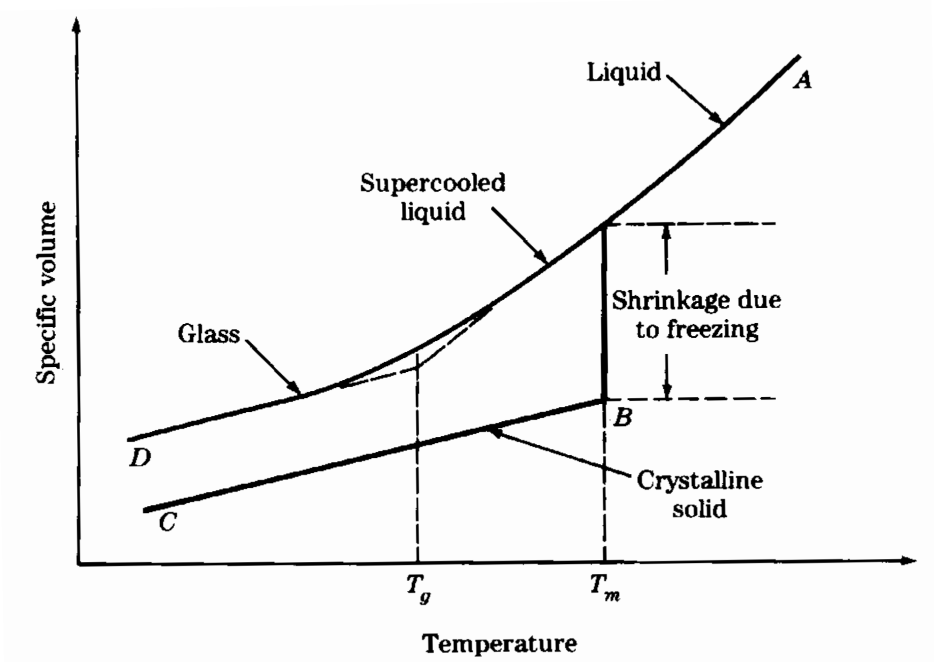
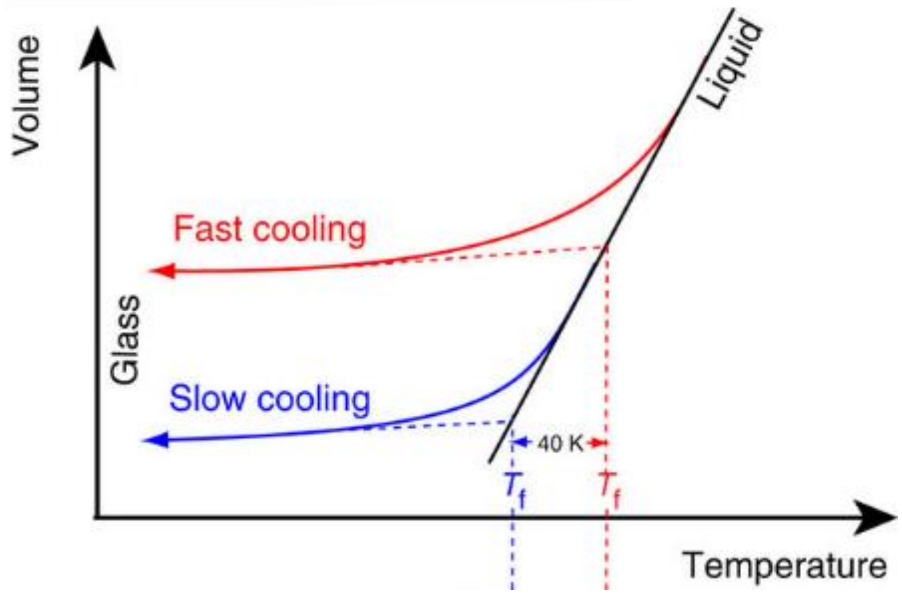
DE LA RECHERCHE À L'INDUSTRIE

# Radiation damages in vitreous wasteforms

www.cea.fr




A glass (or vitreous solid) is a solid formed by rapid melt quenching.

A glass is an amorphous solid that exhibits a glass transition phenomena at $T_g$.

Viscosity

Relaxation time $\tau = \dfrac{\eta}{G}$

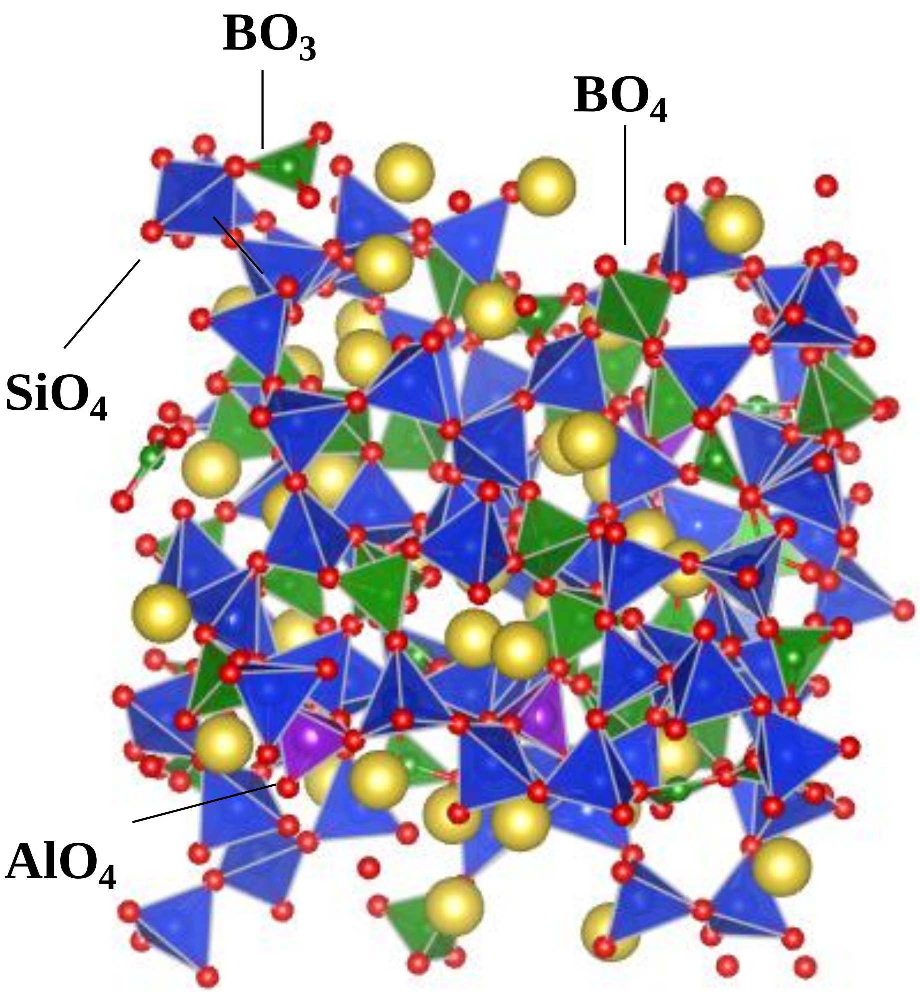
Shear Modulus

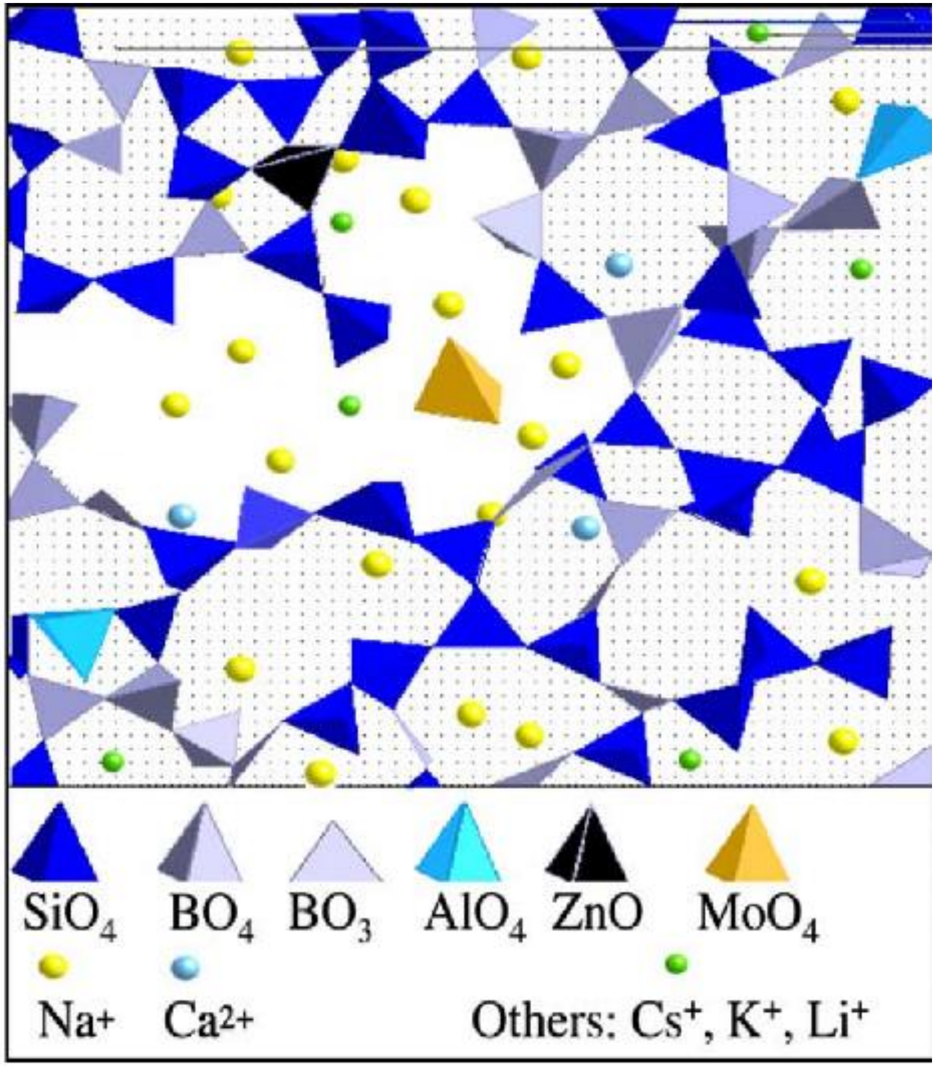
**Glass properties depend on:**

- **Chemical composition**
- **Thermal history during elaboration process**

# Glassy state

- **Short Range Order, SRO : Yes Polyhedra**
- **Medium Range Order, MRO : Yes Angle, Ring statistic**
- **Long Range Order, LRO : No**



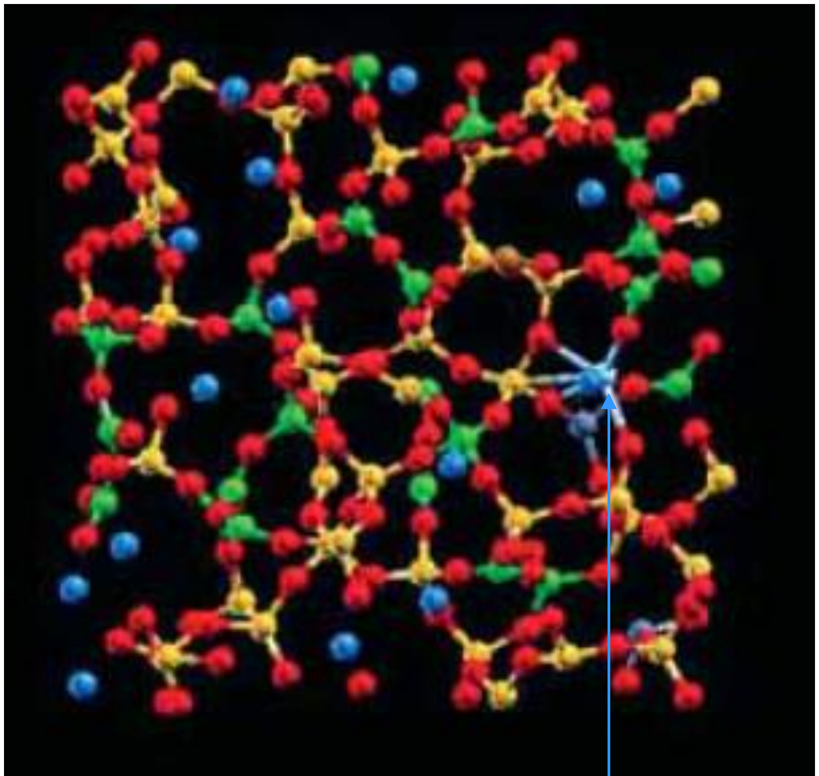



# Complex oxides glasses : French Nuclear Glass

Oxide glass with around 30 oxides

Sodium alumino-borosilicate glass

*L. Cormier, J.M. Delaye, D. Ghaleb, G. Calas, PRB 61 (2001) 14495*



Si B Na O

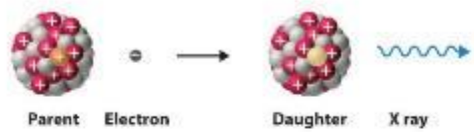
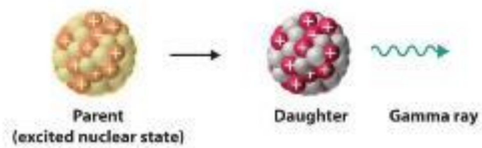
Fission product / Actinide in an octahedric site

**Domaine de composition chimique des verres R7T7 produits dans les ateliers industriels par AREVA - La Hague**

| Oxydes | Intervalle spécifié pour l'industriel (% massique) | | Composition moyenne des verres industriels (% massique) |
|---|---|---|---|
| | min | max | |
| $SiO_2$ | 42,4 | 51,7 | 45,6 |
| $B_2O_3$ | 12,4 | 16,5 | 14,1 |
| $Al_2O_3$ | 3,6 | 6,6 | 4,7 |
| $Na_2O$ | 8,1 | 11,0 | 9,9 |
| CaO | 3,5 | 4,8 | 4,0 |
| $Fe_2O_3$ | | < 4,5 | 1,1 |
| NiO | | < 0,5 | 0,1 |
| $Cr_2O_3$ | | < 0,6 | 0,1 |
| $P_2O5$ | | < 1,0 | 0,2 |
| $Li_2O$ | 1,6 | 2,4 | 2.0 |
| ZnO | 2,2 | 2,8 | 2,5 |
| Ox (PF+Zr+ actinides)+ Suspension de fines | 7,5 | 18,5 | 17,0 |
| Oxydes d'actinides | | | 0,6 |
| $SiO_2$+$B_2O_3$+$Al_2O_3$ | > 60 | | 64,4 |

Monographie DEN : Le conditionnement des déchets nucléaires

# Nuclear Glass or GCM: What type of radiation?

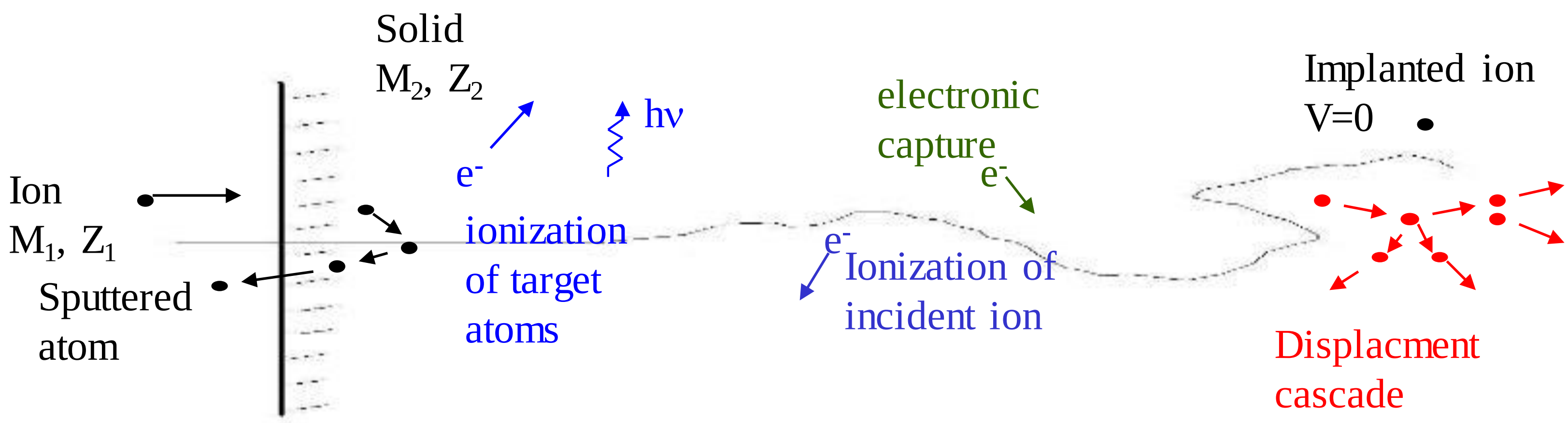
| Decay Type | Radiation Emitted | Generic Equation | Model |
|---|---|---|---|
| Alpha decay | $^{4}_{2}\alpha$ | $^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}X' + {}^{4}_{2}\alpha$ |  |
| Beta decay | $^{0}_{-1}\beta$ | $^{A}_{Z}X \longrightarrow {}^{A}_{Z+1}X' + {}^{0}_{-1}\beta$ |  |
| Positron emission | $^{0}_{+1}\beta$ | $^{A}_{Z}X \longrightarrow {}^{A}_{Z-1}X' + {}^{0}_{+1}\beta$ |  |
| Electron capture | X rays | $^{A}_{Z}X + {}^{0}_{-1}e \longrightarrow {}^{A}_{Z-1}X' + \text{X ray}$ |  |
| Gamma emission | $^{0}_{0}\gamma$ | $^{A}_{Z}X^{*} \xrightarrow{\text{Relaxation}} {}^{A}_{Z}X' + {}^{0}_{0}\gamma$ |  |
| Spontaneous fission | Neutrons | $^{A+B+C}_{Z+Y}X \longrightarrow {}^{A}_{Z}X' + {}^{B}_{Y}X' + C\,{}^{1}_{0}n$ |  |

Actinides: mainly α decays

Fission products: mainly β decays

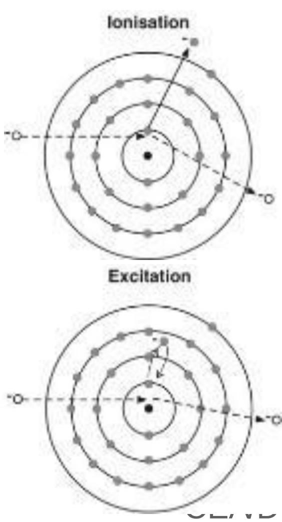
Most of alpha and beta decays

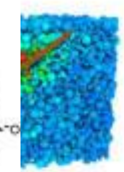
## Due to the various decays: Emission of particles with high amount of energy

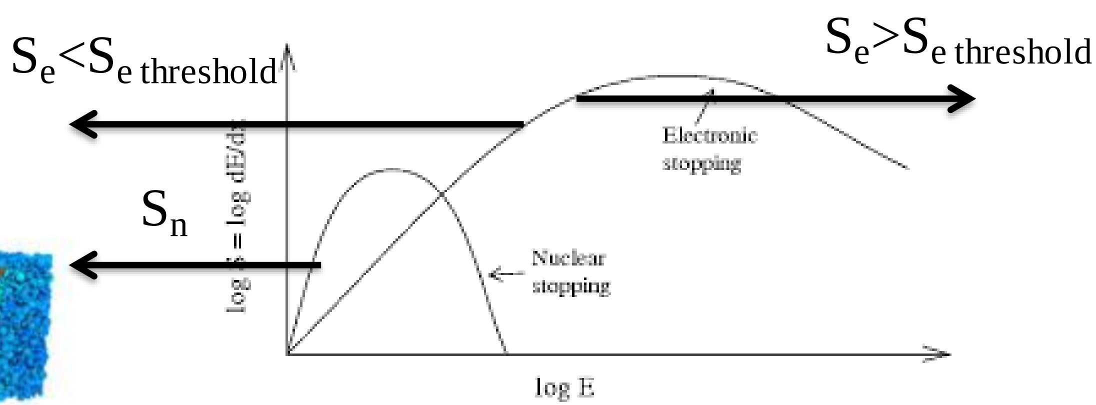


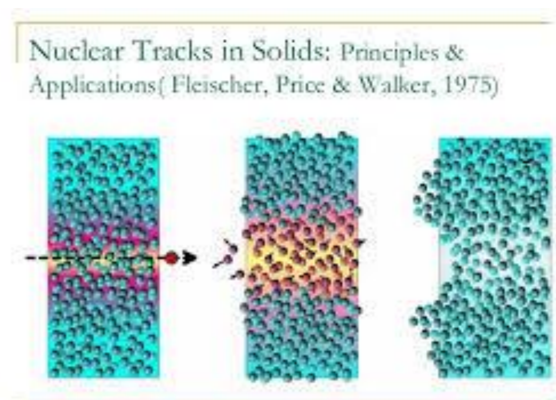

Se = $(dE/dx)_{elec}$ = Electronic energy loss due to collisions with electrons

Sn = $(dE/dx)_{nucl}$ = Nuclear energy loss due to collisions with atoms

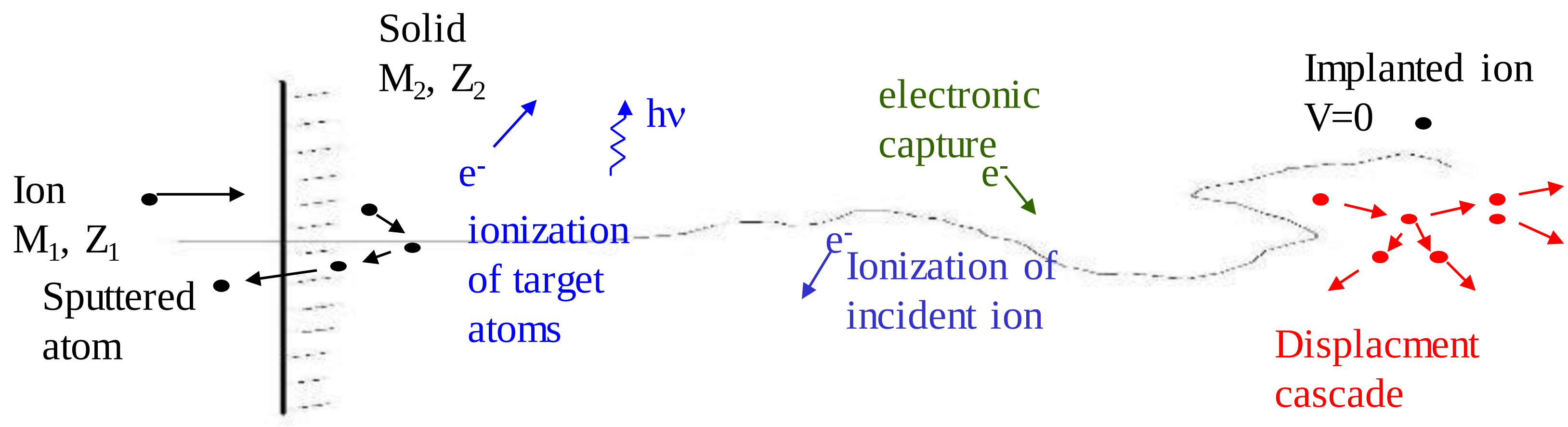


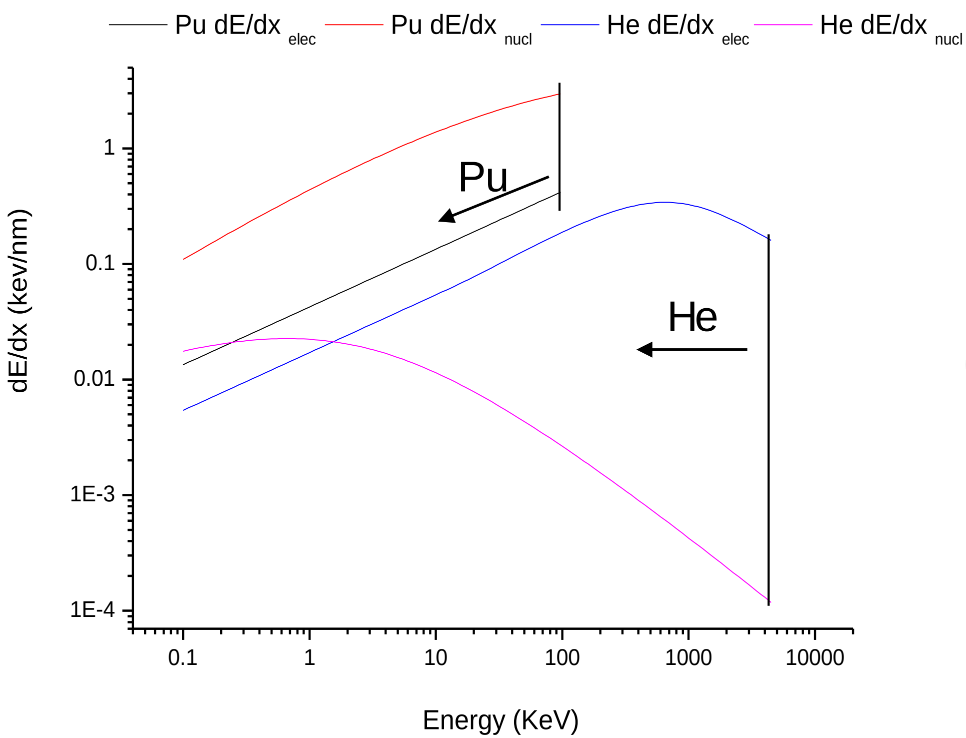



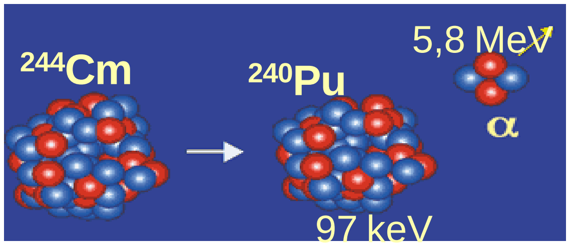


# Interaction with matter



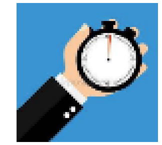





**Mainly nuclear collisions**
**Ballistic damage**
**Displacement cascade**

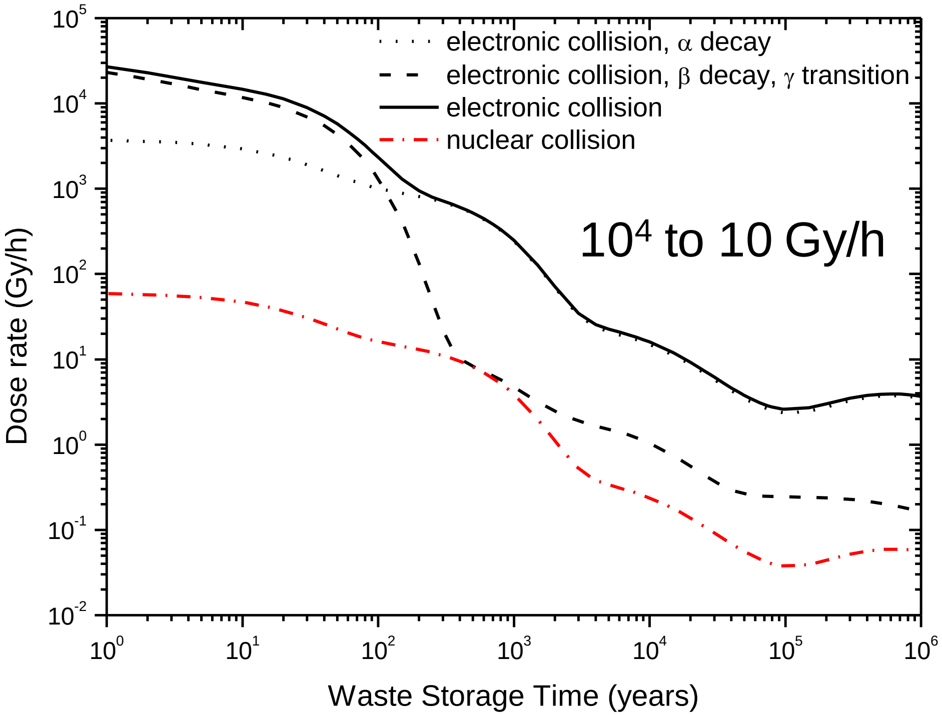

**Mainly electronic collisions**

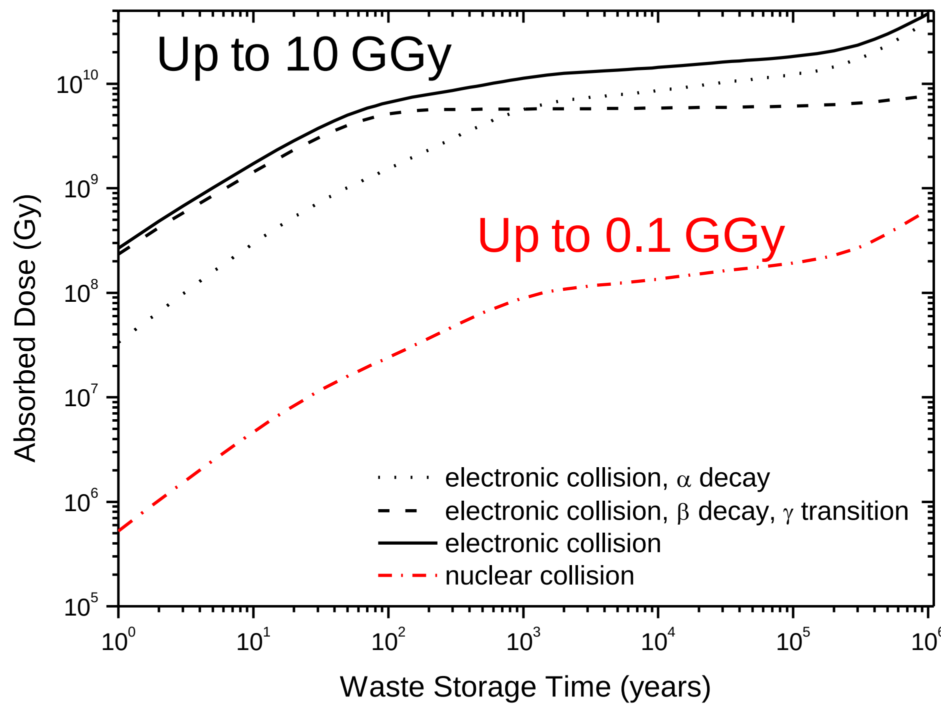
## Important parameters to consider:



- **Dose rate** : absorbed energy per unit of mass of material per unit of time (Gy/s)


- **Dose** : absorbed energy per unit of mass of material (Gy = J/kg)



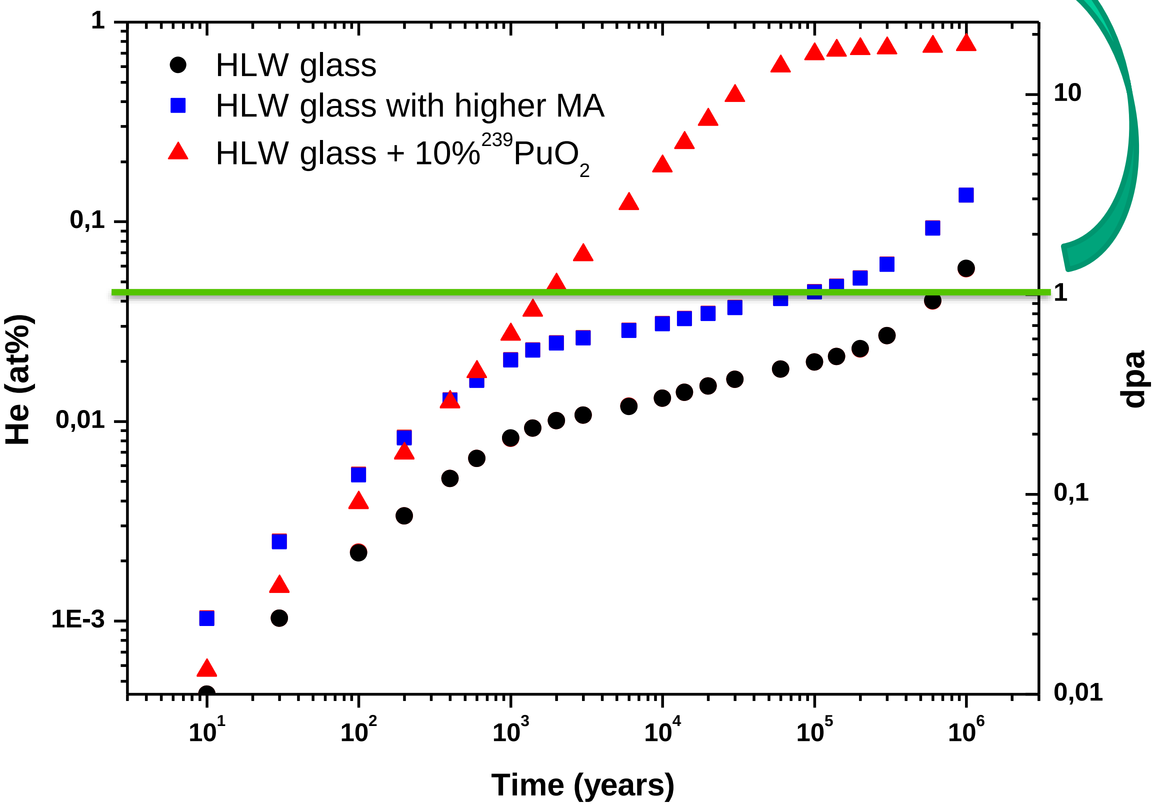



# Interaction with matter

- Nuclear collisions, **dpa** = **displacements per atom**

$$\text{dpa = displacements per atom} = \frac{\text{Number of displaced atoms in volume from NRT equation}}{\text{Number of materials atoms in same volume}}$$

All the atoms have been displaced




$$N_d(T_d) = \begin{bmatrix} 0 & , & T_d < E_d \\ 1 & , & E_d < T_d < 2E_d/0.8 \\ \dfrac{0.8T_d}{2E_d} & , & 2E_d/0.8 < T_d < \infty \end{bmatrix}$$

$$T_D = F_{D,n} = E_0 - F_{D,e}$$

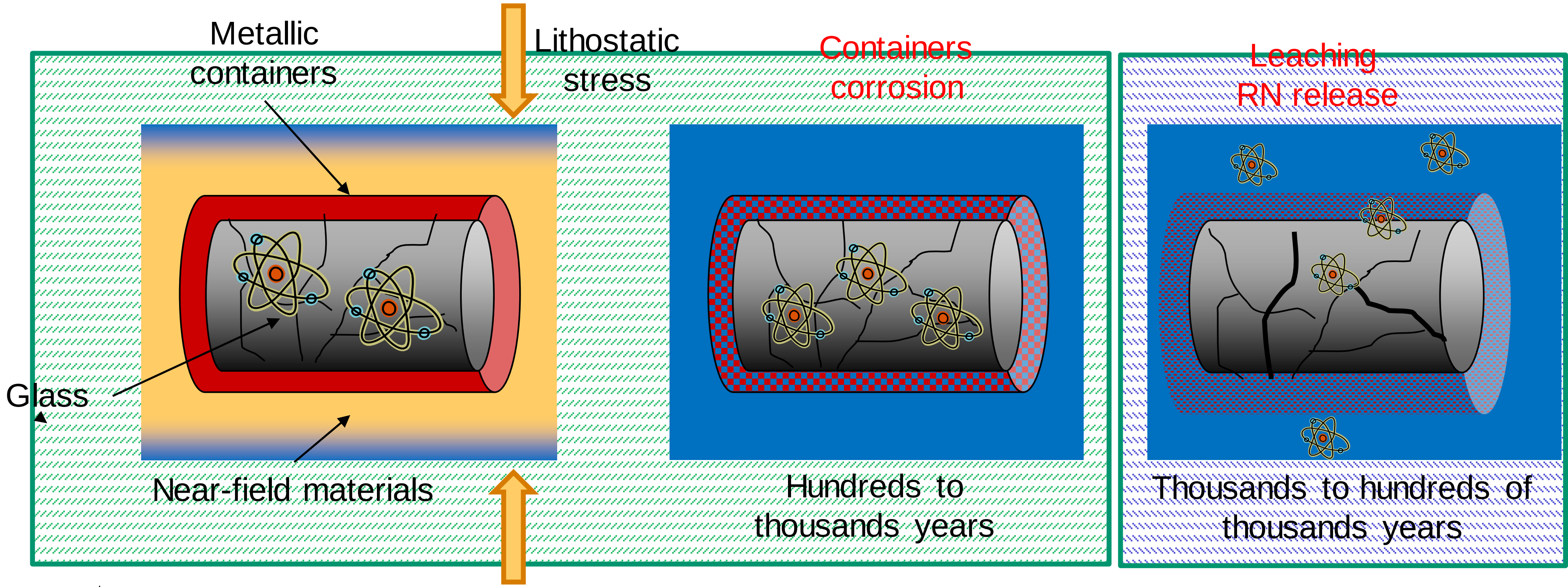
$T_D$=Energy available for damage production

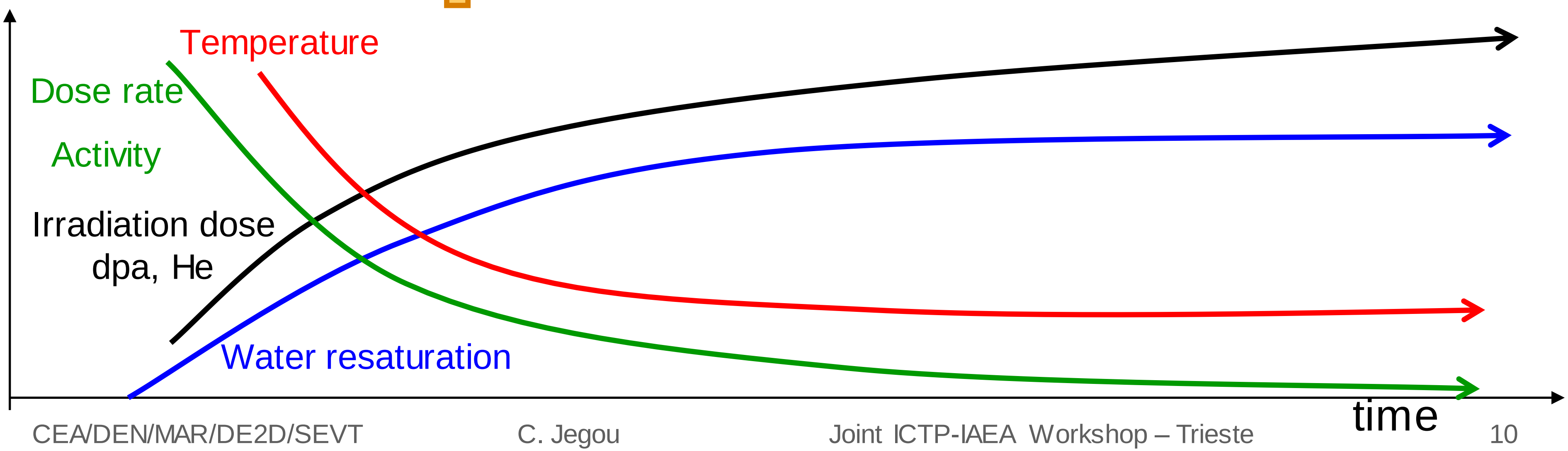
$E_0$=Energy of the particle

$F_{D,e}$=Energy lost to electronic stopping

$E_d$=Threshold displacement energy

# Glass Long Term Behavior – complex ageing scenario



# Glass Long Term Behavior: main past studies?

## Main laboratory studies of alpha decay impact

| | | |
|---|---|---|
| USA (NLs) | 70's-90's | <3 x $10^{18}$ $\alpha$/g |
| UK (AERE) | 70's-80's | <3 x $10^{18}$ $\alpha$/g |
| France (CEA) | 70's- 80's | <3 x $10^{18}$ $\alpha$/g |
| EU (ITU) | 70's-90's | <5 x $10^{18}$ $\alpha$/g |
| JAPAN (JAERI) | 90's | <$10^{19}$ $\alpha$/g |

**Macrosocpic behavior in a limited level of dose**

**but no data on the glass structure !**

Need to improve the understanding of alpha decays effects

To predict long term behavior

To explore nuclear glass limits

To optimize the future glass or glass ceramics composition

Focus on the results of the research program started in 2001 at CEA

# Methodology to simulate alpha decays effects

- **Accelerate the time scale**
- **Dissociate the effects of self-irradiation (*electronic / nuclear*) and *helium generation***
- **Evaluate the effects on the confinement properties**
- **Evaluate the effects on the glass structure**

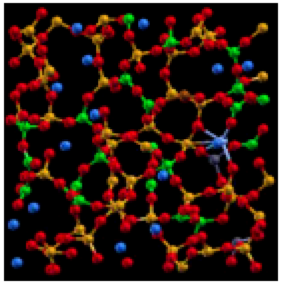
**Propose some models to explain the glass behavior under alpha self-irradiation**

Atalante DHA, CEA

IPN Orsay Lyon, Ganil

OSIRIS, CEA

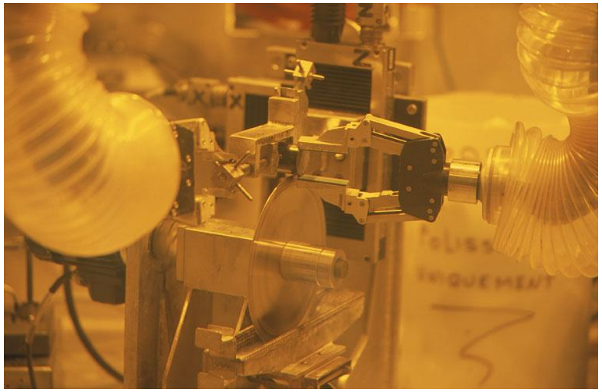
DM, CEA

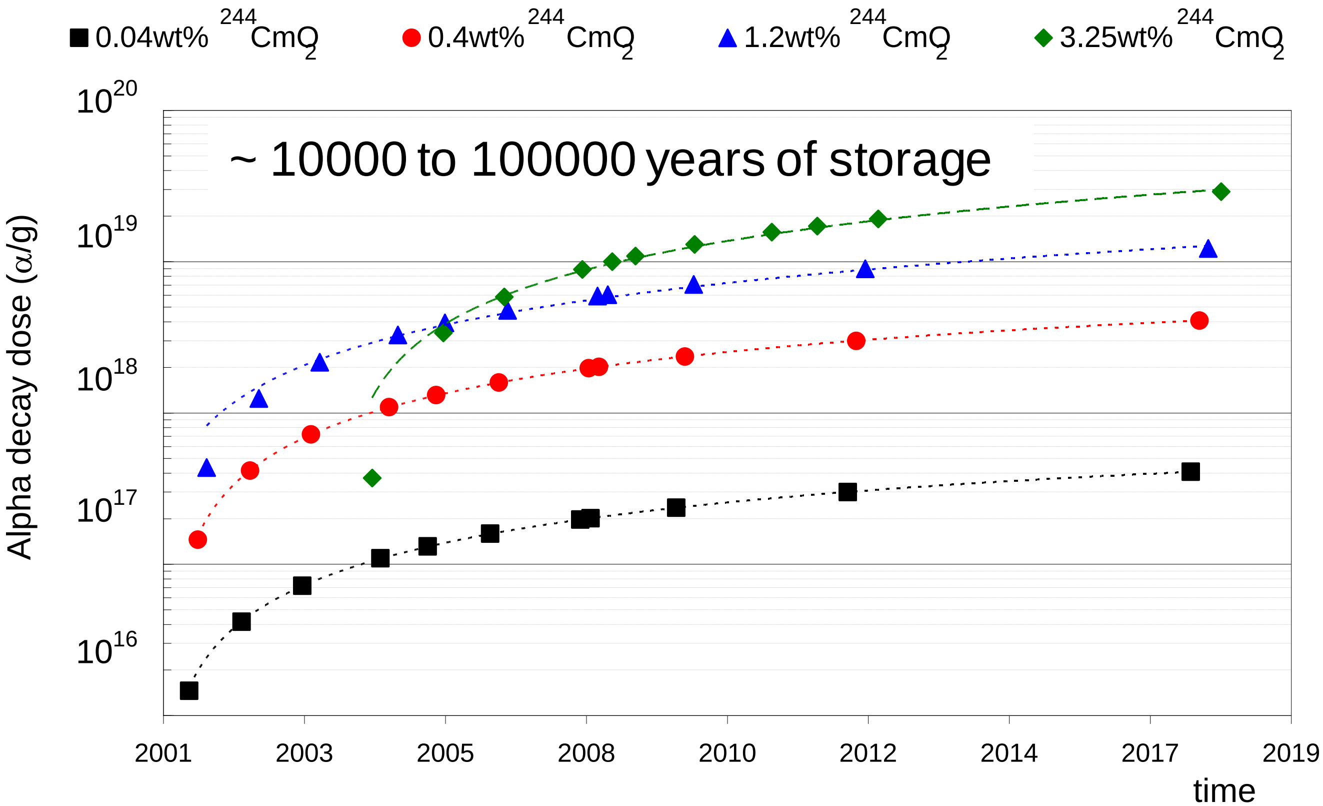


1. **Curium doped glasses**
2. **External irradiation with light and heavy ions**
3. **In pile irradiation : $^{10}B(n,\alpha)^{7}Li$**
4. **Molecular dynamic modeling of ballistic effects**

# Methodology: Cm doping

- SON68 glasses doped with 0.04, 0.4, 1.2, 3.25wt% of $^{244}CmO_2$
- International Standard Glass (ISG) doped with 0.7wt% of $^{244}CmO_2$



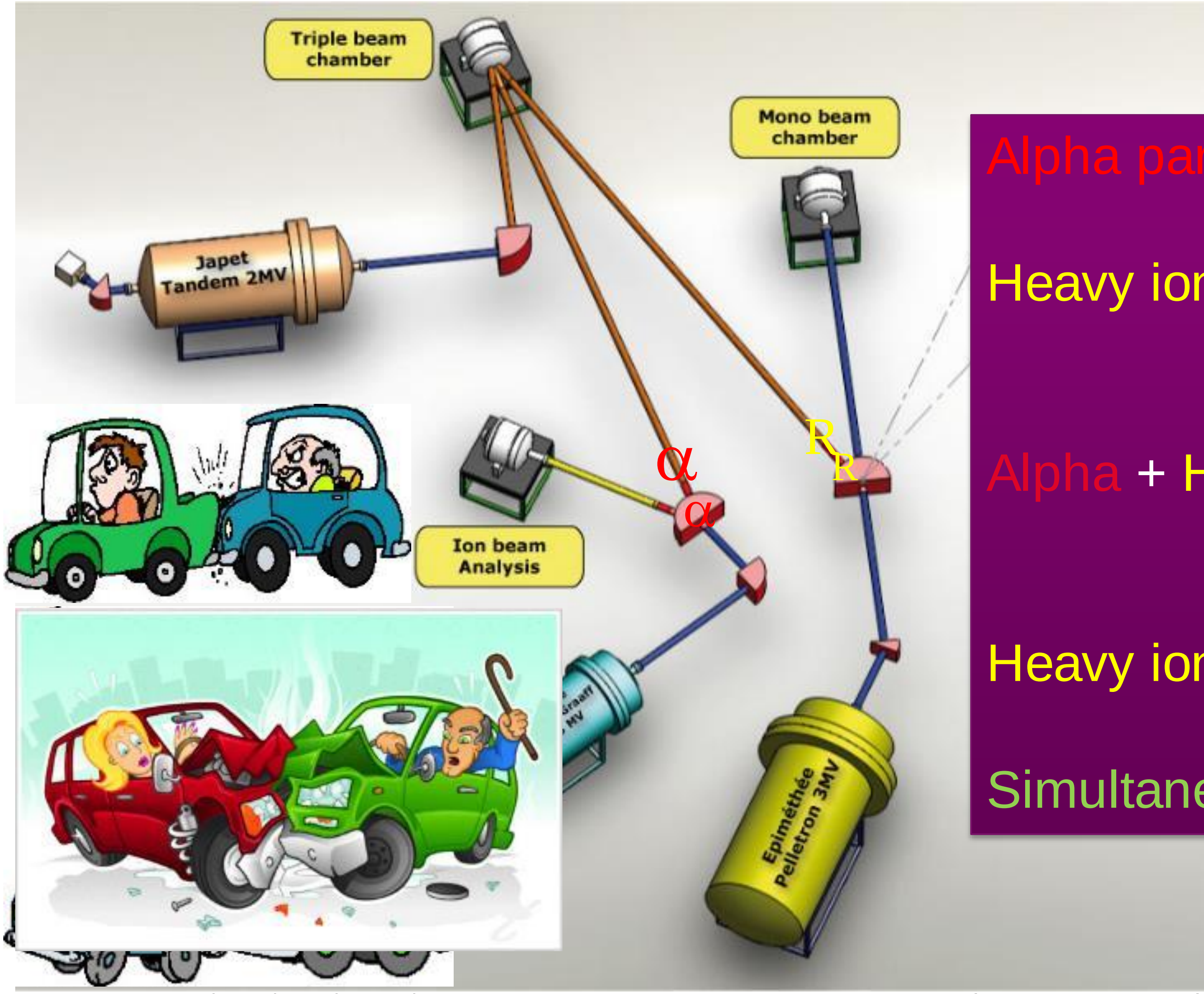



| Mol% | $SiO_2$ | $Na_2O$ | $B_2O_3$ | $Al_2O_3$ | CaO | $ZrO_2$ | Other oxides |
|---|---|---|---|---|---|---|---|
| ISG/CJ4 | 60.1 | 12.6 | 16.0 | 3.8 | 5.7 | 1.7 | |
| R7T7 | 52.8 | 11.3 | 14.1 | 3.4 | 5.0 | 1.6 | 11.8 |

- Initial characterizations of the glasses (homogeneity, chemical composition)
- Periodical characterizations of the glass properties

# Methodology: Ion beam irradiation experiment

Jannus Saclay,Orsay, Ganil




Alpha particles

Heavy ions (RN)

Mono beam

Alpha + Heavy ion

Heavy ion + Alpha

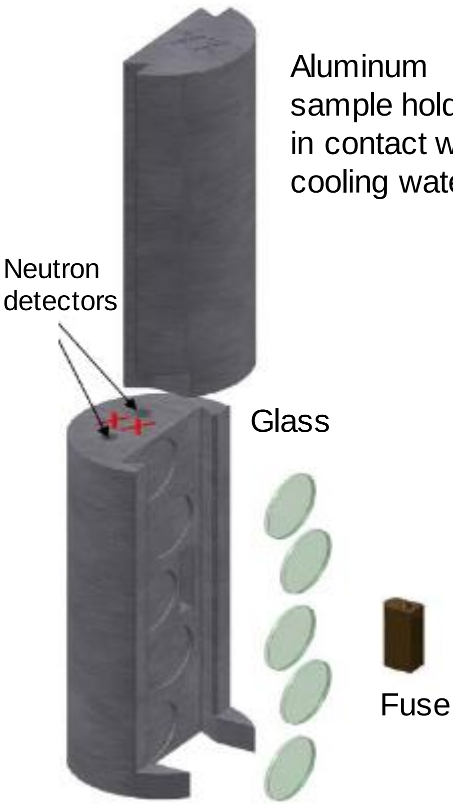
Simultaneous

Double beam

# Methodology: In pile irradiation : $^{10}B(n,\alpha)^{7}Li$

## OSIRIS reactor, CEA SACLAY

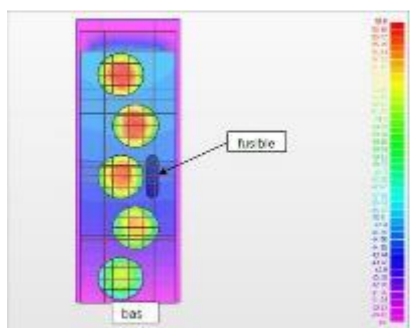
**Glass samples :** polished disks thickness 0.5 mm




| | D1 | D2 | D3 | D4 |
|---|---|---|---|---|
| E (MeV) | He(1.47) + Li(0.84) | | | |
| Fluence (neutron cm$^{-2}$) | $5.9 \times 10^{18}$ | $1.2 \times 10^{19}$ | $3.5 \times 10^{19}$ | $5.2 \times 10^{19}$ |
| Number of events (ion cm$^{-3}$) | $3.5 \times 10^{19}$ | $7.0 \times 10^{19}$ | $2.1 \times 10^{20}$ | $3.1 \times 10^{20}$ |
| $dE/dx_{nucl}$ (keV nm$^{-1}$) | dE/dx(He) <0.03<br>dE/dx(Li) <0.06 | | | |
| $dE/dx_{elec}$ (keV nm$^{-1}$) | dE/dx(He) <0.33<br>dE/dx(Li) <0.56 | | | |
| **$E_{nucl}$ (GGy)** | **0.06** | **0.13** | **0.39** | **0.57** |
| **$E_{elec}$ (GGy)** | **5.16** | **10.45** | **30.69** | **45.71** |
| **Dpa** | **0.27** | **0.54** | **1.6** | **2.38** |

~ 1 million years of disposal

| Mol% | $SiO_2$ | $Na_2O$ | $B_2O_3$ | $Al_2O_3$ | CaO | $ZrO_2$ | Other oxides |
|---|---|---|---|---|---|---|---|
| CJ1 | 67.7 | 14.2 | 18.1 | | | | |
| SON68 | 52.8 | 11.3 | 14.1 | 3.4 | 5.0 | 1.6 | 11.8 |



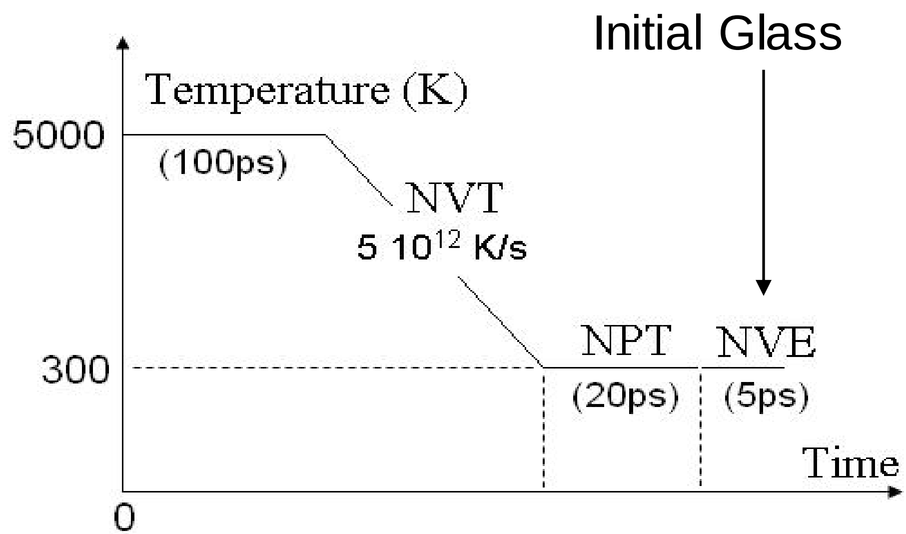

Thermal modeling and fuses observations after irradiation:

T<70°C

# Methodology: Molecular dynamic modeling

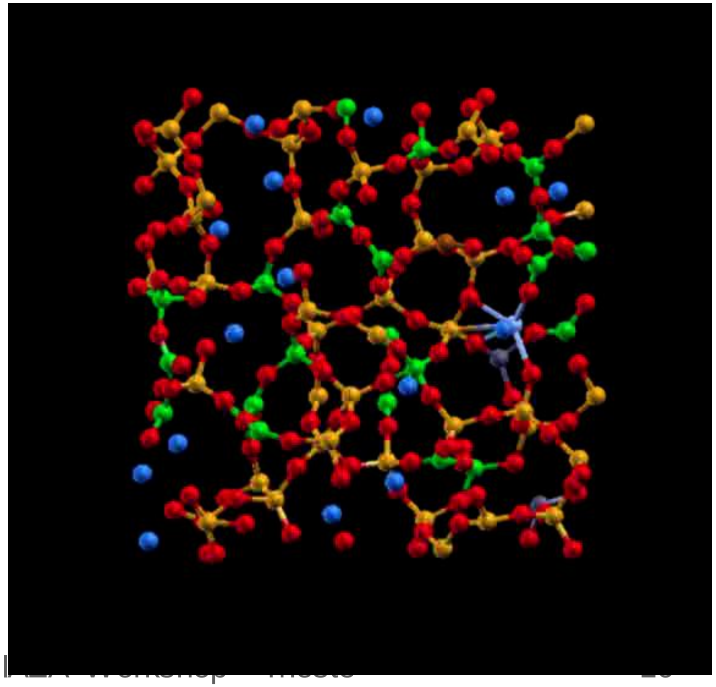
- Simplified borosilicate glasses (CJ1, CJ7)

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + B_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$



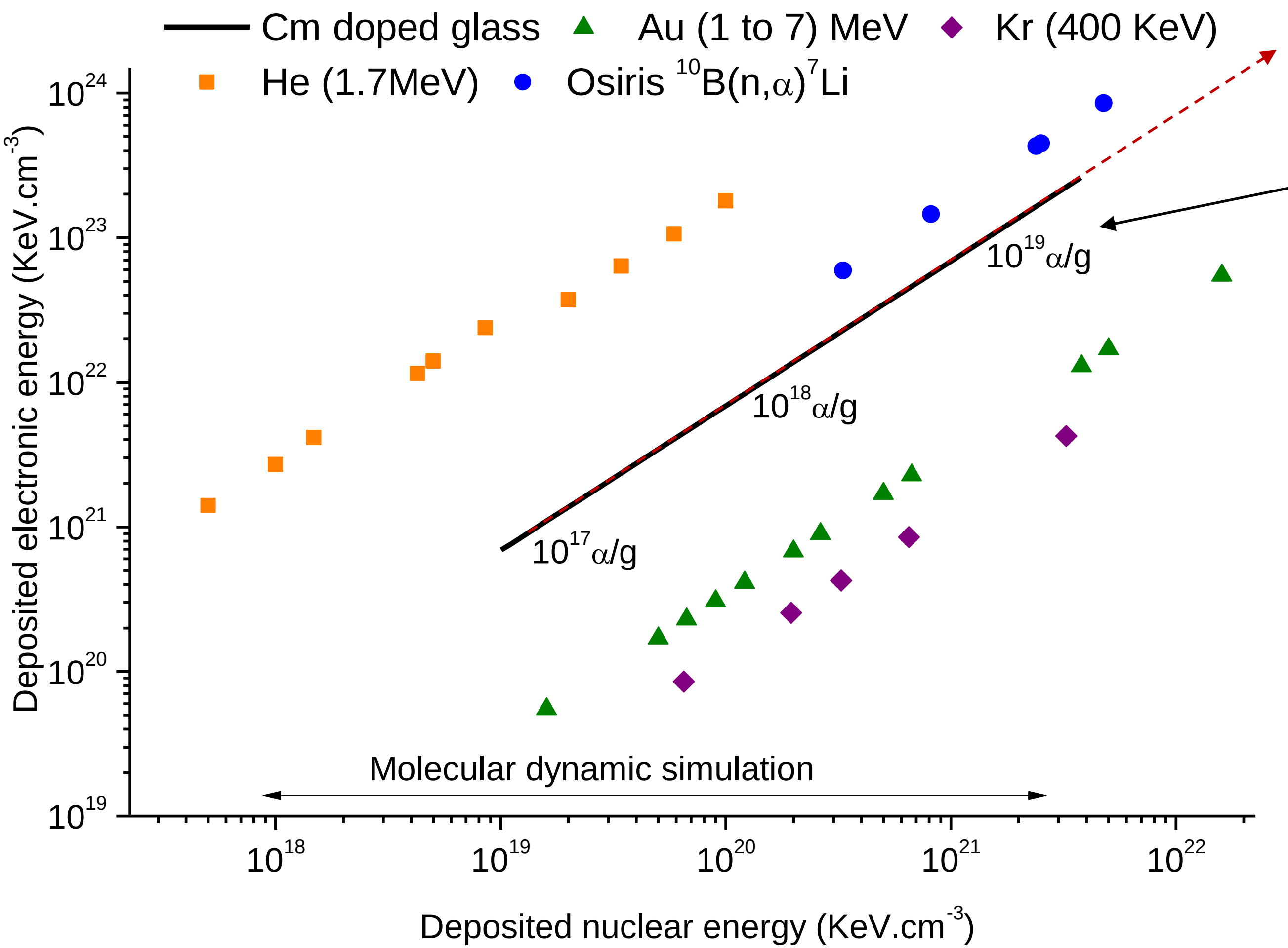

- Accumulation of displacement cascades caused by uranium atoms of energies from 700ev to 70keV

- Characterization of the structural modifications induced by displacement cascades (SRO and MRO)



| Mol% | $SiO_2$ | $Na_2O$ | $B_2O_3$ | $Al_2O_3$ | CaO | $ZrO_2$ | Other oxides |
|---|---|---|---|---|---|---|---|
| **CJ1** | **67.7** | **14.2** | **18.1** | | | | |
| **CJ7** | **63.8** | **13.4** | **17.0** | **4.1** | | **1.8** | |
| *SON68* | *52.8* | *11.3* | *14.1* | *3.4* | *5.0* | *1.6* | *11.8* |

# Methodology: Materials and irradiation conditions




Alpha decay dose scale or time scale

~ 100000 years of storage of nuclear glass

5 to 10 years of storage of $^{244}$Cm glass

**Light ions irradiations (He) : mainly electronic interactions**

**Heavy ions irradiations (Kr, Au) : mainly nuclear interactions**

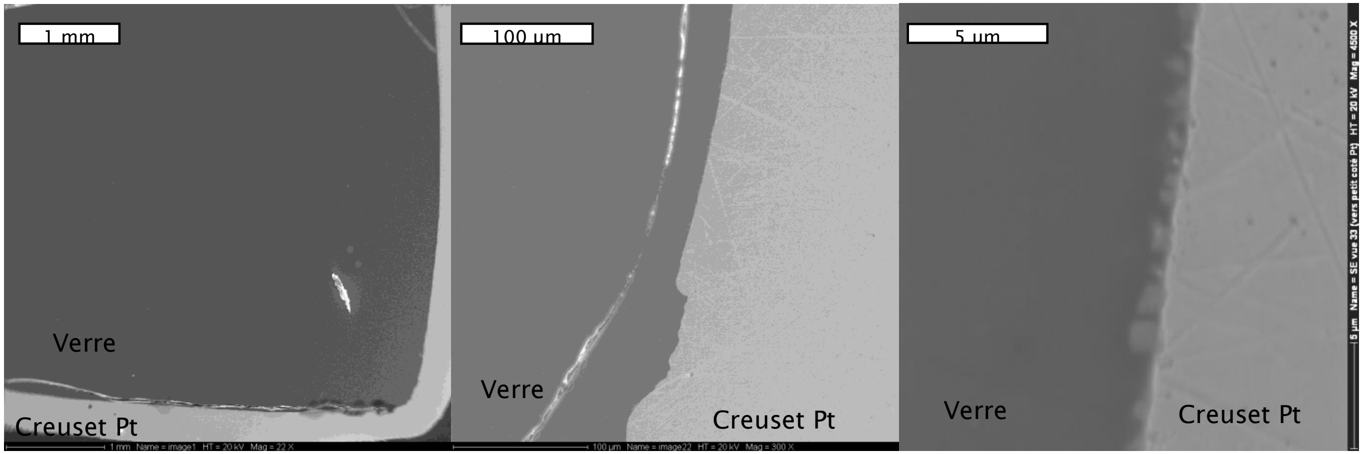
**Doped glasses and OSIRIS irradiation : electronic and nuclear interactions**

**Molecular Dynamics : only nuclear interactions**

**Simulation of at least 100000 years of disposal by various methods !**

# Stability of the metastable glassy state ? Effect on the glass microstructure

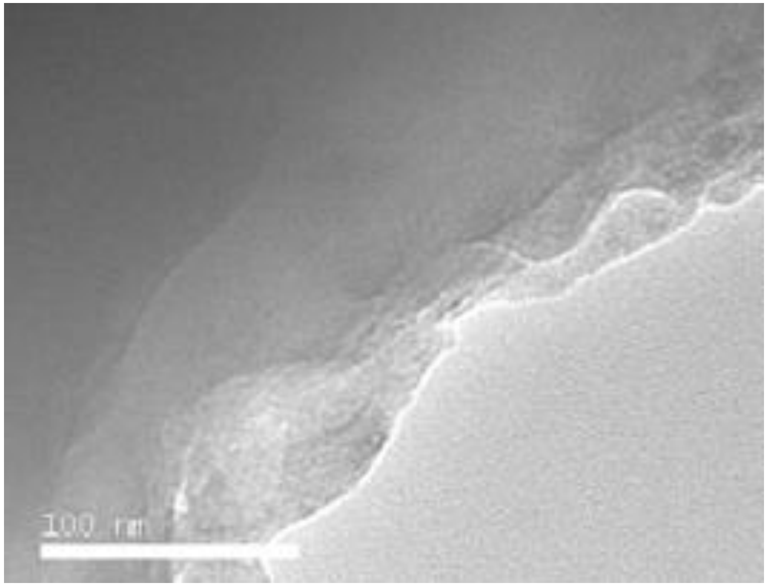
$^{244}$Cm SON 68 glass : SEM (CEA Marcoule), alpha decay dose 2x10$^{19}$α/g




(Around 100000 years of storage)

S. Peuget et al. JNM 44 (2014)

$^{244}$Cm SON 68 glass : TEM (ITU Karlsruhe), alpha decay dose 8x10$^{18}$α/g

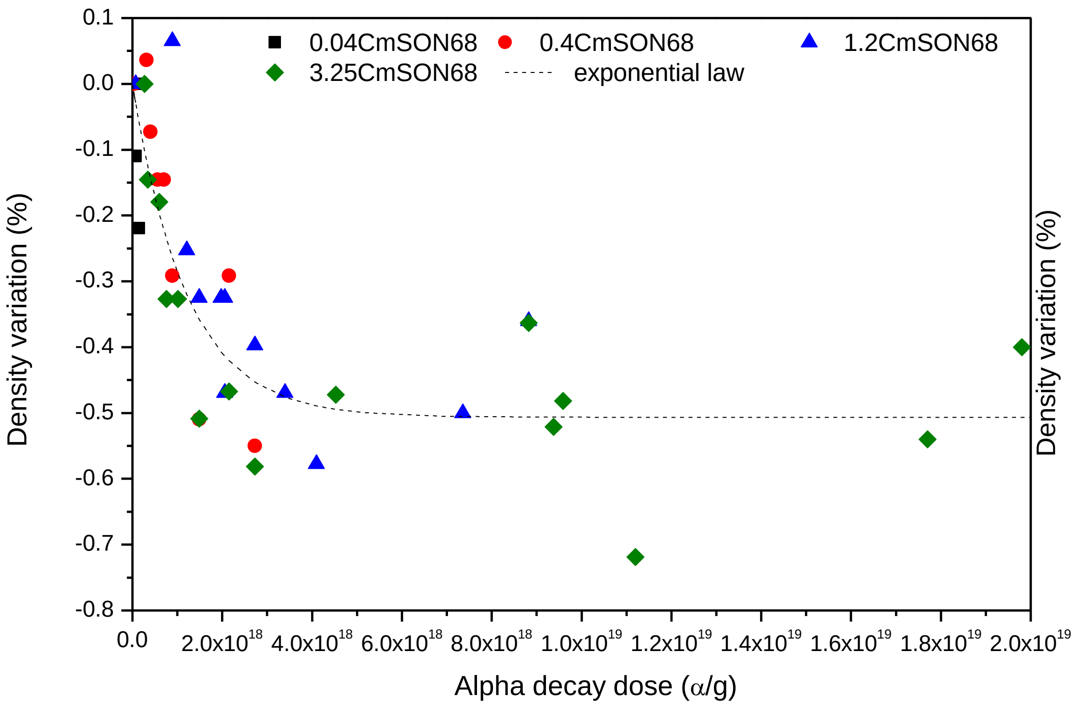



**Homogeneous microstructure**, without bubbles, phase separation or crystallization

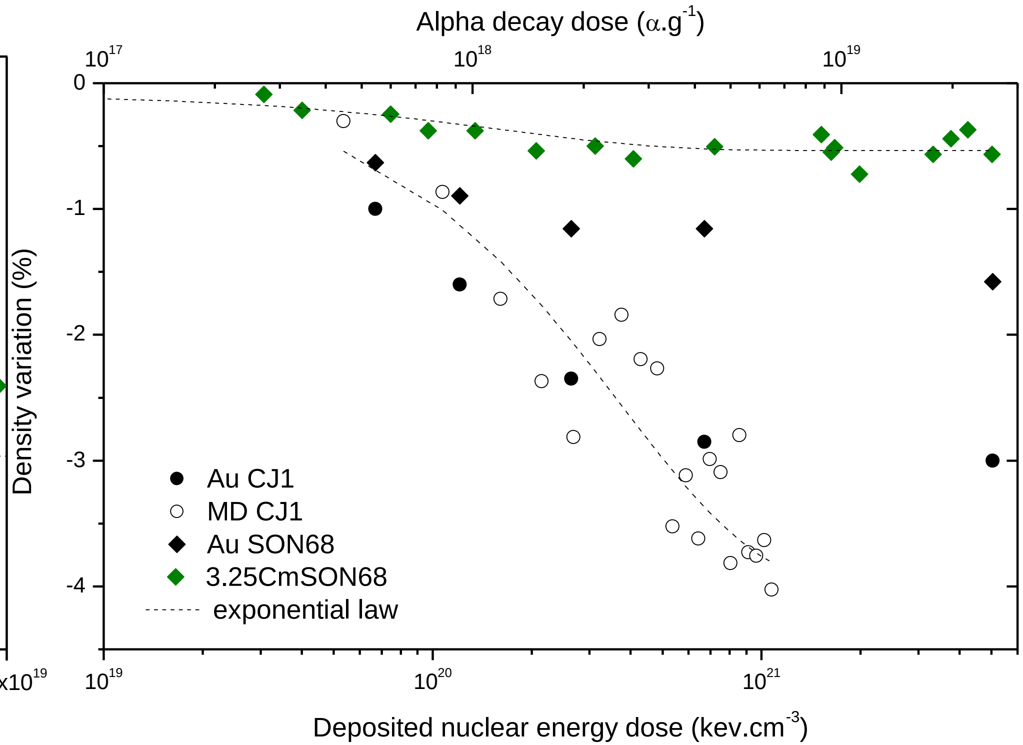
**Stability of the glassy state**

# Stability of the metastable glassy state ? Effect on the macroscopic properties ?

- Slight decrease of the glass density (0.5%)
- No effect of the dose rate
- Stabilization of the evolution at around $4x10^{18}$ $\alpha$/g
- Evolution according to an exponential law (direct impact model)
  - ✓Variations correclty simulated by external irradiations wih heavy ions and MD simulation
  - ✓Swelling level is lower under α decays irradiation (0,5% compared to 1,2% Au irradiation)




S. Peuget et al. J. Nucl. Mat. 354 (2006) 1

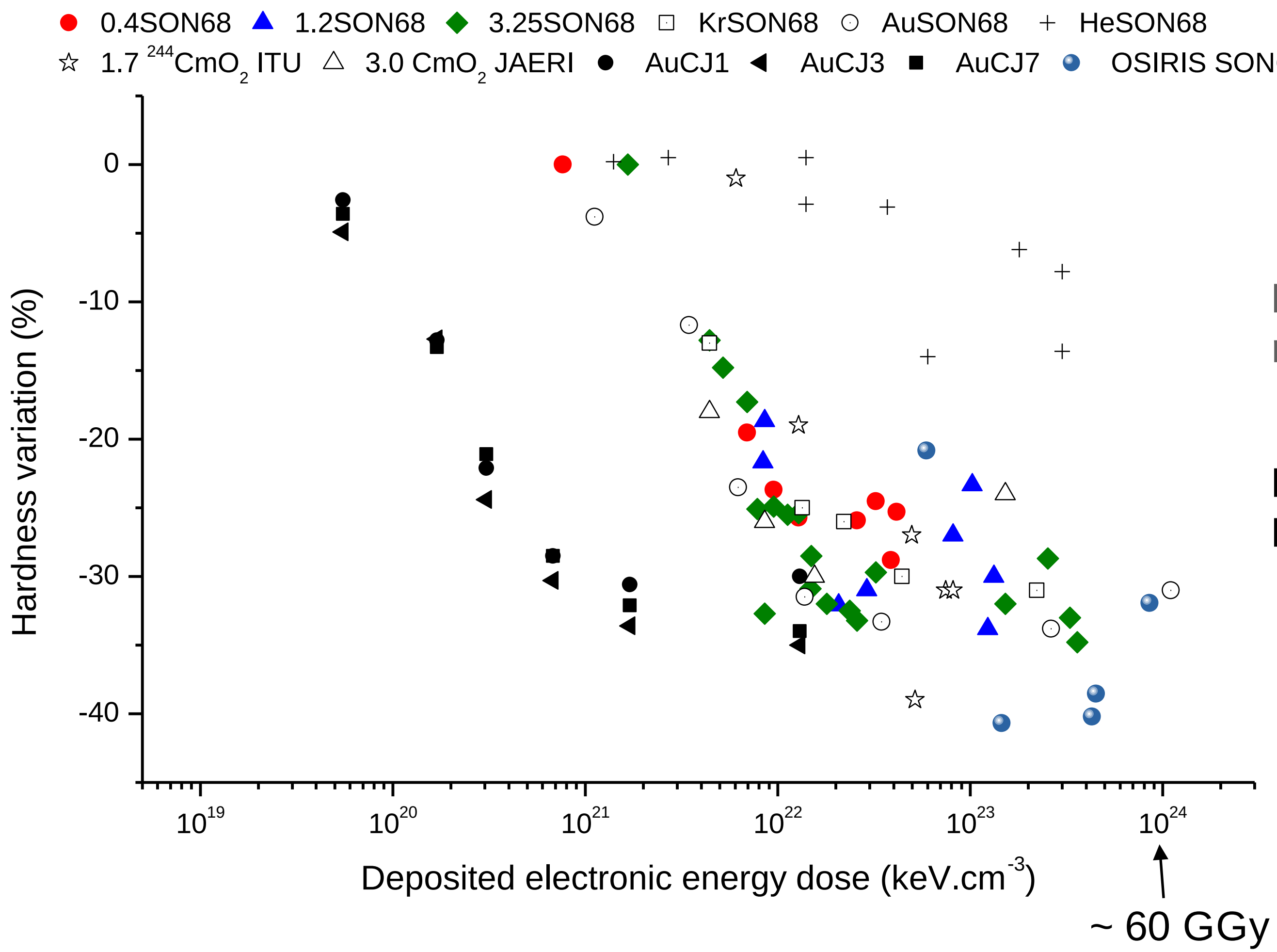



S. Peuget et al. J. Nucl. Mat. 354 (2014) 1

**Mechanical properties: example of hardness**

**Decrease of hardness on curium doped glasses and ions irradiated glasses**

**He induced lower changes**




**Effect of electronic or nuclear interactions?**

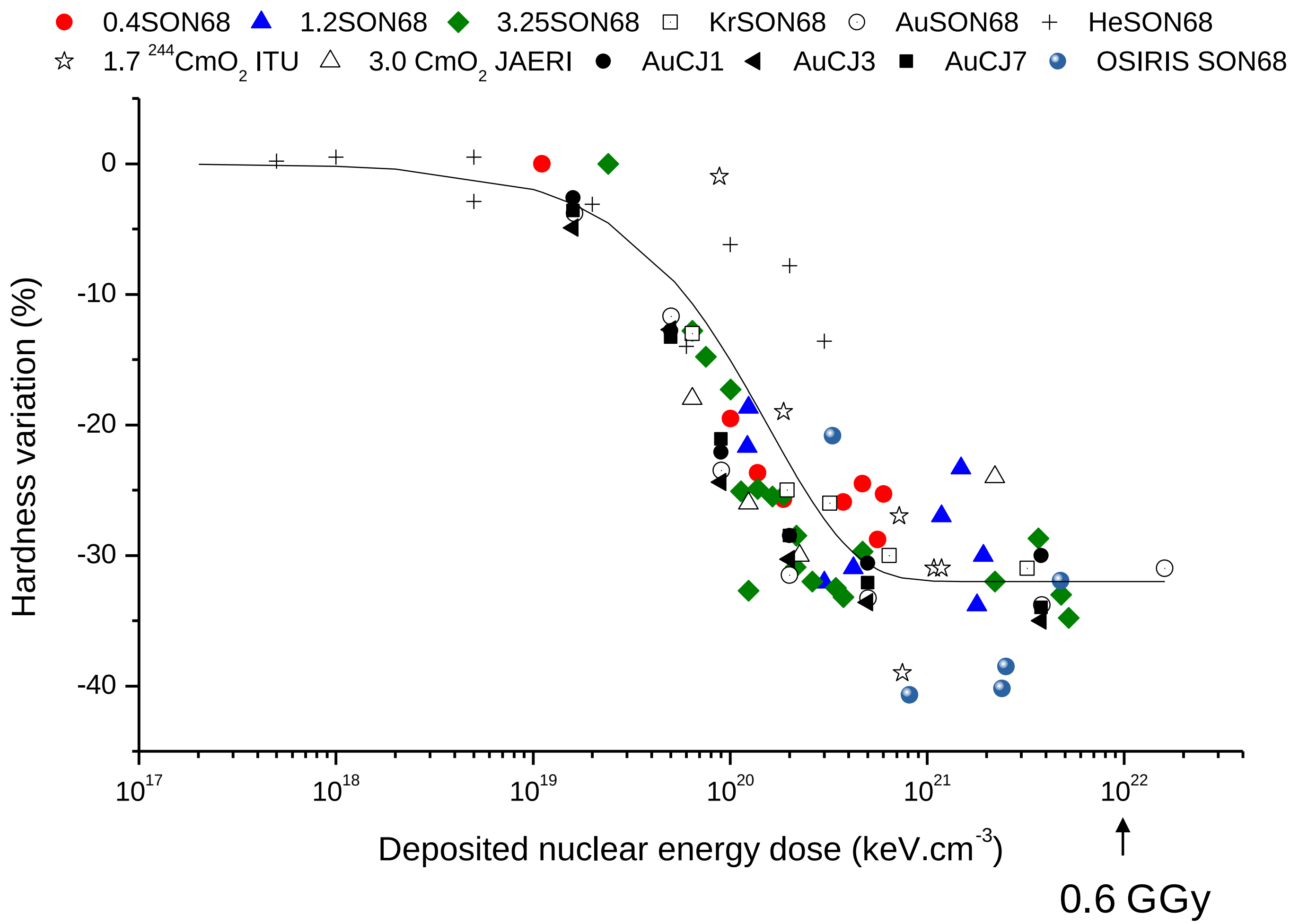
**No agreement versus Electronic dose**

S. Peuget et al, NIMB 246 (2006) 379 S. Peuget et al. JNM 354 (2014) 1 Mir et al. . JNM 469 (2016) 244

**Mechanical properties: example of hardness**

**Decrease of hardness on curium doped glasses and heavy ions irradiated glasses**

**He induced lower changes**




**Effect of electronic or nuclear interactions?**

**Quite good agreement between doped glasses and heavy ions irradiated glasses**

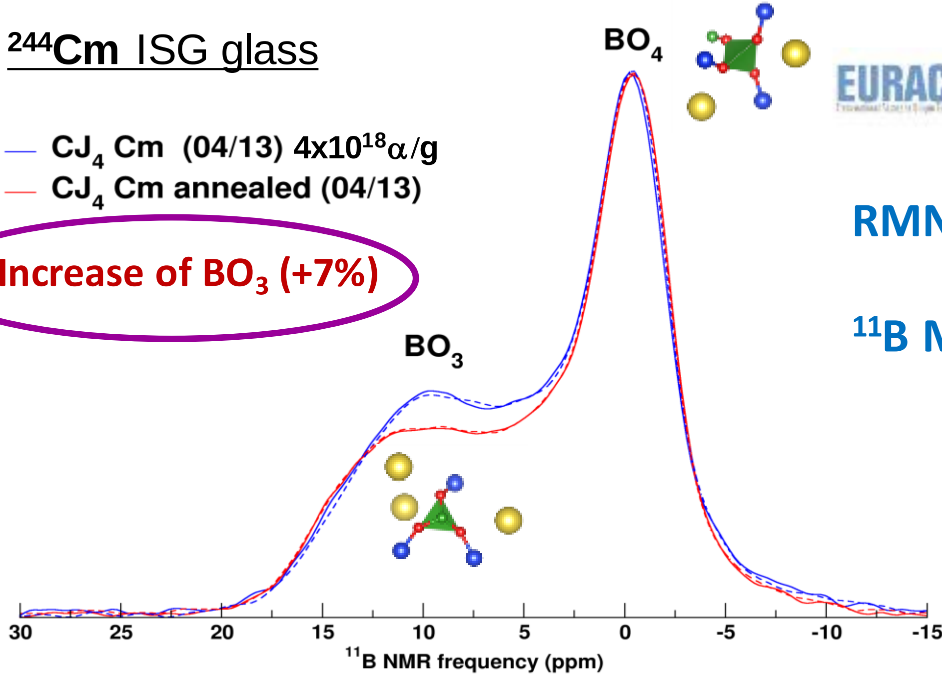
⇩

**Effect induced by nuclear interactions, rôle of RN !**

S. Peuget et al, NIMB 246 (2006) 379
S. Peuget et al. JNM 354 (2014) 1
Mir et al. . JNM 469 (2016) 244

# Stability of the metastable glassy state ? Effect on glass structure : SRO around B

## $^{244}$Cm ISG glass




EURACT-nmr

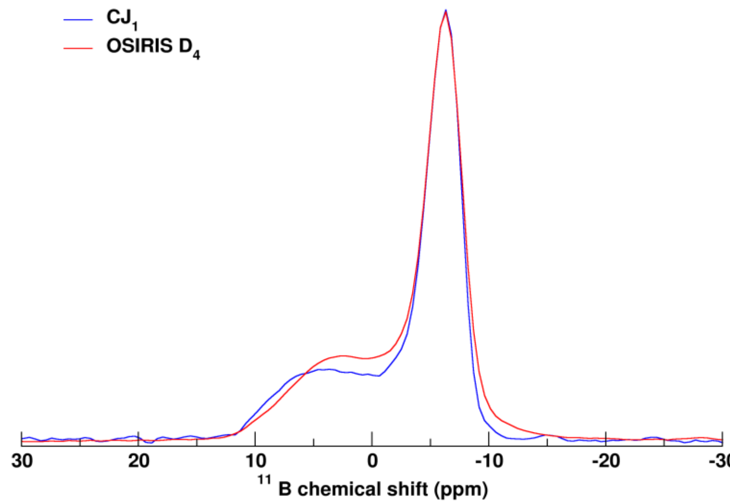
**RMN at ITU**

**$^{11}$B MQMAS**

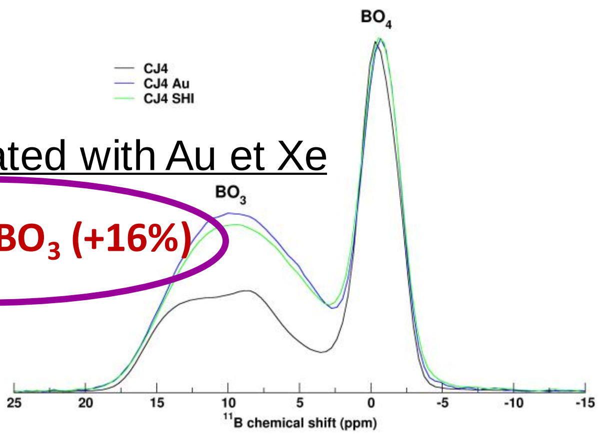
T. Charpentier et al. Scientific Reports 6:25499 (2016)

## CJ1 irradiated in OSIRIS reactor

S. Peuget et al, NIMB 327 (2014) 22-28




## ISG irradiated with Au et Xe



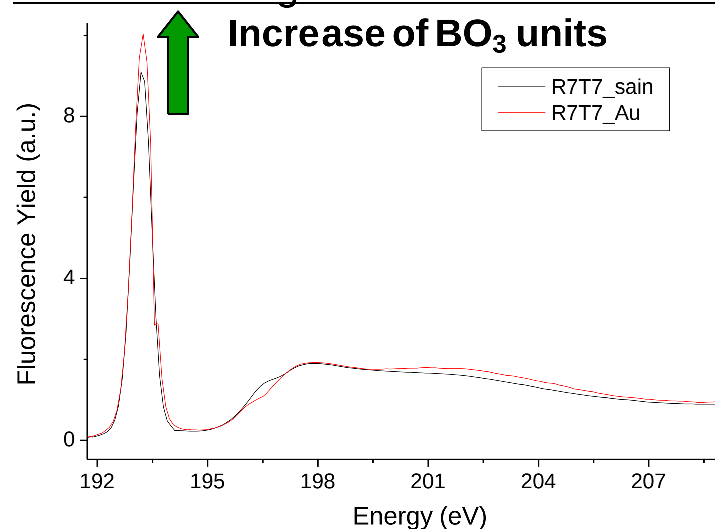

C. Mendoza et al. NIMB 325 (2014) 54-65

**Conclusion :**

**Partial conversion $BO_4$ into $BO_3$ Complex and simplified glasses**

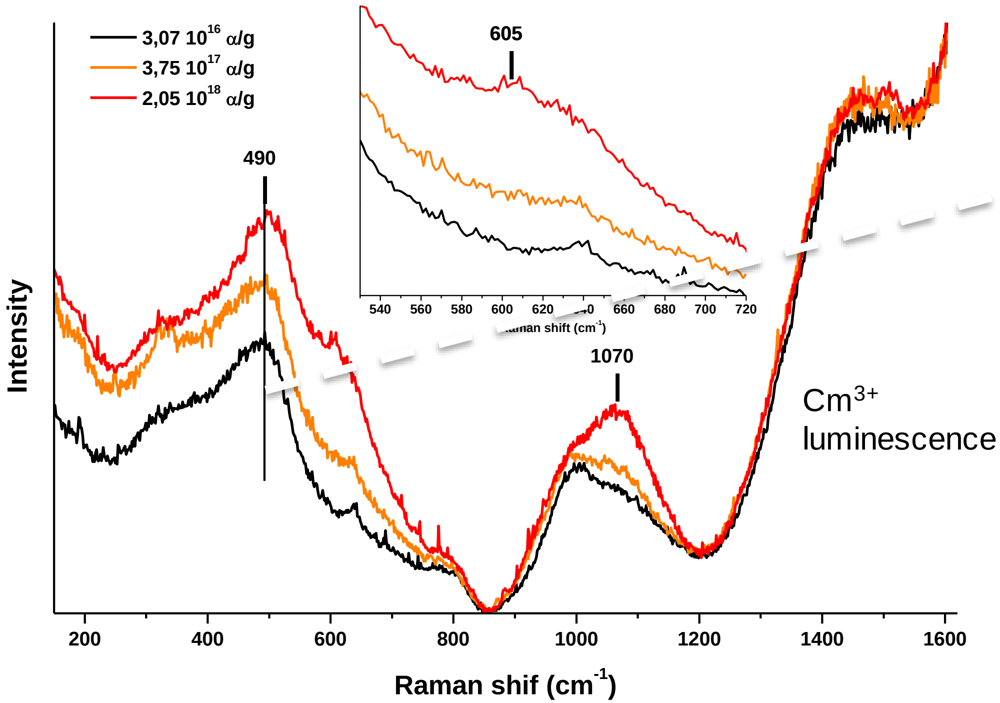
**$BO_3$ increase is lower under α decays irradiation**

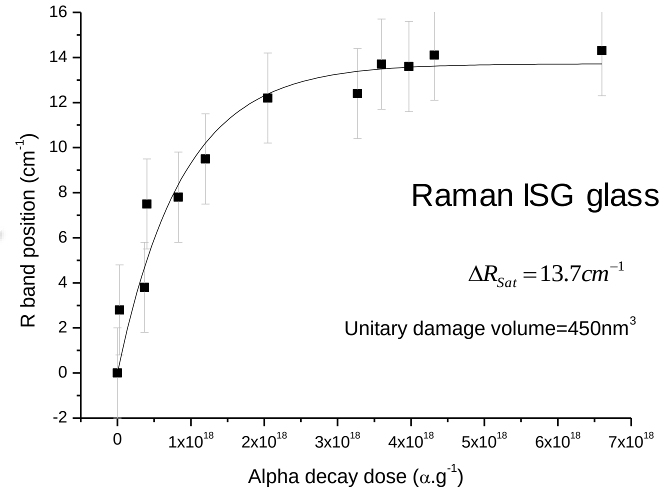
## Xanes B K edge: R7T7 irradiated with Au

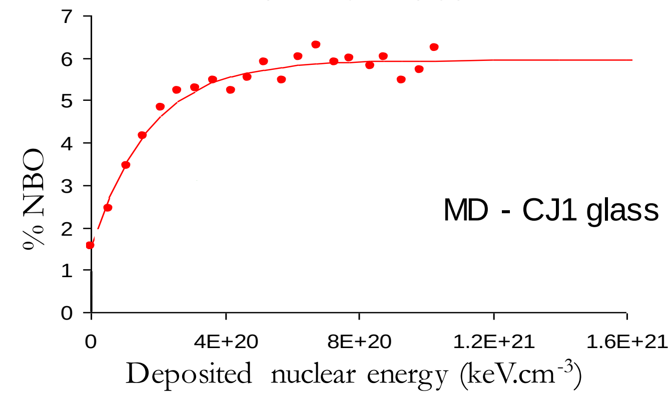



G. Bureau, thesis, (2008)

## Raman spectroscopy on Cm doped ISG (Atalante, DHA)




C. Mendoza et al. Proc. Chem. 7 (2012) 581

- **Increase of Q3 contribution in ISG glass : more NBO**
- **Slight shift of the vibration band around 500cm$^{-1}$**

J.-M. Delaye et al, J. Non-Cryst. Solids 357 (2011) 2763

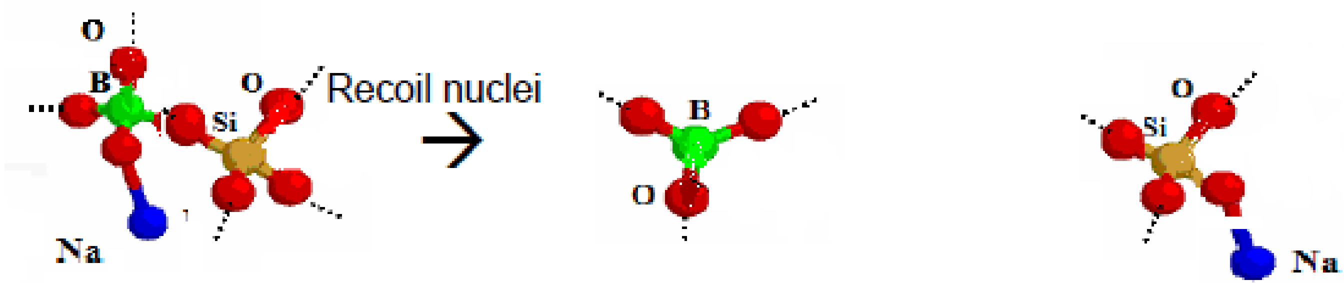
**Decrease of the mean angle between silica tetrahedra**

- **New D2 band on ISG Cm doped glass: 3 members silica rings**
- **Stabilization of the silicon local environment after around 4 x 10$^{18}$ α/g**

# Effects on the glass structure? Summary

## Modification of the Short Range Order

Increase of trigonal boron, increase of NBO



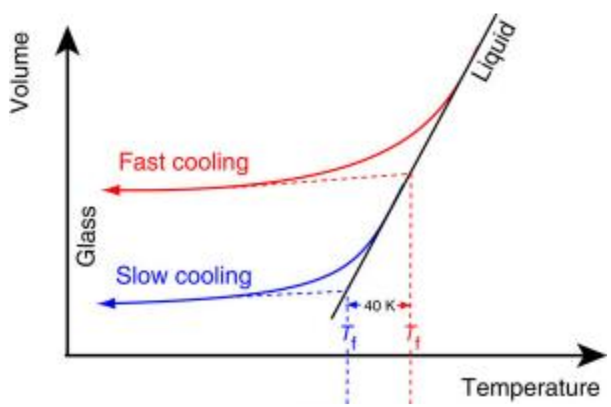

## Modification of the Medium Range Order

Ring statistic modification, increase of glass disorder and Si/B mixing

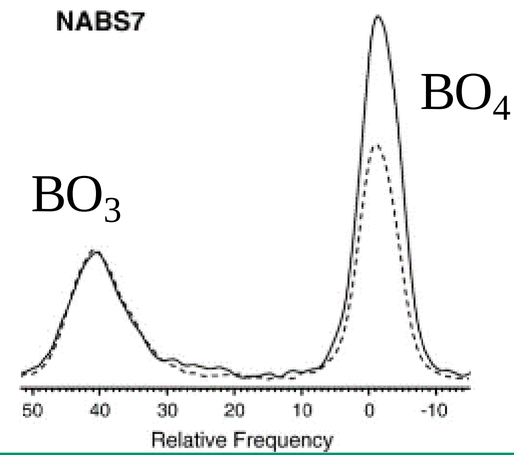
**Effects similar to those induced by thermal quenching of a molten glass**

$BO_4 \xrightarrow{\nearrow T} BO_3 + NBO$

Decrease of the glass density




$^{11}B$ NMR on quenched and annealed glass

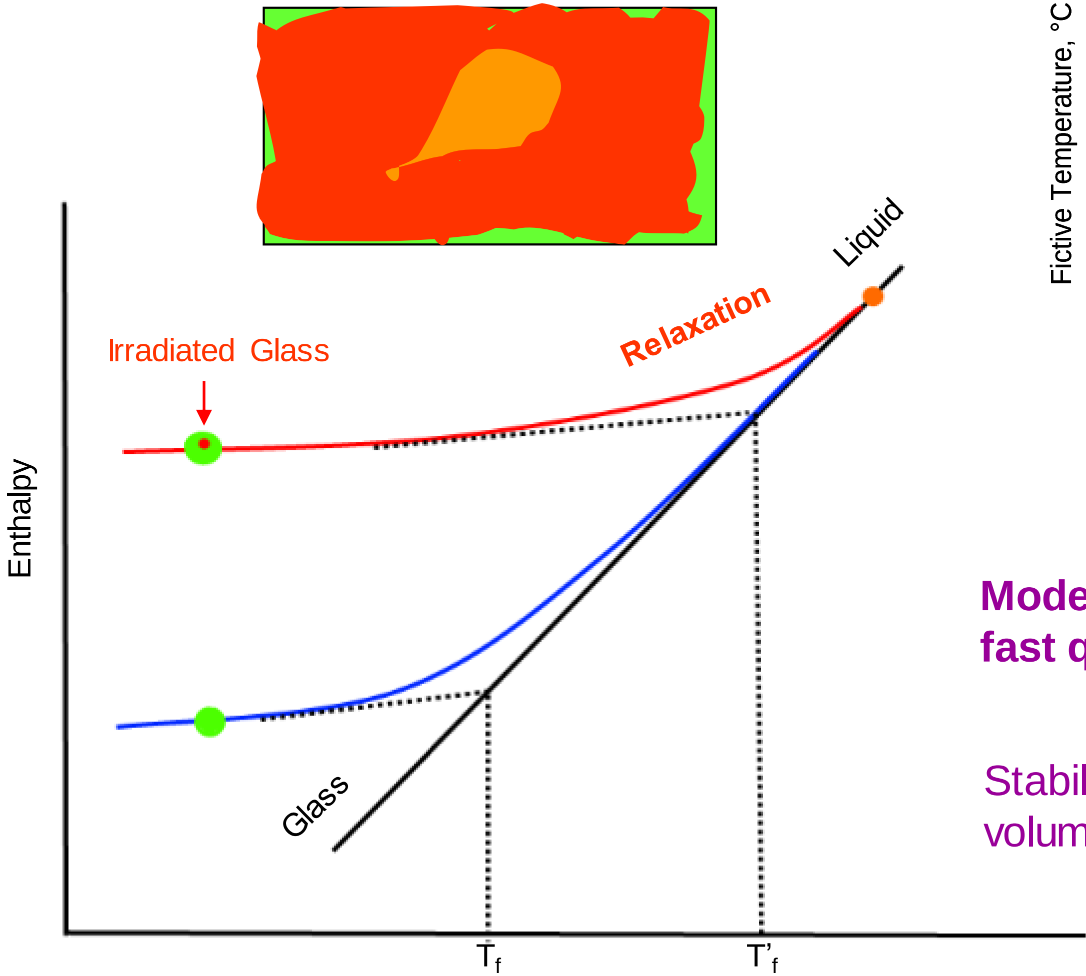



Wu and Stebbins JNCS 356 (2010)

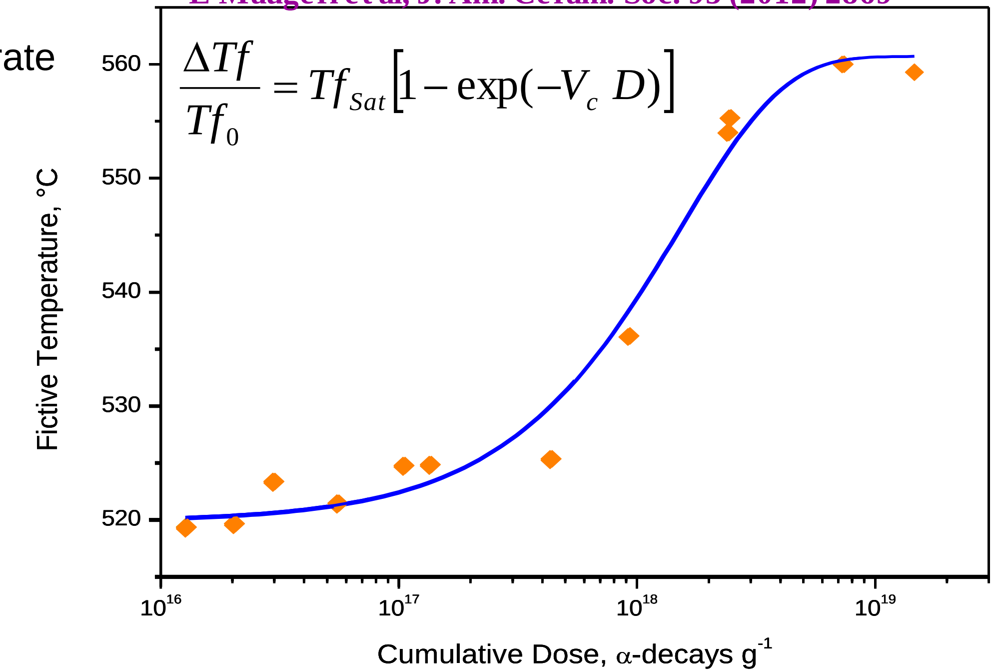
# Understanding of glass behavior under alpha decays

1. Balistic step : disordered state
2. Relaxation step : very important quenching rate

Irradiated zone has a higher fictive temperature




E Maugeri et al, J. Am. Ceram. Soc. 95 (2012) 2869



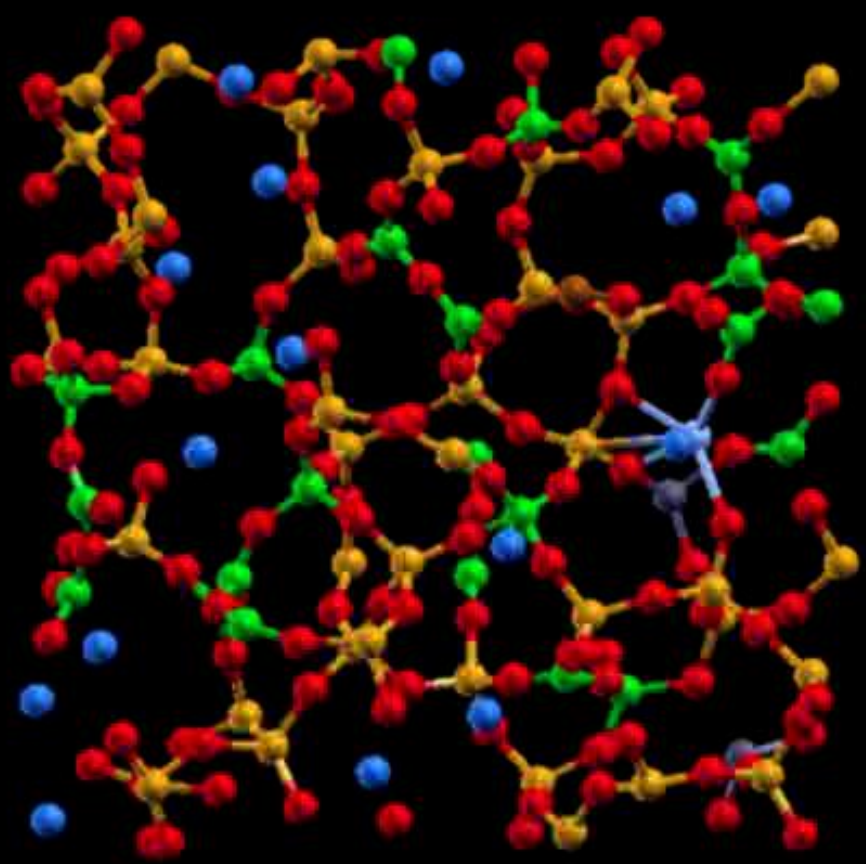

**Model of accumulation of ballistic disordering fast quenching events: "supervitrification"**

Stabilization of a new glass structure when all the volume has been damaged once

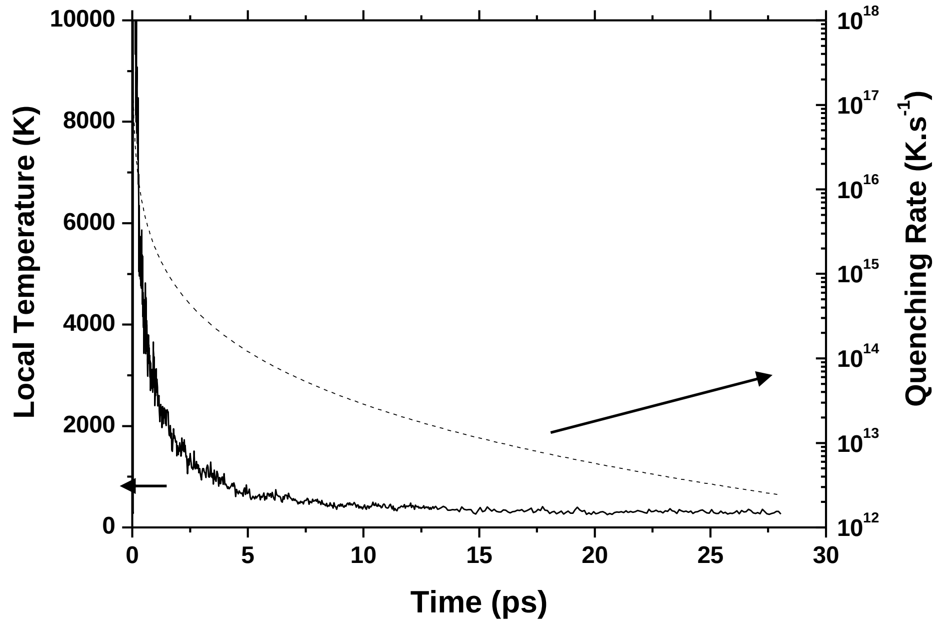
# Effects on the glass structure? Ballistic damage

## What happen in the displacement cascade induced by a recoil nuclei?

JM Delaye, PRB 61 (2000) 14481



1. Balistic phase
2. Thermal phase




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

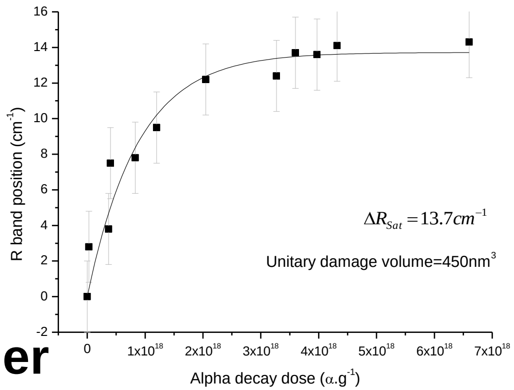
**Very high quenching rate of the disordered state induced by the displacement cascade**

**Supervitrification**

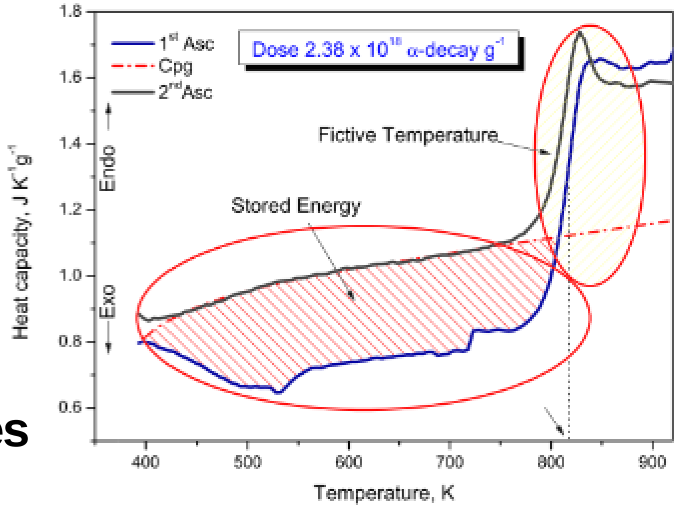
# Characteristics of the irradiated glassy state? α irradiation

## Main effects observed under alpha decay irradiation:

- ✓ **A saturation effect with dose, a new glass structure is reached after around $4x10^{18}$ $\alpha$/g (Nuclear dose ~30 MGy)**




- ✓ **No effect of the dose rate in the relevant range**
- ✓ **Changes at both Short Range Order and Medium Range Order**
  - ✓ **Changes in boron coordination number and glass polymerization index**
  - ✓ **Changes in ring statistic, angle distribution**
- ✓ **A higher fictive temperature after irradiation**
- ✓ **Stored energy of ~100J/g**
- ✓ **Complex glasses are less modified than simple glasses**



## Waste mechanical degradation?

### Can irradiation induce a cracking of the material?

- Due to important swelling under irradiation?
- Degradation of the mechanical properties?
- Due to bubble formation (He bubbles generated by alpha decays)

## Waste mechanical degradation?

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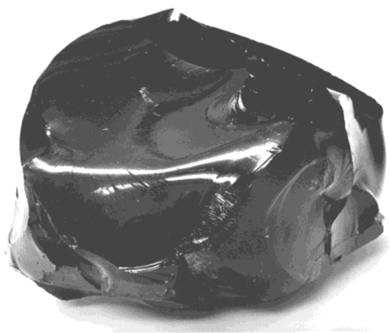
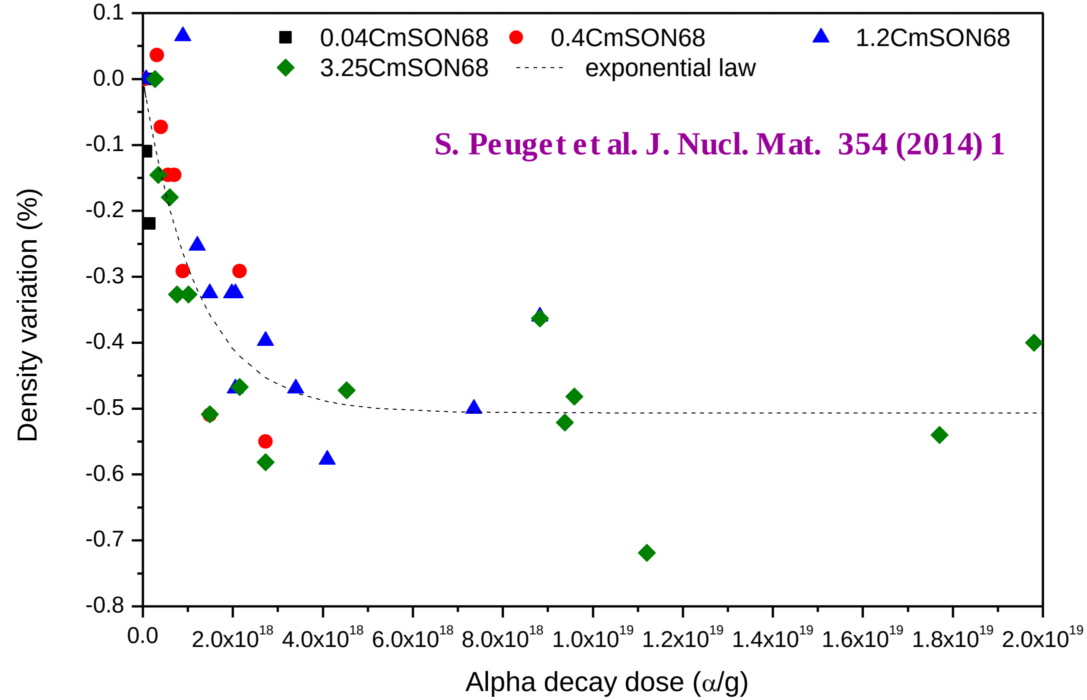
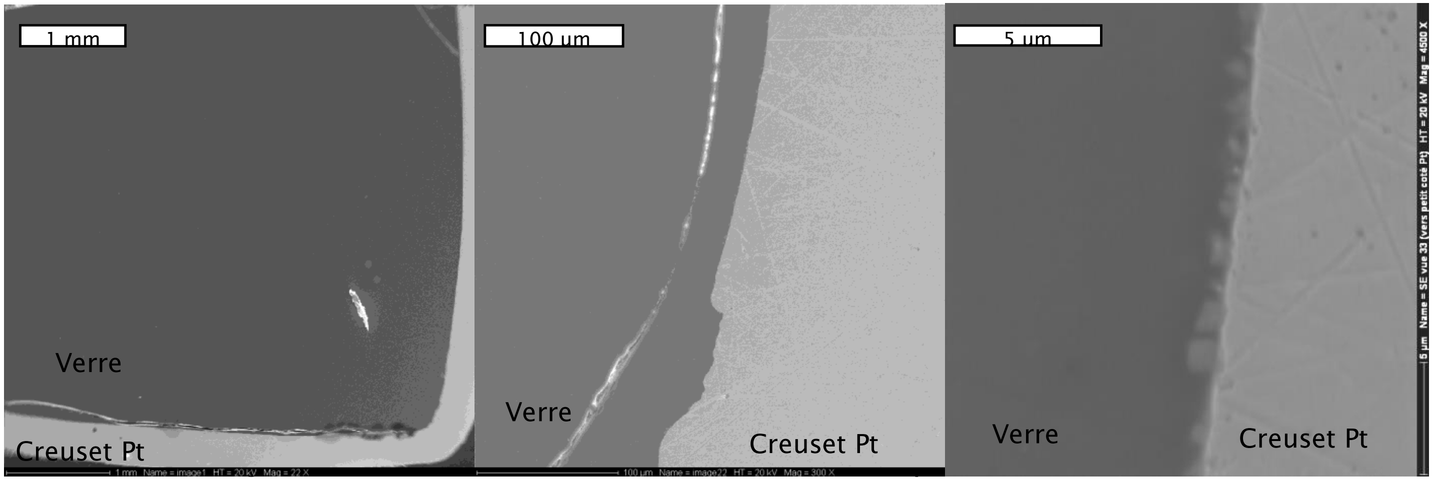


## Important swelling of Homogeneous glass?

Slight variation of the glass density



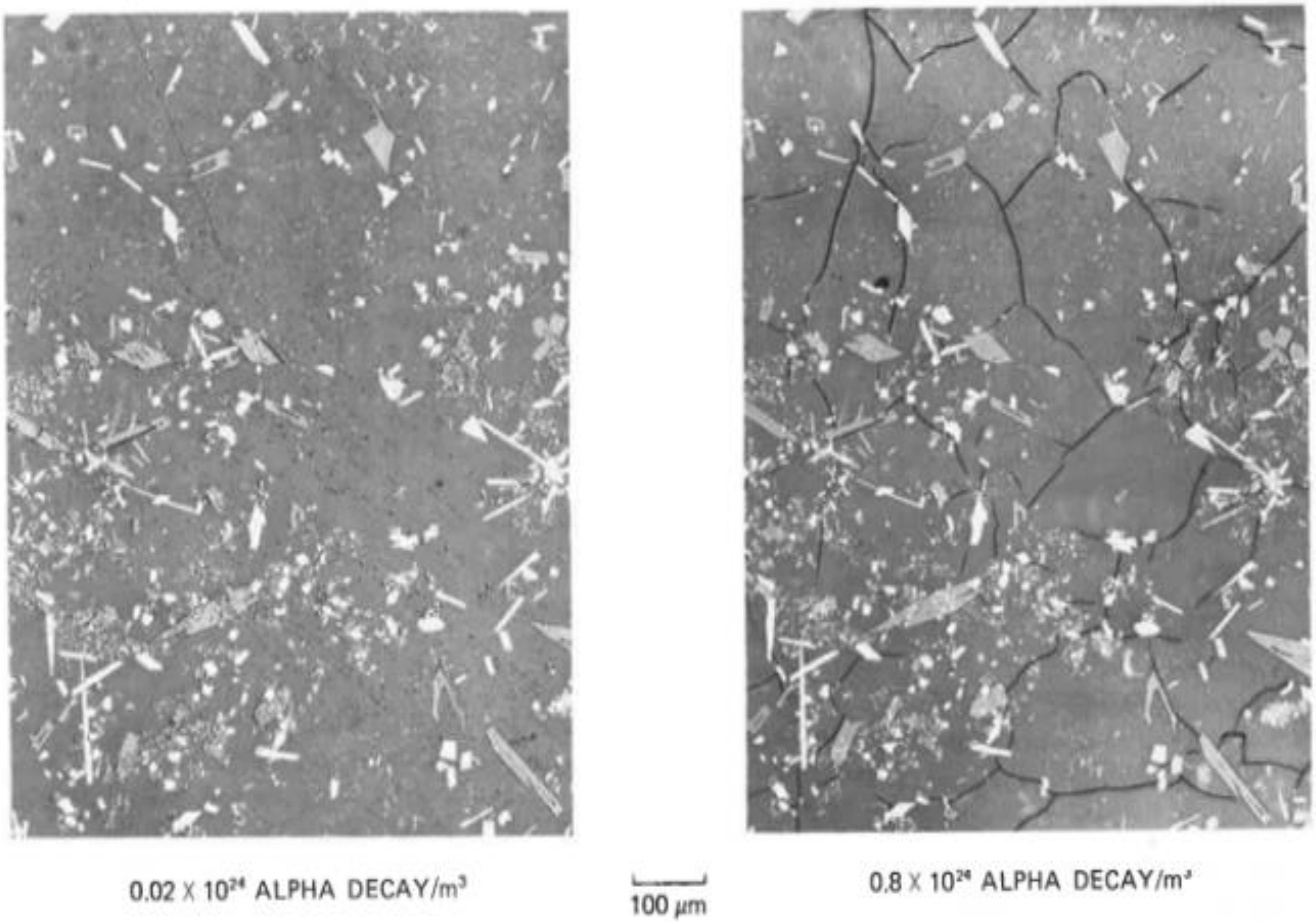

Low swelling level, no microcraking



# WASTE MECHANICAL DEGRADATION?

## Waste form degradation ? GCM?

### Microcracking observed on some GCM




W. J. Weber and F. P. Roberts, Nuclear Technology, vol. 60.,178-198.

Amorphization of the crystalline phases: high swelling level of crystalline phase

**To go further in GCM development:**

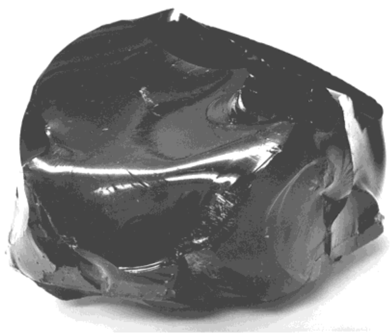
**Need to understand and master the origin of radiation induced cracking**

**Evaluation of the impact of type of phase, density and size of crystalline phases**

## Waste mechanical degradation?

### Can irradiation induce a cracking of the material?

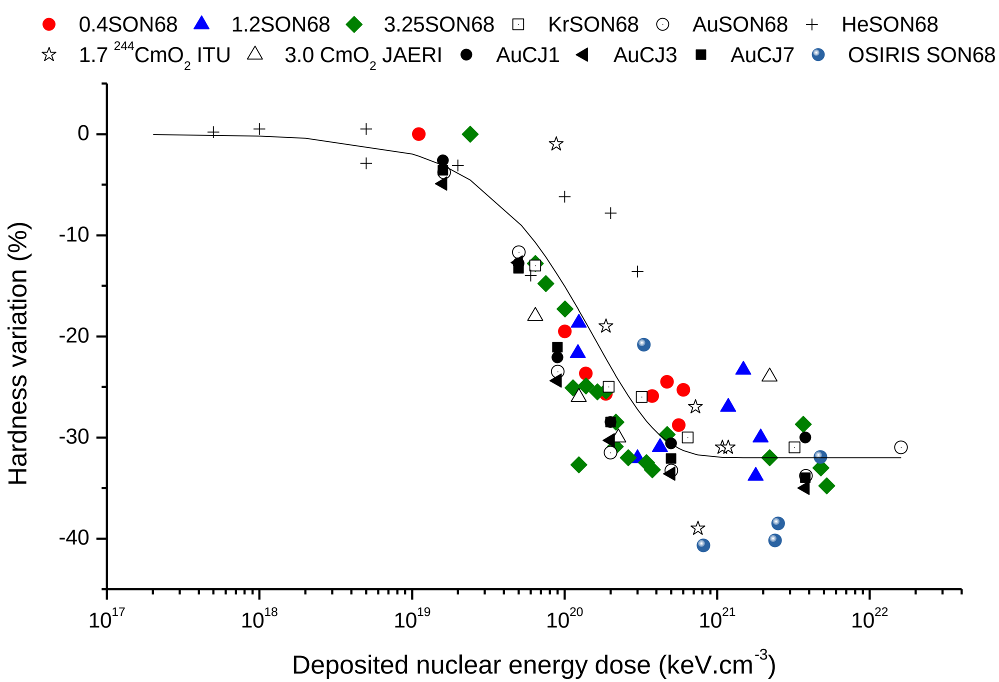
- Due to important swelling under irradiation?
- Degradation of the mechanical properties?
- Due to bubble formation (He bubbles generated by alpha decays)

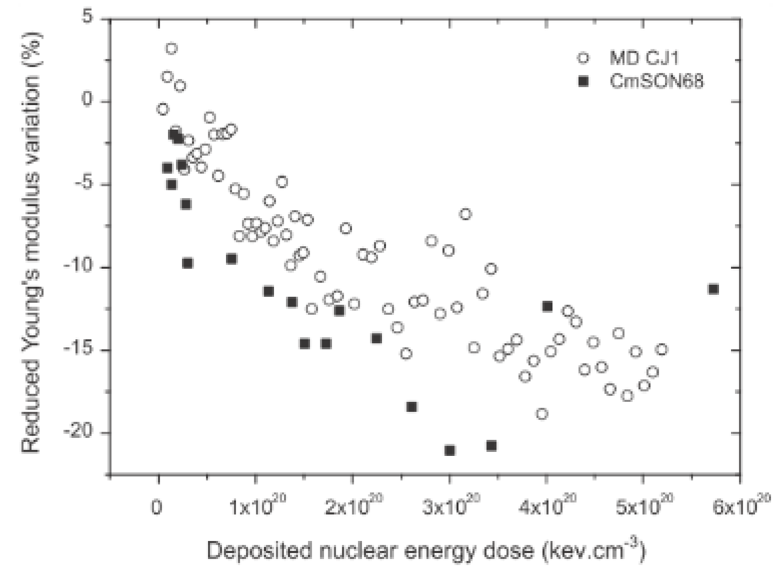


# WASTE MECHANICAL DEGRADATION?

## Degradation of the mechanical properties?

**Decrease of Hardness, Young Modulus, increase of fracture toughness**

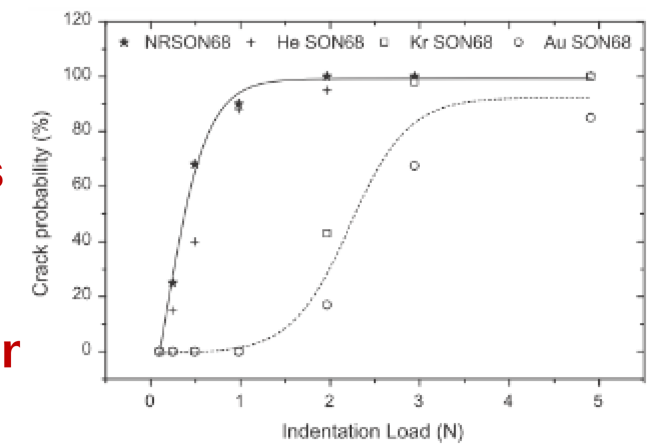



**No significant degradation of the mechanical properties**

**Even slightly better, fracture toughness increase …**

**Origin associated to structural changes under irradiatior**

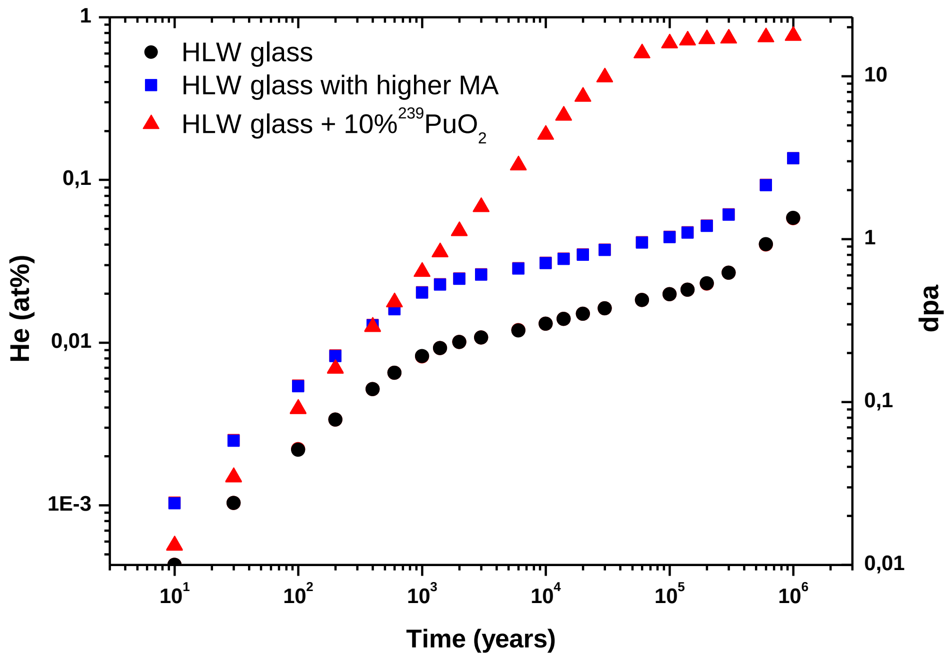


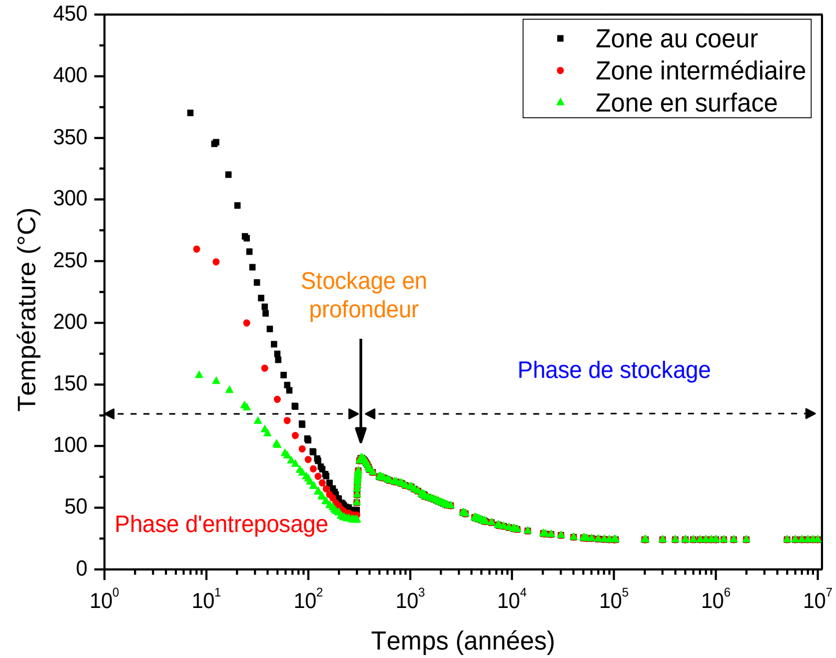
## Waste mechanical degradation?

### Can irradiation induce a cracking of the material?

- Due to important swelling under irradiation?
- Degradation of the mechanical properties?
- Due to bubble formation (He bubbles generated by alpha decays)

## Is there any risk of formation of pressurized He bubbles in a nuclear glass?




- **Helium incorporation mechanism in the glassy network ?**
- **Solubility limit ? Helium bubble formation?**
- **Helium diffusion mechanism?**
- **Impact of radiation damage on these mechanisms?**

# WASTE MECHANICAL DEGRADATION?

## He - METHODOLOGY

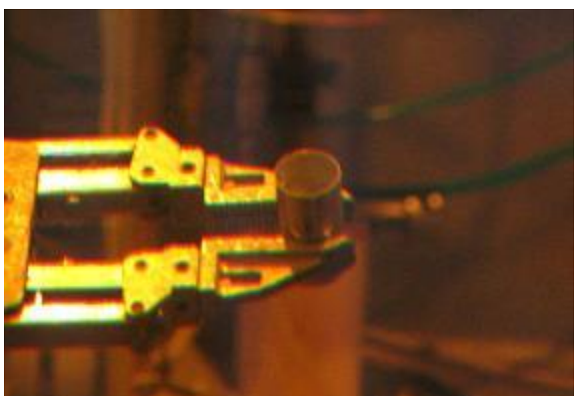
**Irradiation in OSIRIS reactor ($^{10}B(n,\alpha)^{7}Li$)**

**$[He]_{max}$:** $2{,}2 \times 10^{20}$ at./cm$^3$
**dpa:** ~ 1-2

CEA Saclay OSIRIS

**Cm doped glass (alpha decays)**

**$[He]_{max}$:** $4{,}4 \times 10^{19}$ at./cm$^3$
**dpa:** 1



**He Infusion (P, T)**

**Equilibium gas/solid**

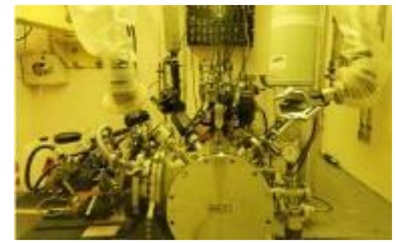
**$[He]_{max}$:** $3{,}5 \times 10^{18}$ at./cm$^3$
**dpa:** 0

CEA Marcoule

**$^3He^+$ implantation :**

**$[He]_{max}$:** $4{,}3 \times 10^{21}$ at./cm$^3$ (local)
**dpa:** 11 (local)

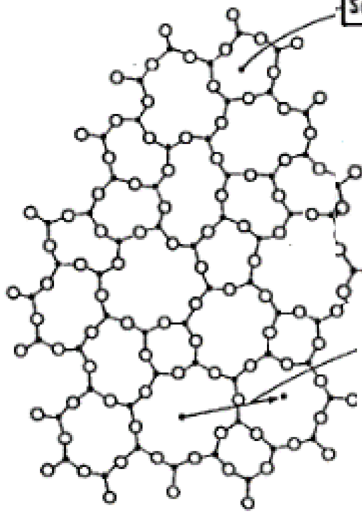
CEMHTI Orléans, LEEL Saclay
**NRA $d(^3He,p)\alpha$**



Jannus Orsay, MIAMI Huddersfield
**in-situ TEM**

# Glass LTB: He incorporation in nuclear glass

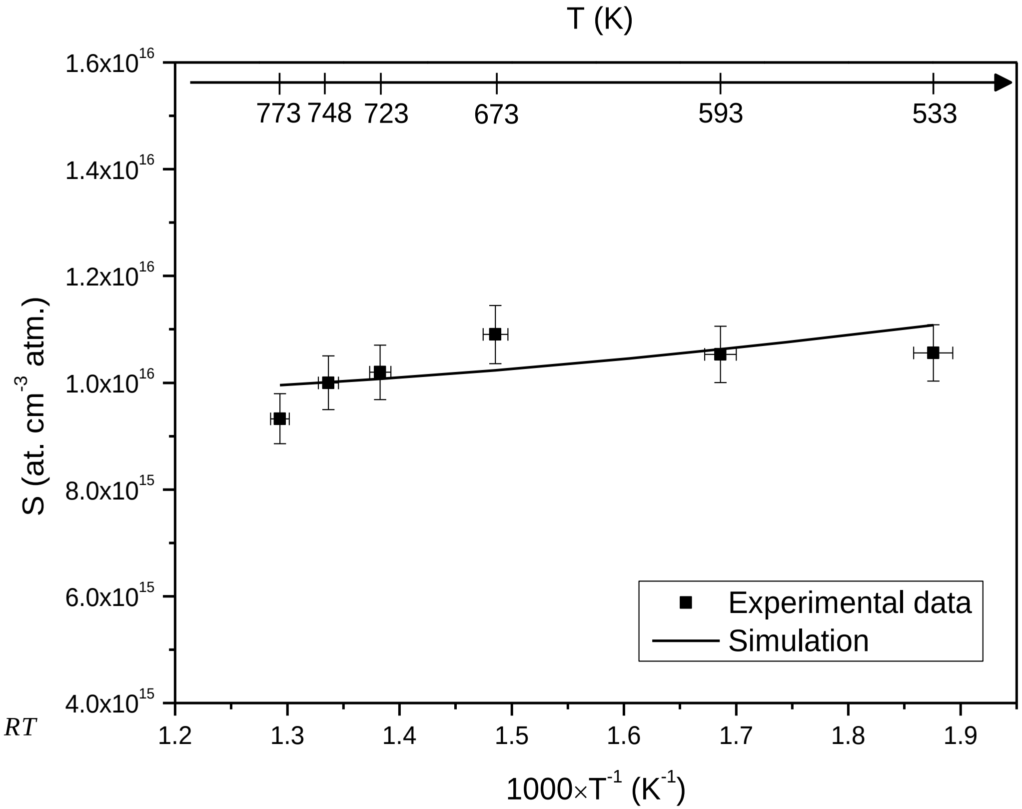
## Incorporation of He in the glass free volume




$$S = \frac{C}{p} = \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} \frac{1}{k_B T} N_S \left(\frac{e^{-h\nu/2k_B T}}{1-e^{-h\nu/k_B T}}\right)^3 e^{-E(0)/RT}$$

*Shackelford J. Appl. Phys. 43 (1972)*

## He infusion experiments




*T. Fares, J. Am. Cer. Soc. 95 (2012) 3854*

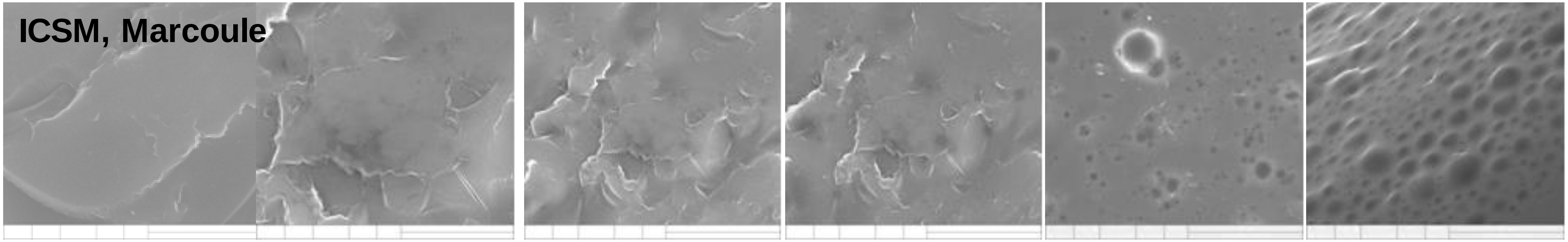
**Density of solubility sites accessible to helium in R7T7 glass: Ns~3x10$^{21}$ sites.cm$^{-3}$**

**Ns~3 at% to confirm by high pressure infusion experiments at JRC-ITU**

# Glass LTB: He incorporation in nuclear glass (Ns=3 at%)

**Physical state of He ?** **Homogeneous generation with equilibrium gas/solide**

**In-situ ESEM during thermal treatment on He infused nuclear glass ([He]=0.001at%)**




352° C 520° C 530° C 540° C 547° C 594° C

**No damage, dpa=0** *Tg* *T (° C)*

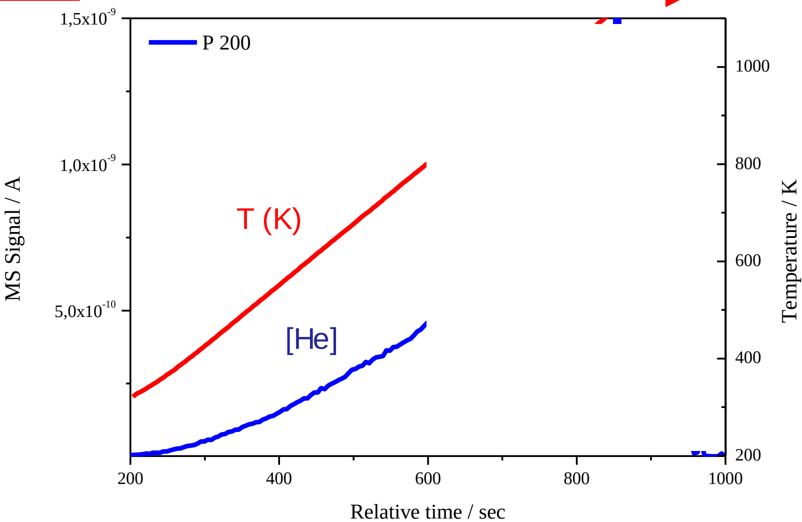
$T<T_G$: No evolution of microstructure
Helium inside the free volume

$T\sim T_G$: Dark zones

- nucleation of He bubbles (1 µm < ø < 10 µm)

$T>T_G$: Formation of bubbles

- migration of bubbles
- release by bursts




*He release*
*ITU QGames*

- **$T<T_g$:** no glass deformation → No bubbles (ø < 50 nm)
- **$T>T_g$:** glass deformation is possible → Bubble formation (ø > 50 nm)

# Glass LTB: He incorporation in nuclear glass (Ns=3 at%)

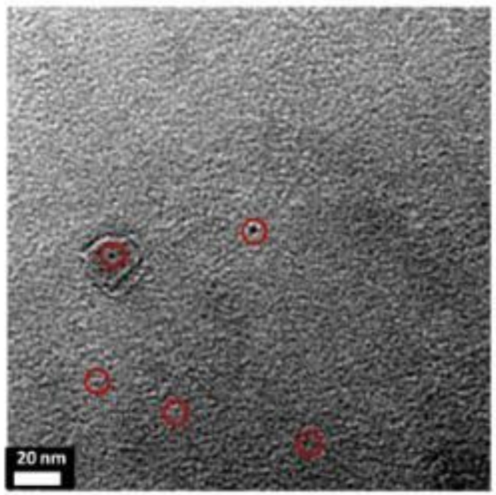
**Physical state of He ?**

**Heterogeneous generation at -130°C with damage**

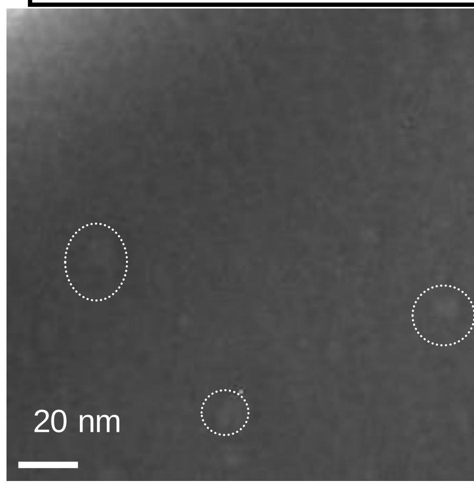
**In-situ TEM during He implantation: Jannus Orsay, MIAMI Huddersfield**

**10 keV, Jannus**

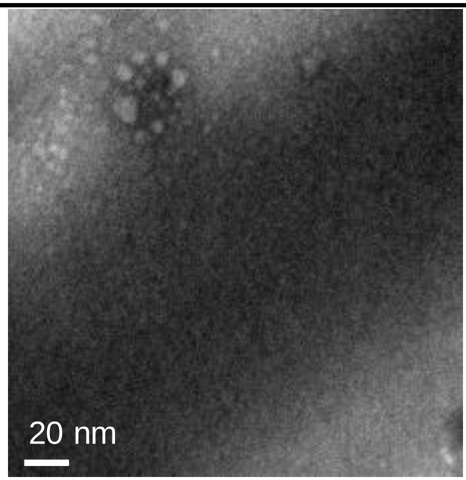
**6 keV, MIAMI**



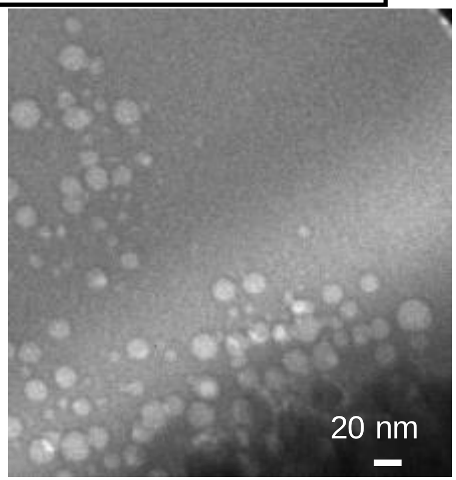

~ $10^{15}$ (0.1 at%, 0.1dpa)




~ 2 x $10^{16}$ (2 at%, ~2dpa)




~ 4 x $10^{16}$(4 at%)




~ 9 x $10^{16}$ (9 at%)

*Ns (~3 at%)*

*F (He.cm$^{-2}$)*

- **[He] < Ns**:

First bubbles observed at ~0,1 at%

Weak evolution of size and density

- **[He ] > Ns**:

Increase of the bubble size

Increase of the bubble density

*R. Bes et al J. Nucl. Mater.* 443 (2013) 544-554

*Gutierrez et al., J. Nucl. Mater.* 452 (2014) 565-568

# Glass LTB: He incorporation in nuclear glass

(Ns=3 at%)

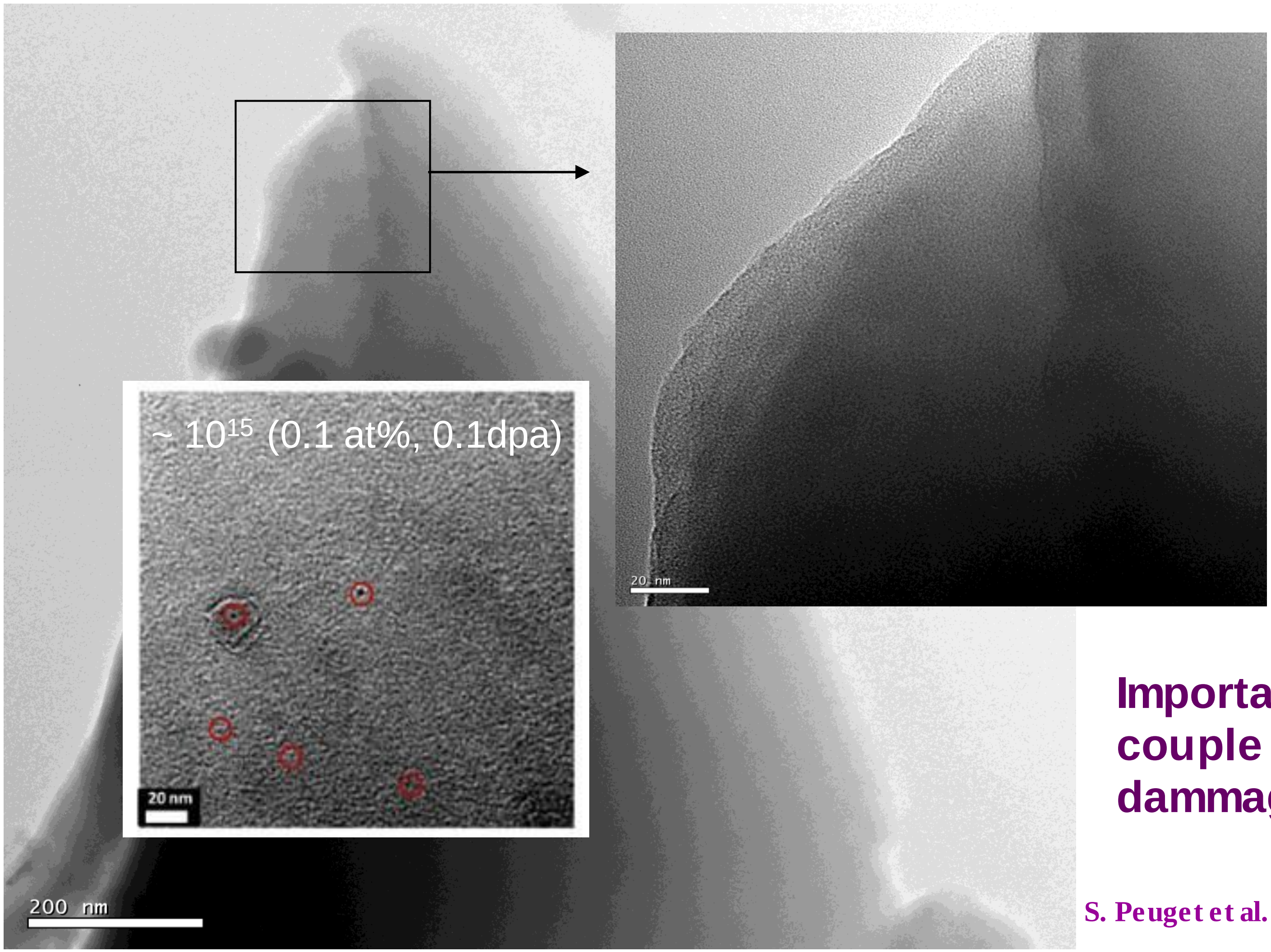
**Physical state of He ?**

**Homogeneous generation <u>at room temperature</u>**

**$^{244}$Cm and OSIRIS irradiated glass $^{10}B(n,\alpha)^{7}Li$ : ~$2x10^{20}$ He/cm$^3$ ( 0.2 at%, ~1dpa)**

(~ $10^6$ ans de stockage)

*TEM (ITU Karlsruhe)*

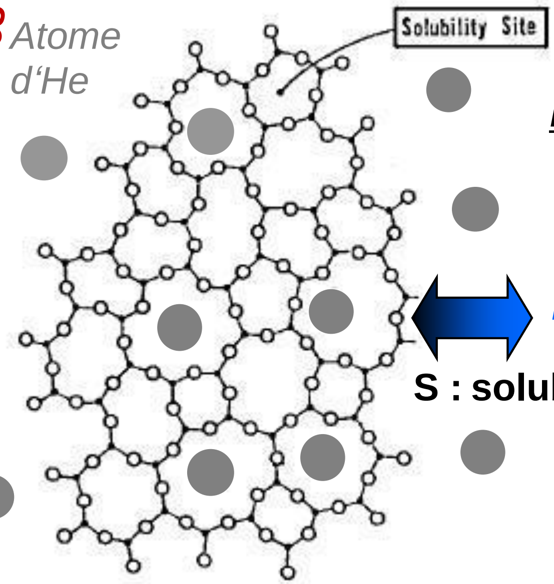



**Importance of the couple T/irradiation dammage**

S. Peuget et al. NIMB 327 (2014) 22-28

# Glass LTB: He incorporation in nuclear glass, summary

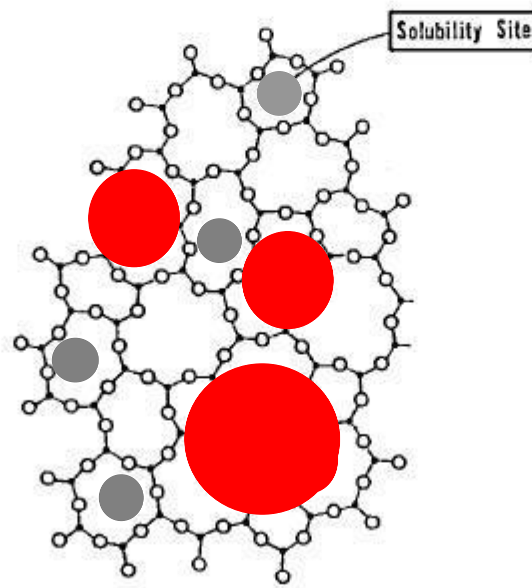
*Solubilisation : equilibrium between solid and gas phases*




***$N_S$ : density of solubility sites***

$P_{He}$

**S : solubility constante**

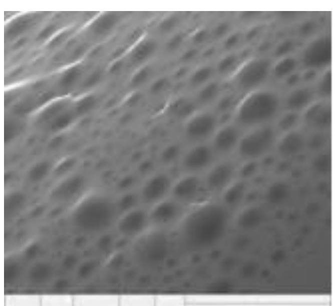



*Incorporation (desintegration, implantation) : out of equilibrium*

*[He] < Ns*

- Helium solubilized in the glass free volume
- Bubble formation for T>Tg (~550°C)

594°C



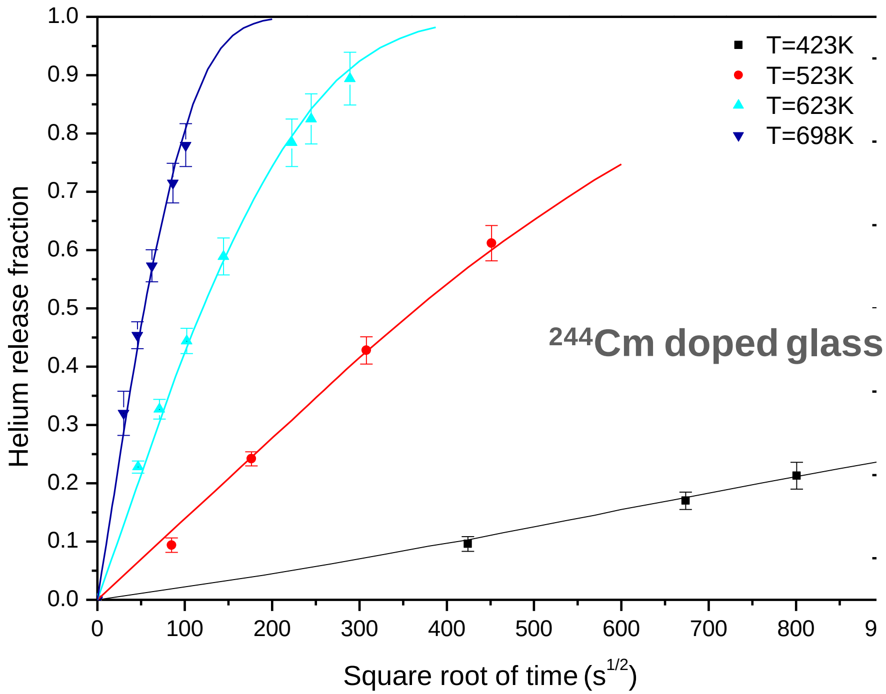
1. [He] < Ns
- He solubilized in the free volume
- Weak probability for He bubble formation
- Importance of temperature and damage?

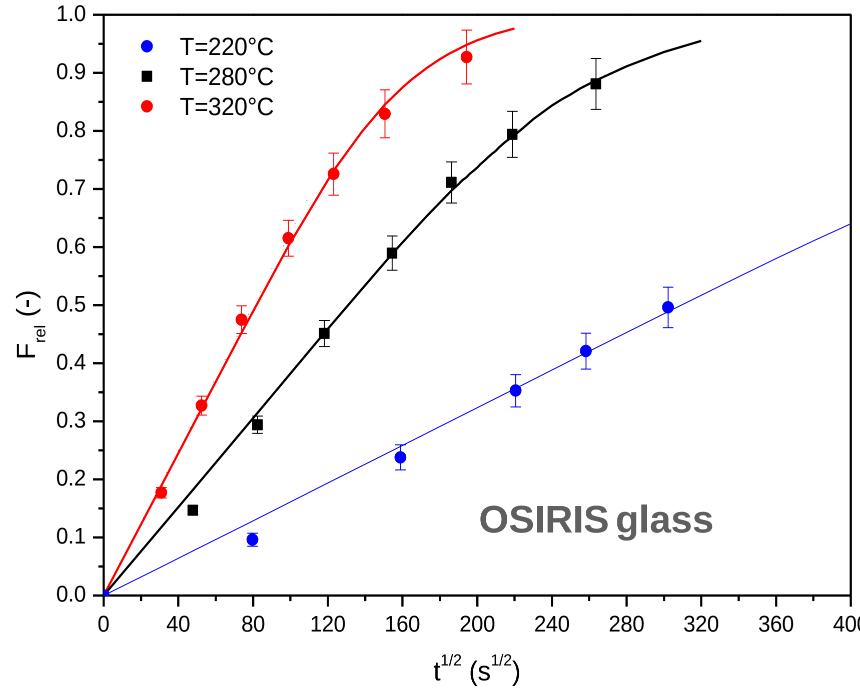
***Disposal conditions: in progress***

2. [He] > Ns
- Bubble formation
- Stress state ?

# Glass LTB: He diffusion in nuclear glass

## Helium release experiment: determination of $D_{He}$



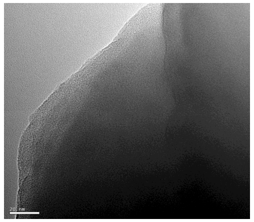




*T. Fares, J. Nucl. Mater. 416 (2011) 236*

*T. Fares, Thèse Univ. Montpellier II (2011)*

DHA, Atalante

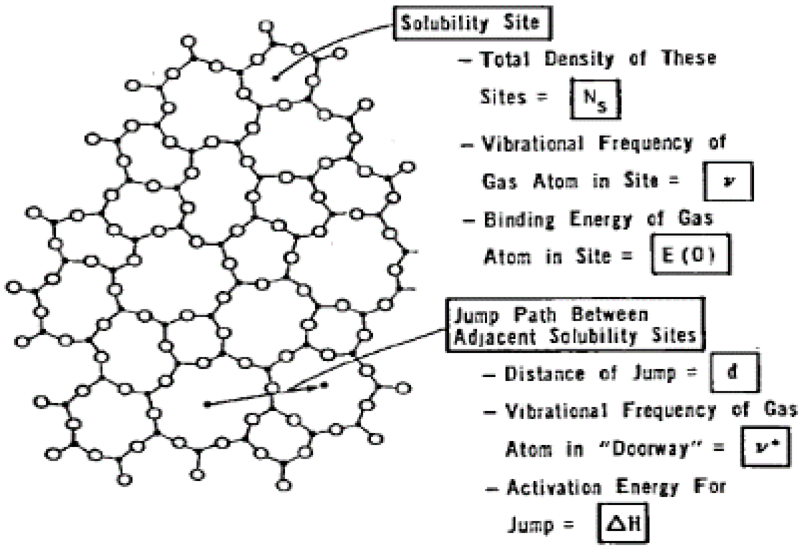
$$\begin{cases} \dfrac{\partial C(x,y,z,t)}{\partial t} = A(x,y,z,t) + D\Delta C(x,y,z,t) \\ A(x,y,z,t) = -\dfrac{dN_{(^{244}Cm)}}{dt} = A_0(x,y,z)\exp\left(-\lambda_{(^{244}Cm)}t\right) \end{cases}$$



**Only a solubilized helium population is needed to fit the data**

**No need to introduce helium bubbles in the model …**

# Glass LTB: He diffusion in nuclear glass

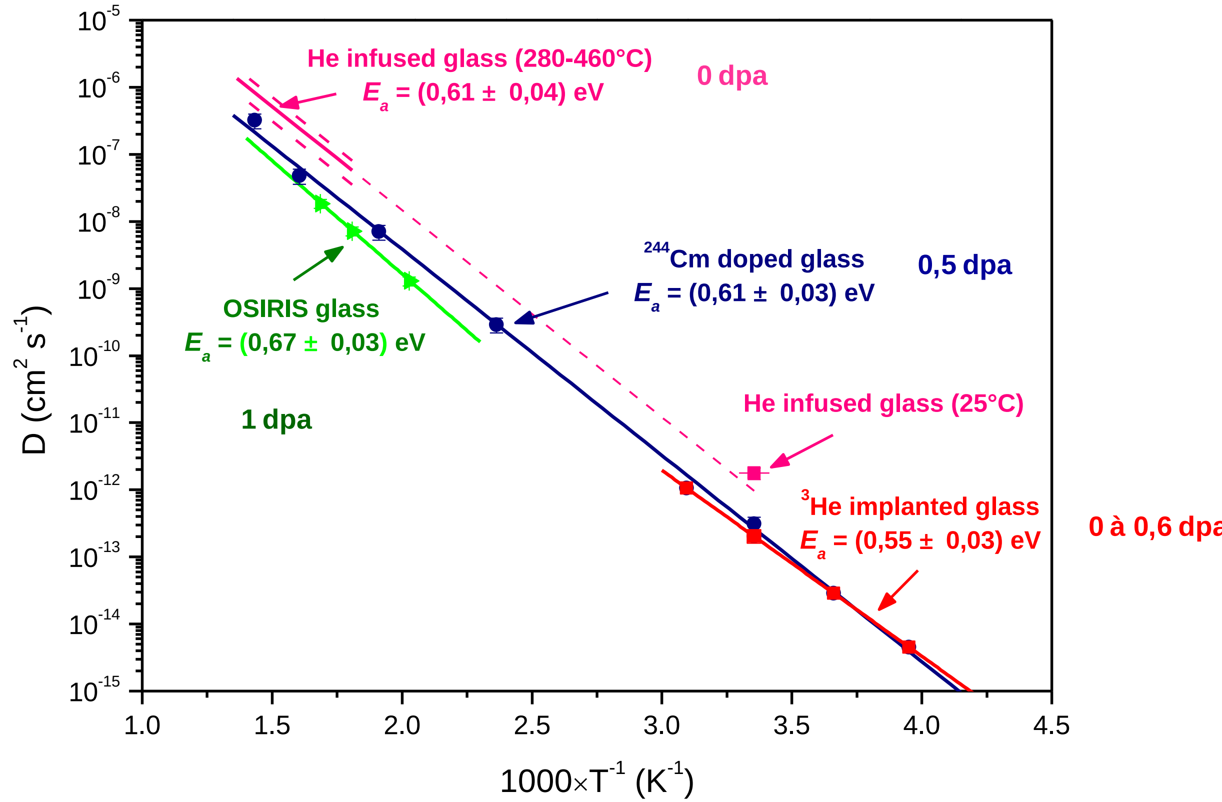



$$D = \frac{1}{6}.d^2.\frac{\nu^3}{\nu^{*2}}.e^{-\Delta H/K_B T} = D_0.e^{-\Delta H/K_B T}$$

*J. Shackelford J. Appl. Phys. 43 (1972)*

*T. Fares, Thèse Univ. Montpellier II (2011)*

*F. Chamssedine J. Nucl. Mater. 400 (2010) 175*



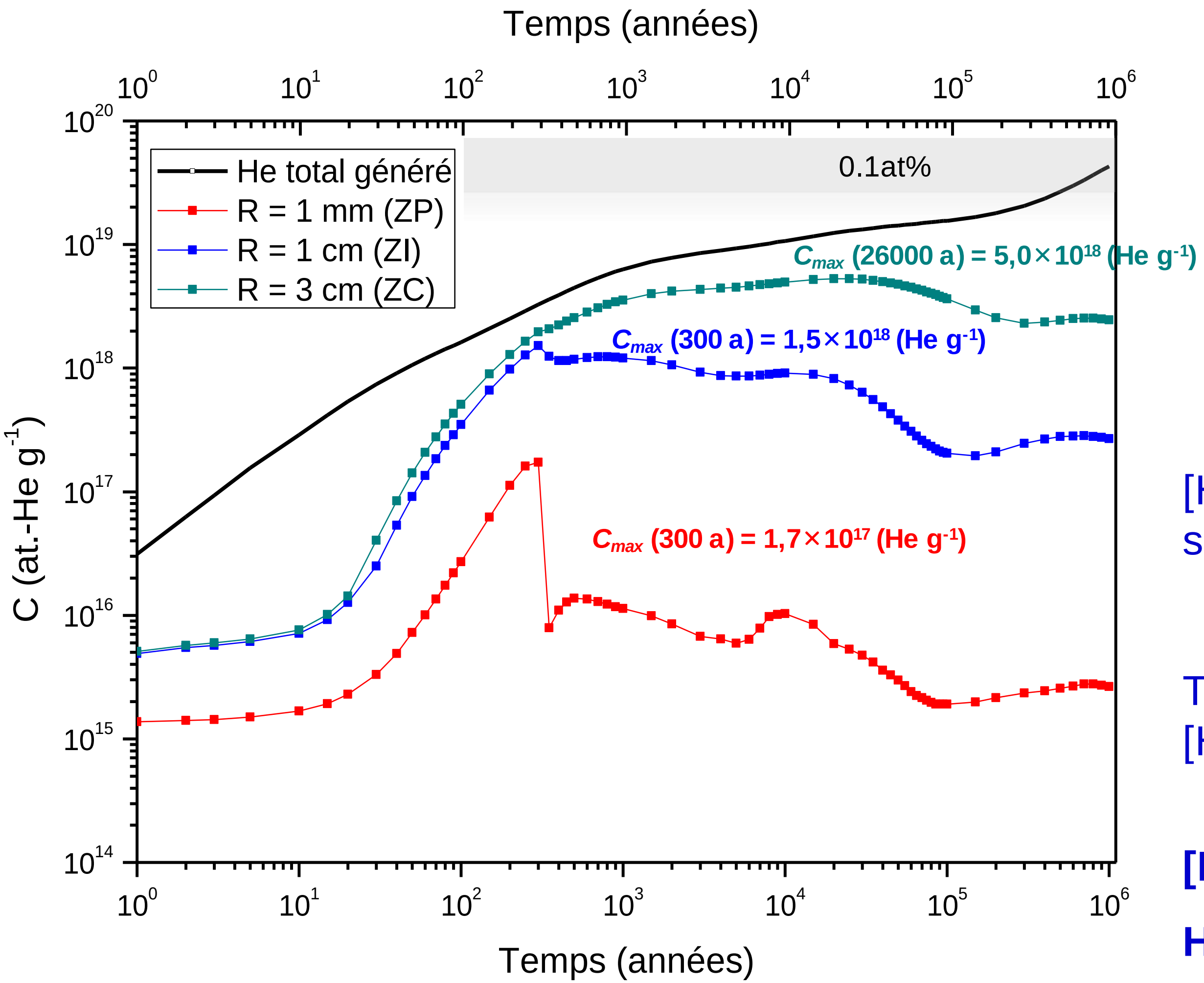

**All data are in quite good agreement**

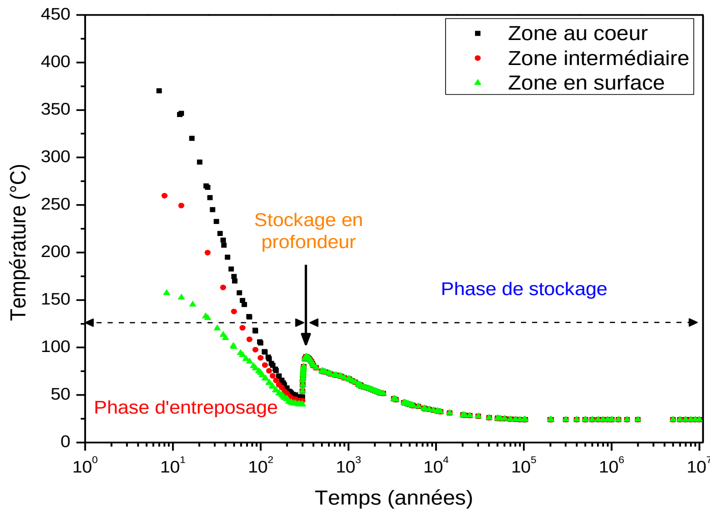
**Ea ~0.6 eV**

**Diffusion through the glass free volume**

**No significant effect of the glass damage on $D_{He}$**

# Glass LTB: modeling of He migration in a canister



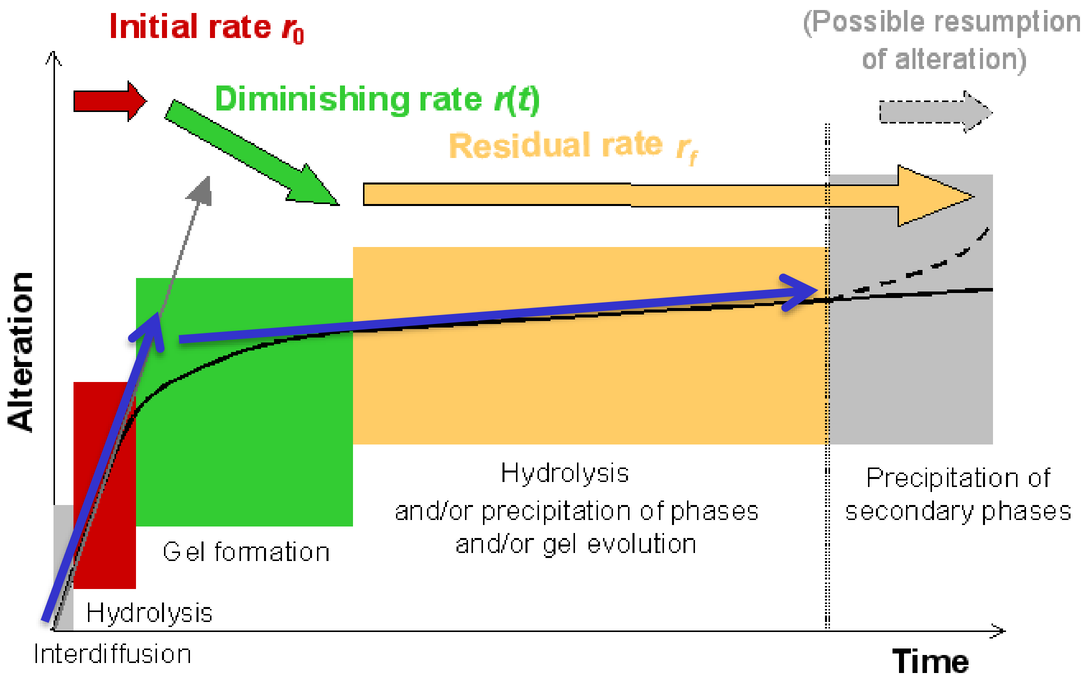

[He]=f(t) is strongly dependent of bloc size

Thermal diffusion can strongly reduce $[He]_{max}$

**$[He]_{max}$<Ns/100**

**He bubble formation is unprobable**

# EFFECTS OF RADIATION ON THE LEACHING BEHAVIOR?

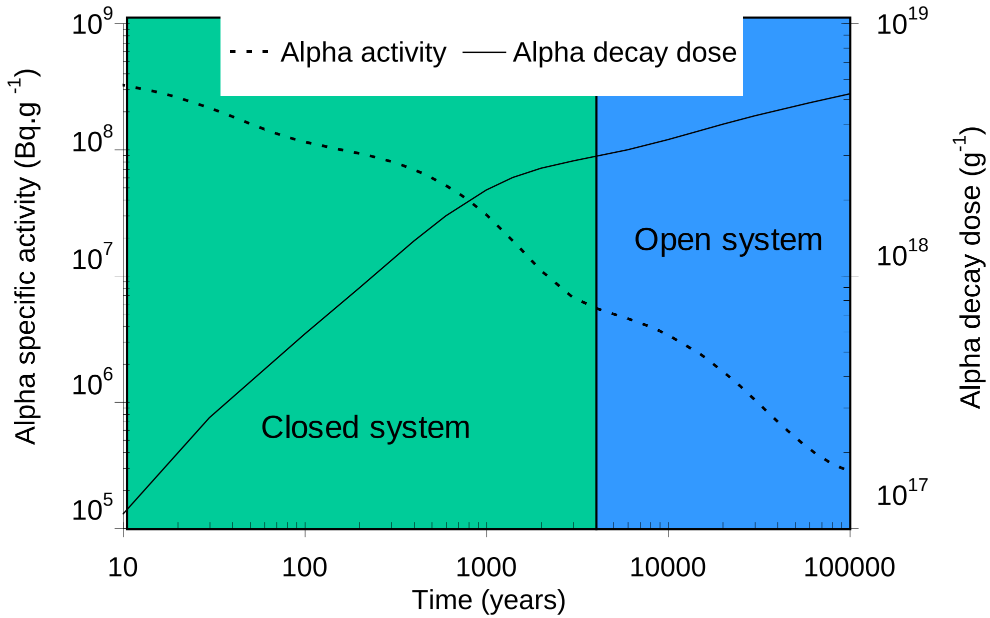



**Two main steps to study:**

1. **Impact on $r_0$**
2. **Impact on residual rate, $r_r$**

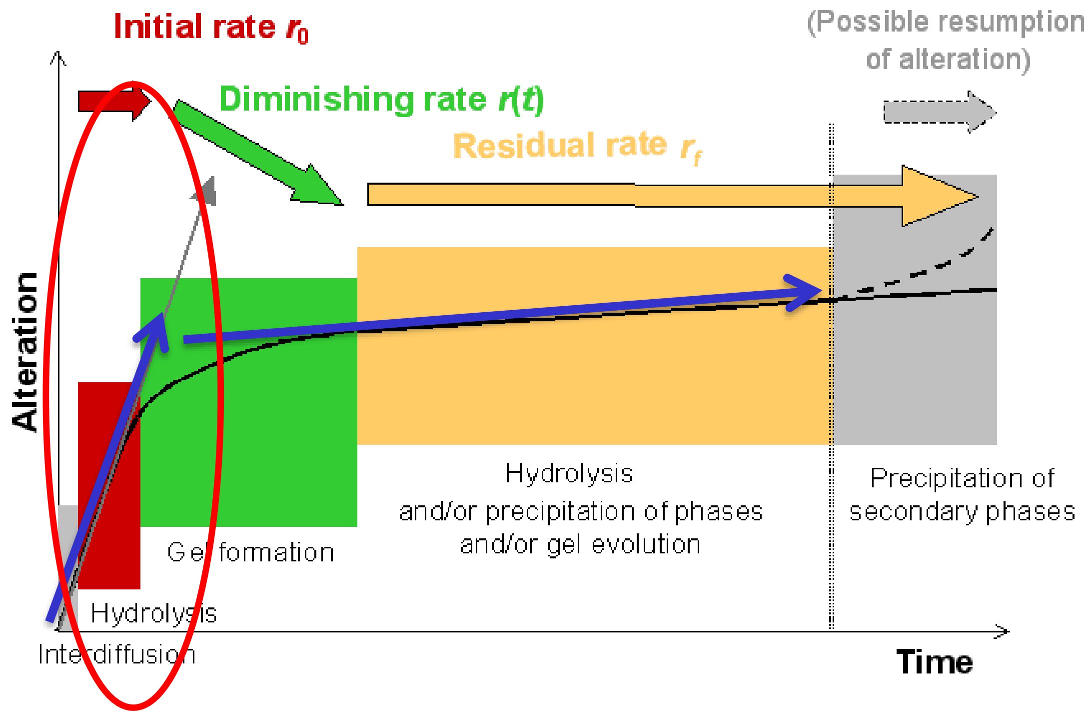
**Two parameters to study:**

1. **Dose rate**
2. **Dose**




**Experiments on radioactive and externally irradiated SON68 glasses**

# EFFECTS OF RADIATION ON THE LEACHING BEHAVIOR?



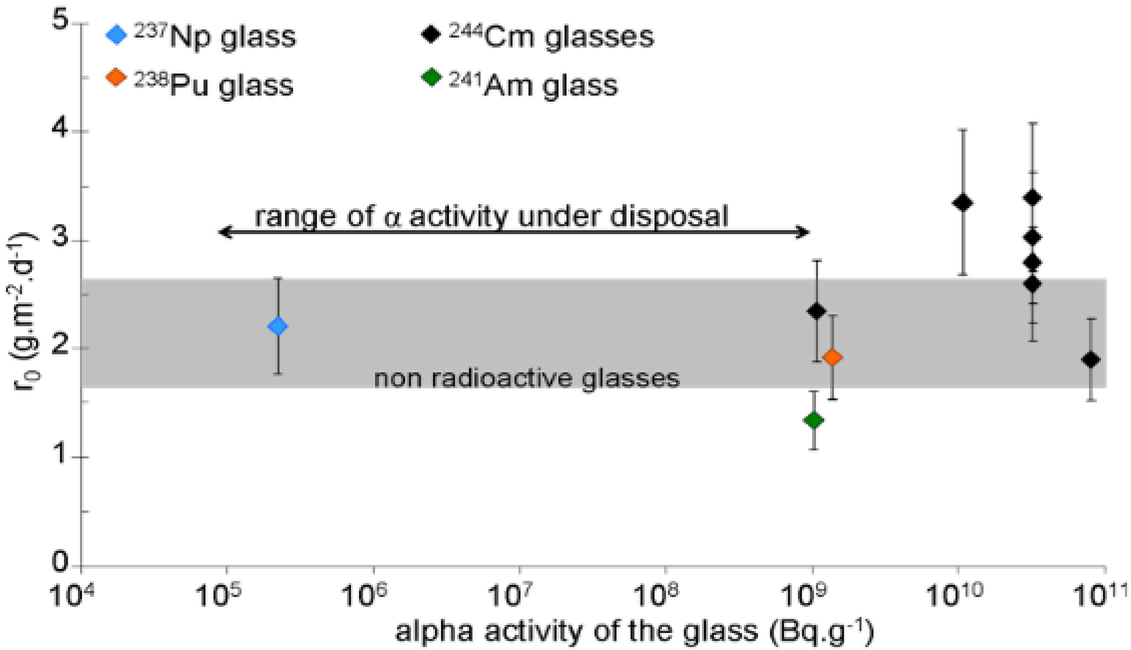

1. **Impact on $r_0$**

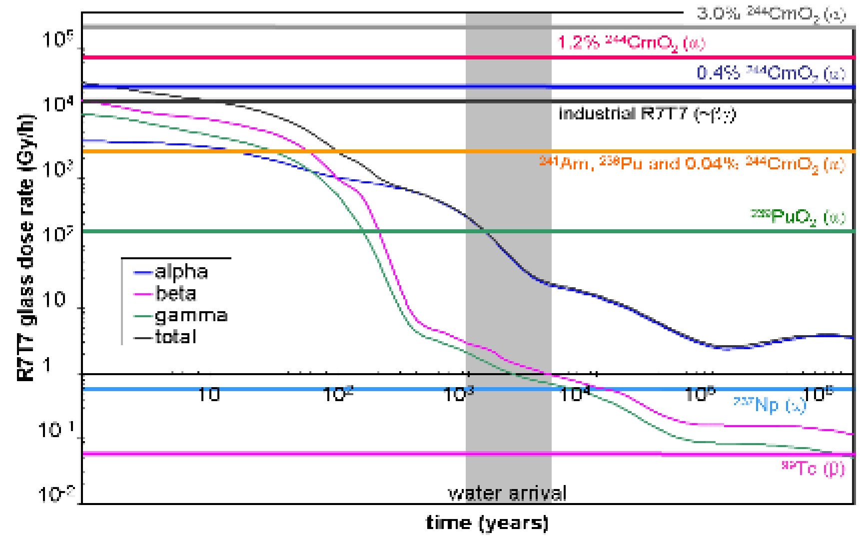
**Two parameters to study:**

1. **Dose rate**
2. **Dose**

# ALPHA DOSE RATE on initial rate R0?

Soxhlet-mode dynamic leach tests or short static tests (low SA/V ratio) on different α doped glasses[1,2]




No significant impact of α activity on $R_0$

[1]S. Peuget et al., JNM 362 (2007)

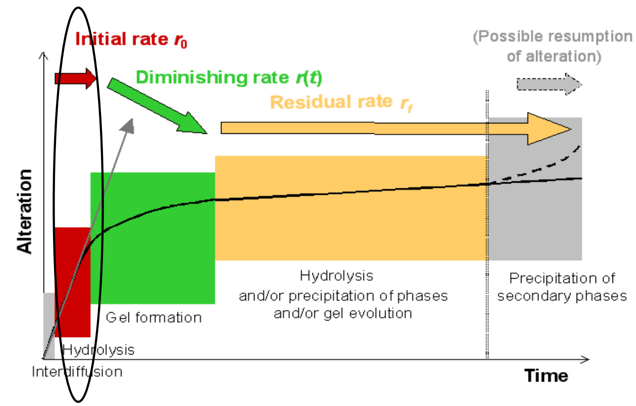
[2]T. Advocat et al., JNM 298 (2001)

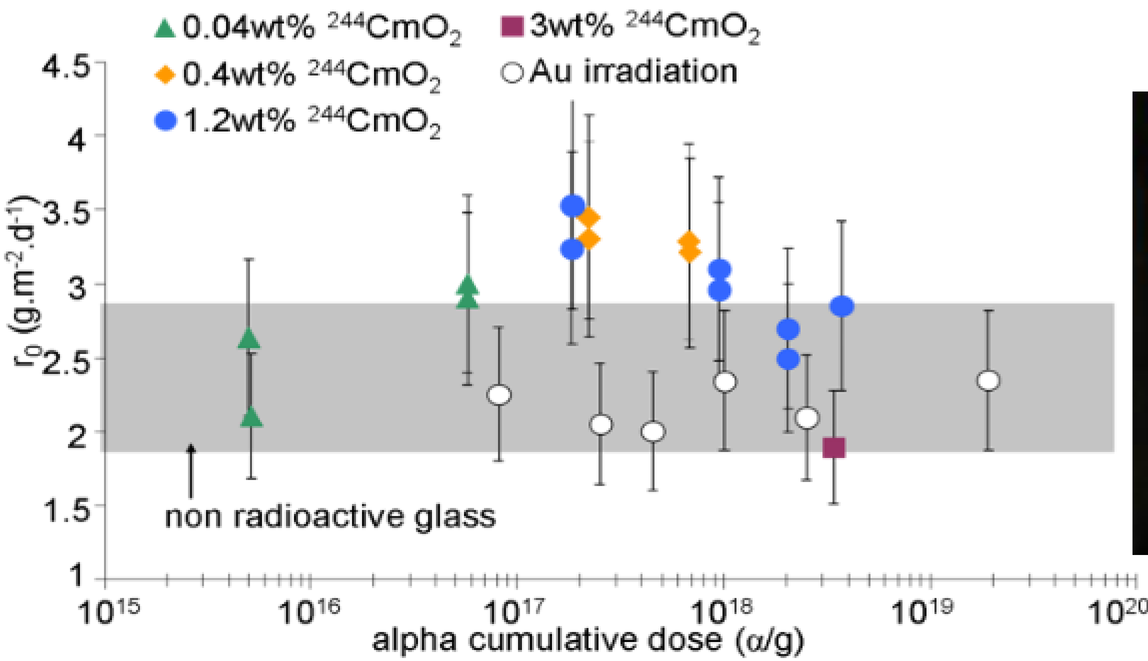
# ALPHA CUMULATIVE DOSE on initial rate R0?

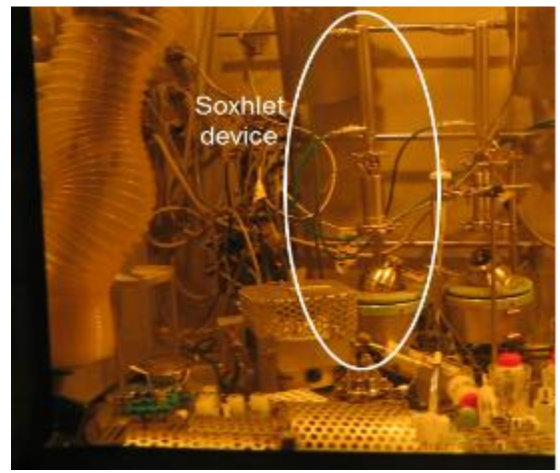
Soxhlet-mode dynamic leach tests (100°C, 1 month) on[1]:

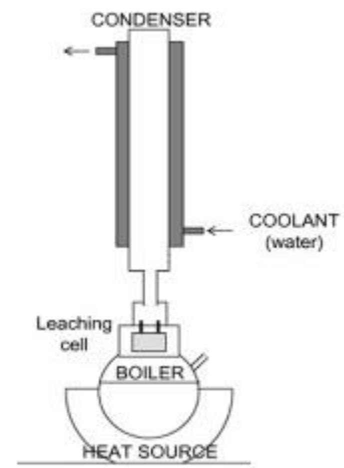
- $^{244}Cm$-doped glasses
- non radioactive glasses previously irradiated by Au ions

$R_0$ determined from solution analysis



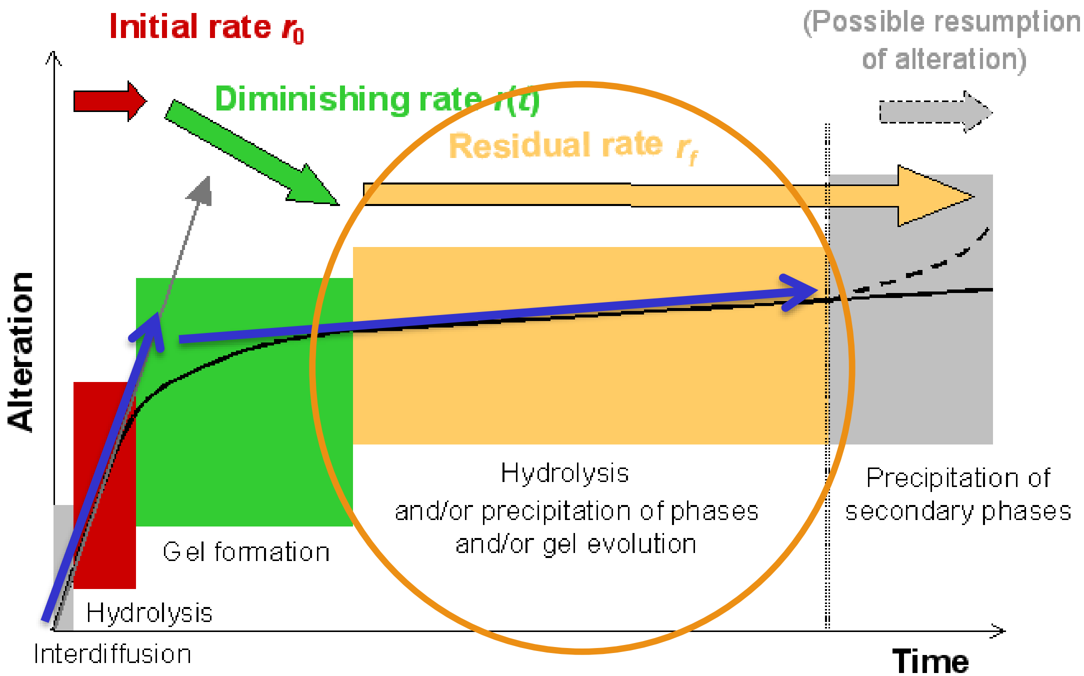




No significant ballistic impact of α cumulative dose on $R_0$

In agreement with data from literature: no impact[2] or less than factor two[3]

[1]S. Peuget et al., JNM 362 (2007) [2]D.M. Wellman et al., JNM 340 (2005) [3]W.G. Burns et al., JNM 107 (1982)

# EFFECTS OF RADIATION ON THE LEACHING BEHAVIOR?




**2.Impact on residual rate, $r_r$**

**Two parameters to study:**

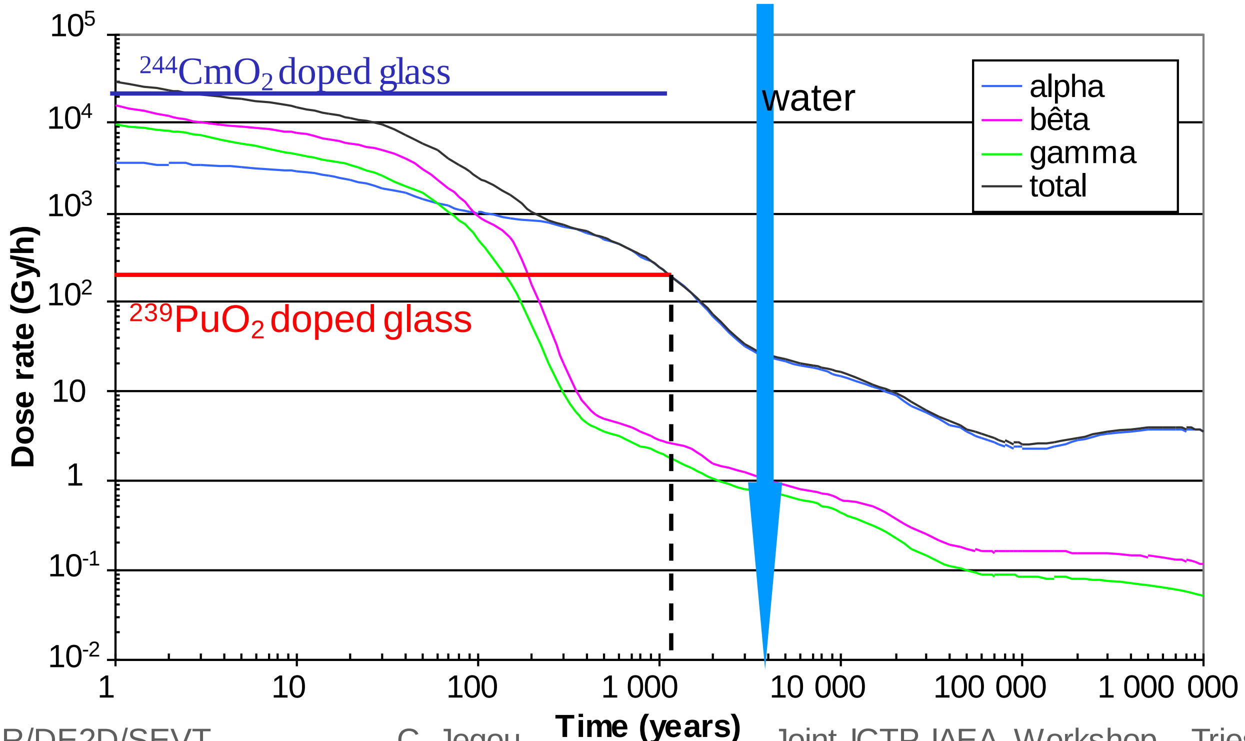
1. **Dose rate**
2. **Dose**

# ALPHA DOSE RATE on residual rate ?

✓ Glass characteristics:

- **2 SON68 doped glasses**

| α-doped glasses | Dose rate (Gy/h) | Dose cumulated before leach exp |
|---|---|---|
| 0.85 wt% of $^{239}PuO_2$ | 150 | ~ $3.7 \times 10^{16}$ α/g |
| 0.4 wt% of $^{244}CmO_2$ | 23,500 | ~ $3 \times 10^{18}$ α/g |



# EXPERIMENTAL

- ✓ Glass samples ground & sieved → 63 – 125 µm fraction powder

$S_{BET}$ ~ 645 $cm^2.g^{-1}$

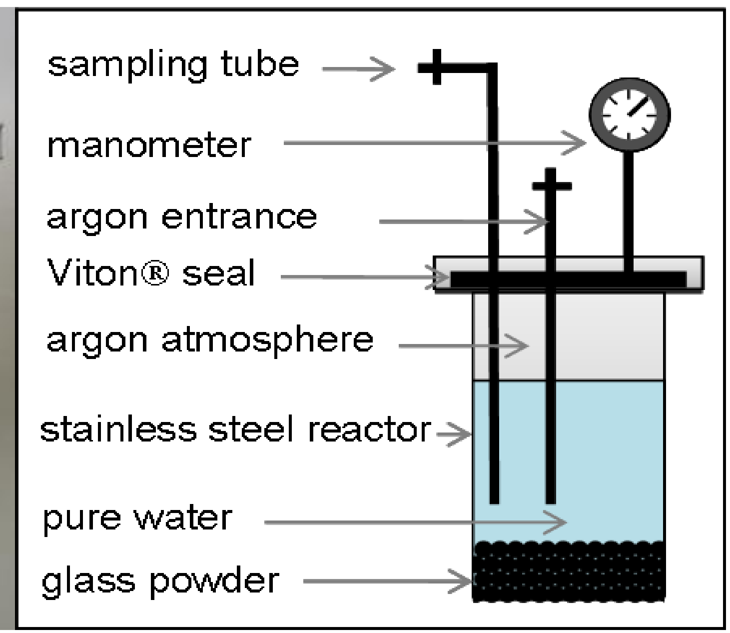
- ✓ SON68 reference glass powder → reference experiment

- ✓ Glass alteration
  - **~10 g of glass powder**
  - **~ 300 mL of pure water**

  } S/V = 20-25 $cm^{-1}$

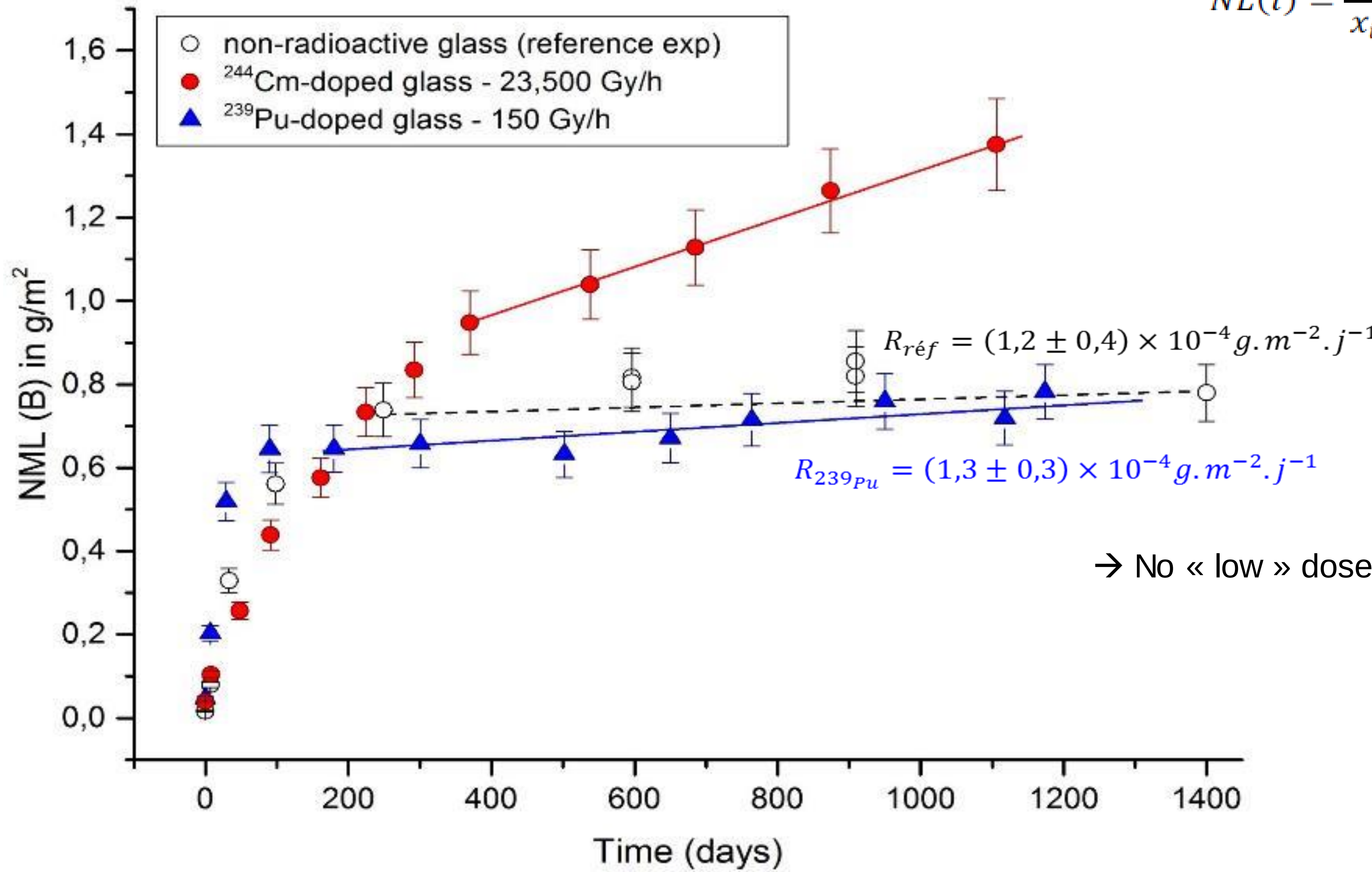
  - **4 Bar Ar overpressure**
  - **90°C**
  - **> 3 years**

- ✓ Analyses:
  - **Regular leachate samples (ICP-AES, ionic chromatography, pH, Eh, radiochemistry)**
  - **Solid analyses after leach test (SEM, TEM, EDX)**



# RESULTS: tracer evolution (B, Na, Li)

$$NL(i) = \frac{C(i)V}{x_i m S} (g.m^{-2})$$

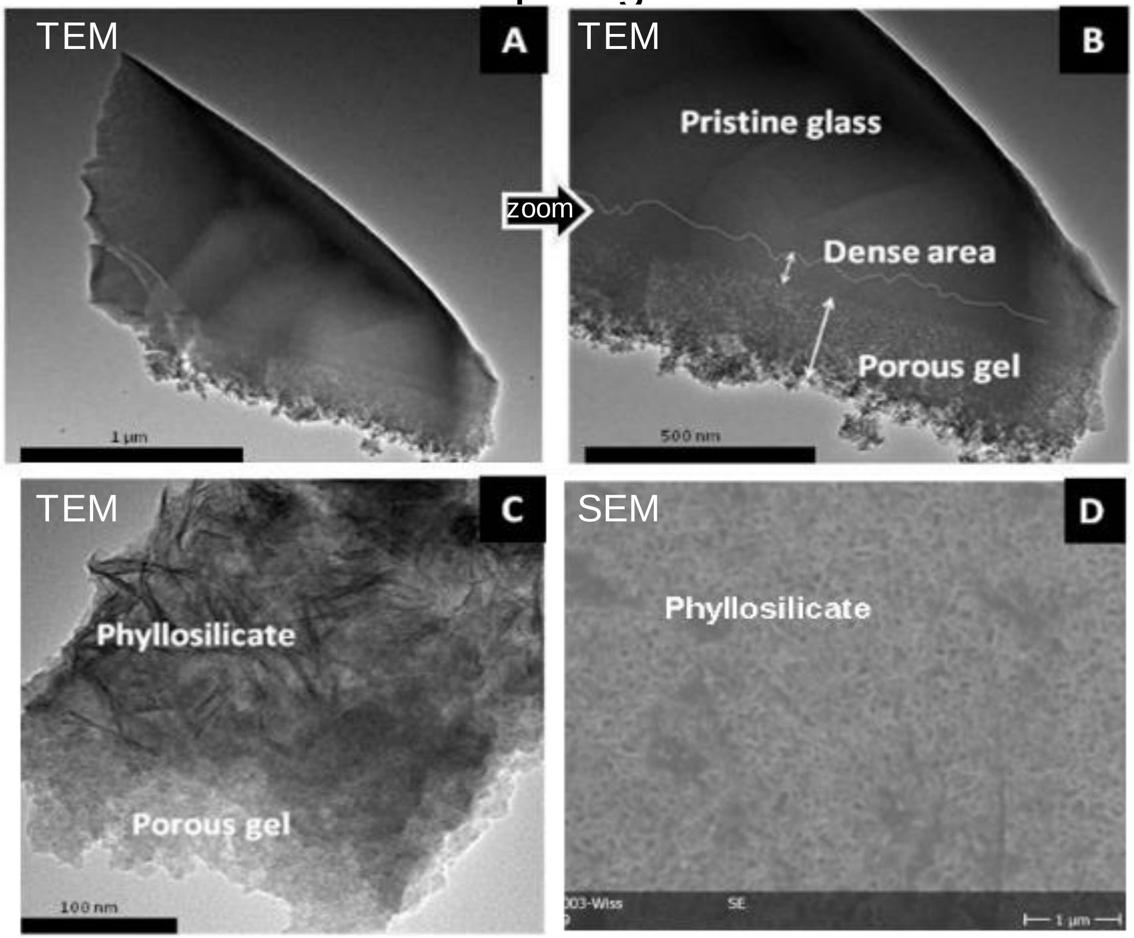



~ similar

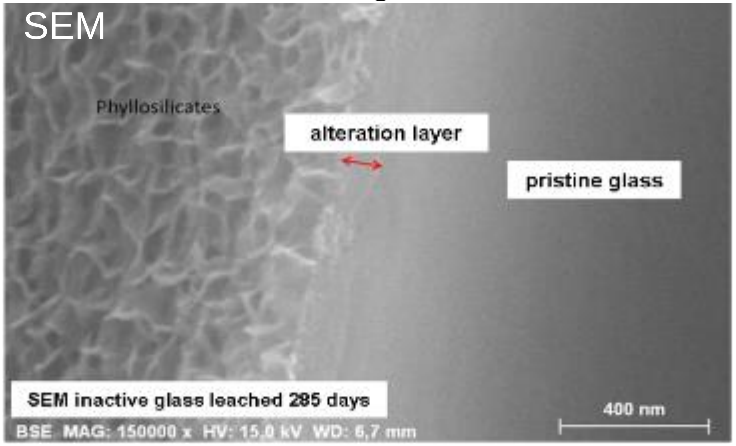
→ No « low » dose rate effect

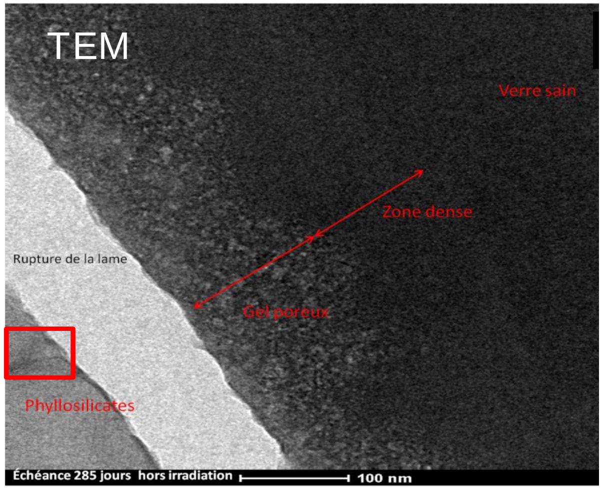
# RESULTS: solid analyses

## Pu-doped glass




## Inactive glass



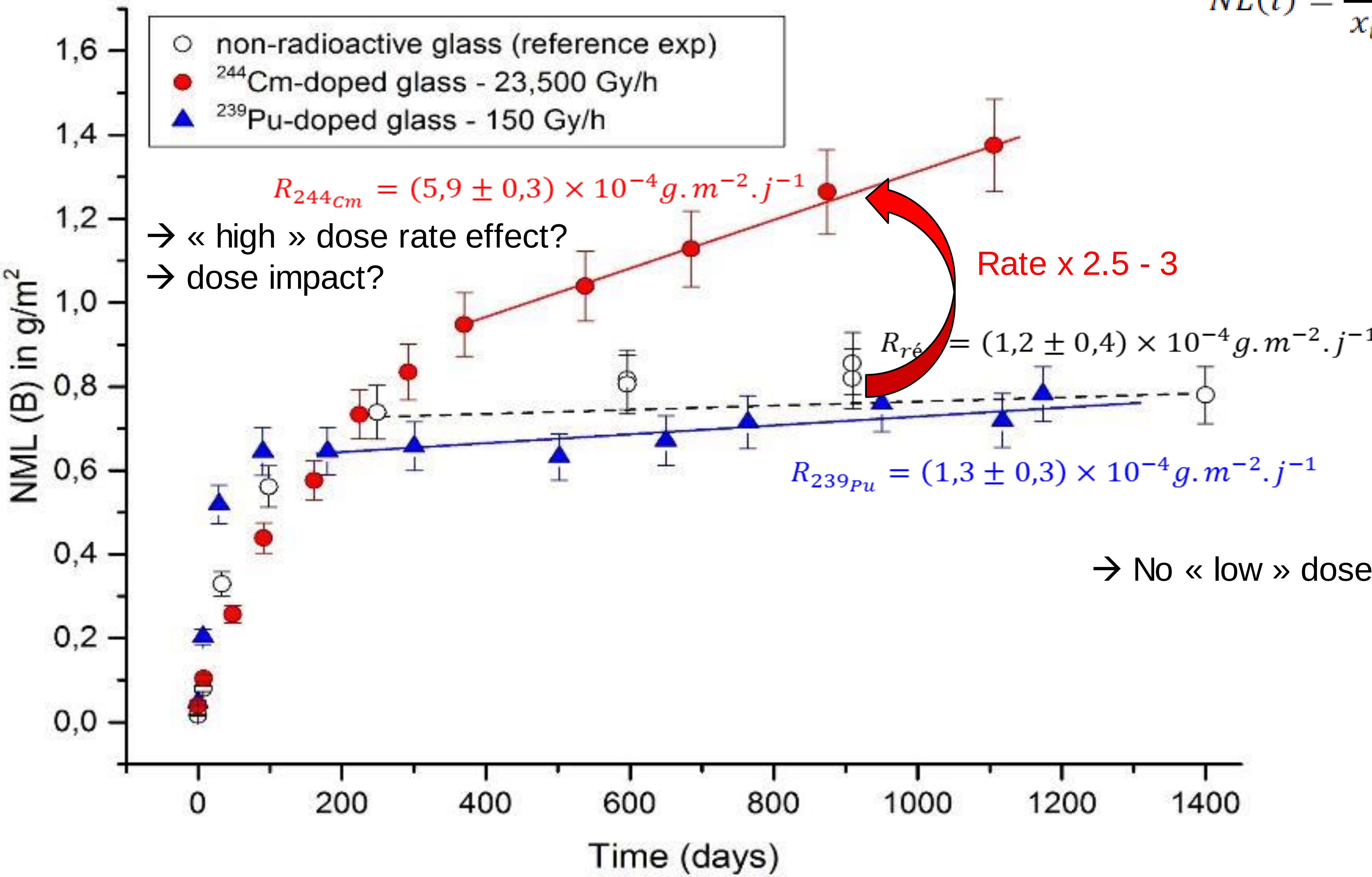




**Alteration layer formed under radiation for $^{239}$Pu-doped glass:**

- Similar to non radioactive one
- Thickness : similar to those calculated from solution releases (300 nm)

# RESULTS: tracer evolution (B, Na, Li)

$$NL(i) = \frac{C(i)V}{x_i m S}\,(g.m^{-2})$$




~ similar

→ No « low » dose rate effect

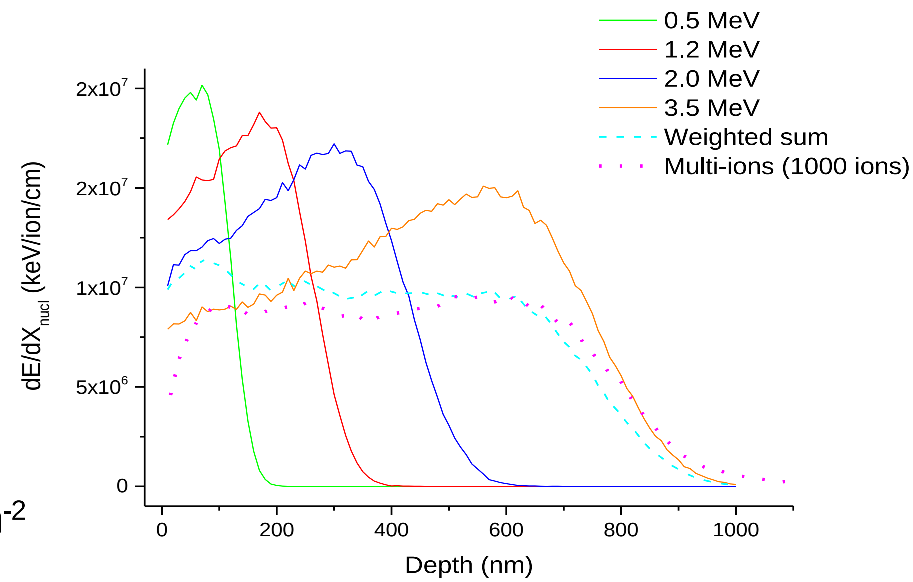
# Glasses and irradiation conditions

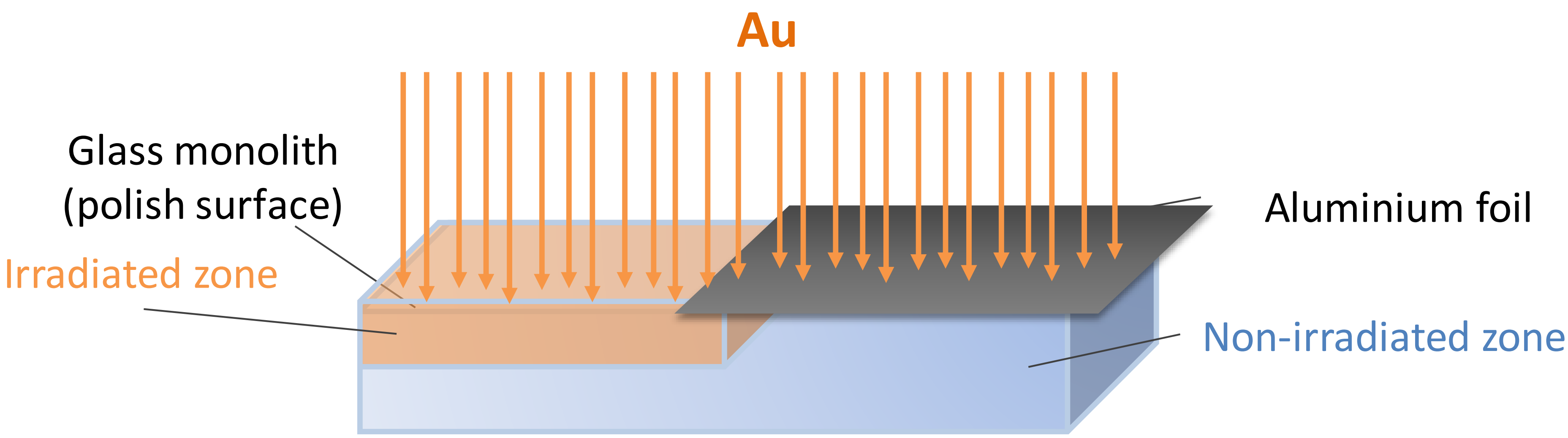
## Simple glass composition

- ISG (International Simple Glass)

## Multiple-energy gold ion irradiation

- 0.5 – 3.5 MeV → ≈ constant ballistic damage
- Energy deposition < ion track formation
- Wide range of fluences: $1.9 \times 10^{12} \rightarrow 5.5 \times 10^{14}$ ions.cm$^{-2}$



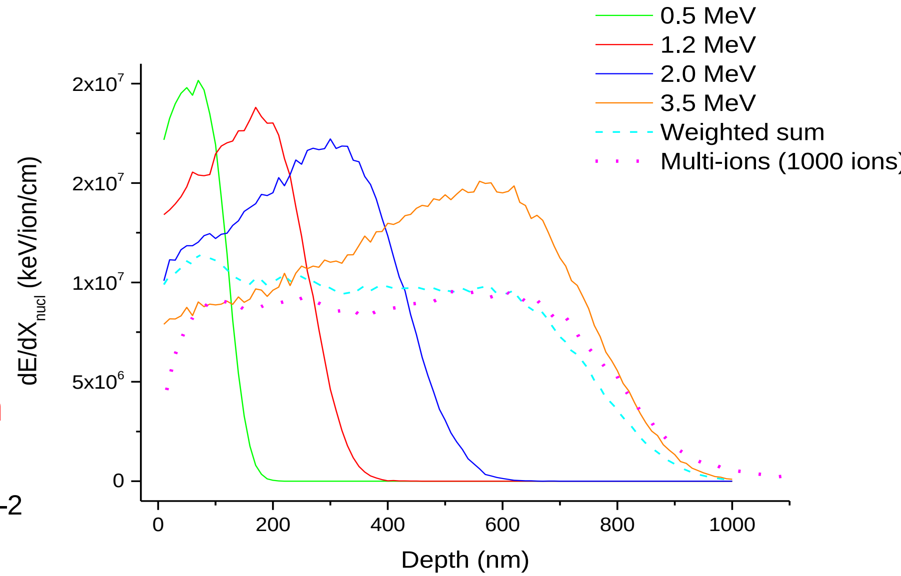



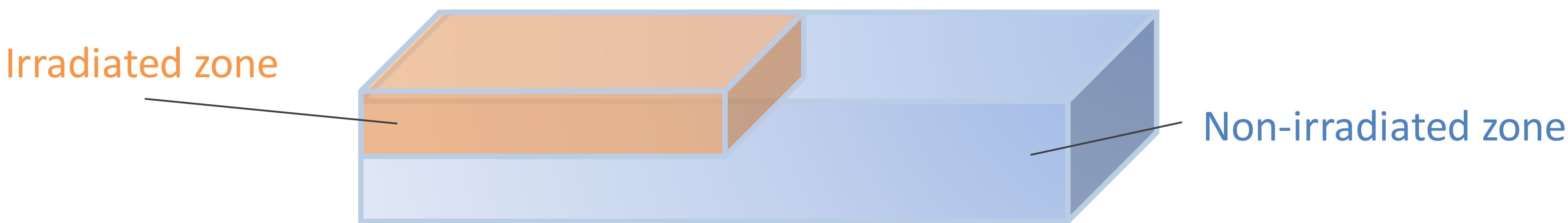
## Simple glass composition

- ISG (International Simple Glass)

## Multiple-energy gold ion irradiation

- 0.5 – 3.5 MeV → ≈ constant ballistic damage 1000 nm
- Energy deposition < ion track formation
- Wide range of fluences: $1.9 \times 10^{12} \rightarrow 5.5 \times 10^{14}$ ions.cm$^{-2}$
- Ballistic dose: 0.7 → 215 MGy



# Leachate and characterizations

## Simple glass composition

- ISG (International Simple Glass)

## Multiple-energy gold ion irradiation

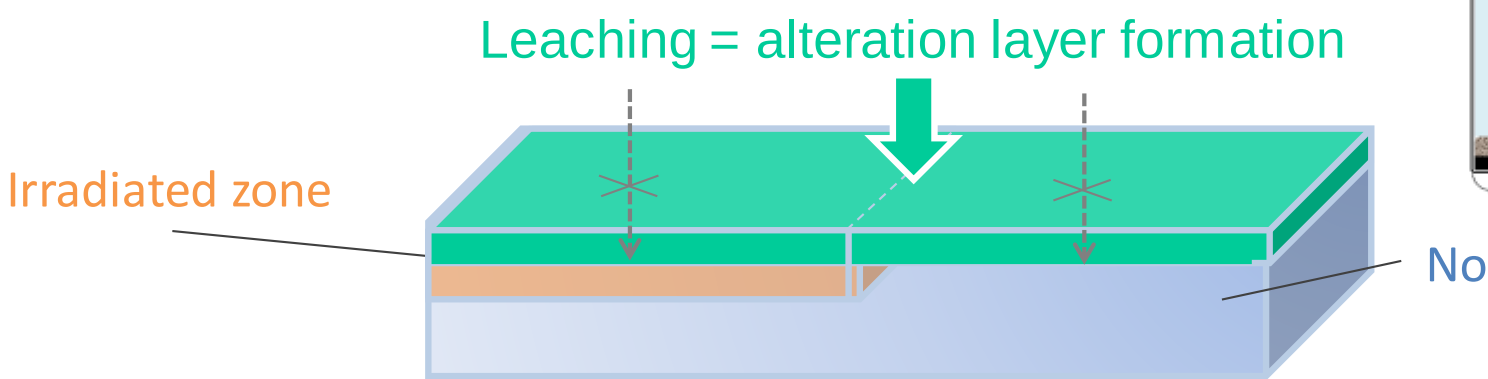
- 0.5 – 3.5 MeV → ≈ constant ballistic damage
- Energy deposition < ion track formation
- Wide range of fluences:
- Ballistic dose: 0.7 → 215 MGy

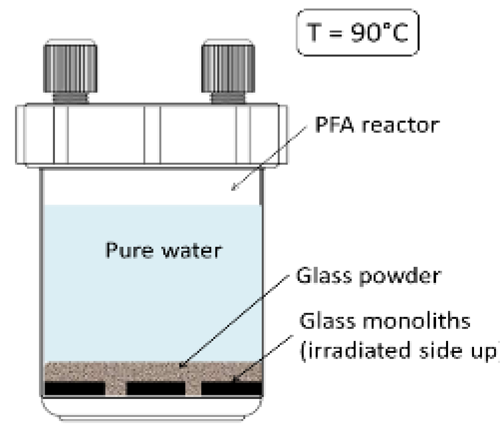
## Alteration protocol

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

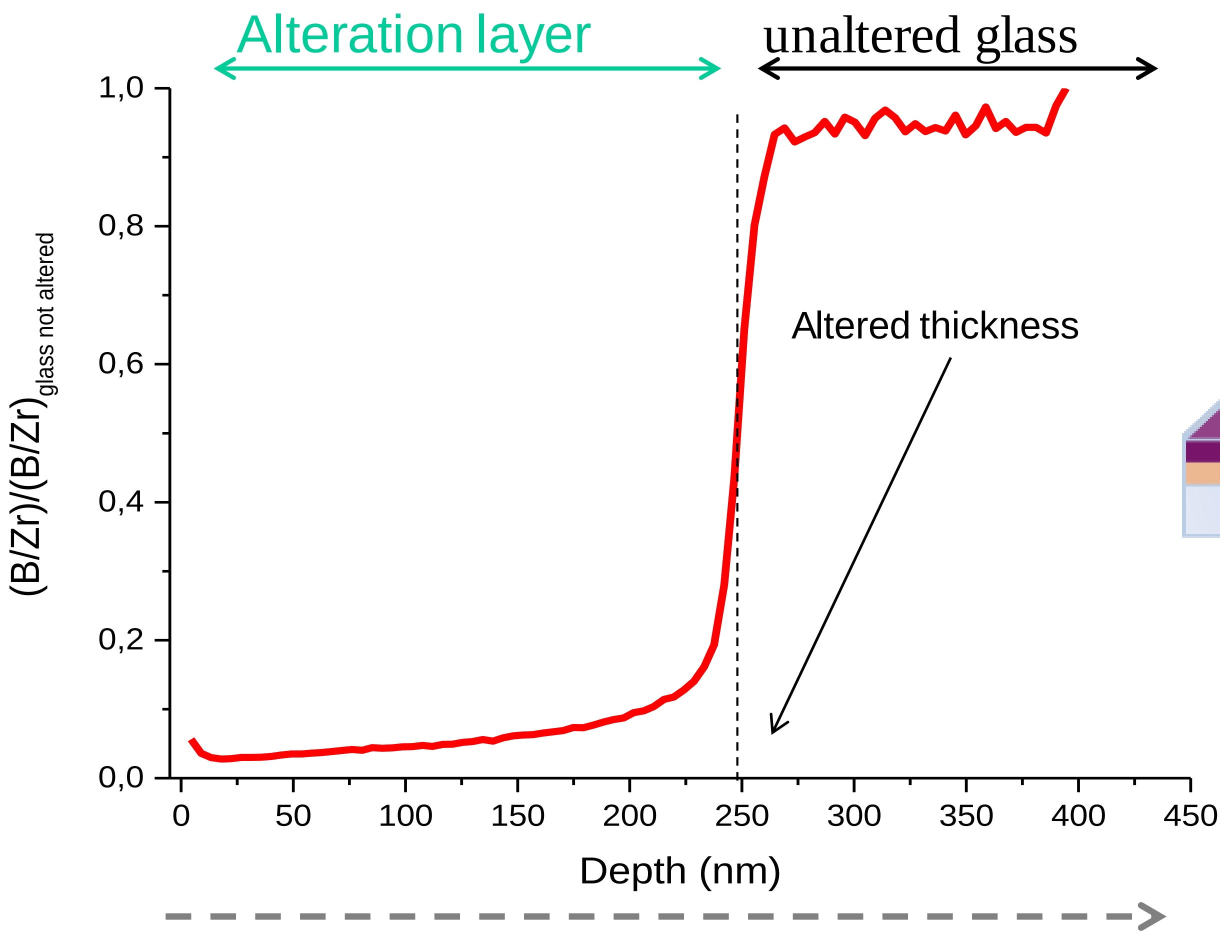
## Altered layer characterization

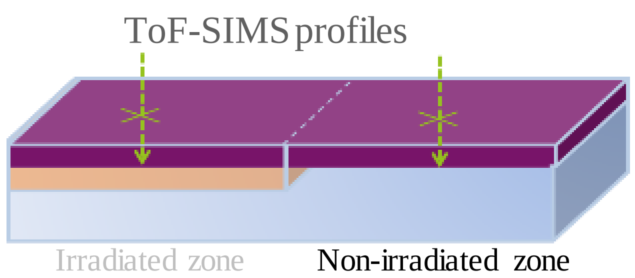
- ToF-SIMS



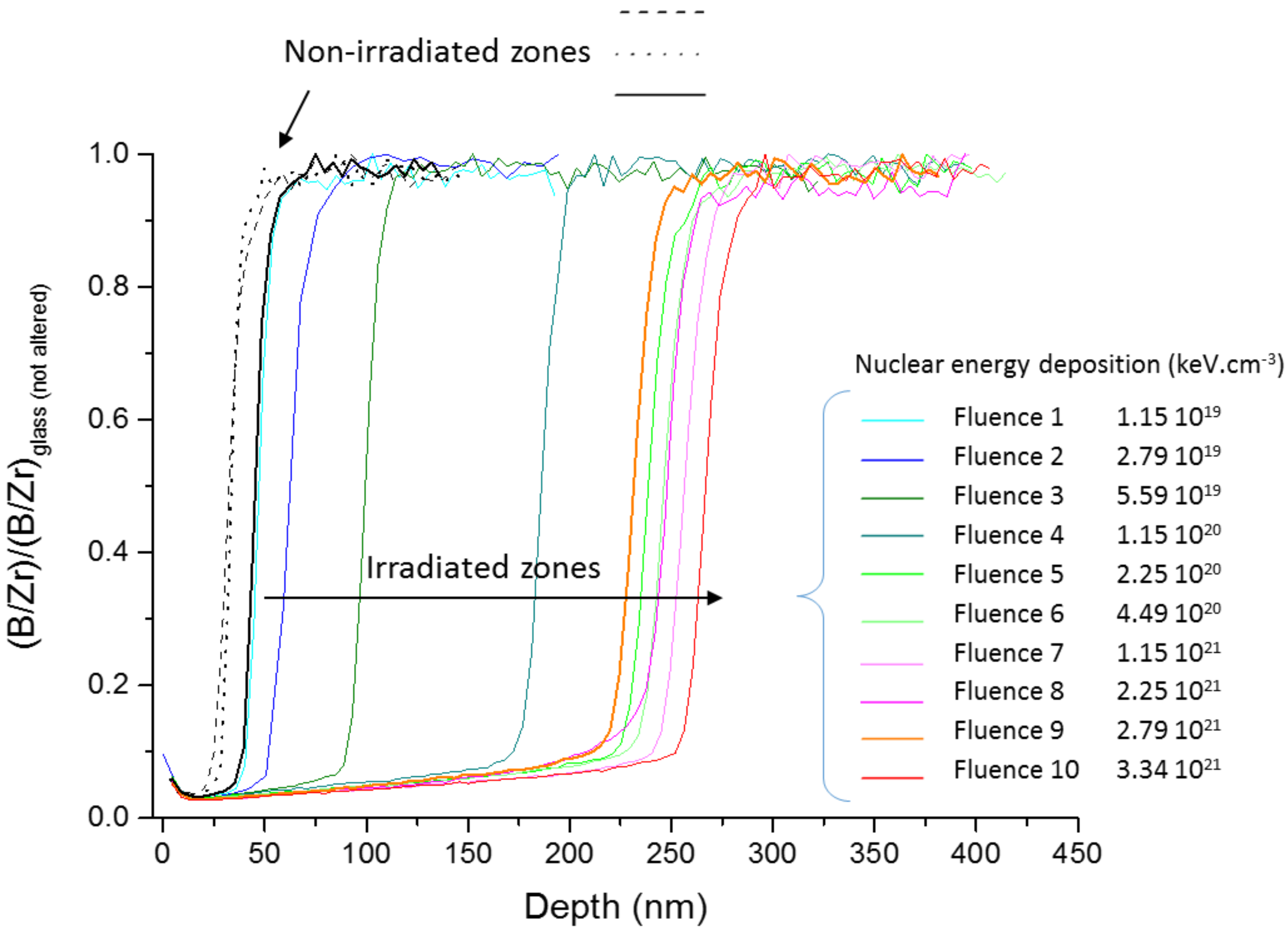

- **Alteration layer thickness determination from boron profile**

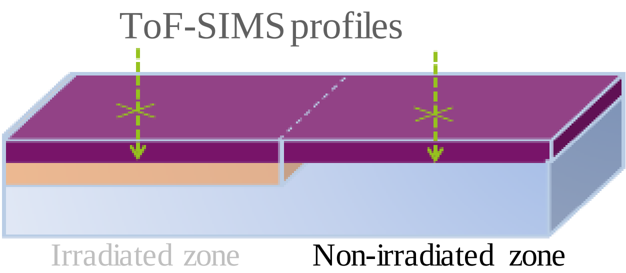



ISG, 13 days of alteration, dose = 145 MGy

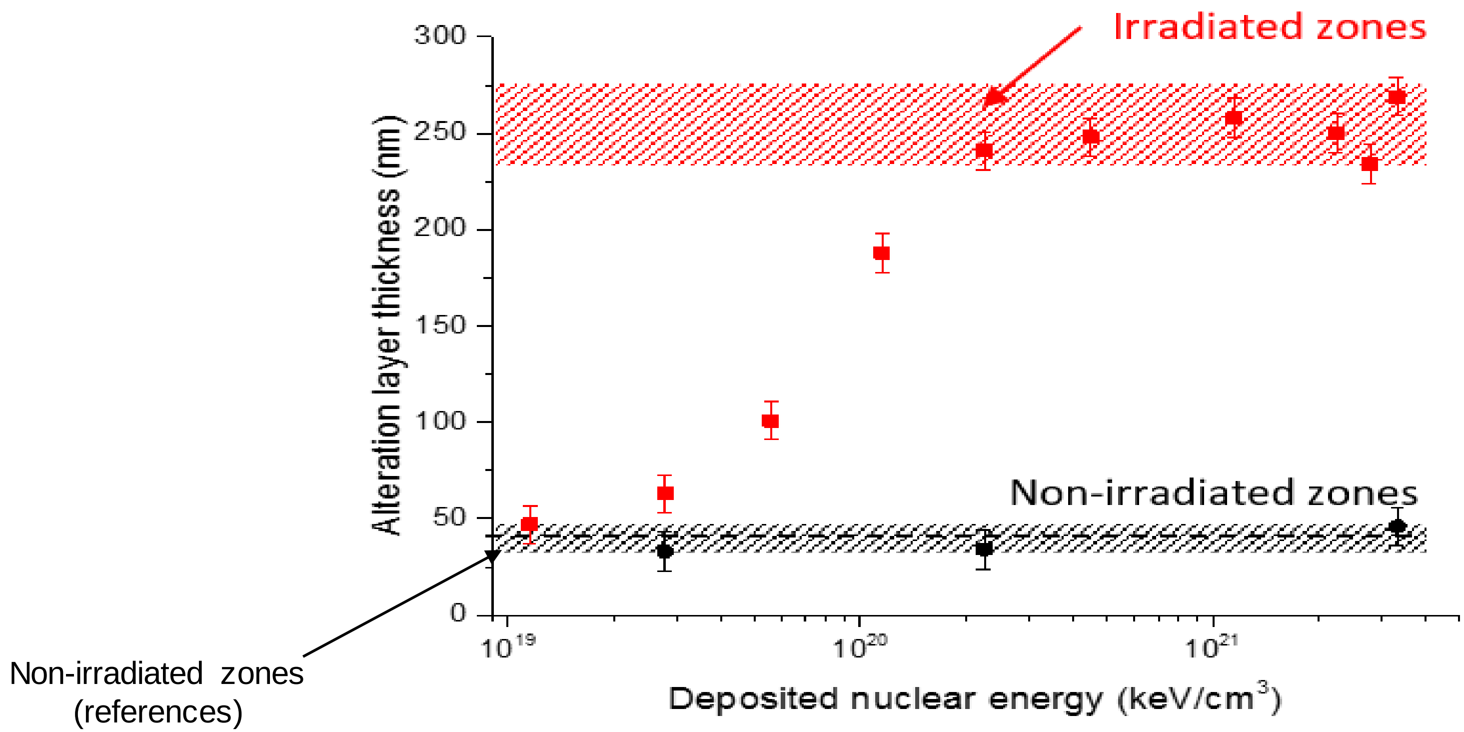
- **Alteration layer thickness determination from boron profile**



## Altered thickness vs fluence

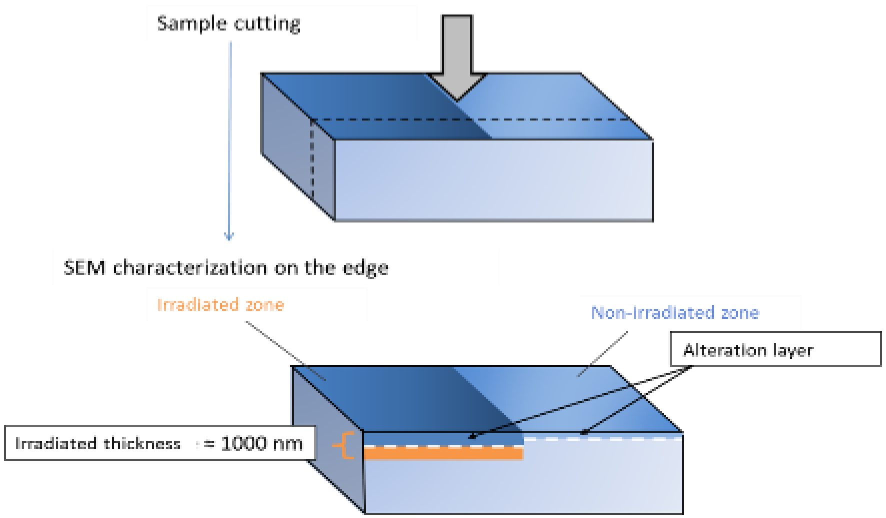
a) ISG glass samples, altered for 13 days

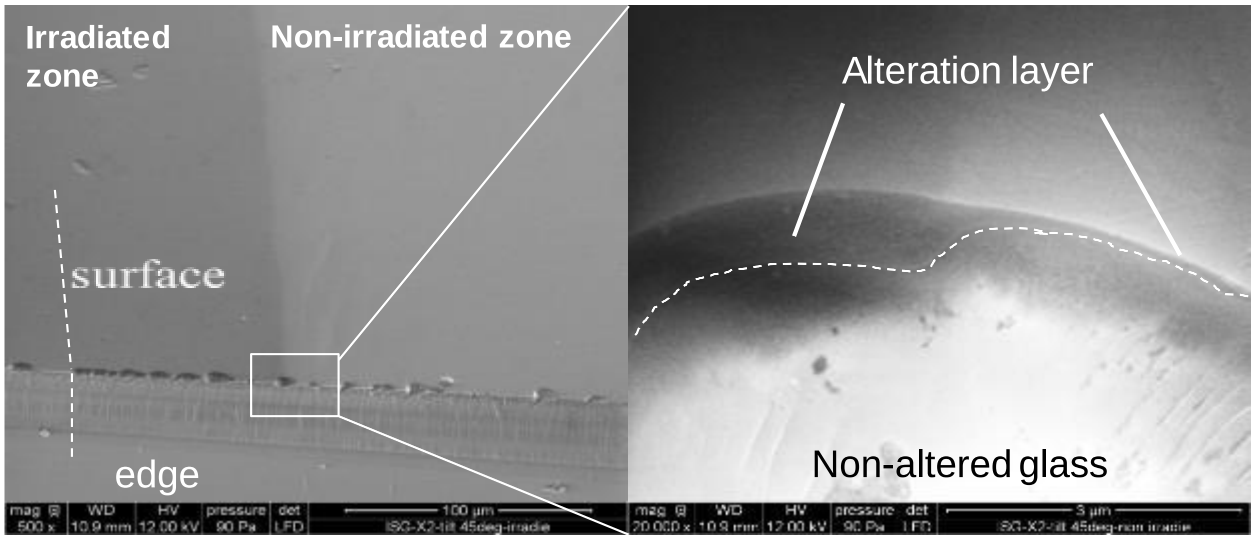



- All non-irradiated zones in agreement
- Increase of alteration layer thickness vs nuclear dose
- « plateau » observed after ≈ 2-4.$10^{20}$ $keV_{bal}/cm^3$

On $^{244}$Cm-doped glass → higher Rr probably due to alpha cumulative dose

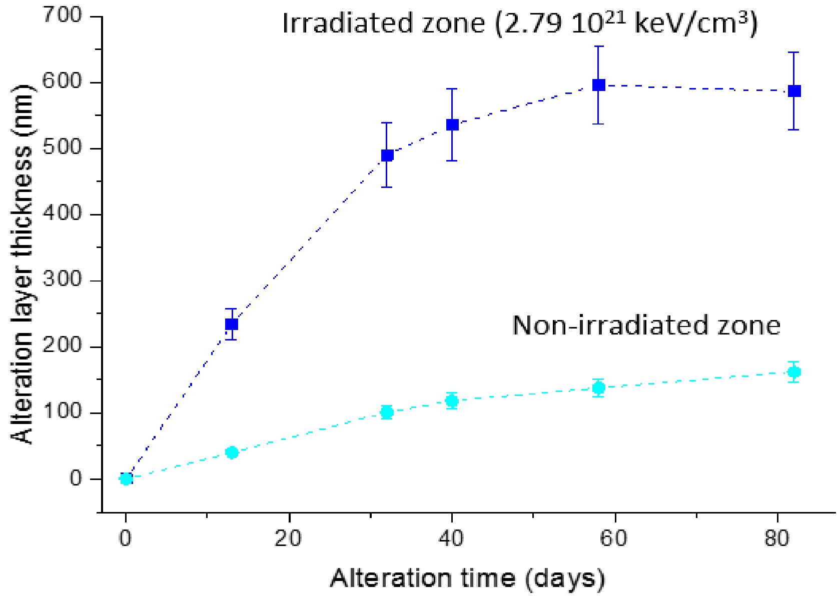
- **SEM:** ISG monolith altered 13 days (fluence = $3.34 \times 10^{21}$ keV/cm$^3$)



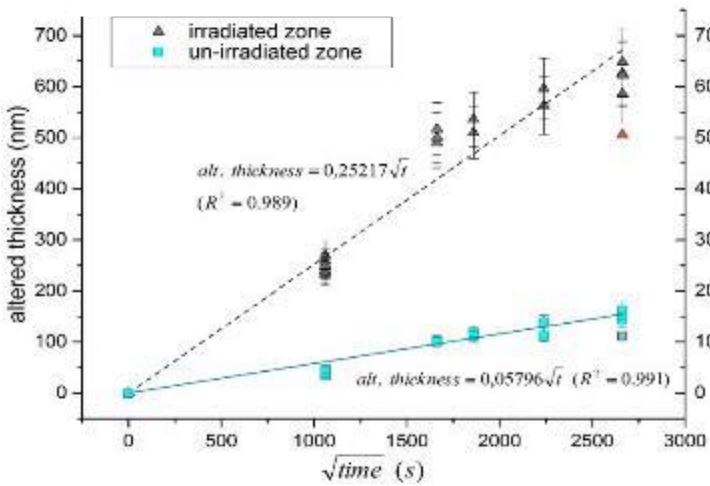



- **Alteration kinetics:** 1 dose, thickness evolution versus time

a) ISG glass (fluence 9)




Diffusive mechanism



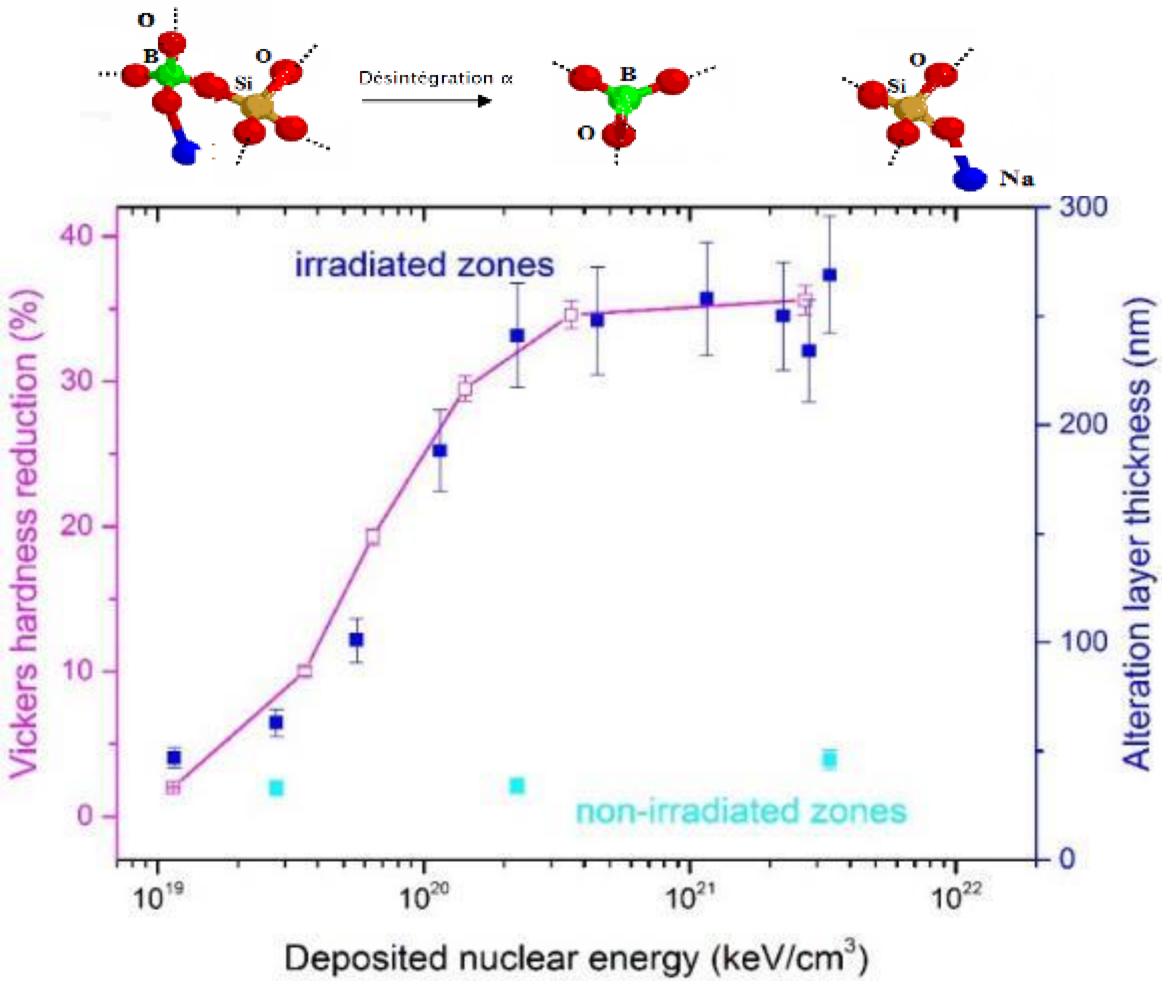

$$T_{alteration\ layer} = 2 \times \sqrt{\frac{D_{app} \times t}{\pi}}$$

| | | $D_{app}$ ($m^2/s$) |
|---|---|---|
| Irradiated zone ($\geq 2.10^{20}$ $keV/cm^3$) | | $5.0\ 10^{-20}$ |
| Non irradiated zone | ×20 | $2.6\ 10^{-21}$ |

Apparent diffusion coefficient increases

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

- Comparison with modifications of glass structure and properties

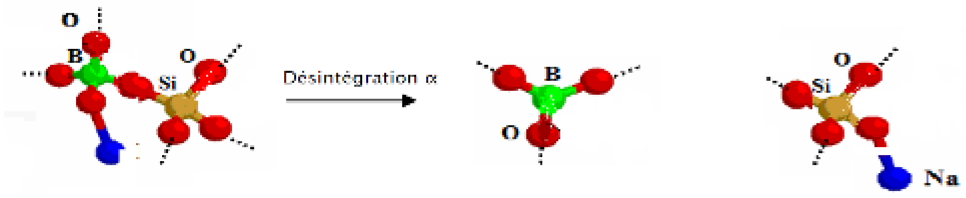



Vickers hardness reduction & altered thickness: same tendency

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

# DISCUSSION

- **Comparison with modifications of glass structure and properties**




→ Increase of free volumes → increase of water or alkali migration?

→ Increase of intern energy → increase of glass reactivity?

Higher increase of alterability on glasses submitted to gold irradiation (x4.5) than on Cm-doped glass (x2.7)

→ Glass composition effect: complex compositions less sensitive to irradiation than simple glasses

→ Recovery effect of α particles in real alpha decay

# CONCLUSIONS & PROSPECTS

Initial alteration rate: no significant effect of alpha irradiation on complex glasses

Residual alteration rate: increase of altered thickness on damaged glasses (x 4.5 max) and plateau reached for doses > $2\text{-}4.10^{20}$ $keV_{bal}/cm^3$ (few $10^{18}$ $\alpha$/g)

⇩

Chemical durability & glass structure / properties similarly affected by irradiation

- Mechanisms: water access and/or increase of local reactivity
- **Long term chemical durability of glass sensitive to its initial structure**

**« simplifed » system vs $^{244}$Cm-doped glass**, also taking into account:

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

**To increase mechanistic undertansding :**

- To explore very initial steps of alteration (water penetration in damaged glasses)
- Atomistic modeling: create a damaged glass, explore water diffusion…
- To study properties of alteration layer formed from damaged glasses

# THANKS TO

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