experimental study
(short-term)

Mechanisms
Kinetic parameters

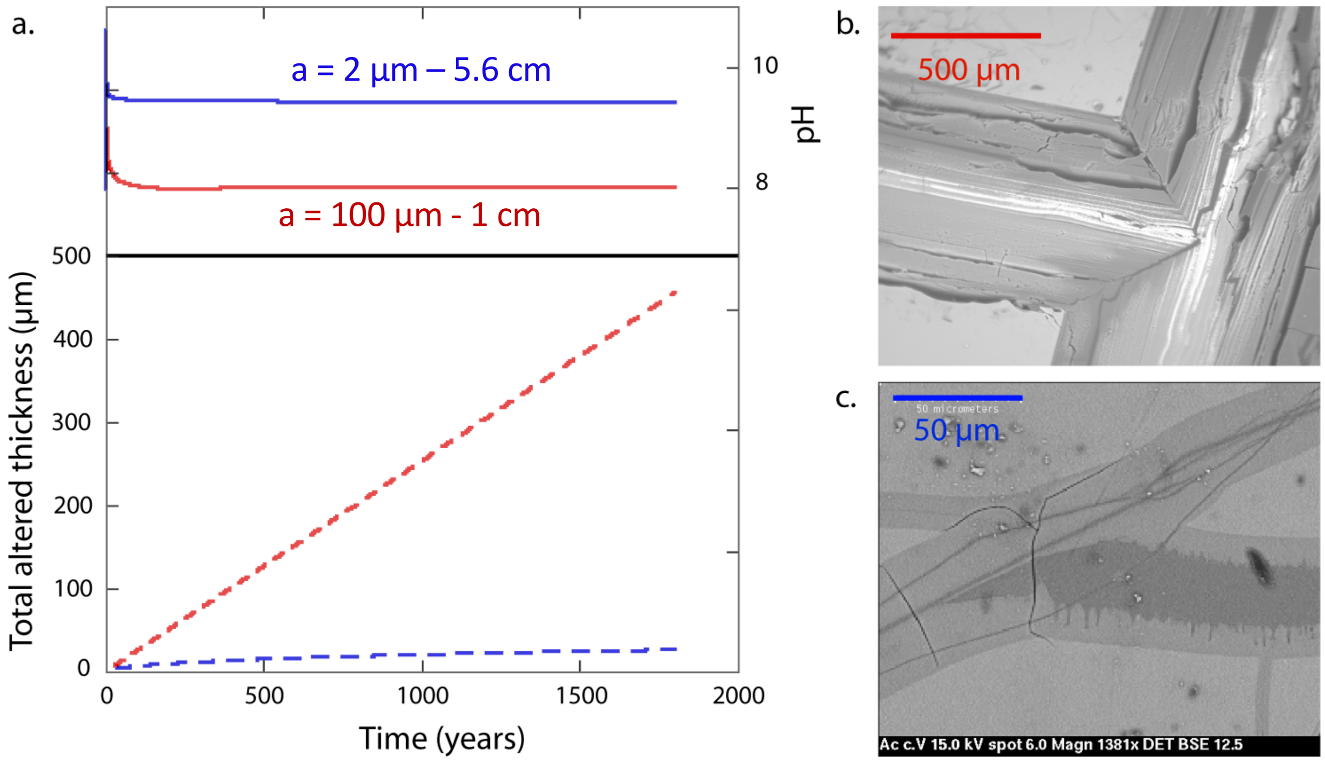
Ancient glass characterization



Long-term simulation

Geochemical model
of glass alteration

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



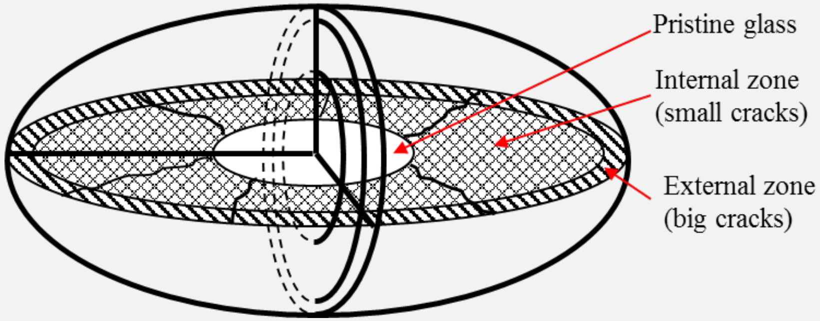
⇒ The external cracks are in contact with a diluted medium → r_0

⇒ Strong coupling between chemistry and transport

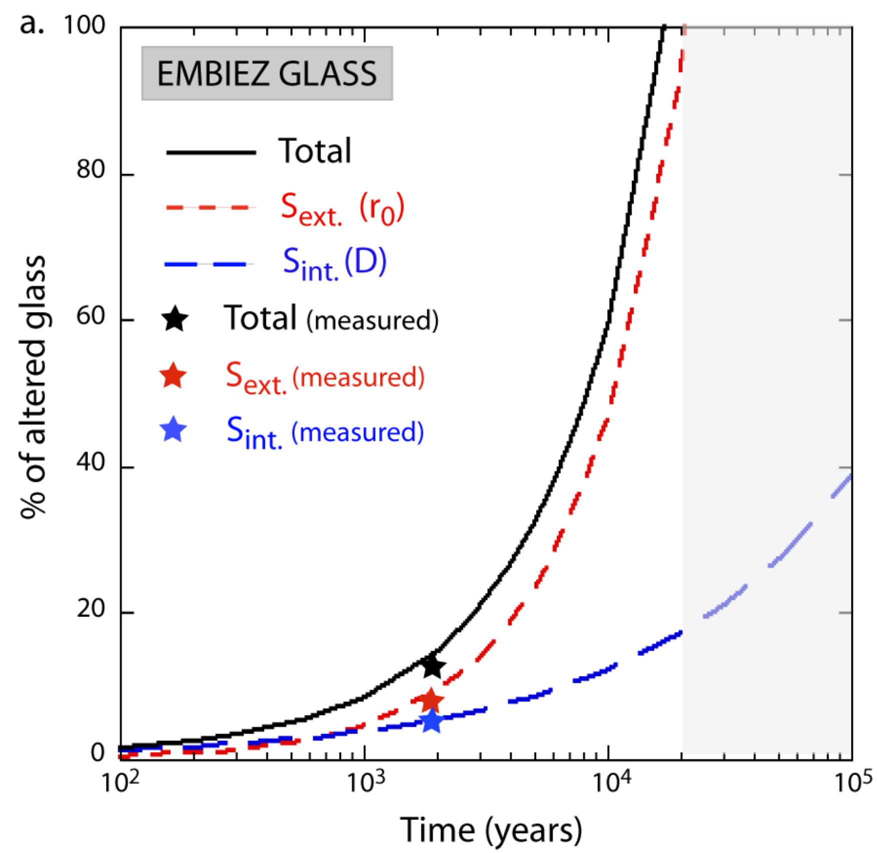
⇒ Good agreement between simulations and observations

⇒ Validation of the predictive capacity of the geochemical model

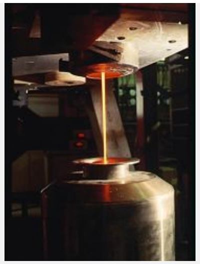
Verney-Carron et al. (2010a,b)



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

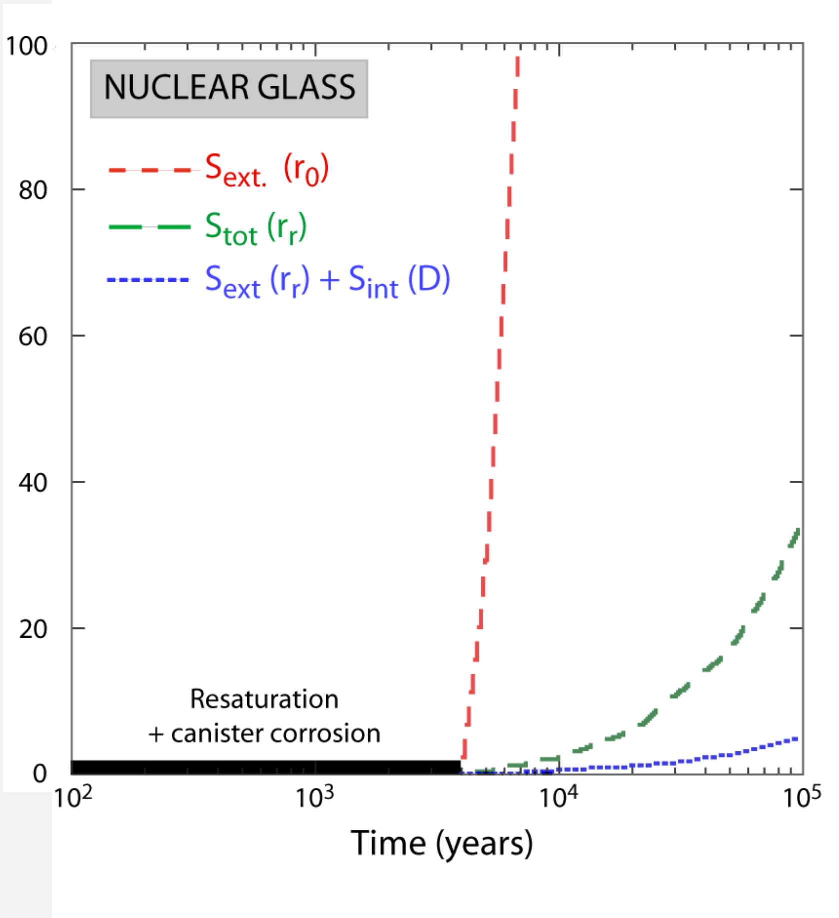


⇒ If only the internal surfaces were leached, more than 650,000 years would be necessary for complete alteration of the Roman glass blocks, but external surfaces alteration would limit the lifetime to about 20,000 years.



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



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

IV. Pre-viking Swedish hillfort glass / LAW glasses

Weaver et al. (2018)

Broborg, Sweden
500 CE

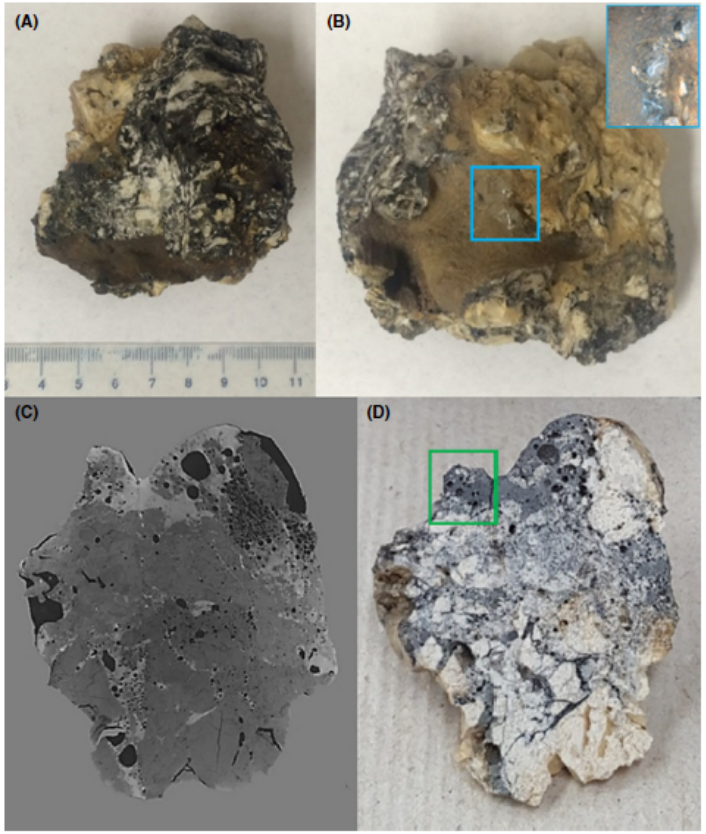


FIGURE 1 Back (A) and front (B) image of the sample from Broborg (inset in B shows higher magnification image of the clear glass), X-ray computed tomography image of plane selected for sectioning (C) and image of cut surface after sectioning (D). Green box represents area selected for high resolution µXRF mapping

⇒ It could be a good analogue of LAW glasses

Outcomes

- No composition analogy BUT

- Important to study other kinds of glasses

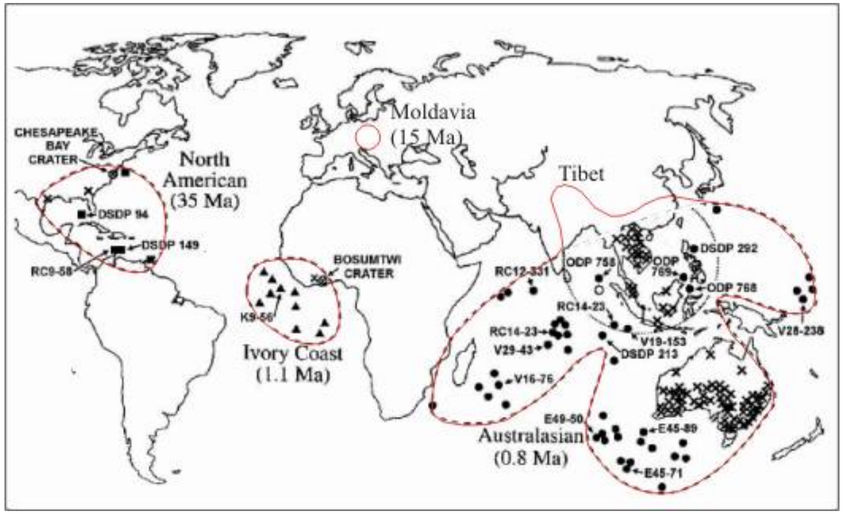
  → General understanding of glass alteration (even minerals) : similar mechanisms but different kinetics.

- Important to continue the modeling work

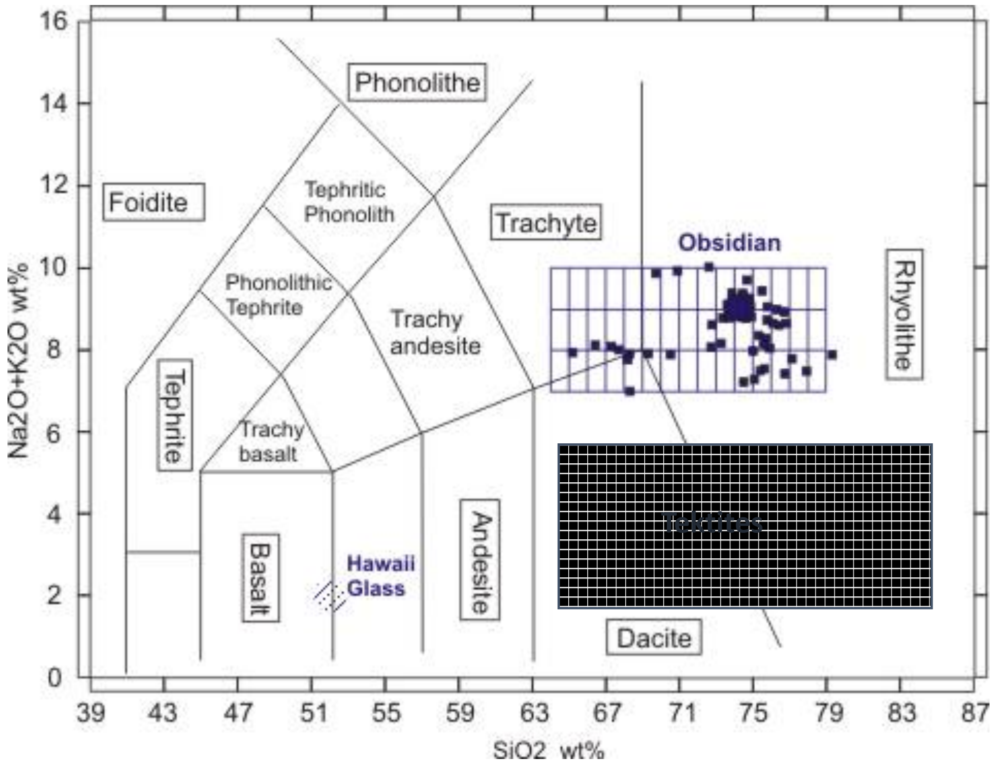
  → To demonstrate the feasibility and the predictive capacity

  → To extend the range of applications of nuclear glass models

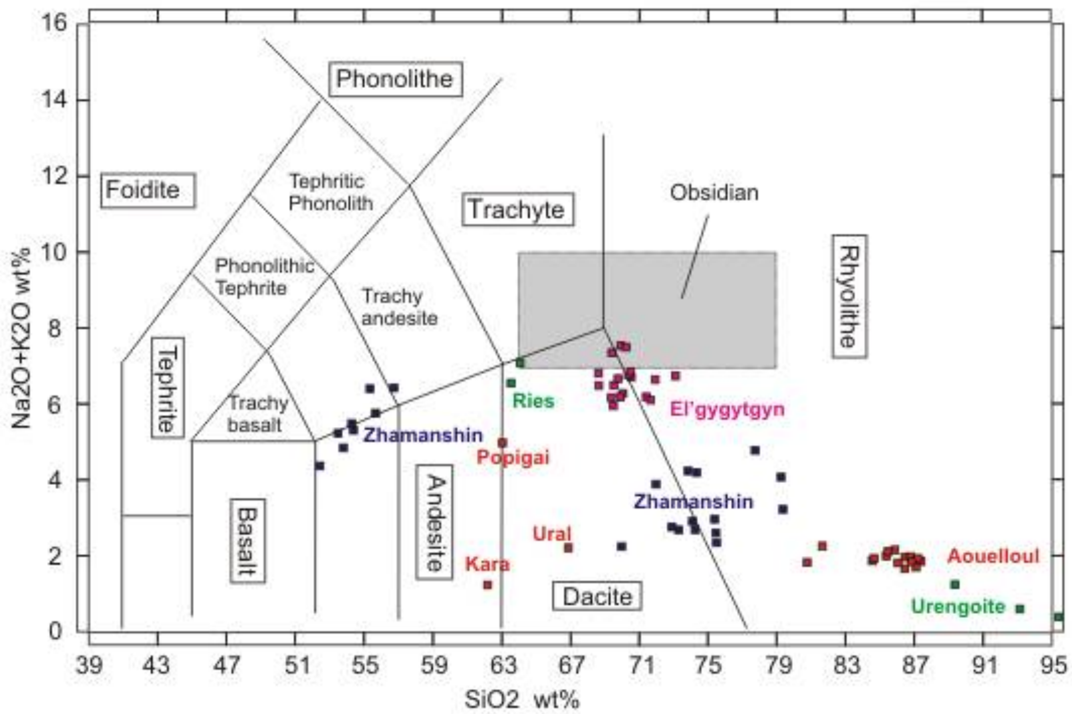
Tektites: rich in Si, Al and low H_2O content



Atacama tektite

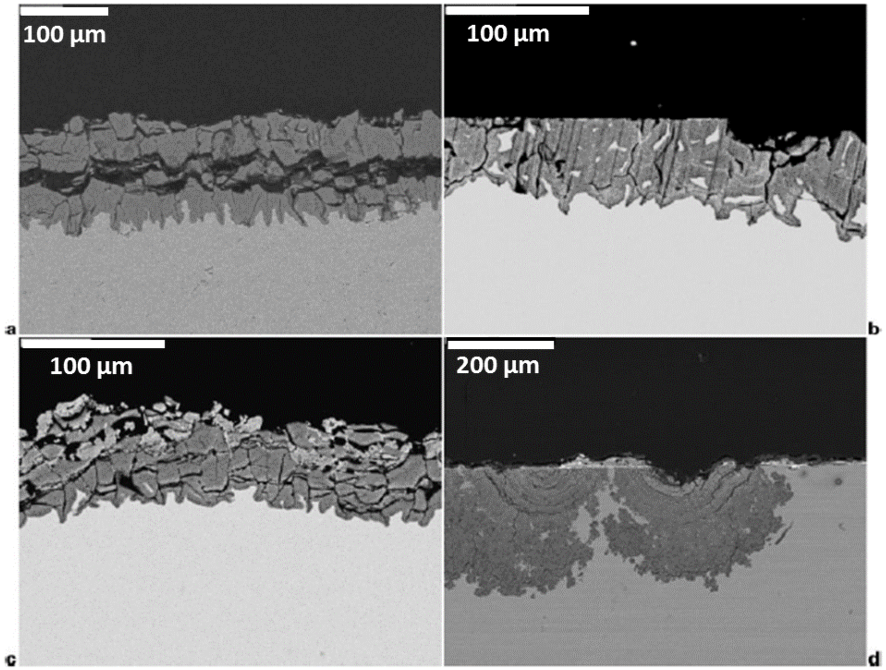


Impactites:

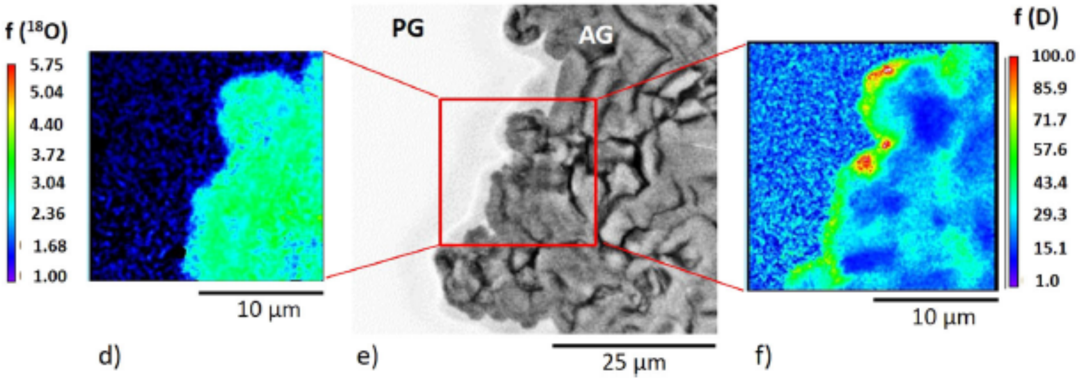


Lybian desert glass

• Stained glass weathered in atmosphere



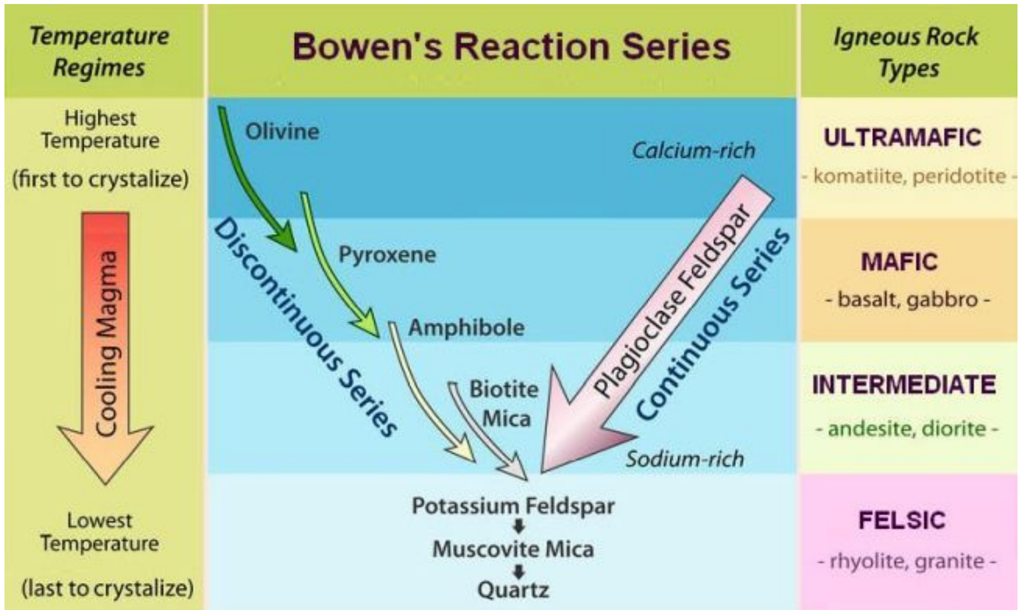
Lombardo et al. (2010)



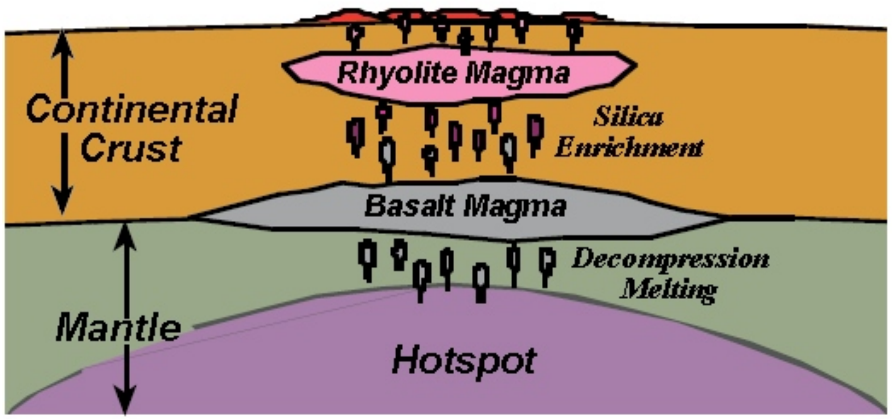
Enrichment in D at the interface of samples exposed at 90 %RH (14 months)

⇒ No protective role of the alteration layer

Magma can have a different composition ↔ partial melting, fractional crystallization, assimilation of surrounding crust.

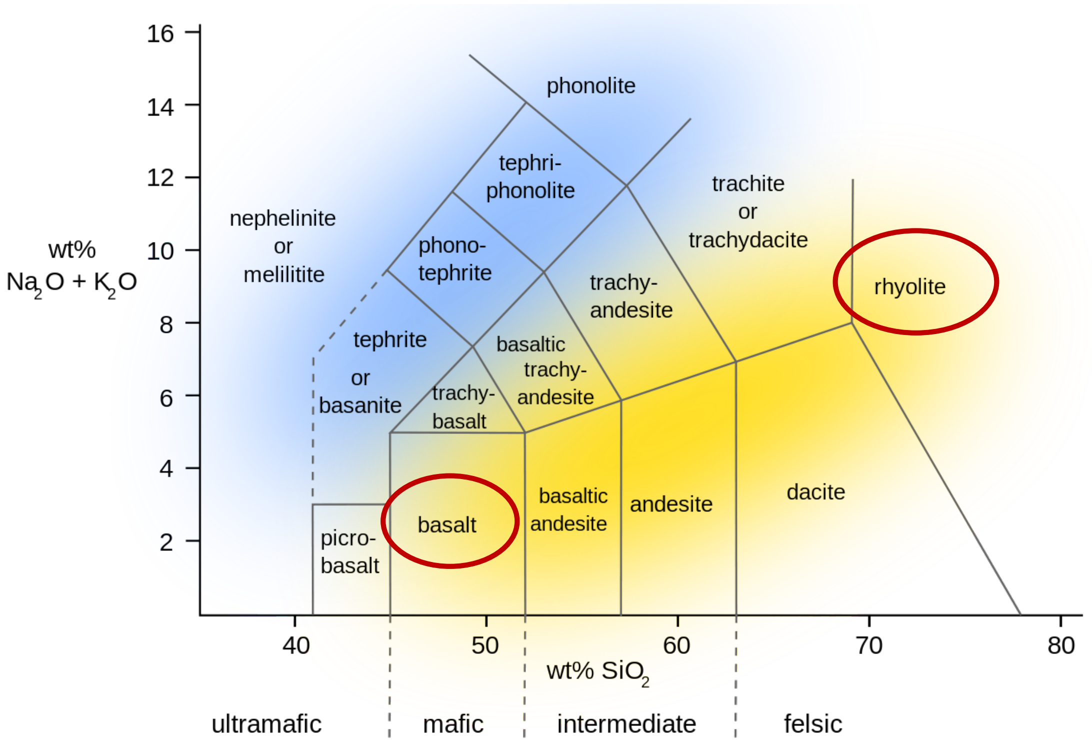


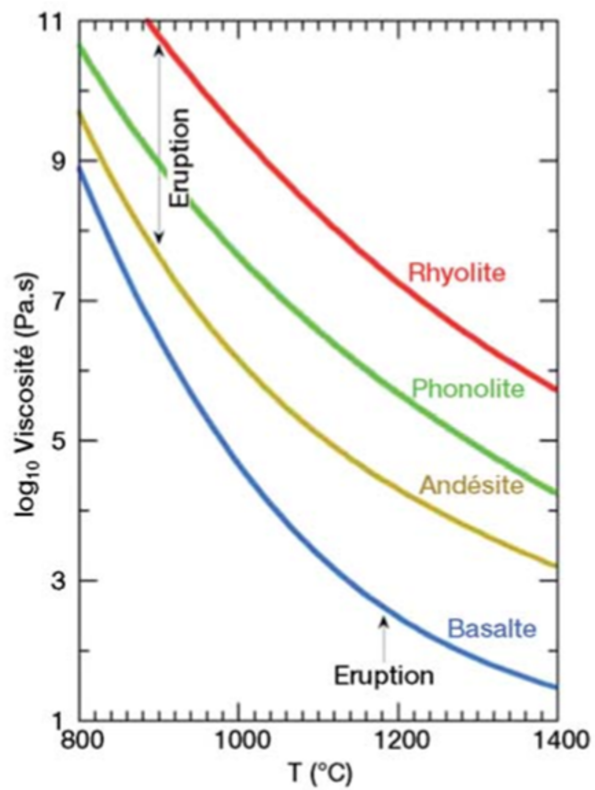
Melting of peridotite (5-20 %) → basalt composition



Melting of continental crust → rhyolite

The composition influences the viscosity and the vitrification.

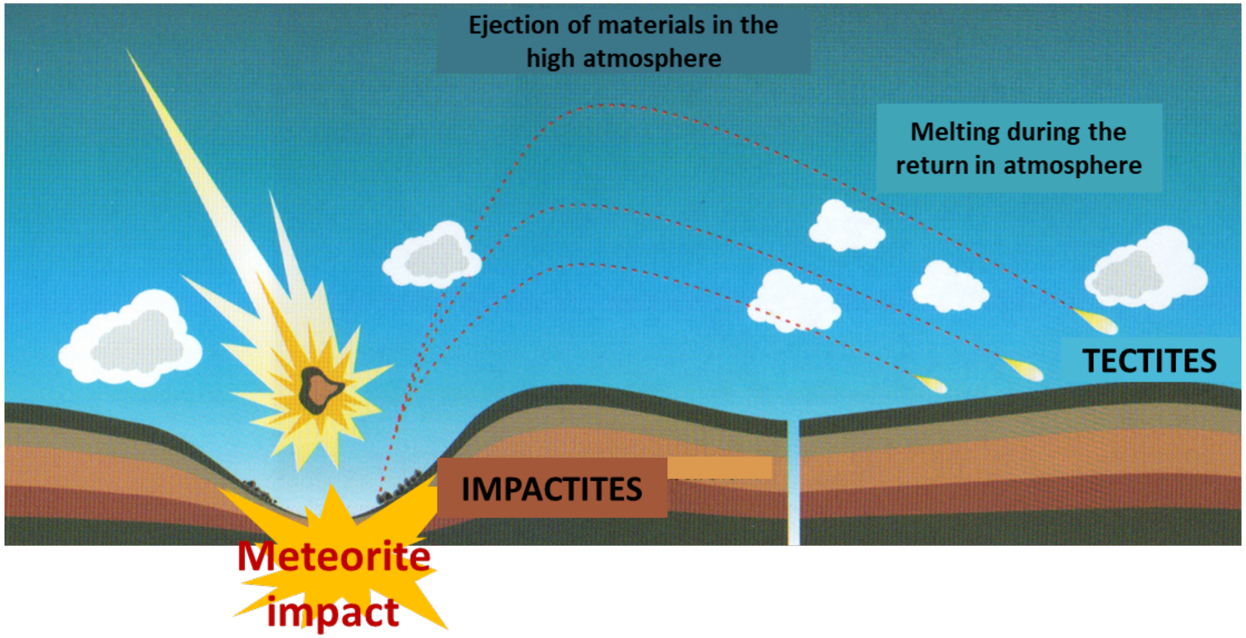




Glass < high viscosity (to inhibit the crystallization) + sudden cooling to chill the material to a glass

- Tektites and impactites

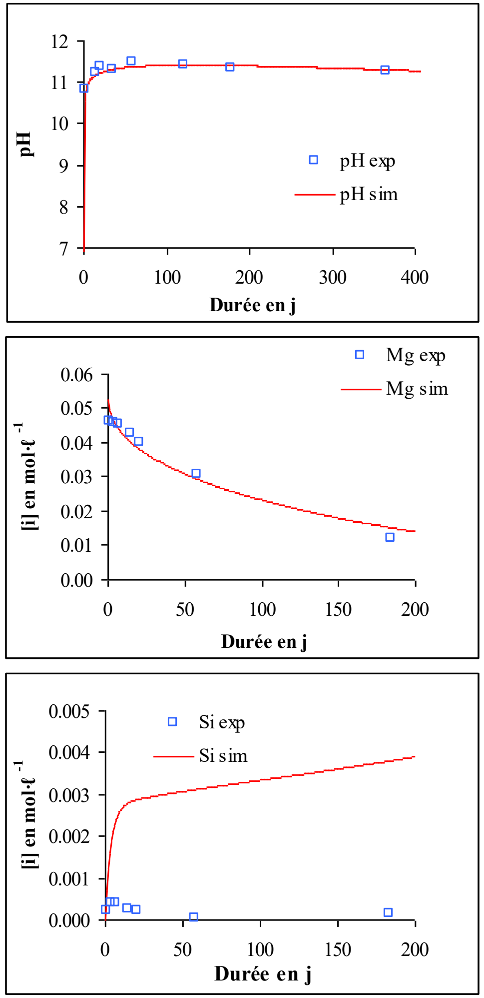
Impactite is formed by the impact of a meteorite and tektites from terrestrial debris ejected far from the impact.



	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
Basalt	49,2	15,7	2,9	1,1	9,5	6,7	3,8	7,3	1,8
Andesite	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
Lybian 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

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