DE LA RECHERCHE À L'INDUSTRIE

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Joint ICTP/IAEA Workshop

Long-term glass leaching: irradiation as a way to refine mechanisms

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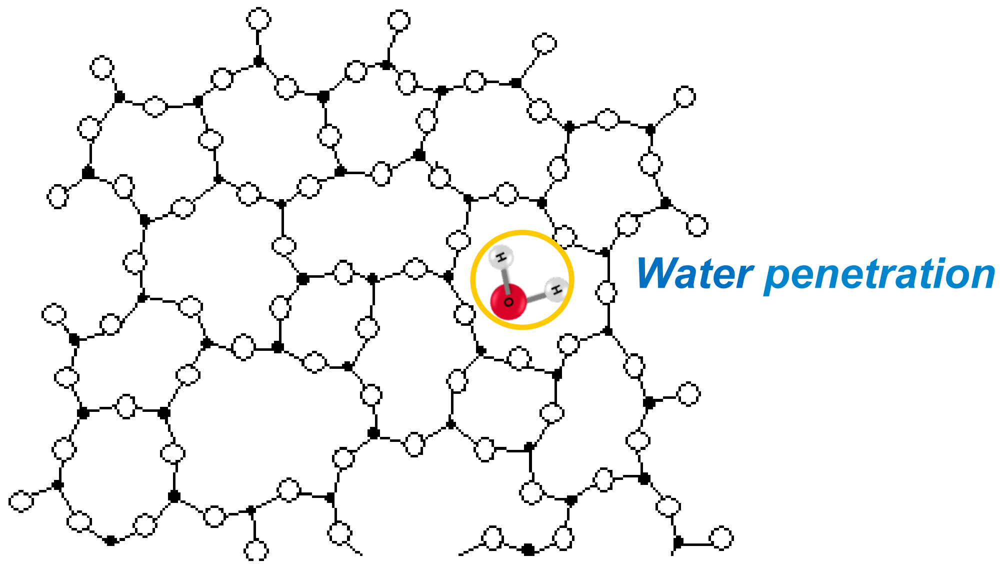
GENERALITIES ABOUT WATER ALTERATION OF GLASSES

AQUEOUS ALTERATION OF GLASSES

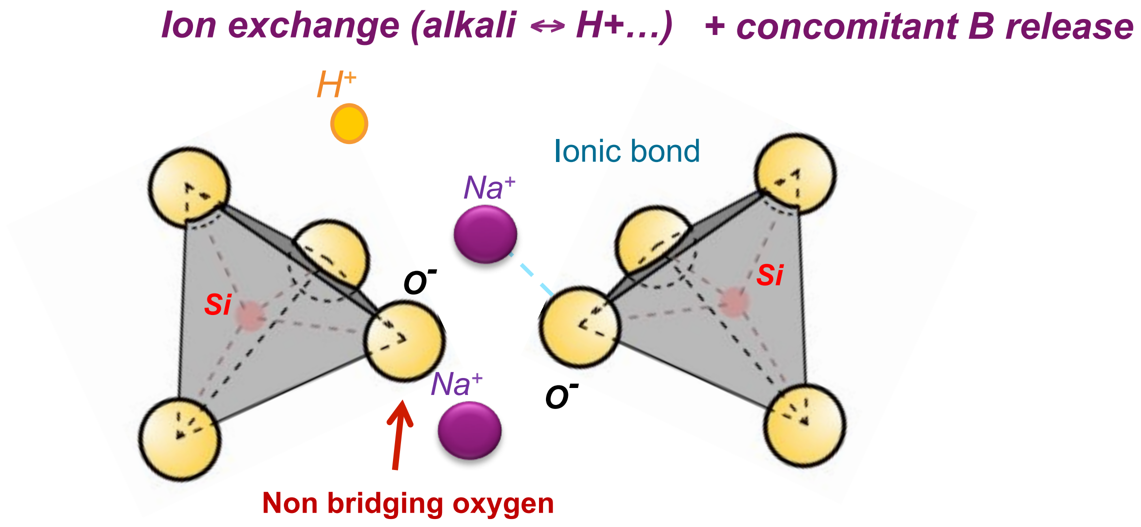
2 mean mechanisms: hydration



R.H. Doremus, J. Non-Cryst. Solids 19 (1975) 137.
T. Chave, Université Montpellier II, 2007.
D. Rebiscoul, J. Non-Cryst. Solids 358 (2012) 2951.

AQUEOUS ALTERATION OF GLASSES

2 mean mechanisms: hydration + interdiffusion



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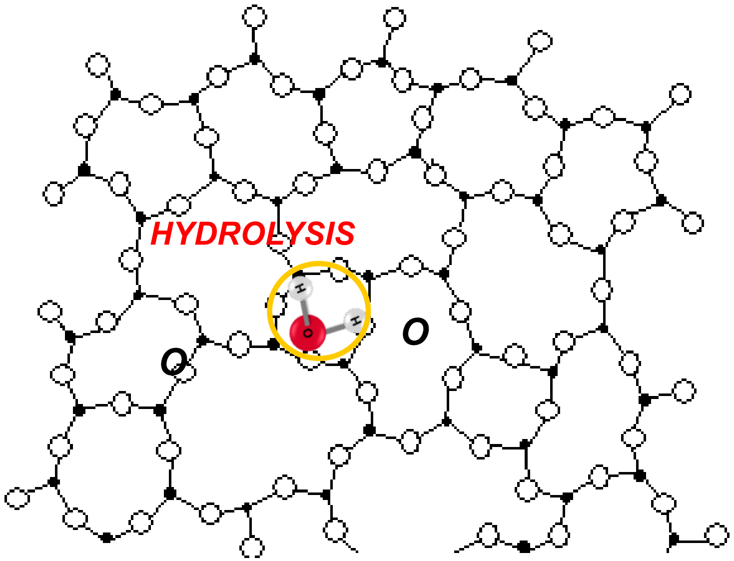
AQUEOUS ALTERATION OF GLASSES

2 mean mechanisms: hydration + interdiffusion

hydrolysis of the glass network



P. Frugier et al., J. Nucl. Mater. 380, pp.8 (2008)
C. Jégou et al., J. Nucl. Mater. 280, pp. 2016 (2000)

AQUEOUS ALTERATION OF GLASSES

2 mean mechanisms: hydration + interdiffusion

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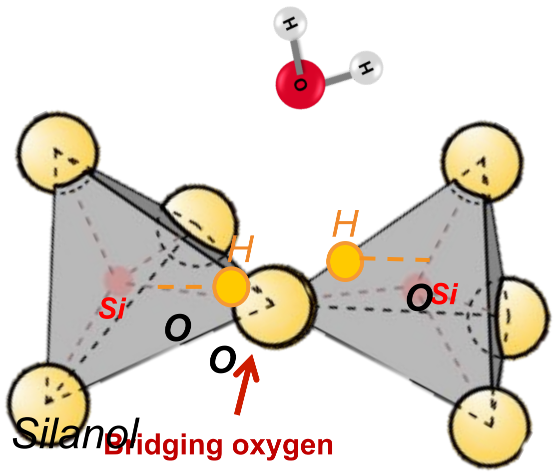
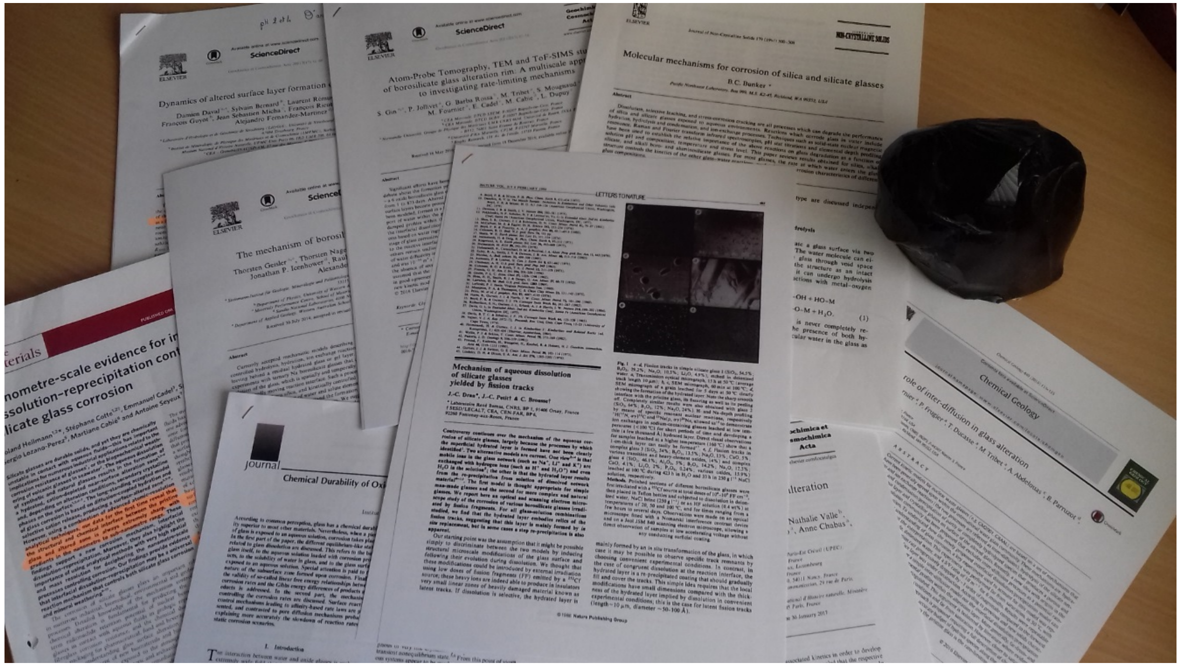


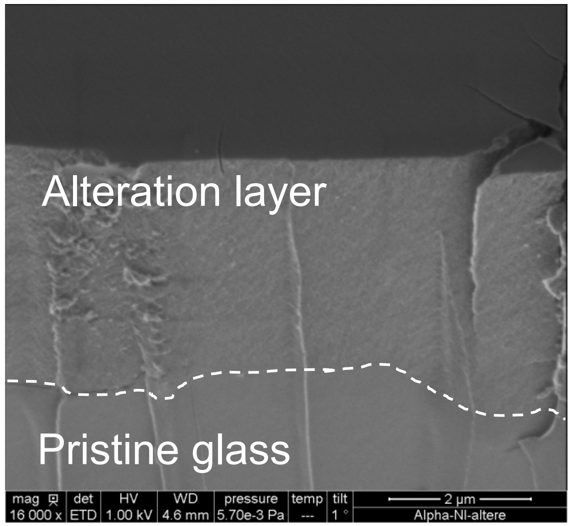
Siloxane bridges

P. Frugier et al., J. Nucl. Mater. 380, pp.8 (2008)
C. Jégou et al., J. Nucl. Mater. 280, pp. 2016 (2000)

AQUEOUS ALTERATION OF GLASSES

Preponderance of
1 mechanism ?
or a set of mechanisms ?
to explain formation of alteration layer





HOW TO GO FURTHER IN MECHANISMS ASSUMPTION?

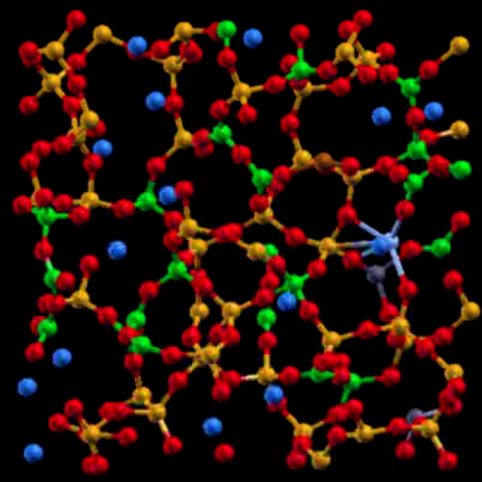
Low energy heavy ion irradiation
→ ballistic interactions

Modifications of
- the glass structure
  - coordination
  - depolymerization

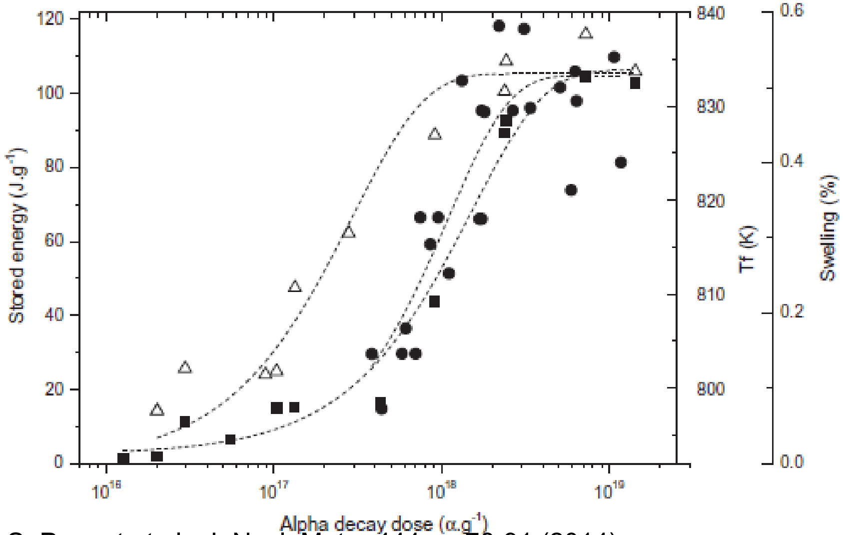
→ Increase of intern energy

- The glass properties
  - ring size
  - swelling, hardness decrease

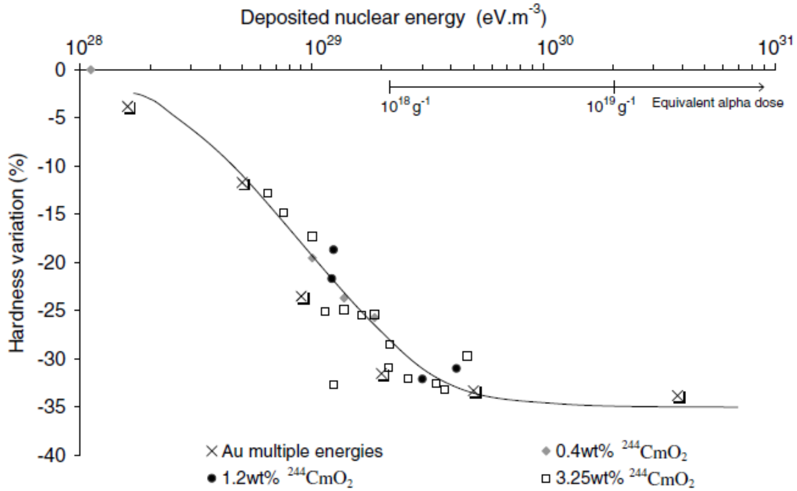
JM Delaye, PRB 61 (2000) 14481



Golden = Si ; Green = B
Blue = Na ; Red = O



S. Peuget et al., J. Nucl. Mater 444, pp76-91 (2014)



HOW TO GO FURTHER IN MECHANISMS ASSUMPTION?

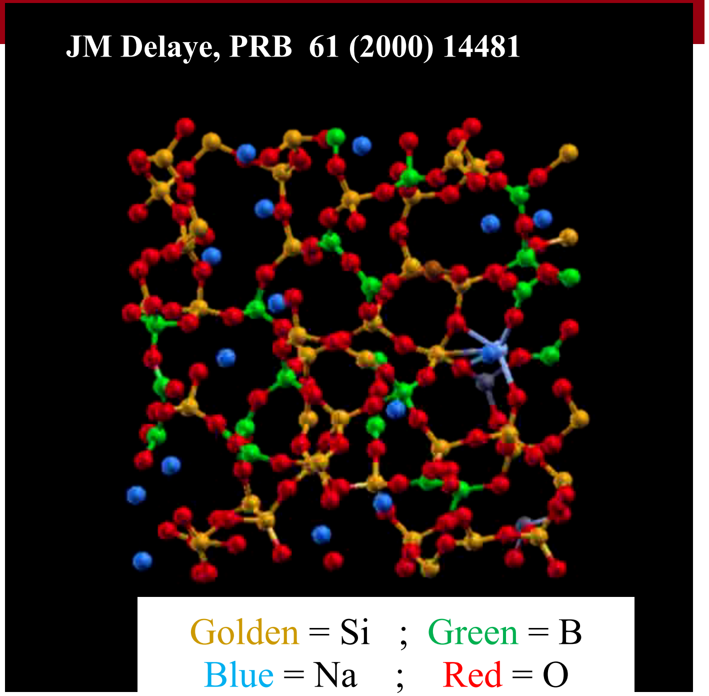
Low energy heavy ion irradiation
→ ballistic interactions

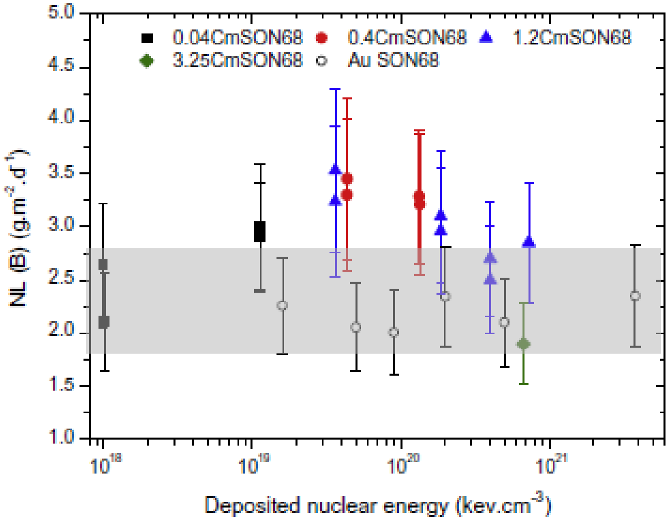
Modifications of
- the glass structure
  - coordination
  - depolymerization

→ Increase of intern energy

- The glass properties
  - ring size
  - swelling, hardness decrease

BUT no modifications of total hydrolysis of glassy network (R_0)





S. Peuget et al., J. Nucl. Mater 444, pp76-91 (2014)

METHODOLOGY

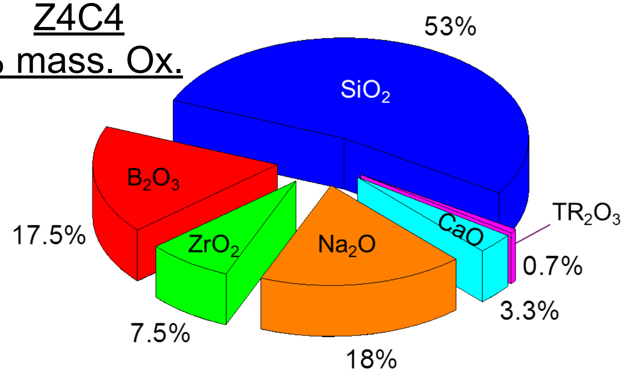
GLASSES AND IRRADIATION CONDITIONS

2 simple glass compositions

- Z4C4-Eu
- ISG (International Simple Glass[1])

	SiO_2	B_2O_3	Na_2O	CaO	ZrO_2	Al_2O_3	Eu_2O_3
Z4C4-Eu $\rho = 2.62\ g.cm^{-3}$	52.34	19.14	17.14	3.19	7.38		0.81
ISG $\rho = 2.50\ g.cm^{-3}$	56.18	17.34	12.17	4.98	3.28	6.06	

Z4C4
% mass. Ox.



[1] S. Gin et al., Materials Today 16(6) (2013)

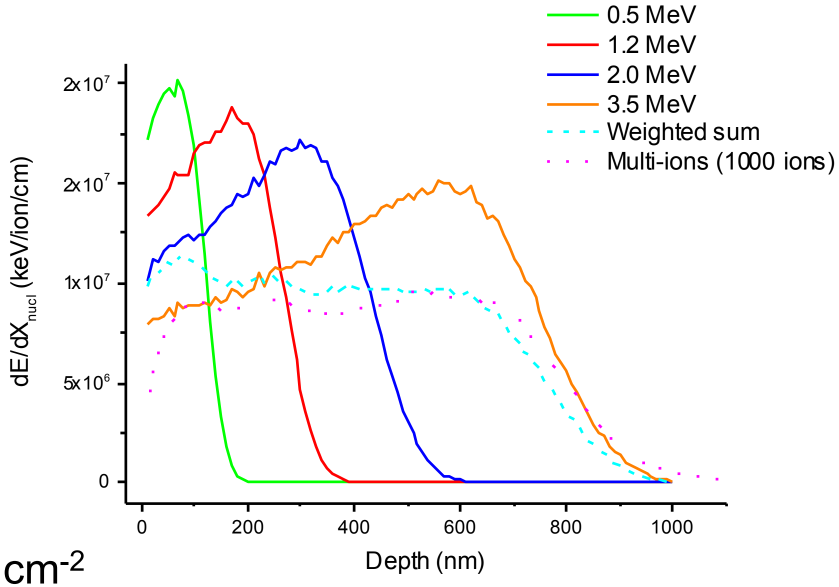
GLASSES AND IRRADIATION CONDITIONS

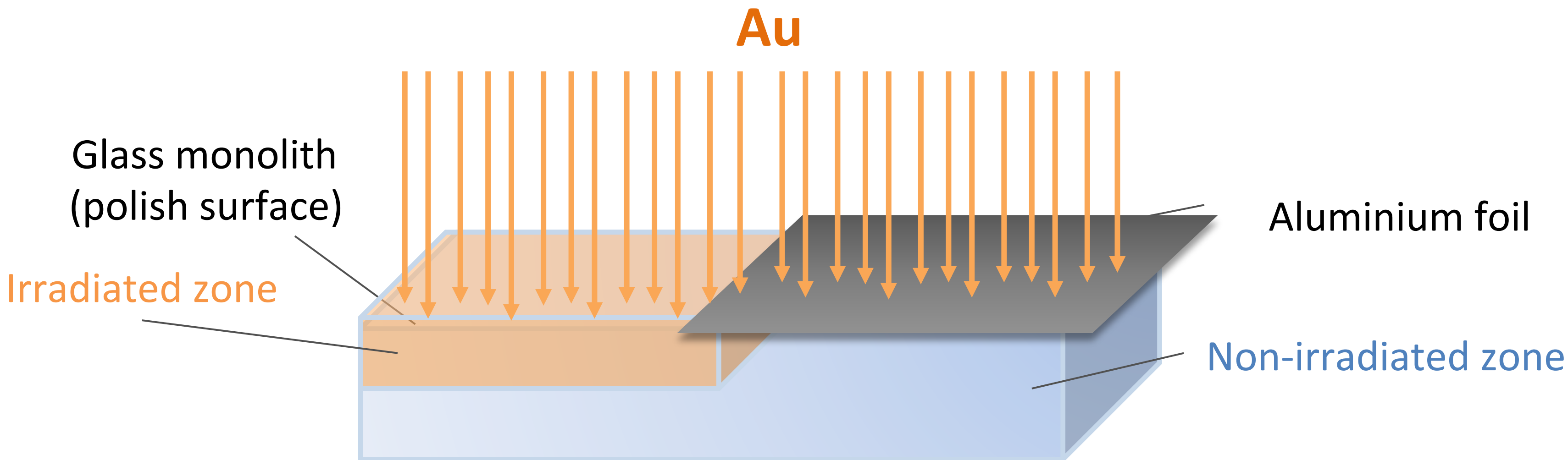
2 simple glass compositions

- Z4C4-Eu
- ISG (International Simple Glass[1])

Multiple-energy gold ion irradiation

- CSNSM, Orsay, France
- 0,5 – 3,5 MeV → ≈ constant ballistic damage
- Energy deposition < ion track formation[2]
- Wide range of fluences: 1,9.10^{12} → 5,5.10^{14} ions.cm^{-2}





[1] S. Gin et al., Materials Today 16(6) (2013)
[2] Mir, A. H., Thèse de l'Université de Caen, 2015.

2 simple glass compositions

- Z4C4-Eu
- ISG (International Simple Glass[1])

Multiple-energy gold ion irradiation

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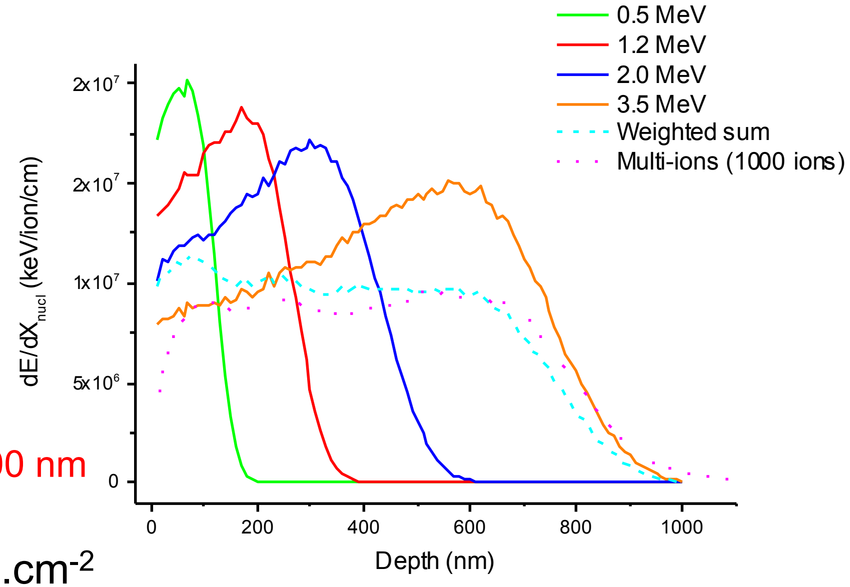
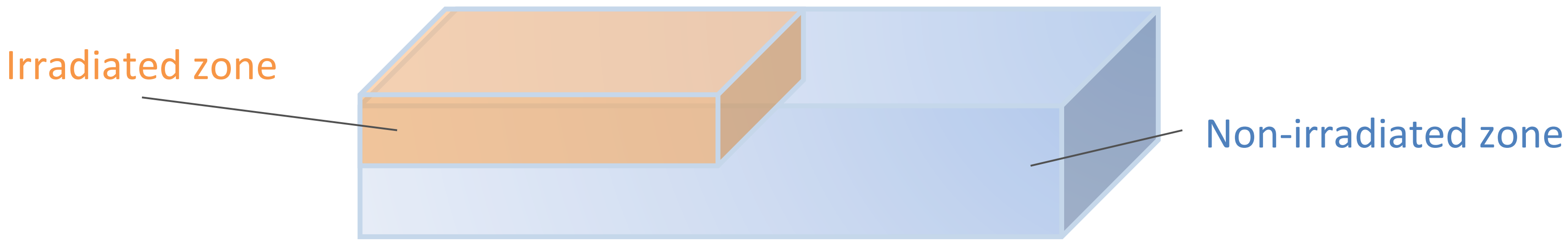
- 0,5 – 3,5 MeV → ≈ constant ballistic damage 1000 nm
- Energy deposition < ion track formation[2]
- Wide range of fluences: $1{,}9.10^{12} \rightarrow 5{,}5.10^{14}$ ions.cm^{-2}
- Ballistic dose: 0,7 → 215 MGy





[1] S. Gin et al., Materials Today 16(6) (2013)
[2] Mir, A. H., Thèse de l'Université de Caen, 2015.

LEACHATE AND CHARACTERIZATIONS

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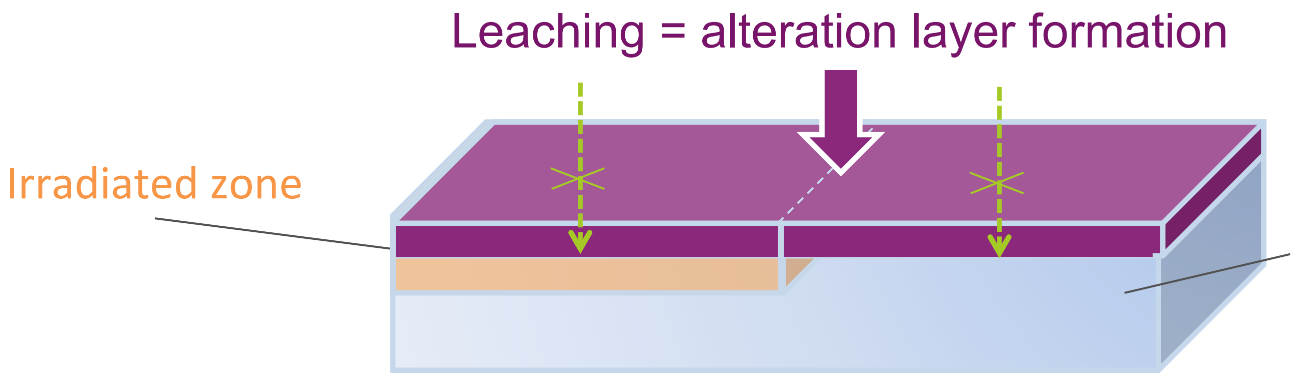
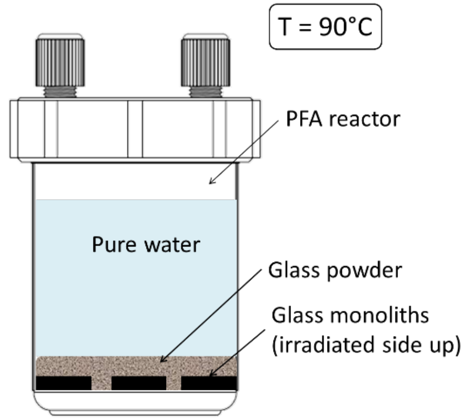
Alteration protocol

- Savillex, 200 cm^{-1}, 90°C
- Glass monoliths sampled regularly

Altered layer characterization

- ToF-SIMS





[1] S. Gin et al., Materials Today 16(6) (2013)
[2] Mir, A. H., Thèse de l'Université de Caen, 2015.

MISE EN ŒUVRE EXPÉRIMENTALE

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Alteration protocol

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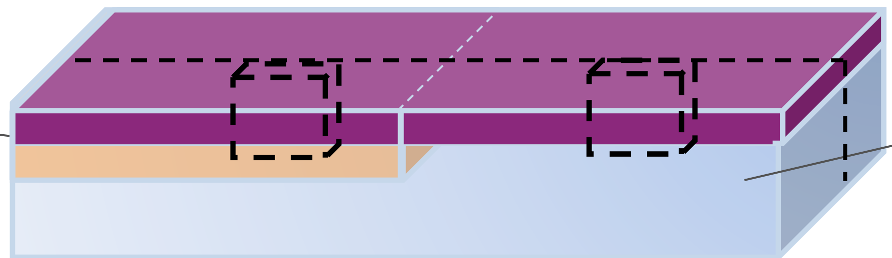
- Glass monoliths sampled regularly

Altered layer characterization

- ToF-SIMS
- SEM
- TEM (FIB lamella)

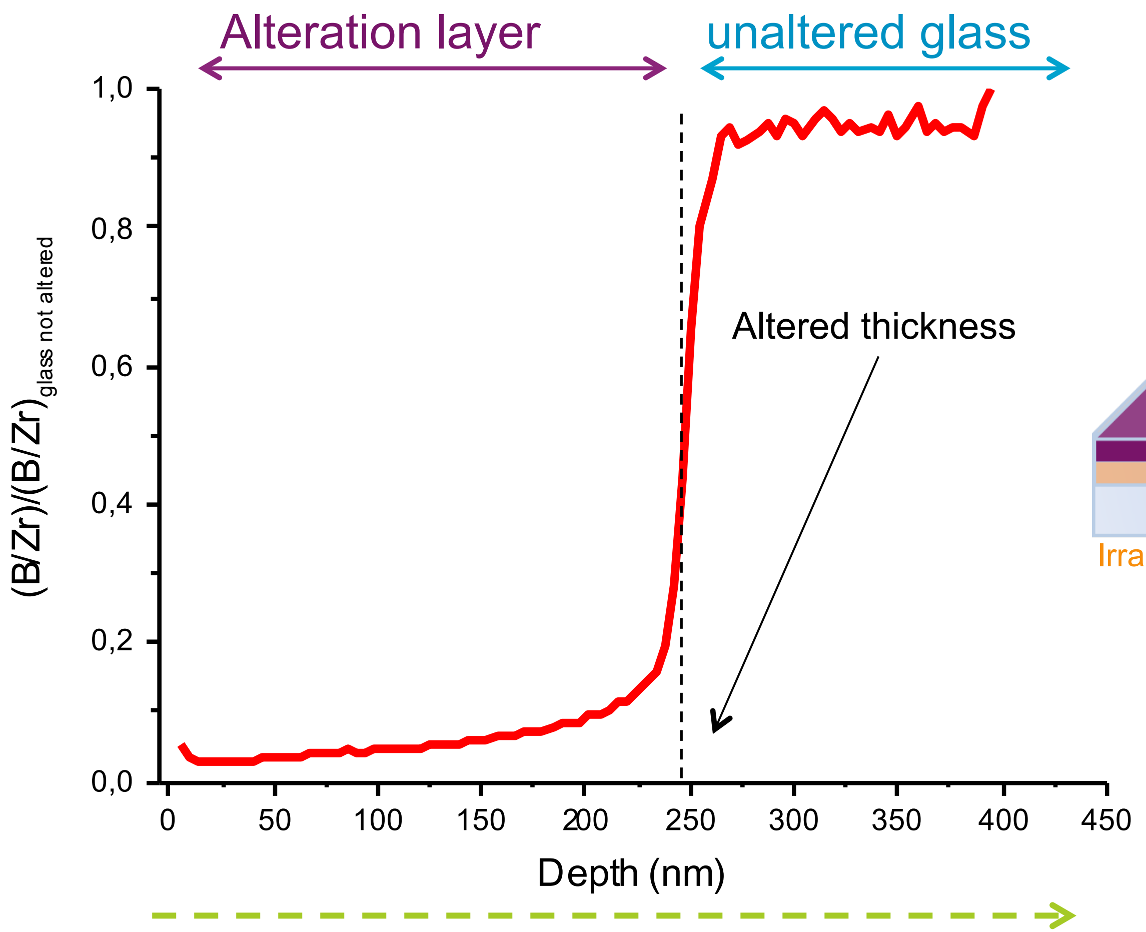


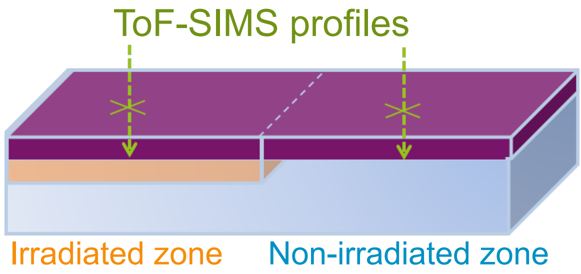
[1] S. Gin et al., Materials Today 16(6) (2013)
[2] Mir, A. H., Thèse de l'Université de Caen, 2015.

RESULTS

TOF-SIMS PROFILES

- **Alteration layer thickness determination from boron profile**

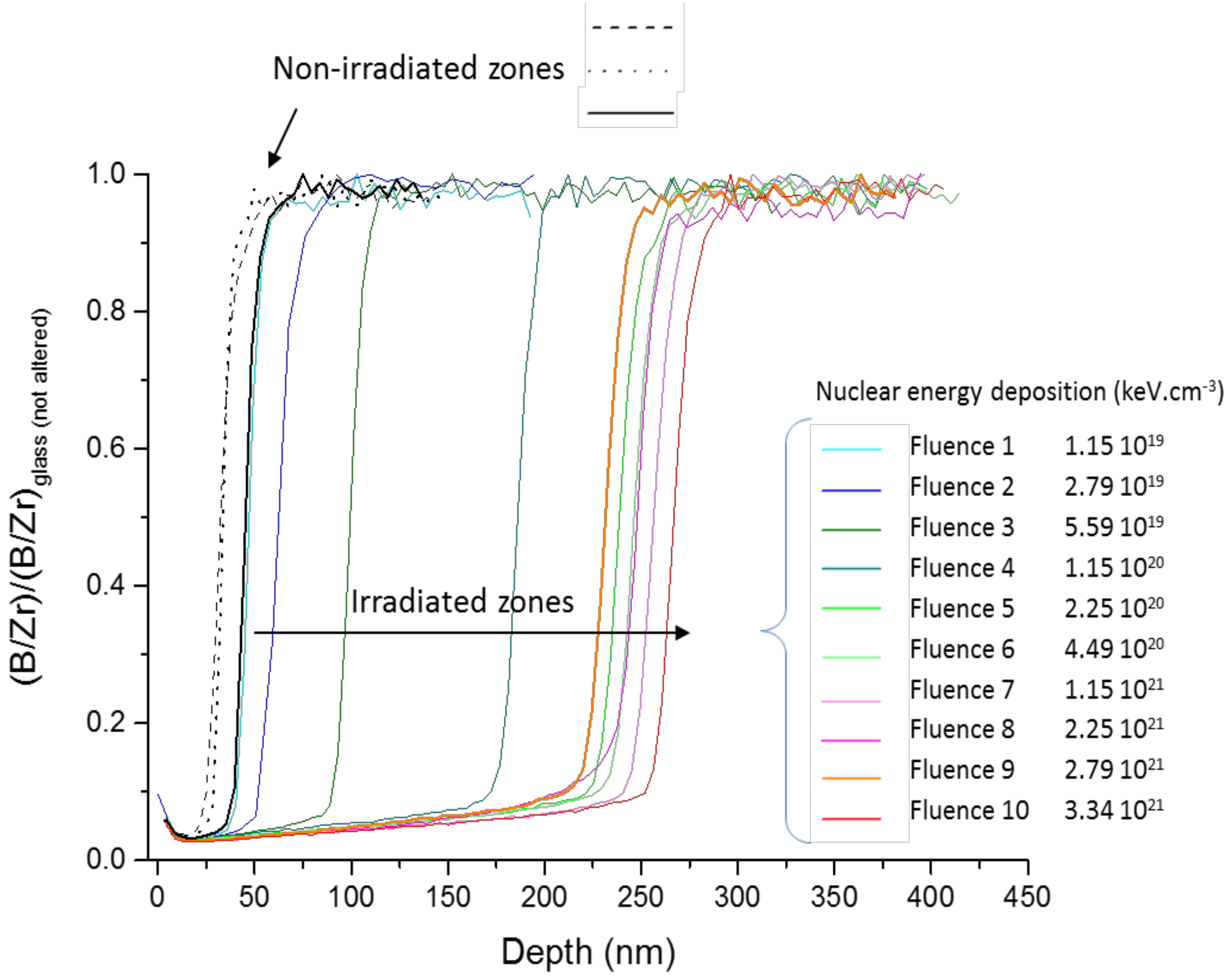


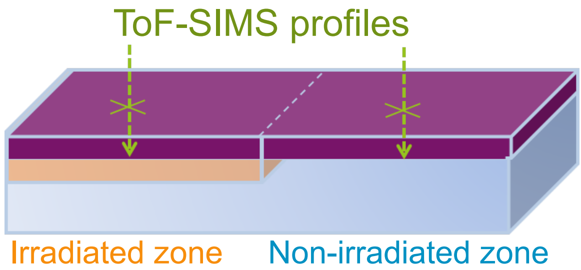


ISG, 13 days of alteration, dose = 145 MGy

TOF-SIMS PROFILES

- Alteration layer thickness determination from boron profile

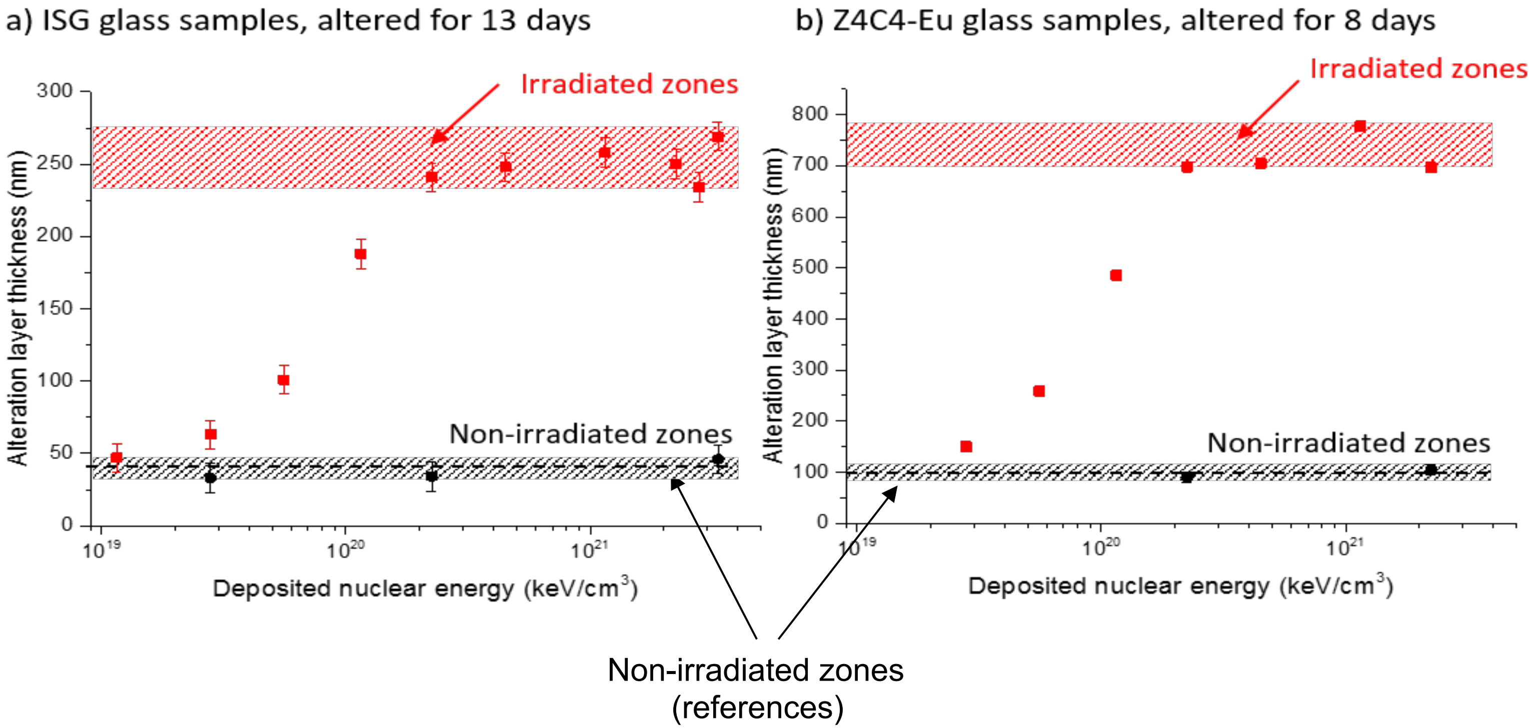




ISG, 13 days of alteration, dose = 145 MGy

TOF-SIMS PROFILES

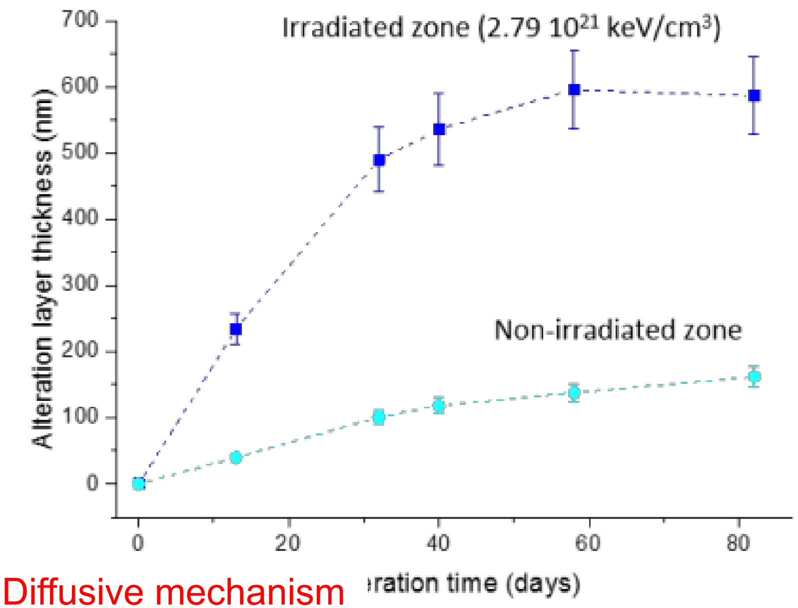
Altered thickness vs fluence

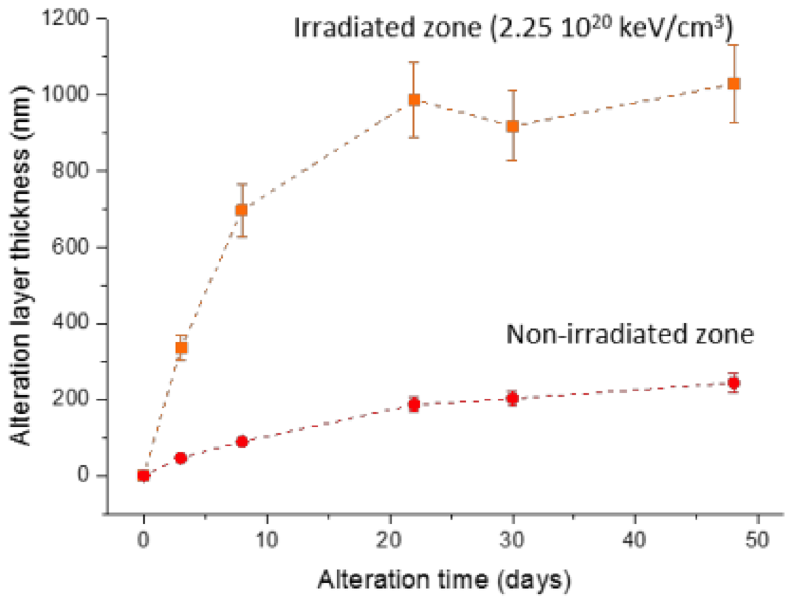


- All non-irradiated zones in agreement
- Increase of alteration layer thickness vs nuclear dose
- « plateau » observed after ≈ 2-4.10^{20} keV_{bal}/cm^3
- Same tendency for the 2 glasses

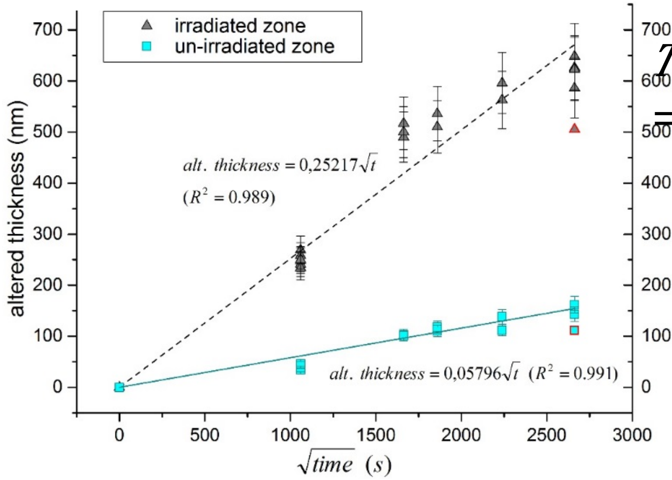
TOF-SIMS PROFILES

- **Alteration kinetics:** 1 dose, thickness evolution versus time





Diffusive mechanism



$$T_{alteration\ layer} = 2 \times \sqrt{D_{app} \times t/\pi}$$

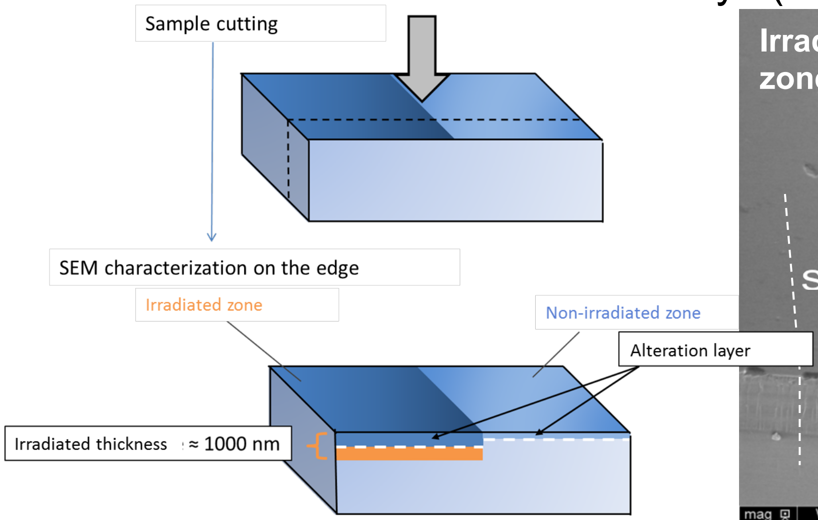
	D_{app} (m^2/s)
Irradiated zone (≥ 2.10^{20} keV/cm³)	$5.0\ 10^{-20}$
Non irradiated zone ×20	$2.6\ 10^{-21}$

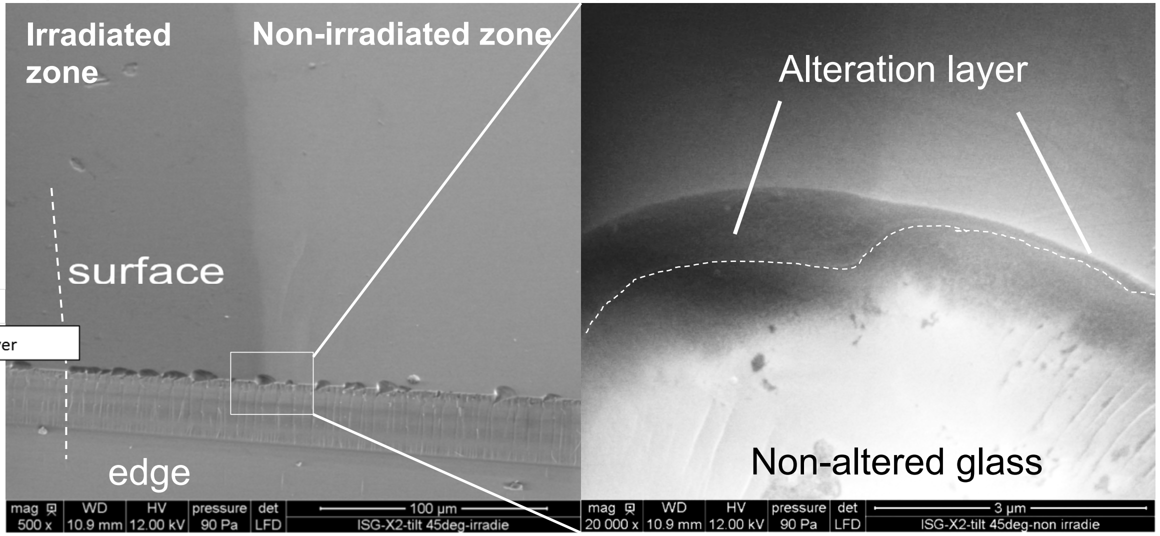
Apparent diffusion coefficient increases

Increase of alteration rate x $\sqrt{20}$ ≈ 4,5

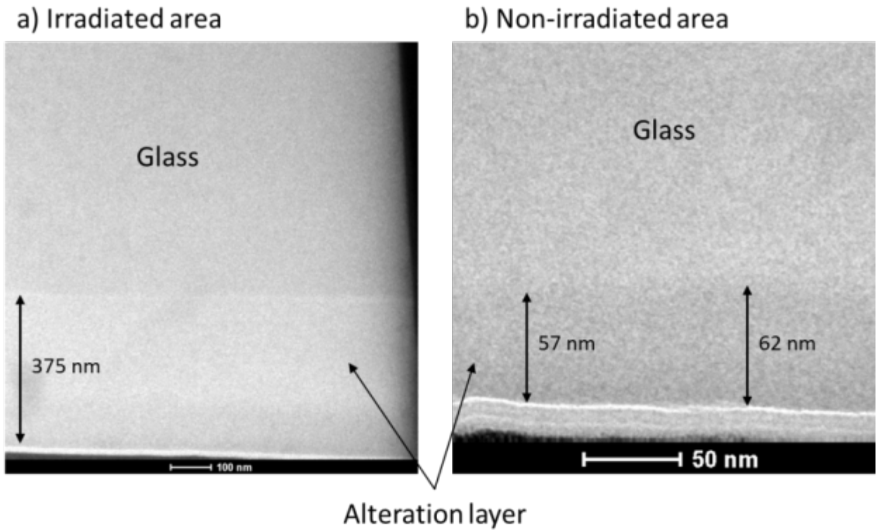
SEM & TEM CHARACTERIZATIONS

- **SEM:** ISG monolith altered 13 days (fluence = 3.34×10^{21} keV/cm^3)





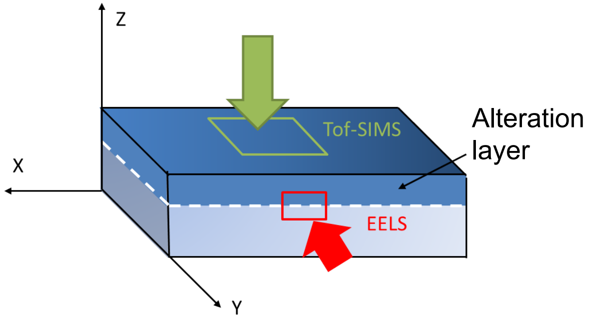
- **TEM:** Z4C4 monolith altered 3 days (fluence = 2.79×10^{21} keV/cm^3)

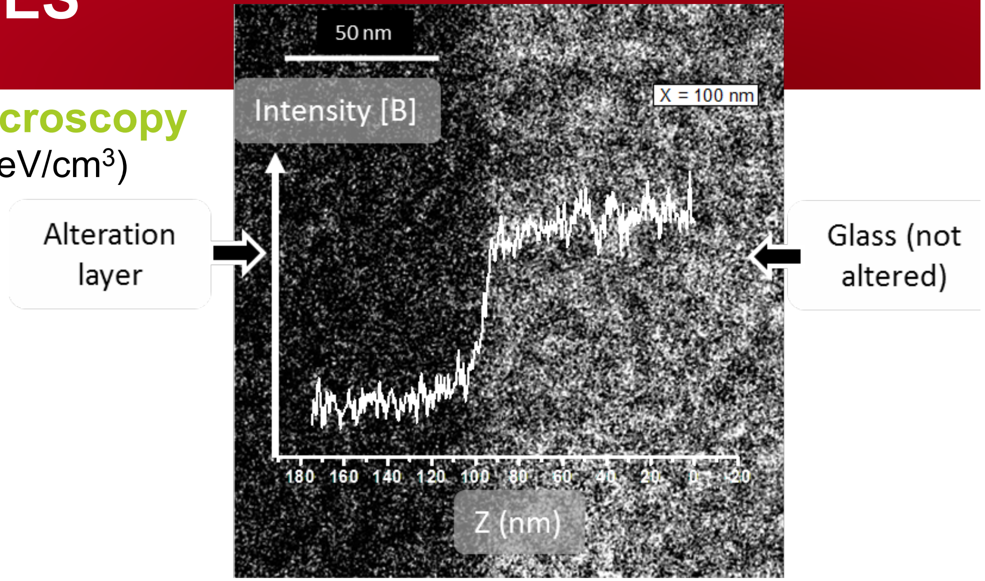


EELS CARTOGRAPHIES

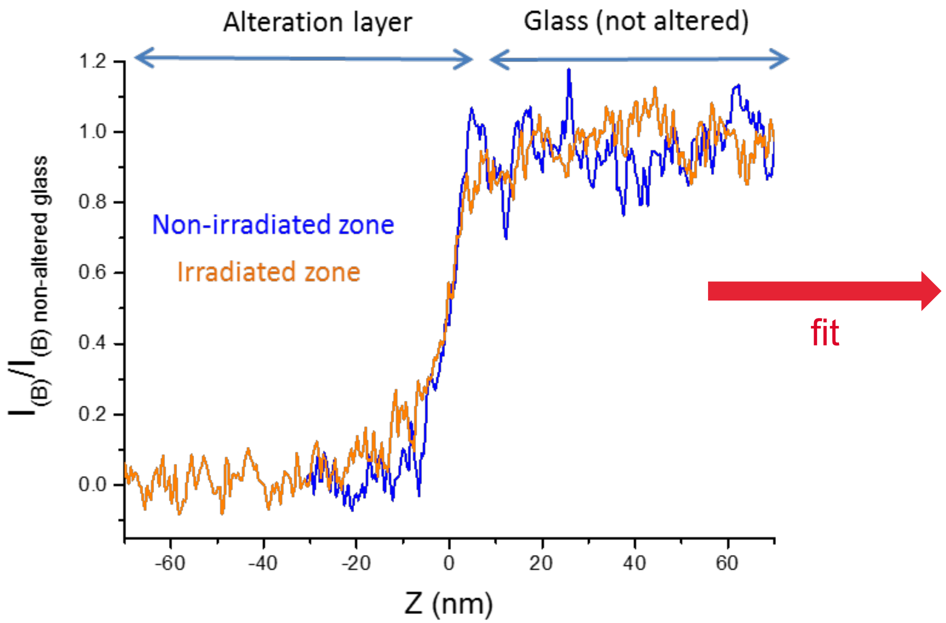
Energy Filtered Transmission Electron Microscopy

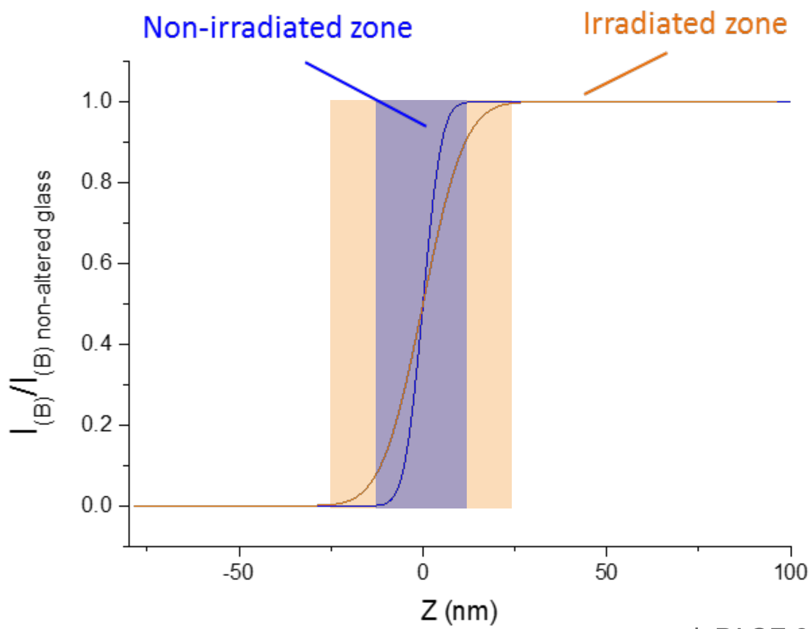
ISG monolith altered 13 days (fluence = 3.34×10^{21} keV/cm^3)





Experimental and fitted boron profile



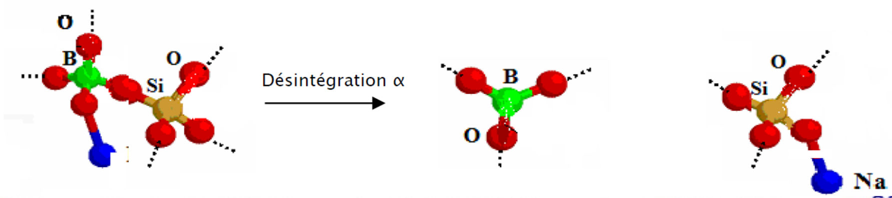


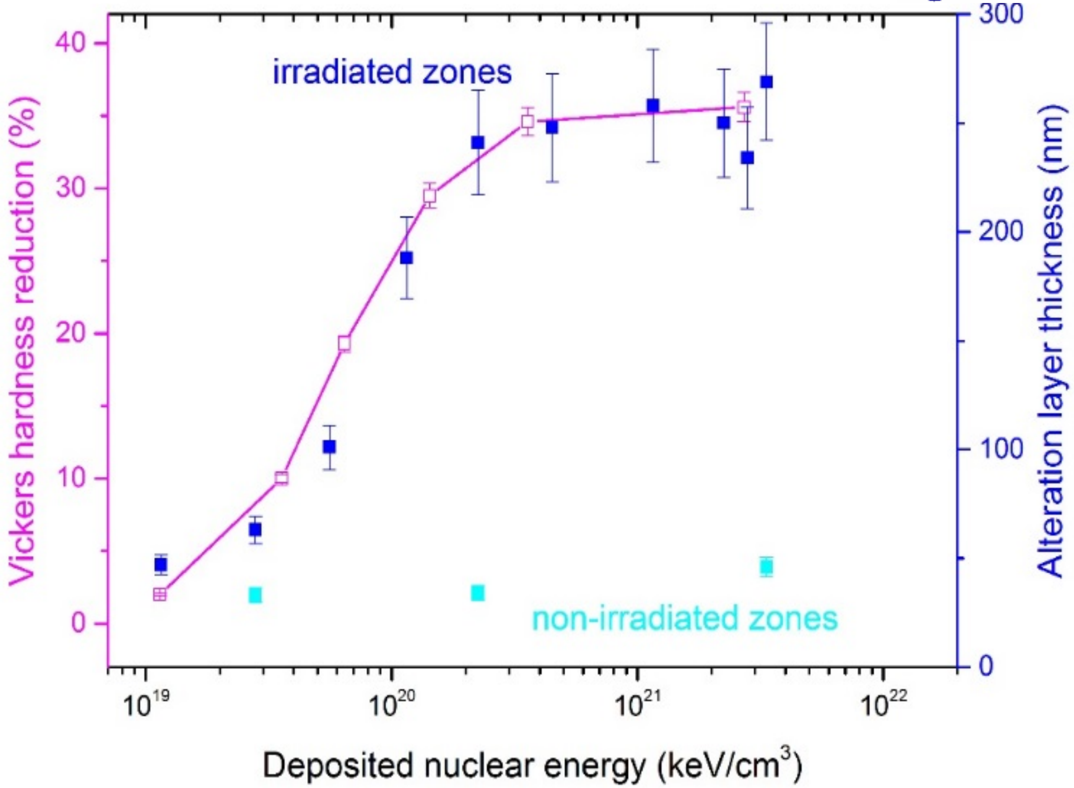
Interface from damaged glass broader than interface from the undammaged one

DISCUSSION

DISCUSSION

Comparison with modifications of glass structure and properties





Vickers hardness reduction[1] & altered thickness: same tendency

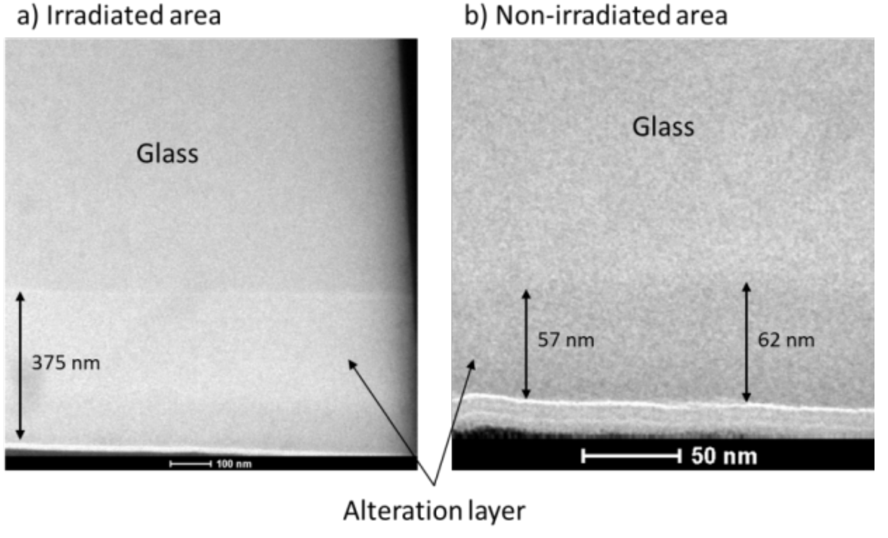
→ Structural / properties & chemical durability similarly affected by the same cause

[1]J. De Bonfils et al., J. Non-Cryst. Solids 356, pp388 (2010)

DISCUSSION

What could be hypothetized?

~~Glass swelling inducing µcracks~~ → increase of open surfaces
→ indirect increase of glass alteration[1]



TEM characterizations

[1]D. M. Wellman et al., J. Nucl. Mater. 340, pp149 (2005)

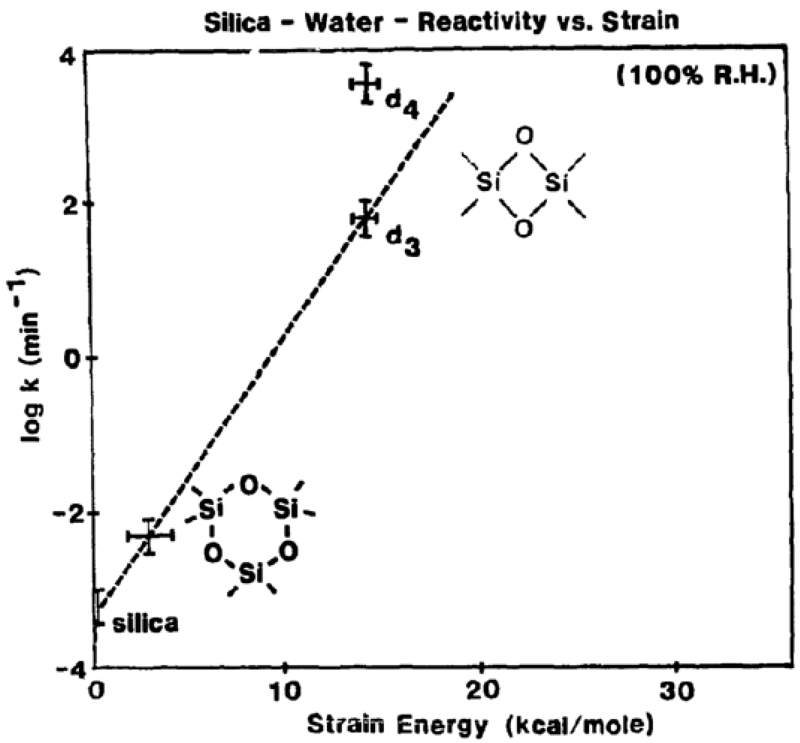
DISCUSSION

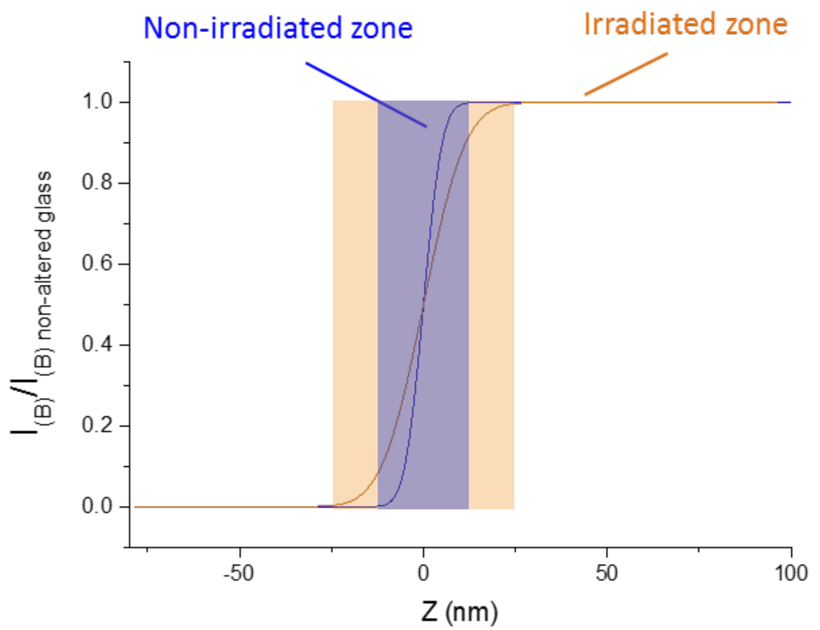
What could be hypothetized?

Increase of medium range order distributions (rings statistic, angles…)

→ Modification of the glass free volume

→ Modification of water access in irradiated glass[1]





[1]B. C. Bunker et al., J. Non-Cryst. Solids 179, pp300 (1994)

DISCUSSION

What could be hypothetized?

Increase of stored energy[1]

→ Increase of glass reactivity

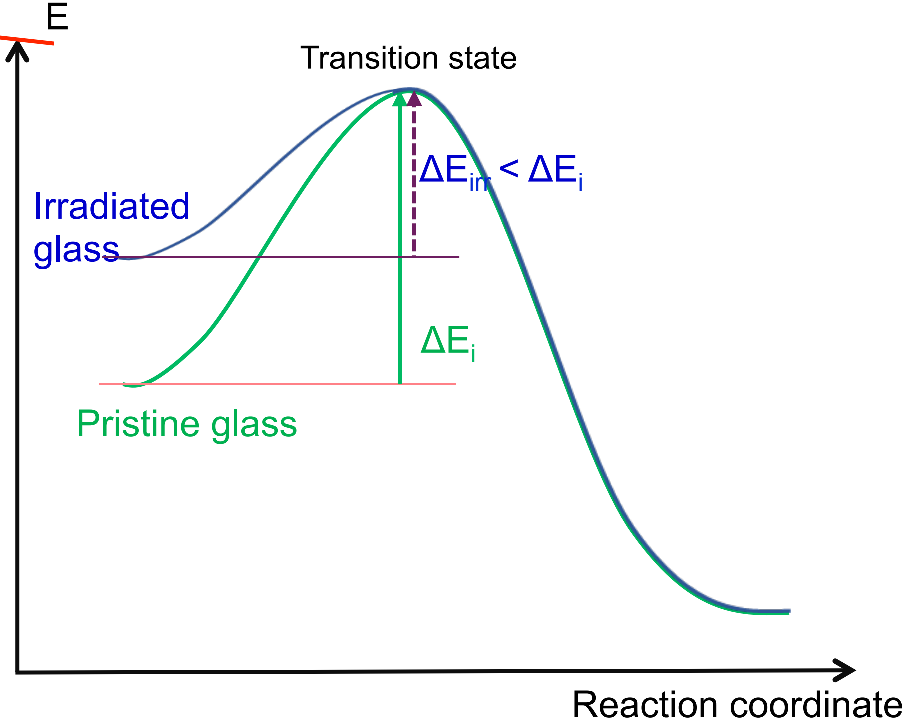
of weakly bonded elements (alkalis, B…)

of elements from glassy network

local SiO_4 hydrolysis

~~total SiO_4 hydrolysis~~

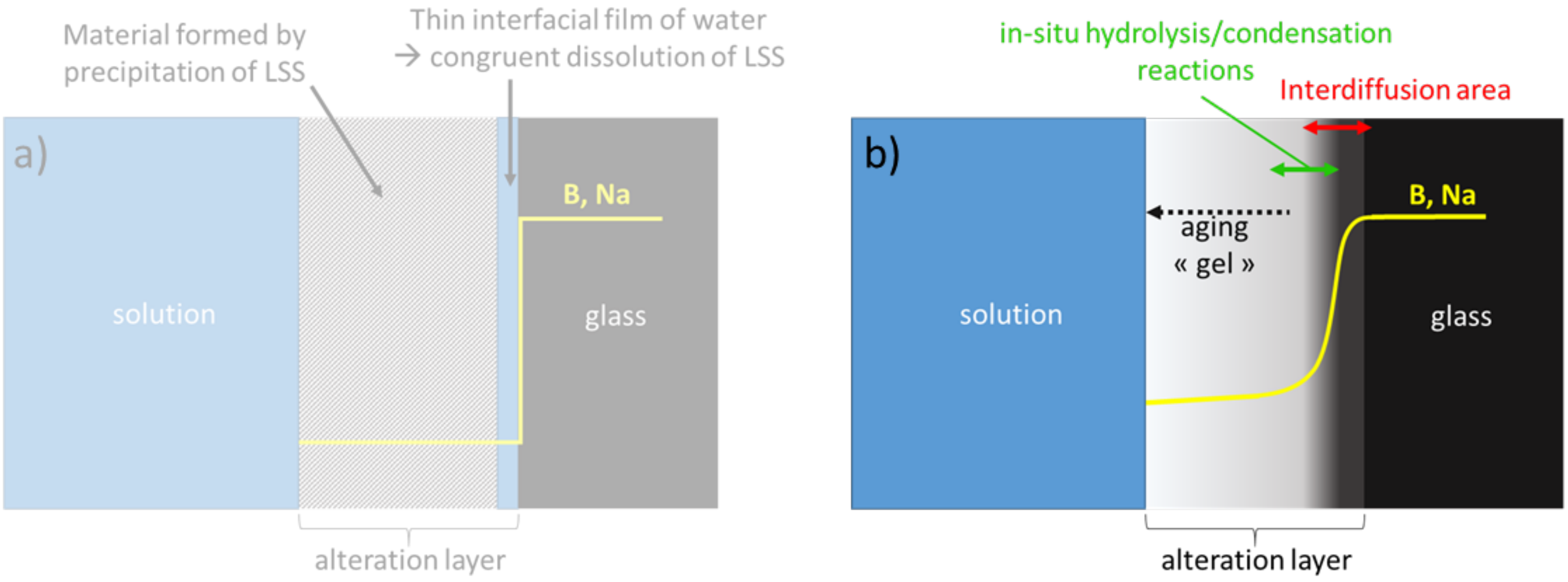
Initial alteration rate (i.e. total hydrolysis) not modified by such an irradiation[2]



[1]E. Maugeri, J. Am.Ceram.Soc. 95, pp2869 (2012)

[2]S. Peuget et al., J. Nucl. Mater 444, pp76-91 (2014)

WHAT ABOUT MECHANISMS?



Here, previous irradiation affects glass alteration

→ hypothesis of effect on total hydrolysis ruled out

→ hypothesis of increase of local reactivity or water migration in agreement

CONCLUSIONS & PROSPECTS

Increase of altered thickness on damaged glasses (x 4.5 max)
Plateau reached for doses > $2\text{-}4.10^{20}$ keV_{bal}/cm^3

⇩

- Chemical durability & glass structure / properties similarly affected by irradiation
  - Mechanisms: water access and/or increase of local reactivity
- Chemical durability of glass sensitive to its initial structure

« simplifed » system, also taking into account:

- Glass composition: simple glass more sensitive than complex glasses
- Recovery effect of α particles in real alpha decay[1] → « Dual Beam » irradiations

To increase mechanistic undertansding :

- To explore very first time of alteration[2] (water penetration in damaged glasses)
- Atomistic modeling: create a damaged glass, explore water diffusion[3]…

1 Mir, A. H., Thèse de l'Université de Caen, 2015.
2 D. Rébiscoul et al., J. Non-Cryst. Solids 358, pp. 2951 (2012) & C. Mansas et al., J. Phys. Chem. C 121, pp.16201 (2017)
3 G. K. Lockwood et al., J. Nucl. Mater. 430, pp.239 (2012)

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And you for your attention

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SECM / LMPA