INSTITUT DE CHIMIE
SEPARATIVE DE MARCOULE

Are mesoporous silicas resistant to radiation damage ?

X. Deschanels, Y. Lou, S. Dourdain, C. Rey

Xavier.deschanels@cea.fr

CEA, ICSM – UMR 5257 CEA-CNRS-UM-ENSCM, 30207 Bagnols-sur-Cèze Cedex, France

XXth Colloque Ganil – 15-20 October 2017

Marcoule Institute for Separation Chemistry

Joint Research Unit (UMR 5257) between CEA, CNRS, Montpellier University, and Chemistry School of Montpellier ENSCM.

Research teams

Hybrid Materials for Separation (**LHYS**, D. Meyer)

Ions at Interfaces (**LIIA**, O. Diat)

Ion separation using supra-molecular self-assembled colloids(**LTSM**, S. Pellet-Rostaing)

Sonochemistry in Complex Fluids (**LSFC**, S. Nikitenko)

Nanomaterials for Energy and Recycling processes (**LNER**, X. Deschanels)

Evolving interfaces in materials (**LIME**, N. Dacheux)

optimiser la séparation

Anticiper le cycle de vie

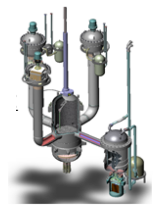
chimie verte

méthodes et théories

comprendre la séparation

GEN IV Nuclear reactors

Fuel fabrication



Back end of fuel cycle

Support teams

Study of matter in Environmental Conditions (**LM2E**, R. Podor)

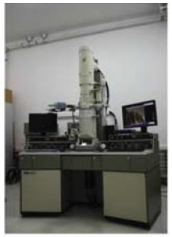
Mesoscopic Modelling and Theoretical Chemistry (**LMCT**, J.-F. Dufrêche)

Small and wide Angle x-ray Scattering (SWAXS)

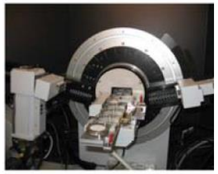
X-ray reflectivity and Grazing incidence X-ray diffraction

And DTA/TGA, N2 , Kr and H2O adsorption-desorption, GC-MS, X-ray fluorescence....

MEB FEI quanta 200 ESEM FEG



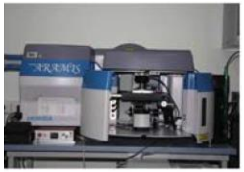
MET



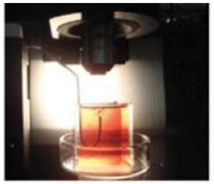
Diffraction (Brucker D8 ADVANCE)

ICP OES

RMN Brucker 400 Mz



Raman



ONL

Understand Separation | Optimize separation | Green chemistry | Anticipate life-cycle | Methods and theory

Context and goals

Mesoporous materials :

- 2 nm < d_{pore} < 50 nm (IUPAC definition)
- Mesoporous materials enable access to (strong) curvatures in solid state chemistry
- Mesoporous materials are error tolerant and tend to reorganise spontaneously

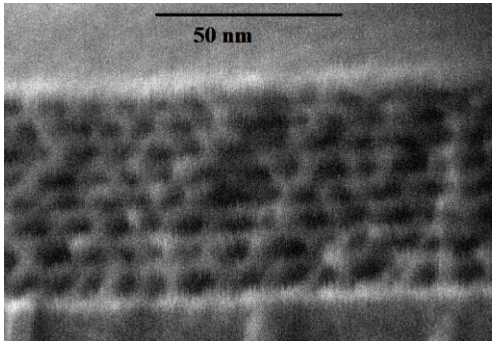
Radiation tolerance?

- Interfaces act as sinks for irradiation induced point defects (Frenkel pairs)
- Size of “displacement cascade” ~ Size of the mesoporosity

Mesoporous silica

- Size and organization of the mesoporosity can be easily tuned (elaboration by sol-gel process)
- Many studies on radiation behavior of dense silica and several on Vycor glass (Klaumunzer)

Mesoporous SiO_2 layer deposited on Si wafer



P. Makowski, X. Deschanels, A. Grandjean, D. Meyer, G. Toquer, F. Goettmann, New. J. Chem. 36 (2012) 531
S. Klaumünzer, Nucl. Instr. Meth. Phys. Res. B 225 (2004) 136-153, 191 (2002) 356-361, 166-167 (2000) 459-464

Elaboration of the film

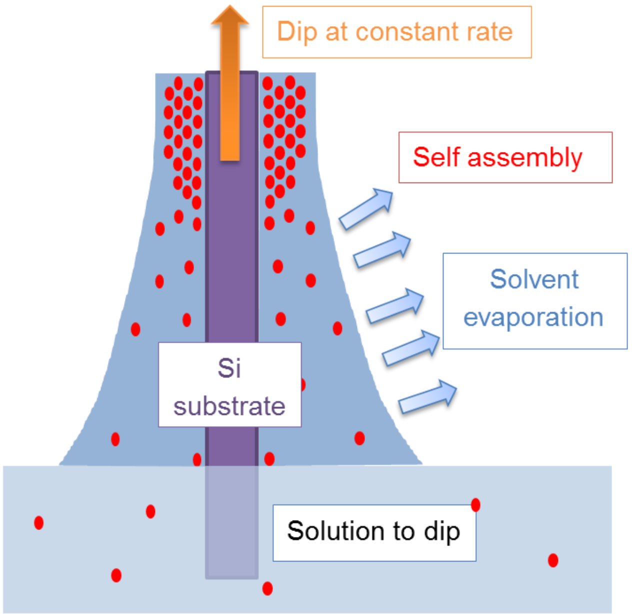
Sol-Gel route

Hydrolysis : $Si\text{-}(OR_4) + x\ H_2O \rightarrow (OH)_x\text{-}Si\text{-}(OR)_{4\text{-}x} + x\ R\text{-}OH$

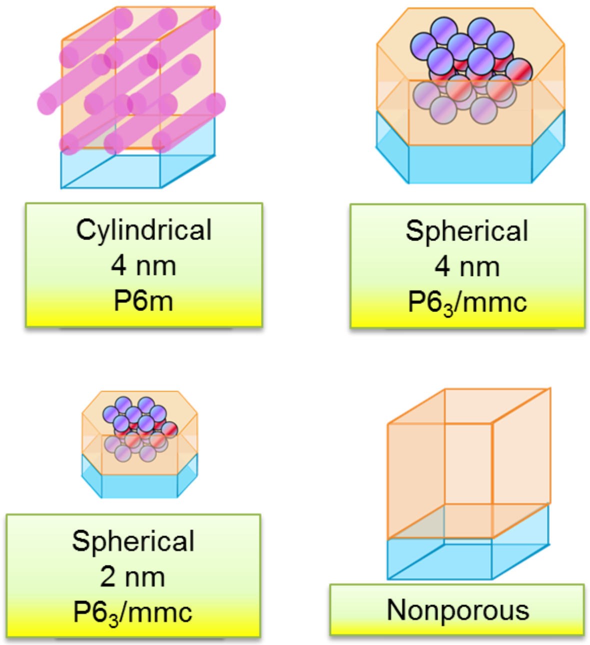
Condensation : $(OR_3)\text{-}Si\text{-}OH + HO\text{-}Si\text{-}(OR_3) \rightarrow (OR_3)\text{-}Si\text{-}O\text{-}Si\text{-}(OR_3) + H_20$

	CTAB : CHBrN	Spherical 3D Ø~ 2-3 nm
Templating agent :	P123: COH…	Cylindrical 2D Ø~ 4 nm
	F127: COH…	Spherical 3D Ø~ 4 nm

- Dip coating

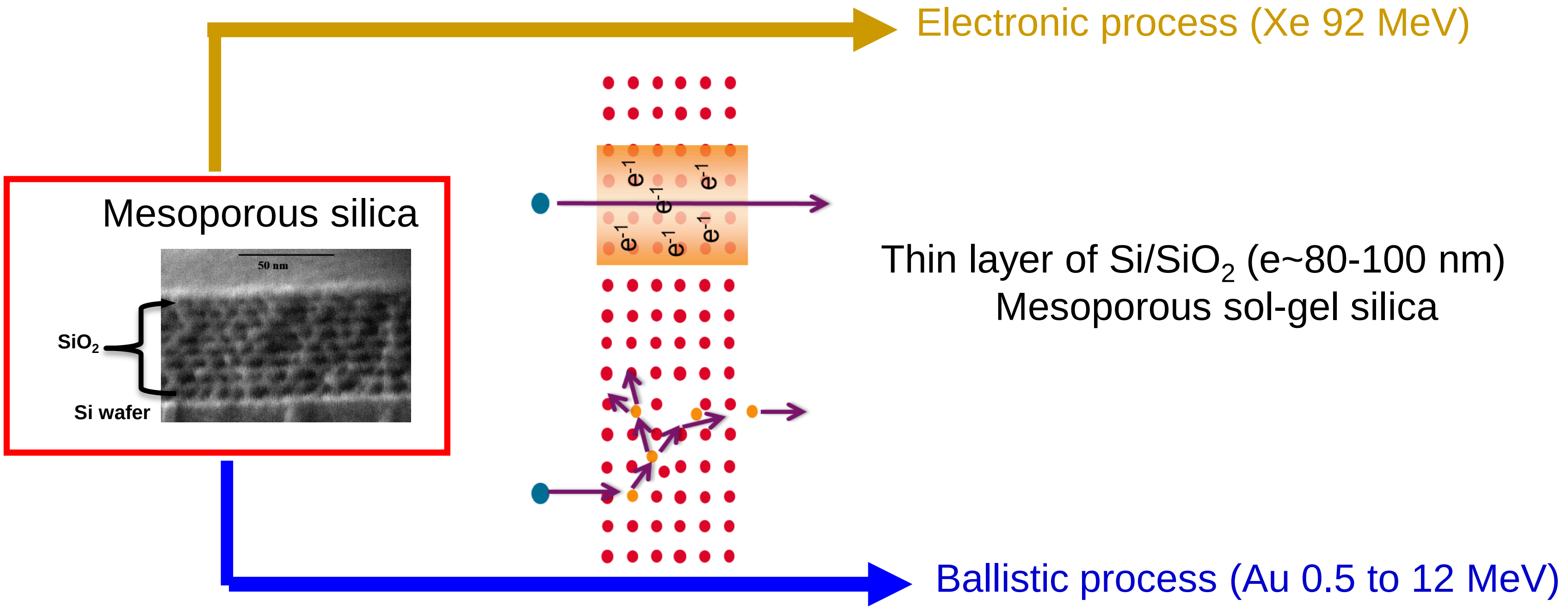


- Obtained morphologies



Dourdain, S.; Bardeau, J.-F.; Colas, M.; Smarsly, B.; Mehdi, A.; Ocko, B. M.; Gibaud, A., *Appl. Phys. Lett.* **2005,** *86* (11), 113108

Objectives and Methodology



✓Analysis techniques: X-ray reflectivity, FTIR, SEM

Objectives

- Mesoporous structure evolution as well as silica network as a function of irradiation conditions
- Influence of stopping power, dose, pore morphology…
- Understanding of damage mechanisms

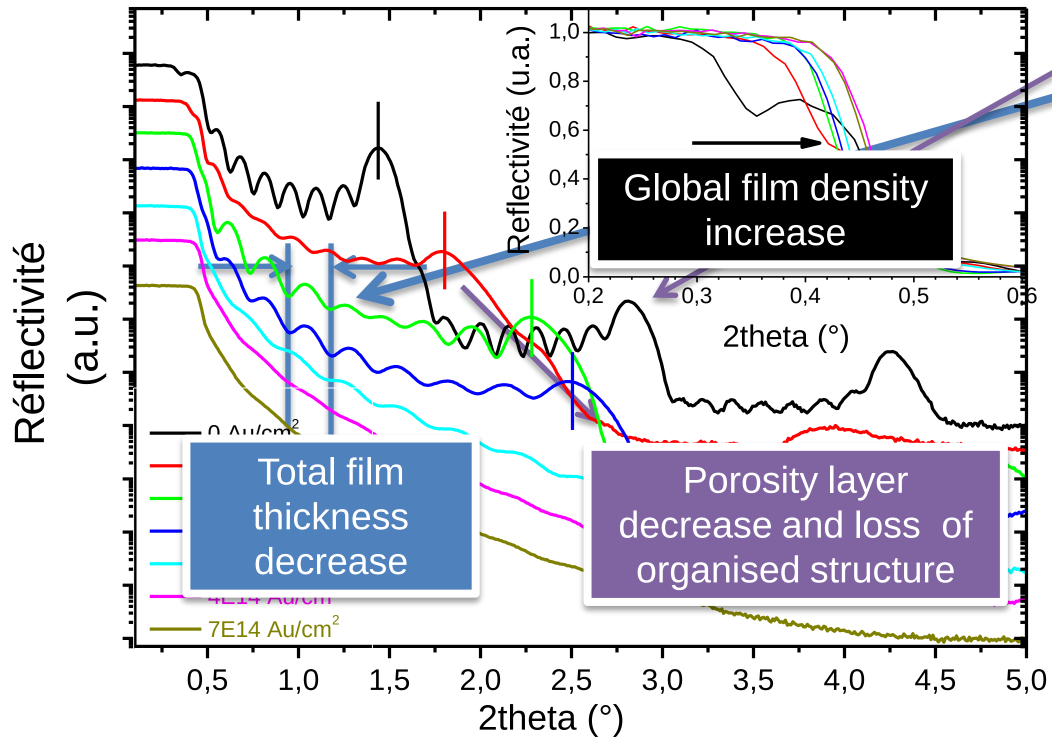
Irradiation conditions

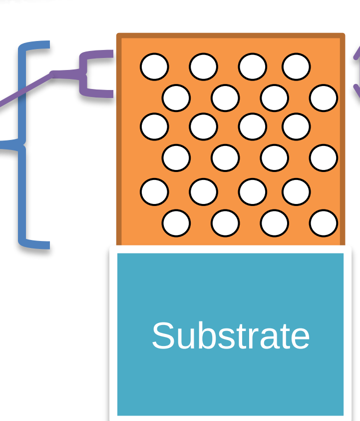
	Ion	Sample	dE/dx Elec (keV/nm)	dE/dx Nucl (keV/nm)	dpa at fluence 10^{14} cm^{-2}
JANNuS Saclay	Au 0,5MeV	2D cyl 4nm 3D sph 2nm 3D sph 4nm Non porous	0,85	3,1	0,33
JANNuS Saclay	Au 3MeV	2D cyl 4nm	1,8	2,1	0,18
JANNuS Saclay	Au 7MeV	2D cyl 4nm	2,4	1,5	0,099
JANNuS Saclay	Au 12MeV	2D cyl 4nm	2,7	1,1	0,081
Irrsud	Xe 92MeV	2D cyl 4nm	11	~0	~0

- Annealing at 400°C for sol-gel samples aims to stabilize the SiO_2 structure

Au 0.5 MeV- XRR measurements
Effect of fluence

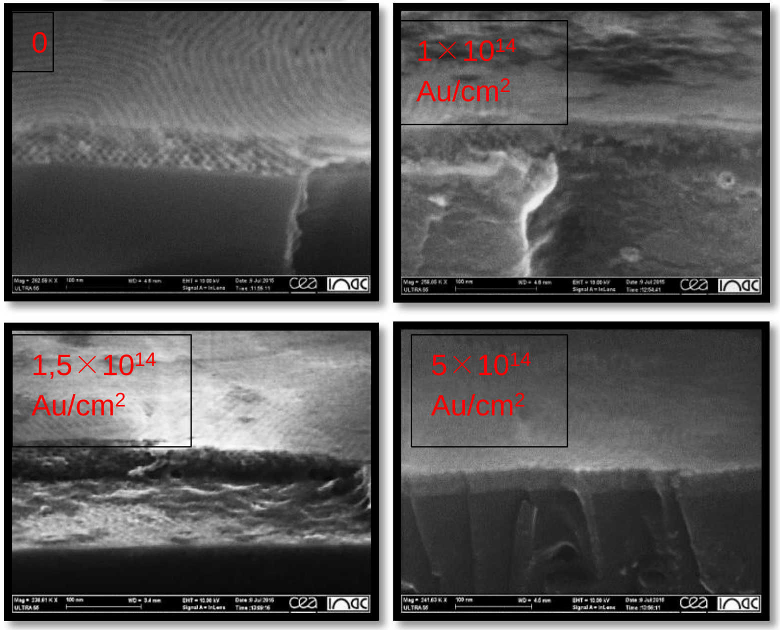
2D Cyl 4 nm - 1 dpa ~ 3x10^{14}ion/cm^2





$$t = \frac{2\pi}{\Delta Q_{z,Bragg}}$$

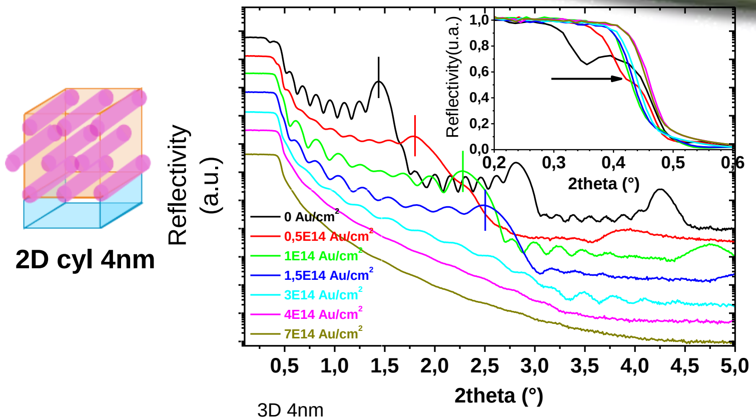
$$T = \frac{2\pi}{\Delta Q_{z,Kiessig}}$$

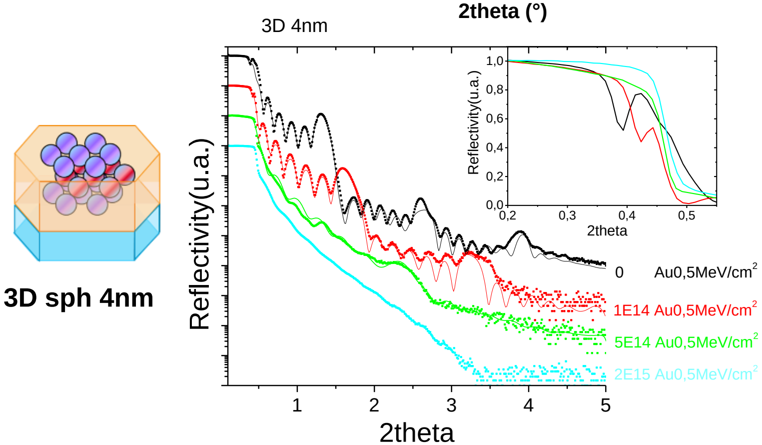


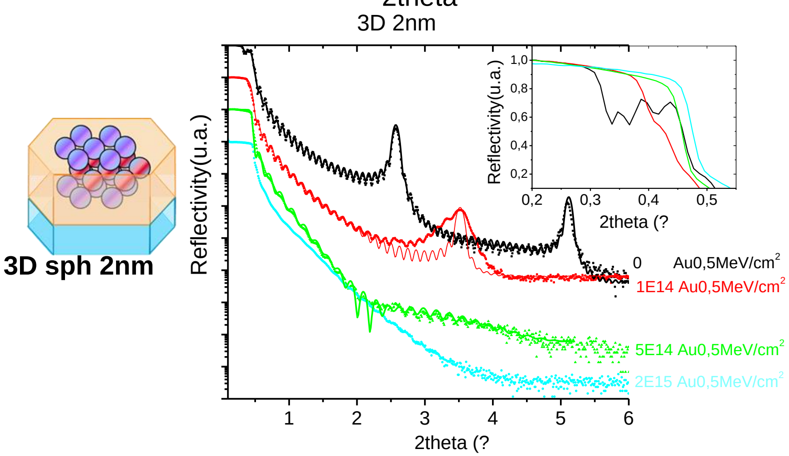
- **Amorphisation, compaction and deformation of pores (XRR measurments)**
- **Confirmation by SEM observations**

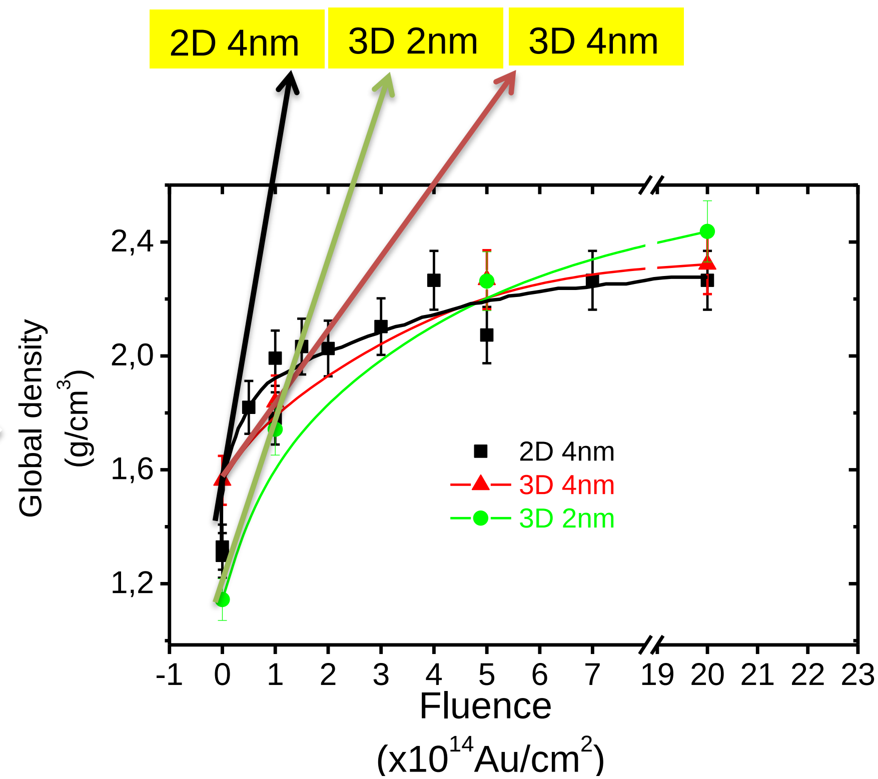
« Structure evolution of mesoporous silica under heavy ion irradiations of intermediate energies », Y. Lou, S. Dourdain, C. Rey, Y. Serruys, D. Siméone, N. Mollard, X. Deschanels *Microporous mesoporous materials* 251 (2017)

Au 0.5 MeV- XRR measurements
Structure effects







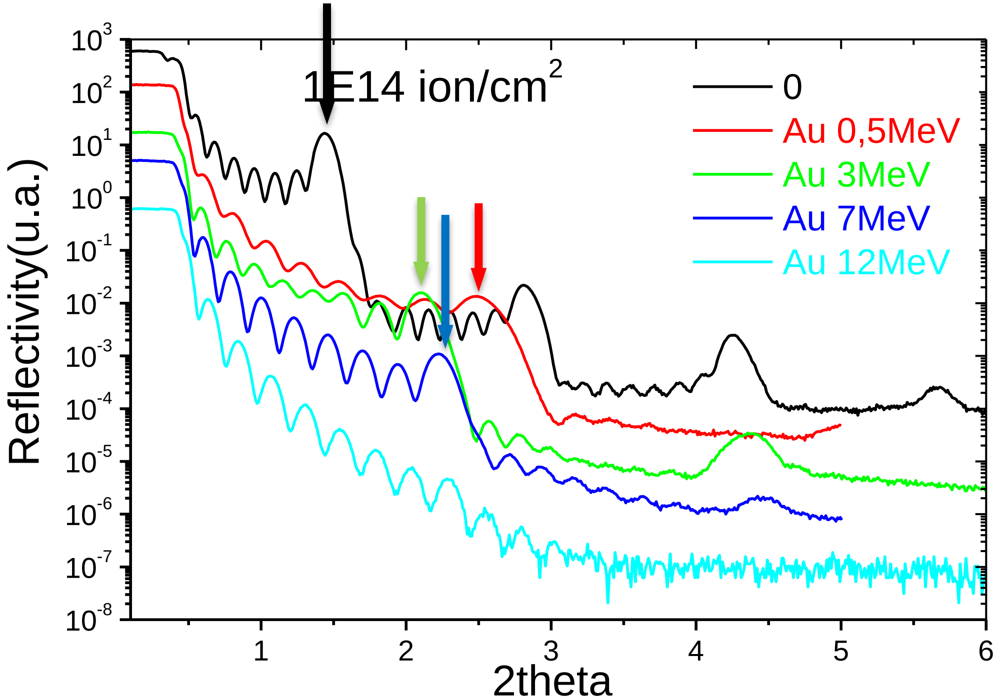


Damage effect on the material:

- 2D 4nm > 3D 2nm > 3D 4 nm
- Cylindric > spheric
- Small pores > large pores

Au irr. - XRR measurements
Stopping power

2D cyl 4nm



Au 0,5-3-7-12 MeV
Ion energy↑ ballistic effect↓ & electronic effect ↑

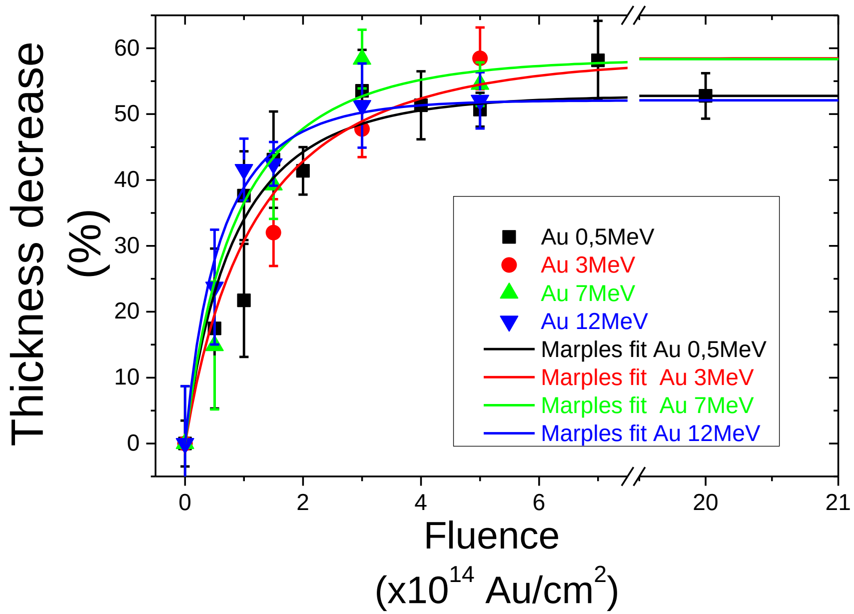
Damage effect

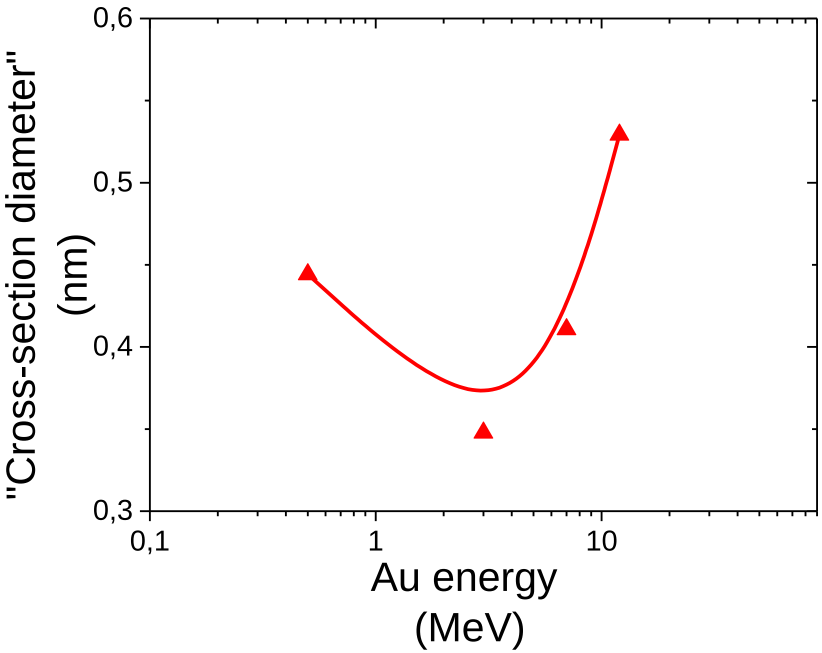
- Au 12MeV > Au 0.5 MeV > Au 7 MeV > Au 3 MeV
- Damage less important when electronic and ballistic effects are mixed

Au Irr. – XRR measurments Stopping power

2D cyl 4nm

$$\frac{\Delta\rho}{\rho_0} = \left(\frac{\Delta\rho}{\rho_0}\right)_{sat} (1 - exp(-\sigma\Phi))$$





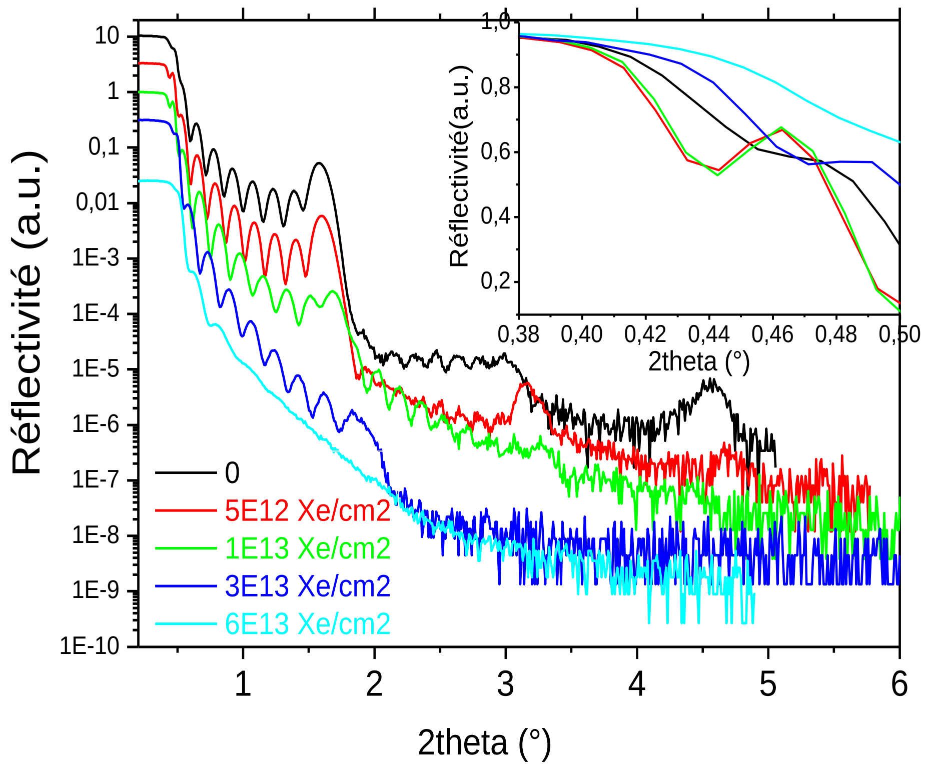
Quantitative confirmation

U shape form for the plot of Cross section versus Energy

- Au 12MeV > Au 0.5 MeV > Au 7 MeV > Au 3 MeV
- Antagonism effect between electronic and ballistic stopping power

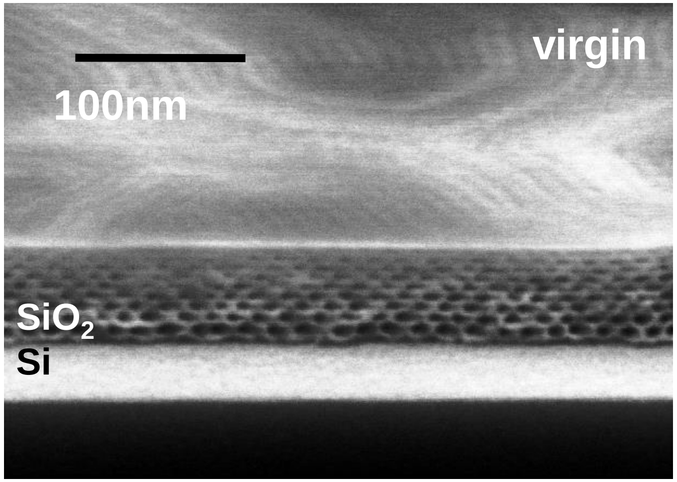
Marples, J. A. C., Dose rate effects in radiation damage to vitrified radioactive waste. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 1988, 32 (1), 480-486.

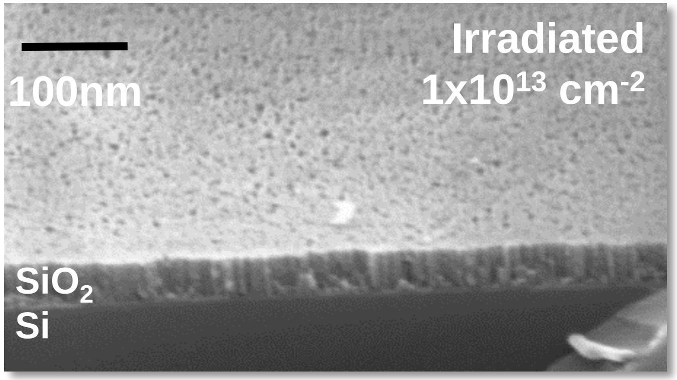
2D Φ~4nm, ^{129}Xe, 92MeV, 11 keV/nm



- Collapse of the mesoporous structure for high fluence
- Observation of track by SEM

dE/dx> track formation in dense SiO_2

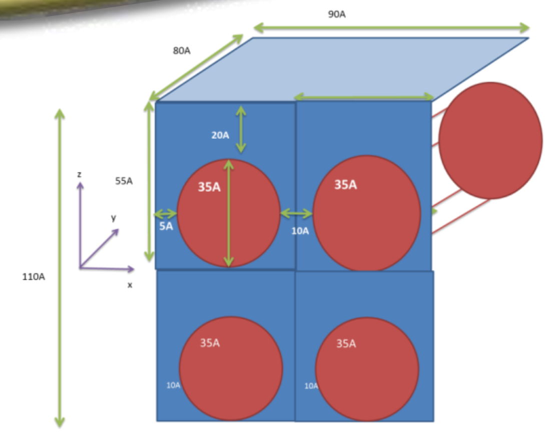


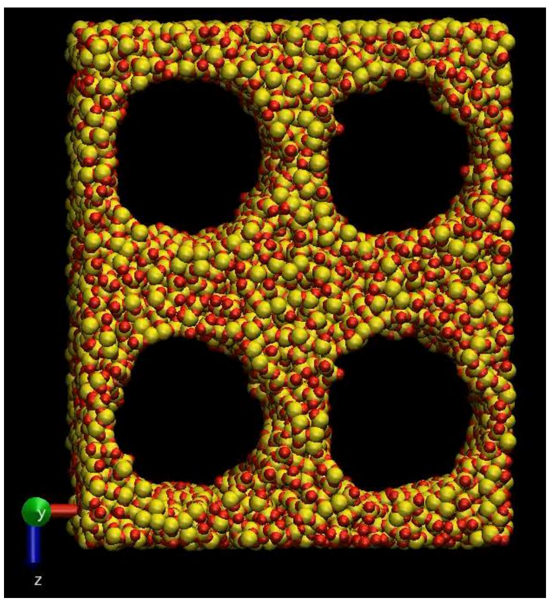


Dourdain, S.; Deschanels, X.; Toquer, G.; Grygiel, C.; Monnet, I.; Pellet-Rostaing, S.; Grandjean, A., Radiation damage of mesoporous silica thin films monitored by X-ray reflectivity and scanning electron microscopy. *JNM* **2012,** *427* (1–3), 411-414

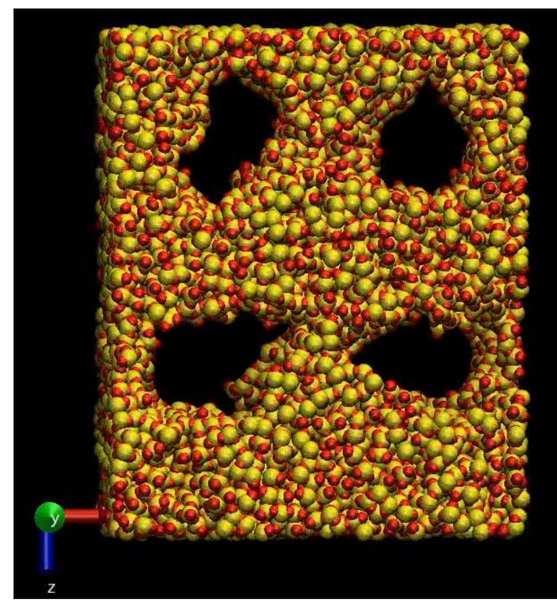
Ballistic effects - Modelling

Modelling
- Structure similar to thin layer 2D cyl-hex 4 nm
- Box creation: MonteCarlo
- Irradiation simulation : Molecular dynamics (Ballistic effects only)





Mesostructure evolution (up to 1,2 dpa)

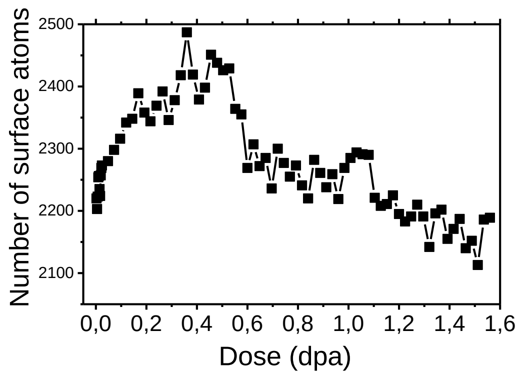


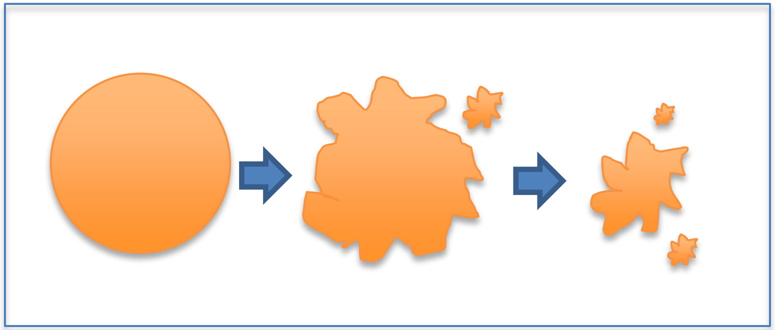
- Mesopore collapse and deformation of the mesoporous structure
- Box shrinkage

Ballistic effects - Modelling

- Surface atoms (Voronoï)

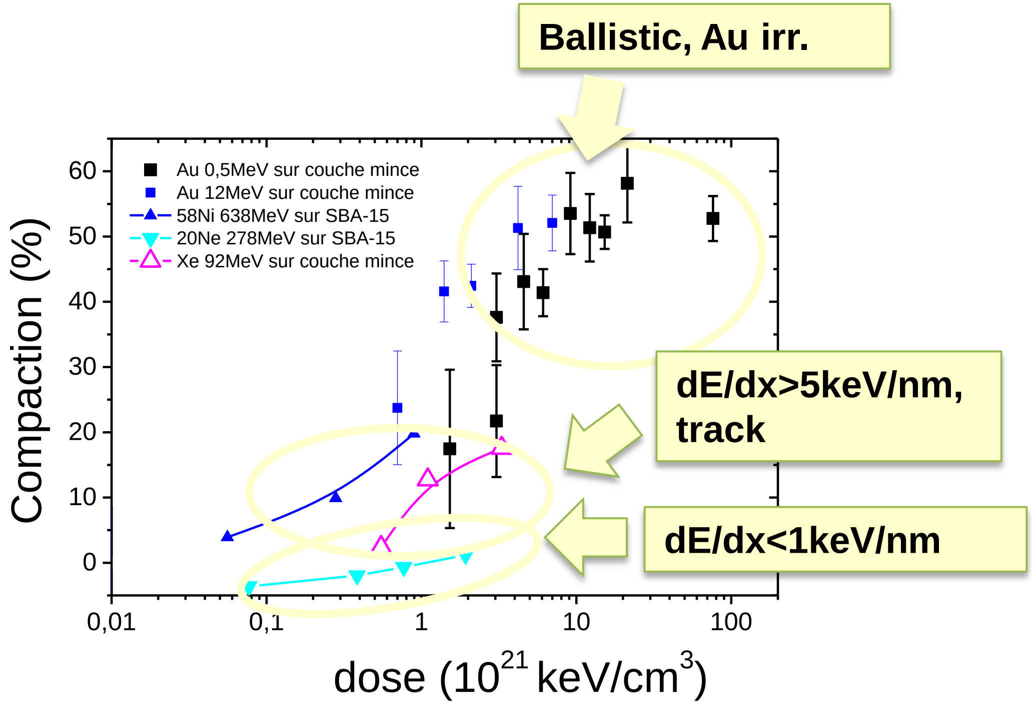
- Number of surface atoms





- At first, up to 0.4 dpa, increase of the nb. of surface atoms, ie rugosity and pore formation in the wall of the silica network
- For higher damage, decrese in the nb. of surface atoms, ie collapse of the mesoporous structure

Conclusions

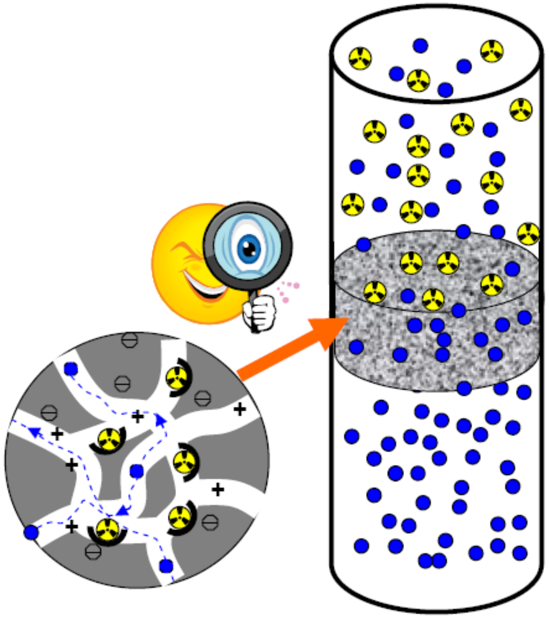


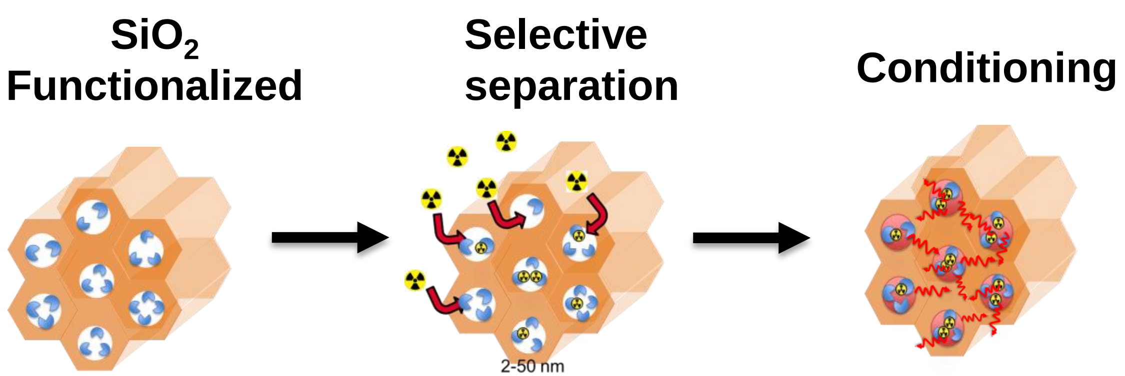
- Compaction is dependant on the stopping power of the ions
- Ballistic effects lead to higher damage than electronic ones
- The size of the mesopore is a crucial parameter

In some extent mesoporous materials present tolerance to radiation **damage**

Separation – conditioning process

- **Nuclear waste management**
  - Adsorption of the selected radionuclide
  - Encapsulation of the radionuclide by subsequent collapse of the structure (Thermal stress, chemical stress…)





Pore collapse
(Thermo-mechanical or radiation stress)

- **Field of application**
  - Outflows coming from dismantling sites

Thank you for your attention

Thanks to C. Grygiel, I. Monnet, F. Durantel at GANIL facility

Thanks to Y.Serruys and all the staff of JANNUS-Saclay

Thanks to B.Siboulet and J-M.Delaye for modelling study

Thanks to EMIR network for irradiation and to the GDR Needs «Déchets » for funding

Institut de Chimie Séparative de Marcoule
UMR 5257 | CEA – CNRS – UM – ENSCM
Site de Marcoule | Bâtiment 426 | BP 17171 | F-30207 Bagnols-sur-Cèze Cedex
T. +33 (0)4 66 79 60 87 | F. +33 (0)4 66 79 76 11
http://www.icsm.fr