Institute Separative Chemistry of Marcoule (ICSM)

Behavior of mesoporous thin films (SiO_2, C) under ion irradiation

Adaptive Nanomaterials Laboratory for Energy

A. AZEDDIOUI, P. de LAHARPE, C. REY, G. TOQUER, C. GRYGIEL*, X. DESCHANELS

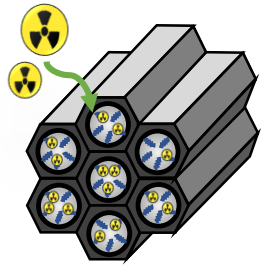
ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, France
*CIMAP, CEA-CNRS-ENSICAEN-UNICAEN Bd. Henri Becquerel, Caen, France

Xavier.deschanels@cea.fr

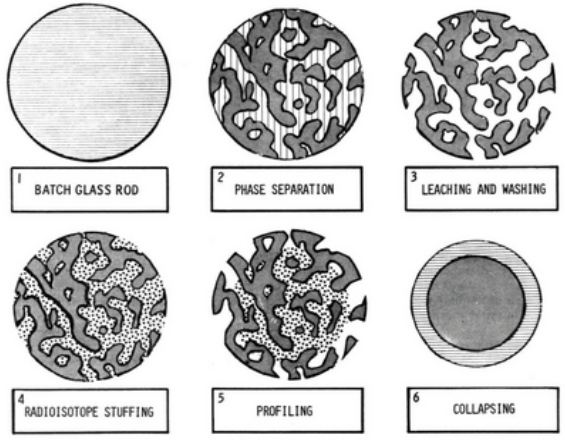
Mesoporous silica and nuclear

Model materials → Silicas

- ✓ Chemically similar to **glass**
- ✓ **Mesoporous** : Φ = 2 - 50 nm
- ✓ **Organized**
- ✓ High surface area (500–1000 m^2/g), easily functionalized, selective for radionuclides
  - → Applications: nuclide separation and packaging



Vycor glasses (Simmons 1979)



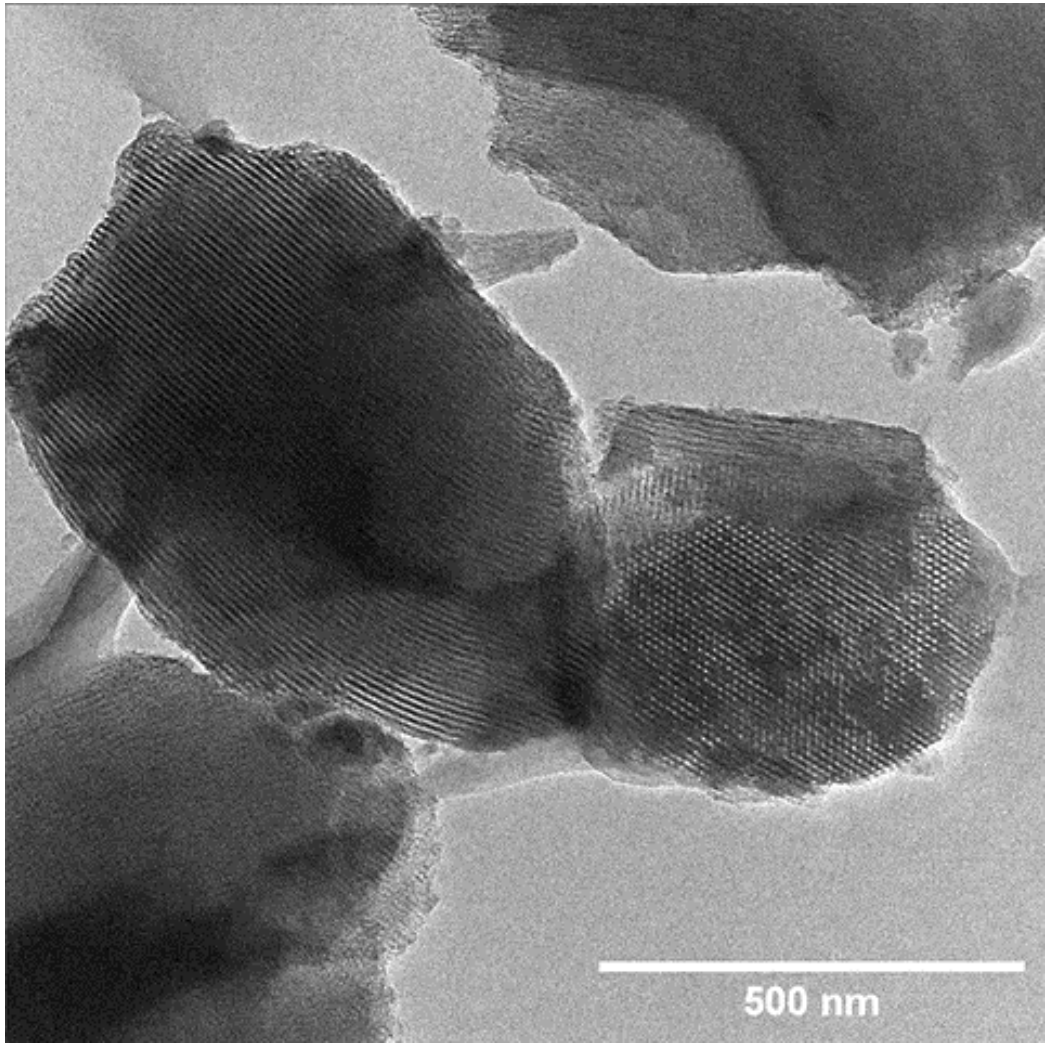
Radiation damage in mesoporous silica

Simmons, J. H., *and al., Nature,* ***1979, 278 (5706), 729-731***

Makowski, P., and al., New Journal of Chemistry, ***2012, 36,3,531–541***

Mesoporous silica – Previous studies

- Xe: 600keV – SiO_2 mesoporous SBA-15 at -160°C
  ϕ<6.25E+14 ions/cm²
- **Collapse of the mesoporosity**



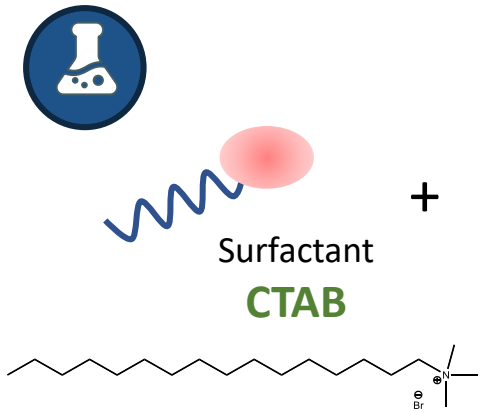
Radiation damage in mesoporous silica

↓

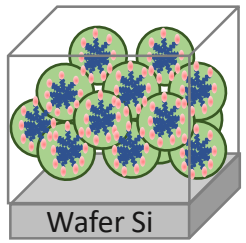
Densification

MIAMI-2 platform Huddersfield University
Collaboration **Anamul. H Mir**

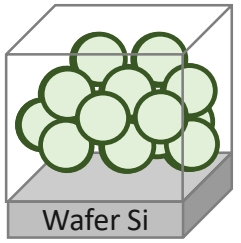
Synthesis: Mesoporous silica thin film (sol-gel process)



Evaporation-Induced Self Assembly (EISA)



calcination
400°C

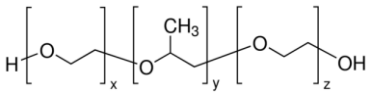


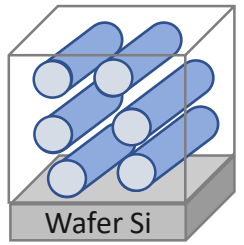
ICc

3D Spherical pore diameter
2-3 nm

Visual aspect

Surfactant
P123



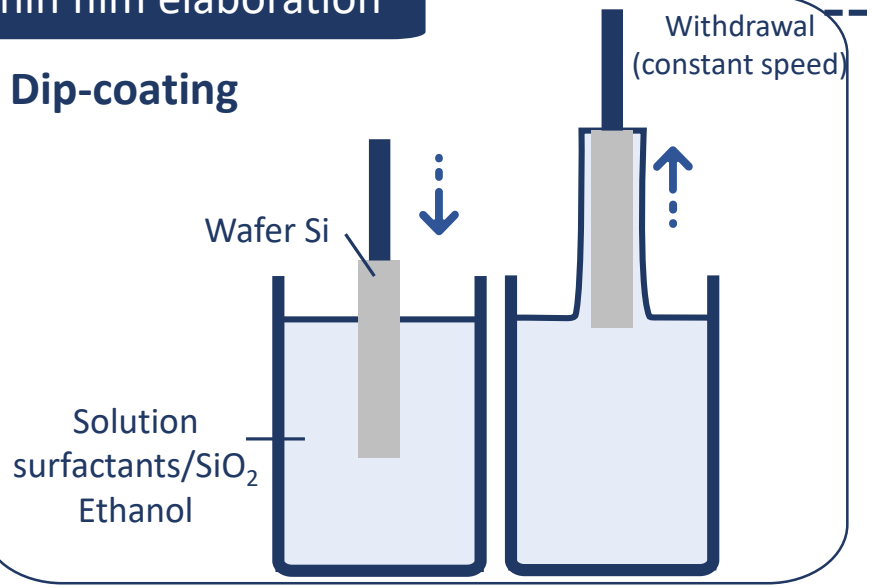


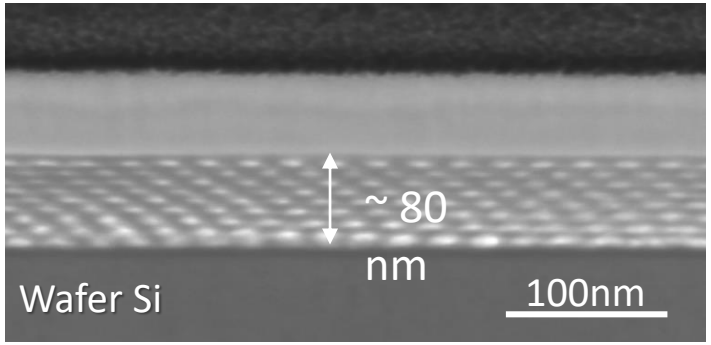
IPc

2D Cylindrical pore
diameter 4 nm

Thin film elaboration

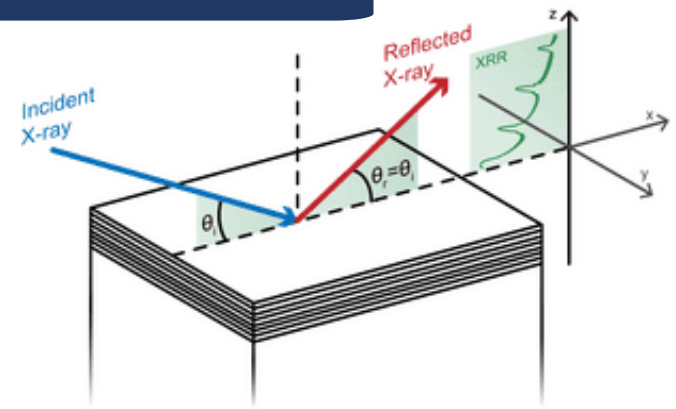
Dip-coating





Cross-section SEM

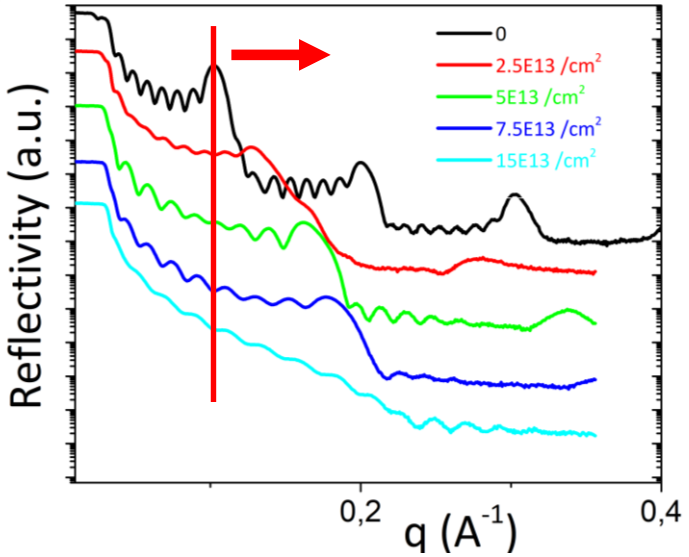
Thin film characterization

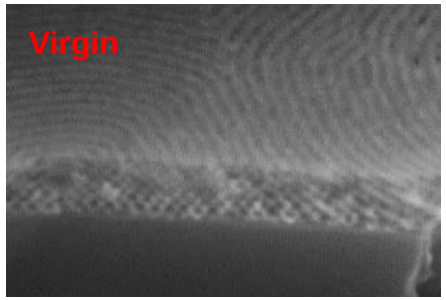


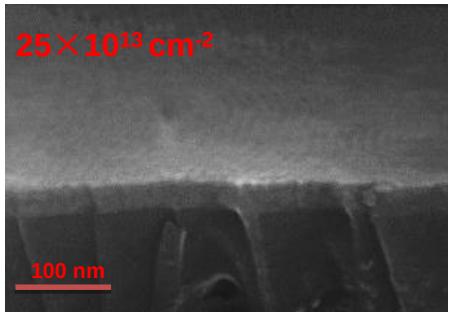
Zhao, D., *et al.*, *Science* ***1998, 279 (5350), 548-52***

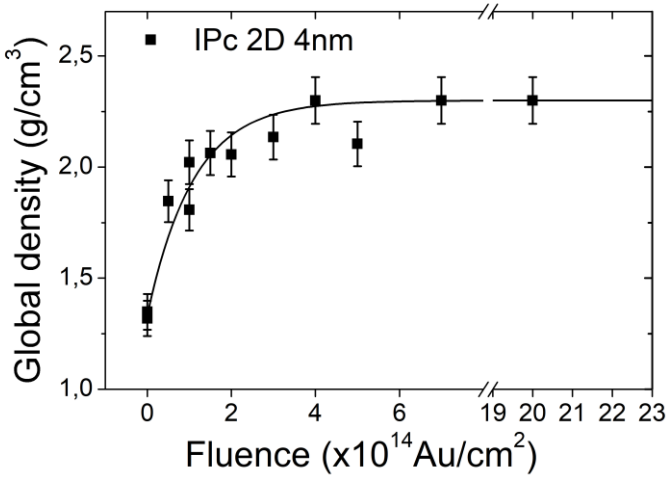
Mesoporous silica (IPc): Collapse versus stopping power

Au 0,5 MeV : dE/dx=4,2keV/nm

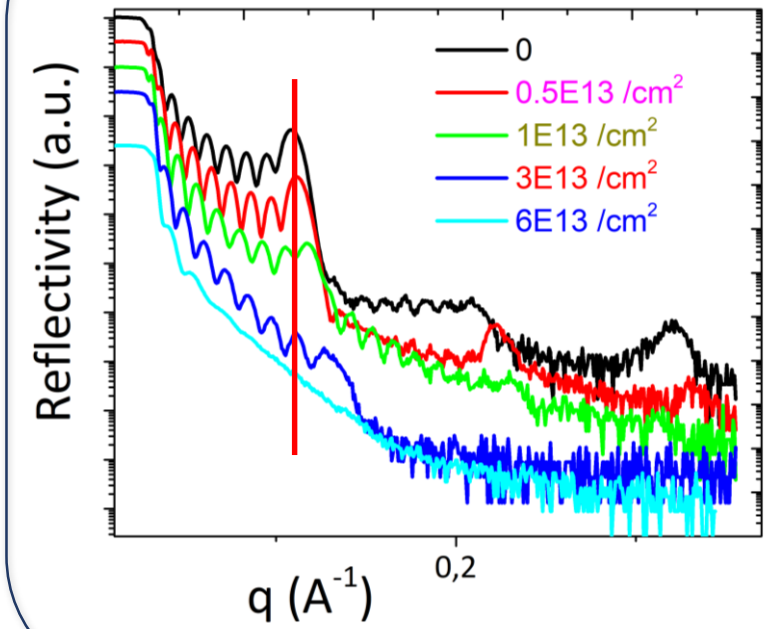




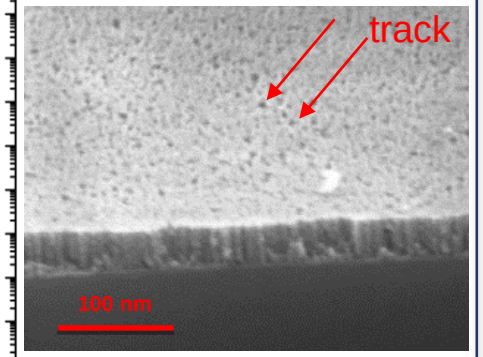




Xe 92MeV : dE/dx=11keV/nm



10^{13} cm^{-2}

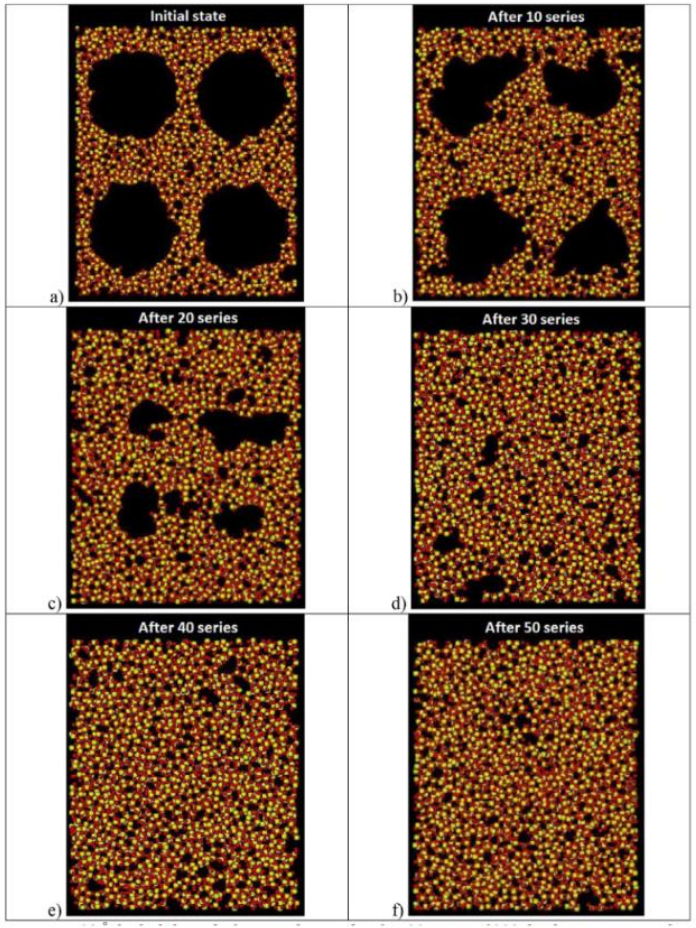


Mesostructure collapse

- High dE/dx → Track formation
- Low dE/dx → to be precise

Mesoporous silica – Modelling ballistic process

Molecular dynamics of 1.2 keV U impact



Progressive shrinkage of the porous structure with the accumulation of **ballistic effect**

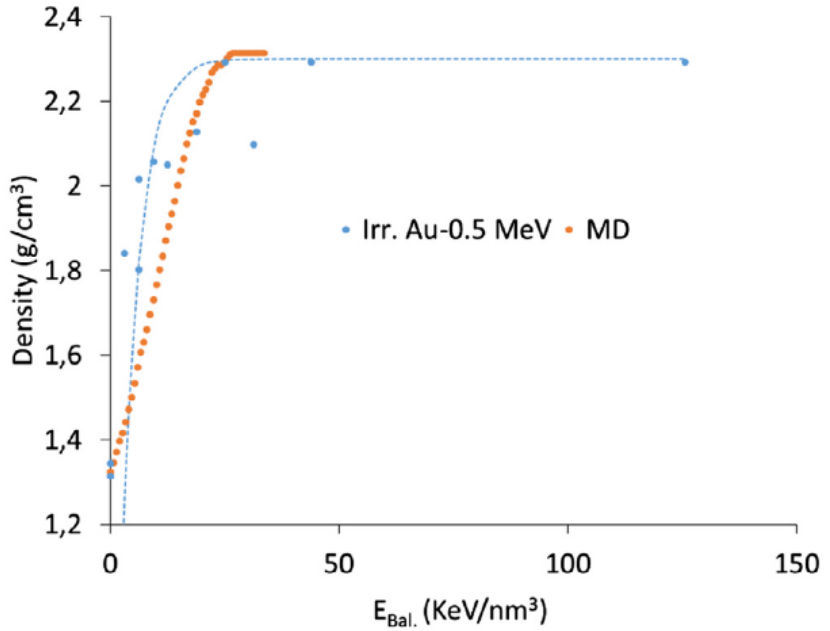


Fig. 12. Comparison between experimental and modelling results. E_{bal} corresponds to the energy deposited by ballistic effects.

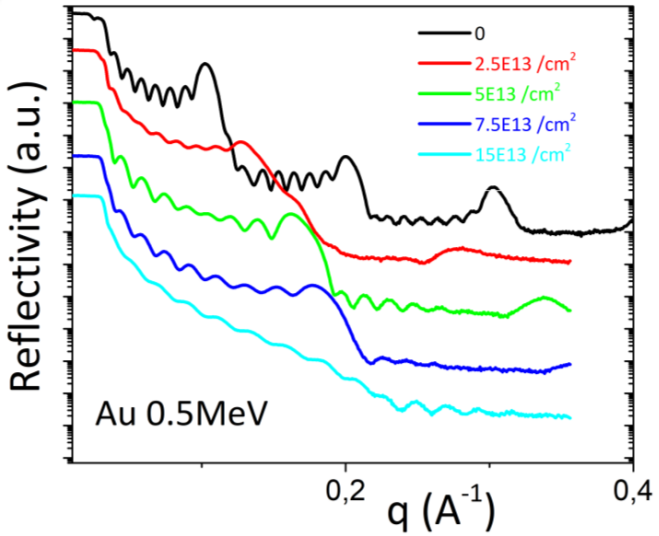
Possible **densification** mechanism:

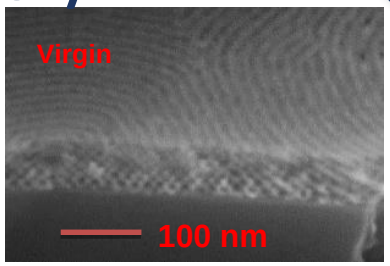
→ **Low temperature sintering process assisted by ballistic diffusion**

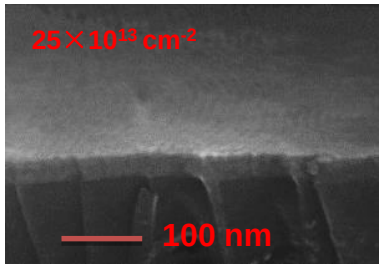
Lou, Y. and al., Journal of Non-Crystalline Solids, 2020, **549, 120346**
Lin, J. and al., Microporous and Mesoporous Materials **2021, 328, 111454**

Mesoporous silica (IPc) - Irradiation versus Heating

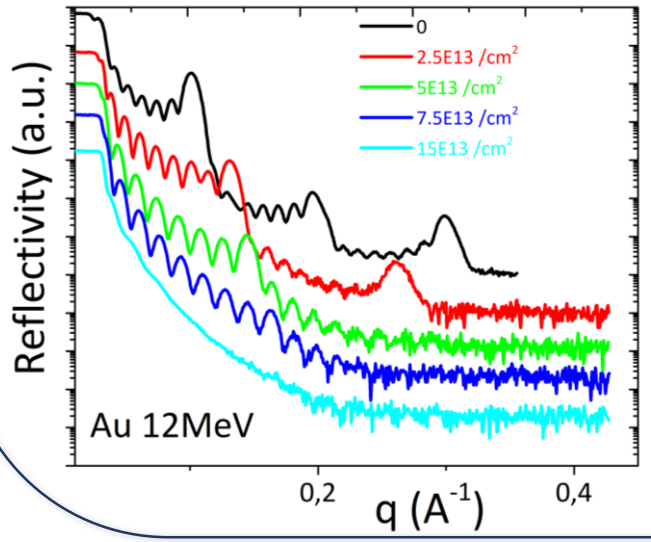
Au 0,5 MeV : dE/dx=4,2keV/nm

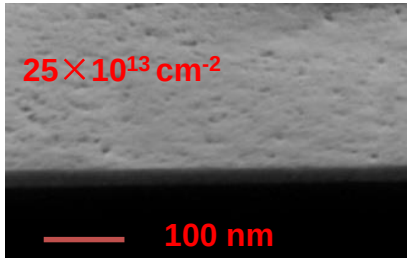




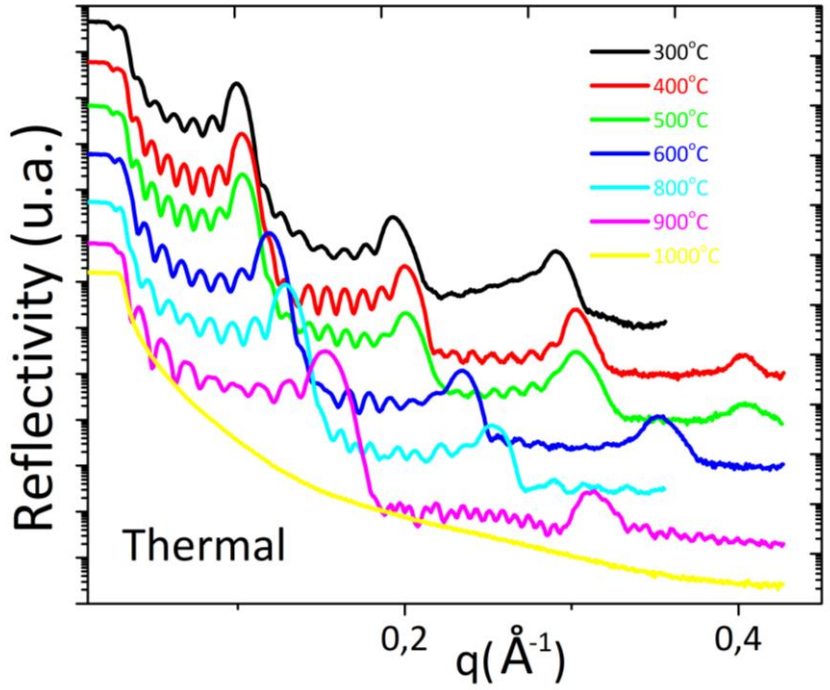


Au 12 MeV : dE/dx=3,8keV/nm





Heating : 300 to 1000°C



Analogy between heating and irradiation at low-stopping-power

Irradiation-induced **sintering process**

Problematic of the study

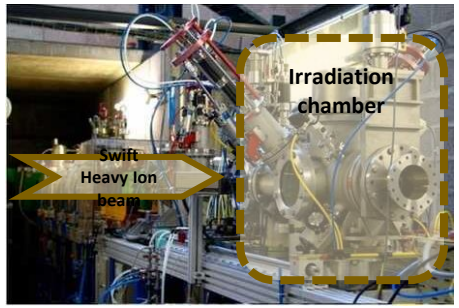
Observed **densification** mechanism:

⇢ Irradiation-induced **sintering process** within mesoporous silica

⇒ Contribution of irradiation and heating were performed simultaneously (ballistic/electronic processes, stopping power)

Lou, Y. and al., Journal of Non-Crystalline Solids, 2020, **549, 120346**
Lin, J. and al., Microporous and Mesoporous Materials **2021, 328, 111454**

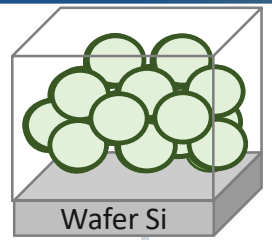
Methodology



GANIL

JANNUS

ICc and ICp



Characterization

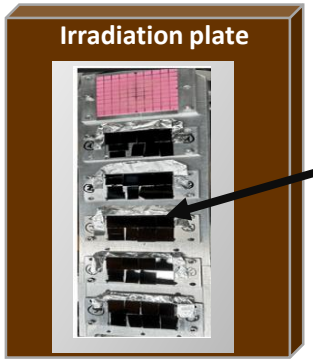
Characterization
- **X-ray reflectivity** : density, thickness, roughness
- **FTIR** : Si-O-Si network
- **SEM/TEM** : morphology

Irradiation :
- **Electronics** (Ar, Ne)
- **Ballistics** (Au)

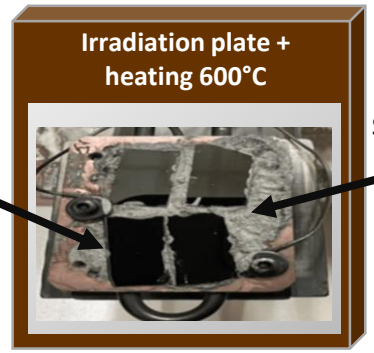
Irradiation

Irradiation + Heating

Heating only



Sample



silver glue

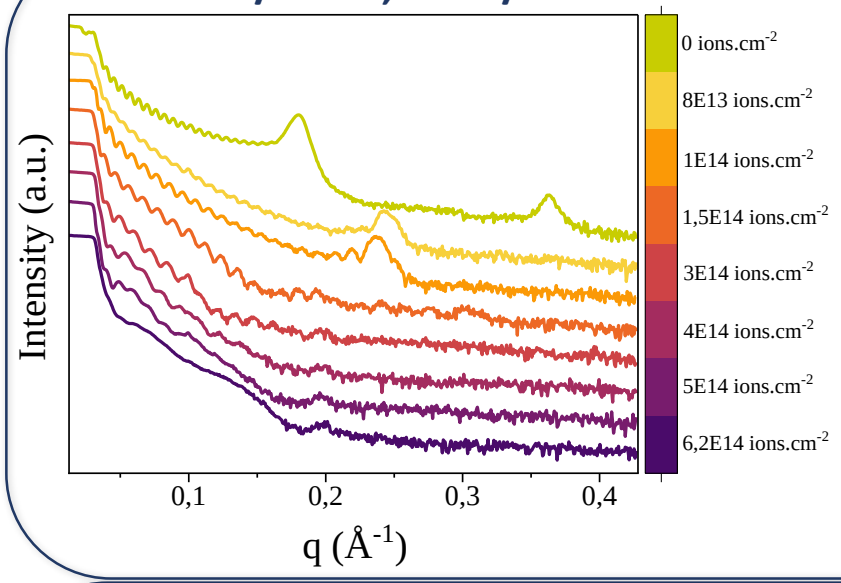
Electronic (Se)

Ion	Energie MeV/A	Se keV/nm	Sn keV/nm	Flux Ions/(cm².s)	Beamline
^{22}Ne	0.98	**2.2**	2.79E-03	7~8e9	IRRSUD GANIL, Caen
^{36}Ar	0.98	**4.5**	1.00E-02	8~9e9	IRRSUD GANIL, Caen
^{197}Au	0,025	1.0	**3.2**	6~9e10	JANNUS, Orsay

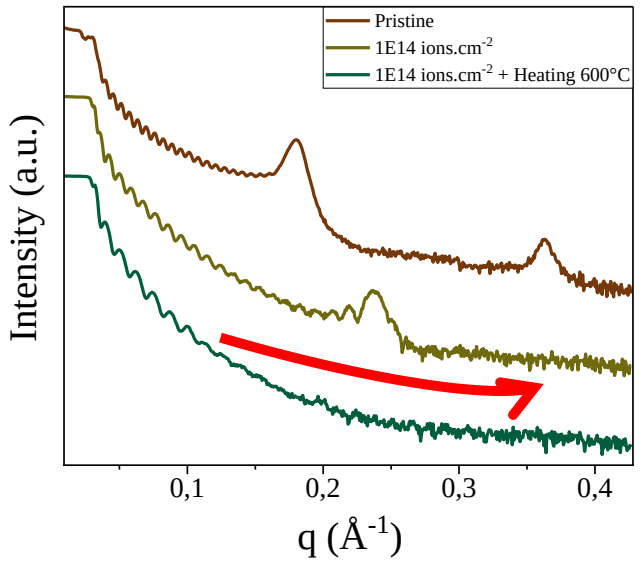
Ballistic (Sn)

Mesoporous silica ICc - combined effect of T + radiation

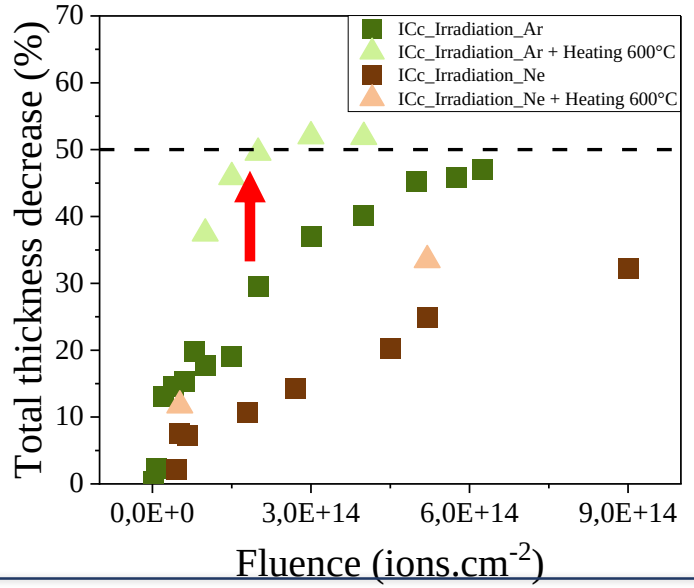
^{36}Ar – dE/dx =4,5 keV/nm



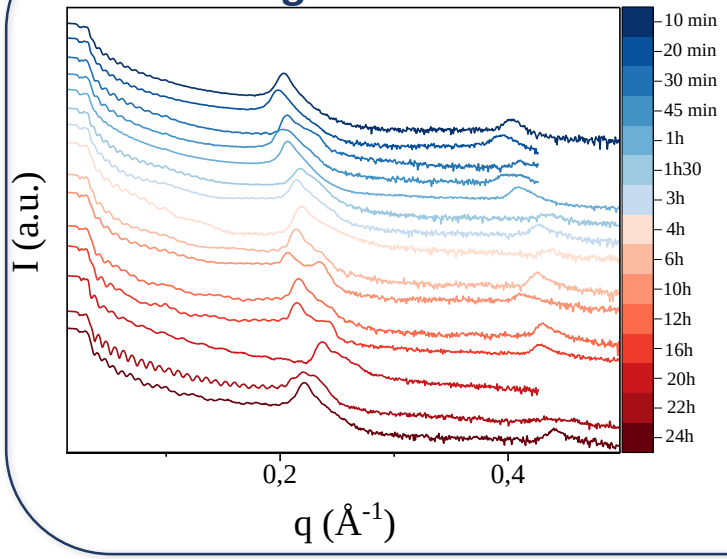
^{36}Ar - dE/dx = 4,5keV/nm + 600°C/4h



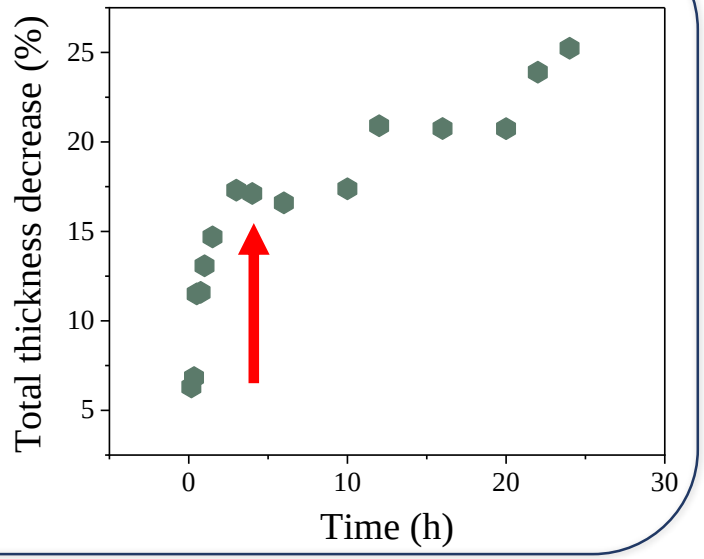
Densification



Heating 600°C



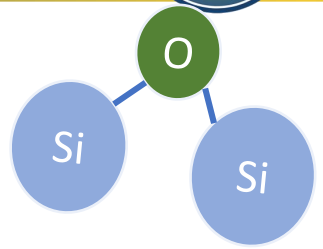
Densification



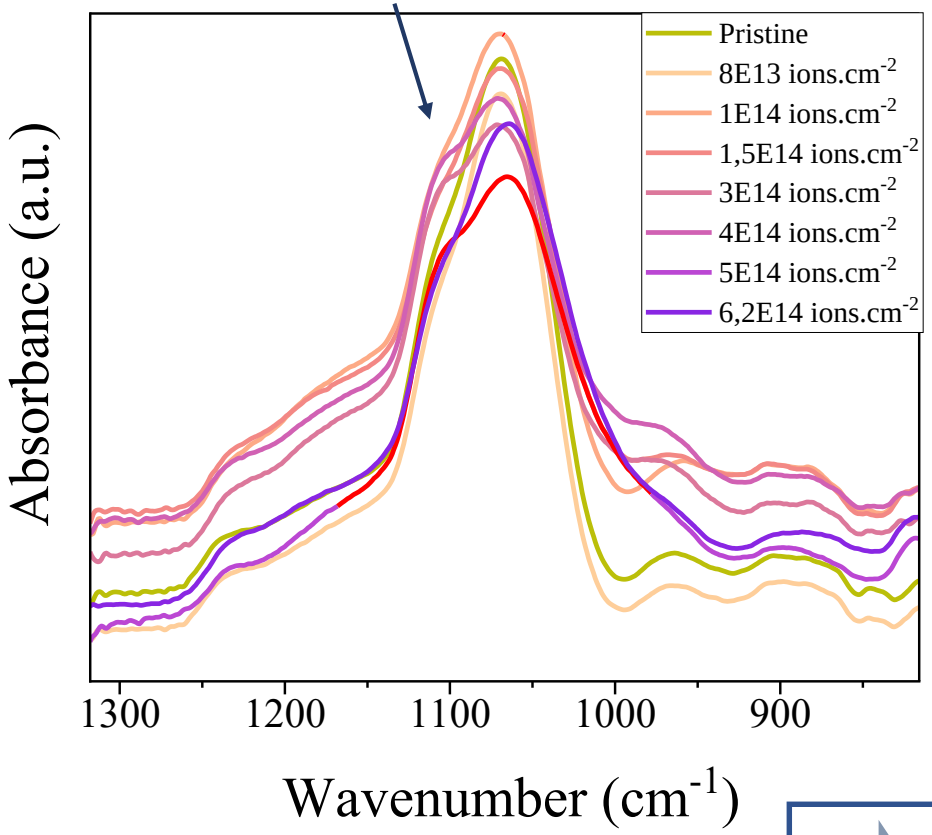
- **Decrease in overall intensity → Interfacial roughness increase**
- **Irradiation in electronic regime → Additional effect temperature + irradiation**

Mesoporous silica ICc - FTIR analyses transmission mode

^{36}Ar 0.98 MeV/A

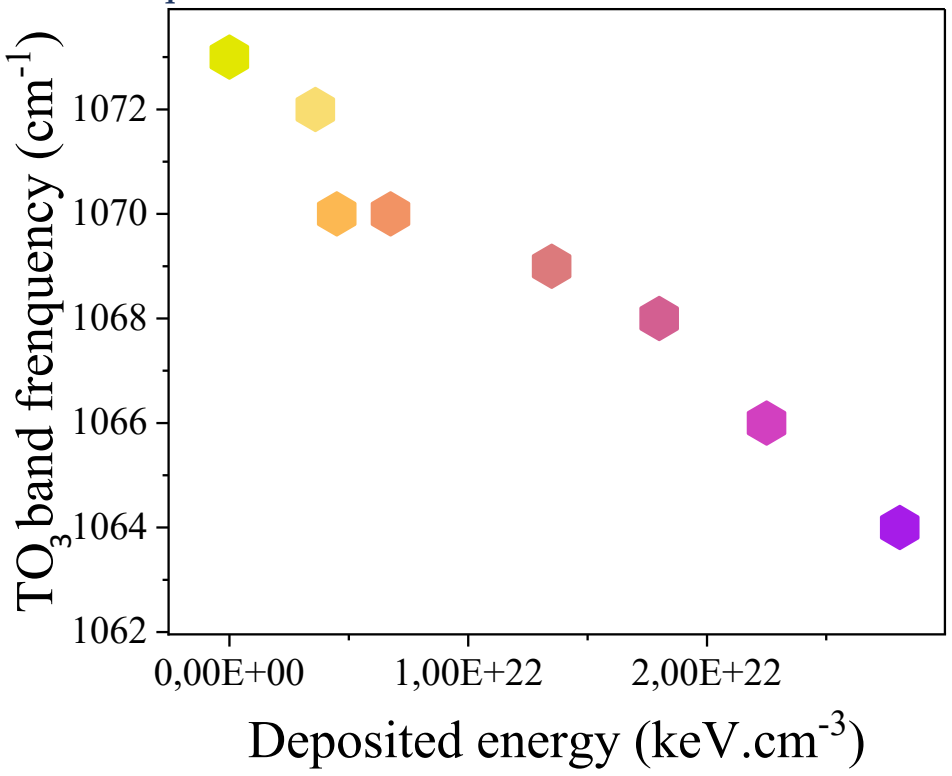


Si–O–Si TO_3 band→ Shift and intensity decreases with fluence



Shoulder (Si–OH)
→ Gradually disappears

The main band shifts to lower frequencies

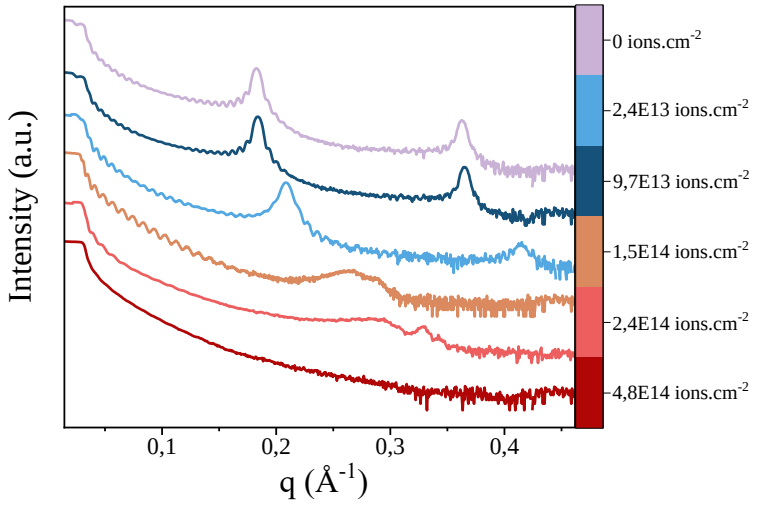


Si-OH intensity decrease → **Si-O-Si condensation**
TO_3 shift → **Angle decrease**

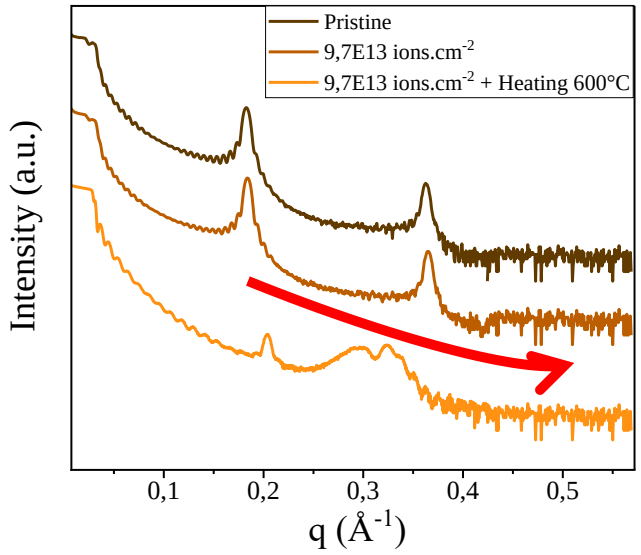
Devine, R. A. B., and Co. NIMB **1994,** *91.*
Innocenzi, P.; and Co. *J. Phys. Chem. B* **2003,** *107*

Mesoporous silica ICc - combined effect of T + radiation

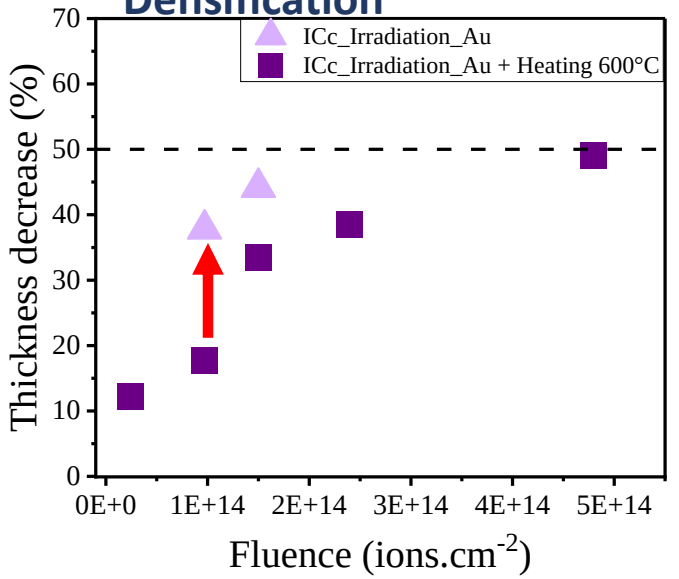
^{197}Au 0,5MeV-dE/dx=4,2 keV/nm



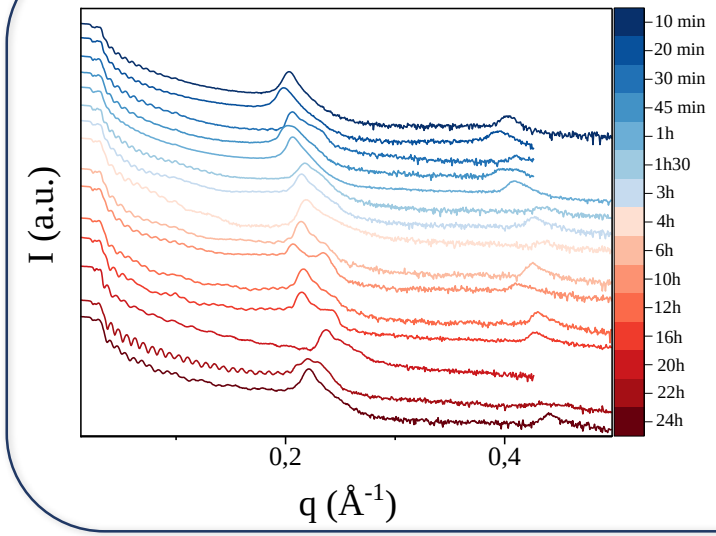
^{197}Au-dE/dx=4,2keV/nm+600°C/20min



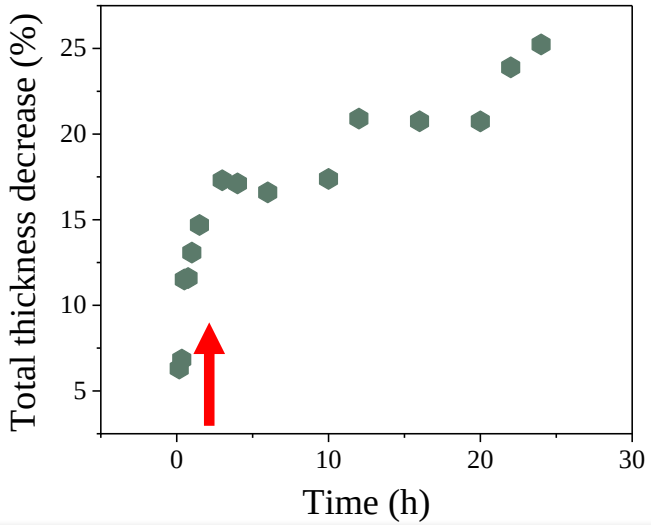
Densification



Heating 600°C



Densification



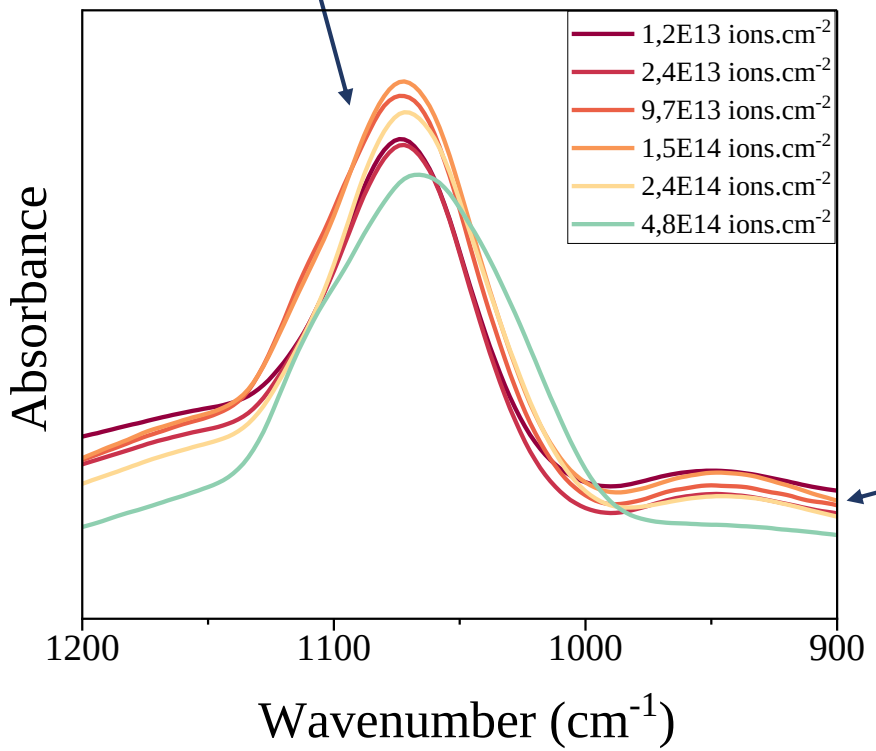
Irradiation ballistic regime

Additional effect temperature + irradiation

Mesoporous silica ICc - FTIR analyses transmission mode

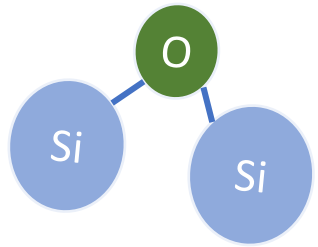
^{197}Au 0.5 MeV

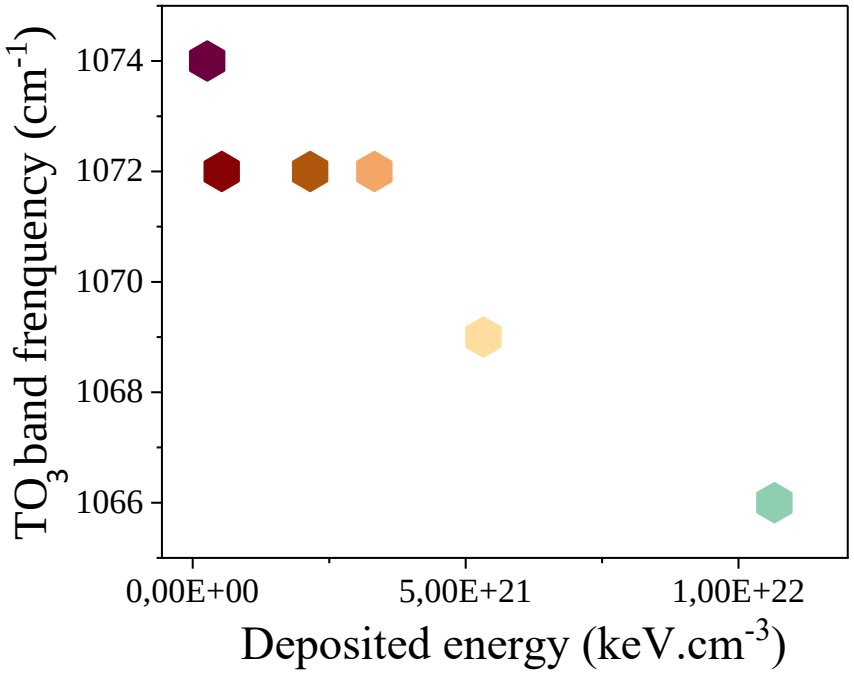
Si–O–Si TO_3 band → Shift and intensity decreases with fluence



Shoulder (Si–OH)
→ Gradually disappears

TO_3 band shifts to lower frequencies



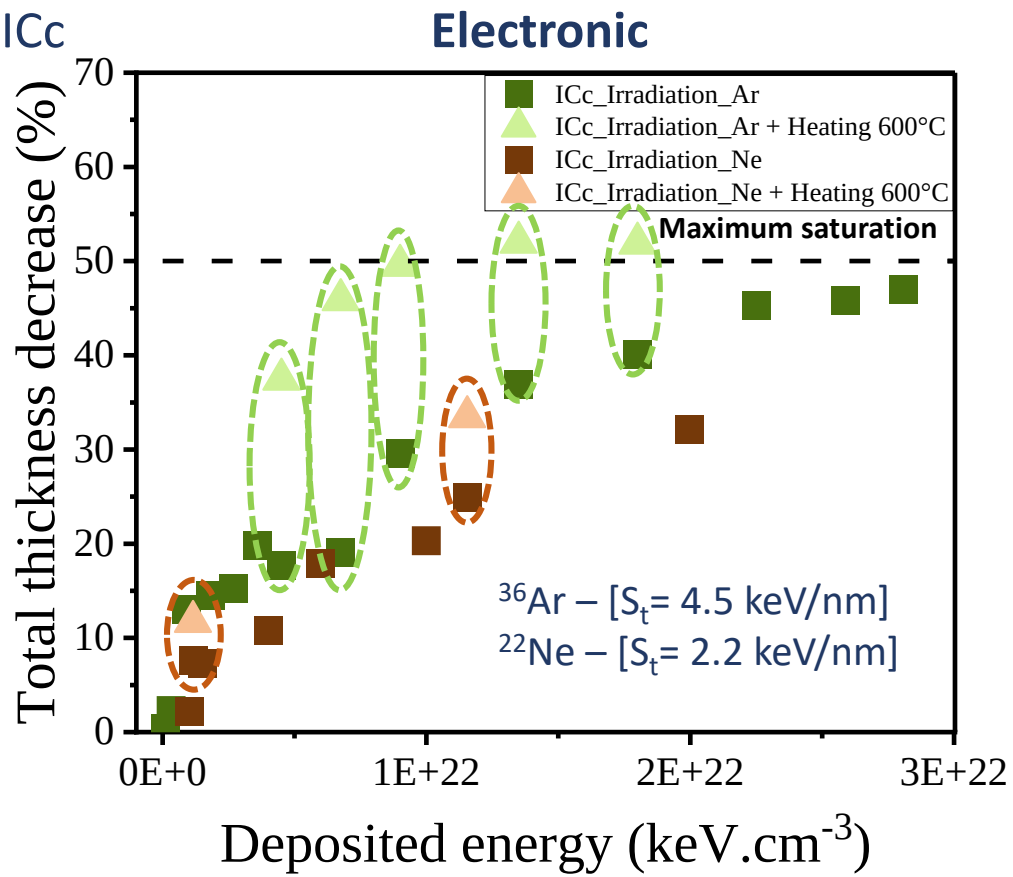


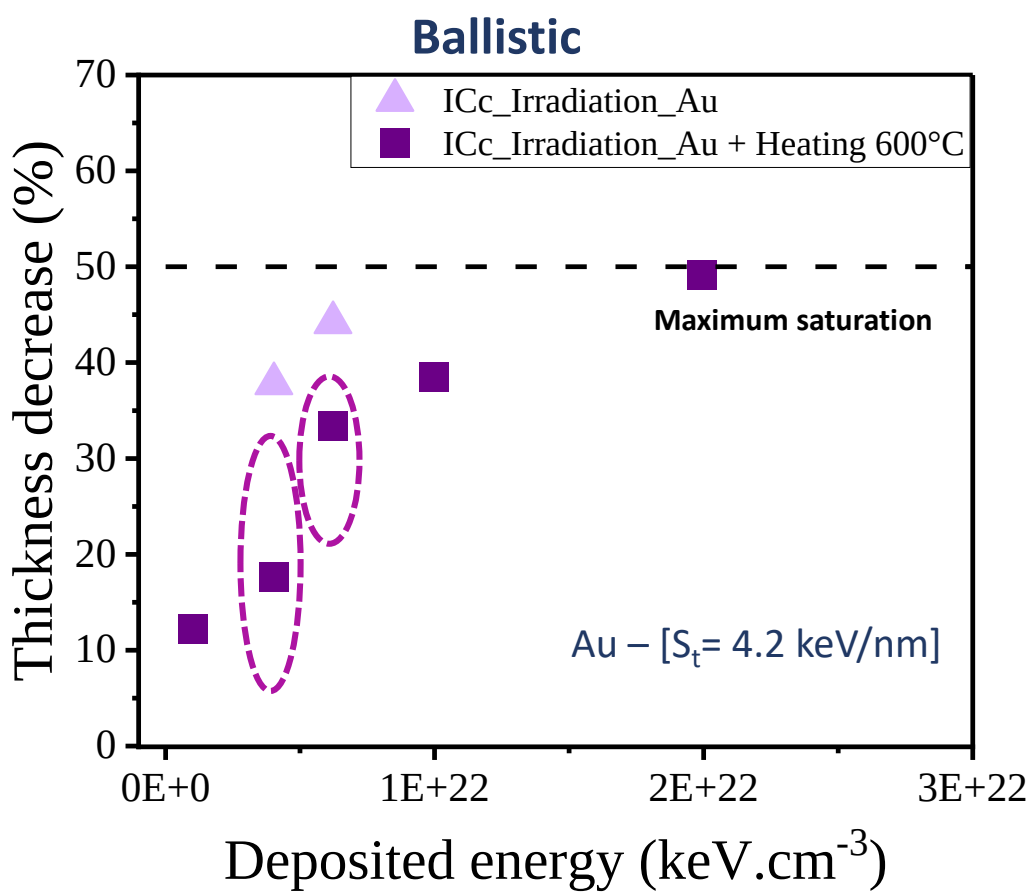
Si-OH intensity decrease → **Si-O-Si condensation**
TO_3 shift → **Angle decrease**

Devine, R. A. B., and Co. NIMB **1994,** *91.*
Innocenzi, P.; and Co. *J. Phys. Chem. B* **2003,** *107*

Results irradiation vs heating : ballistic/electronic effects

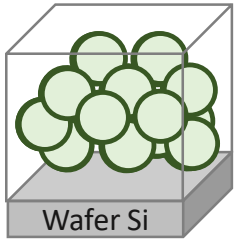
ICc





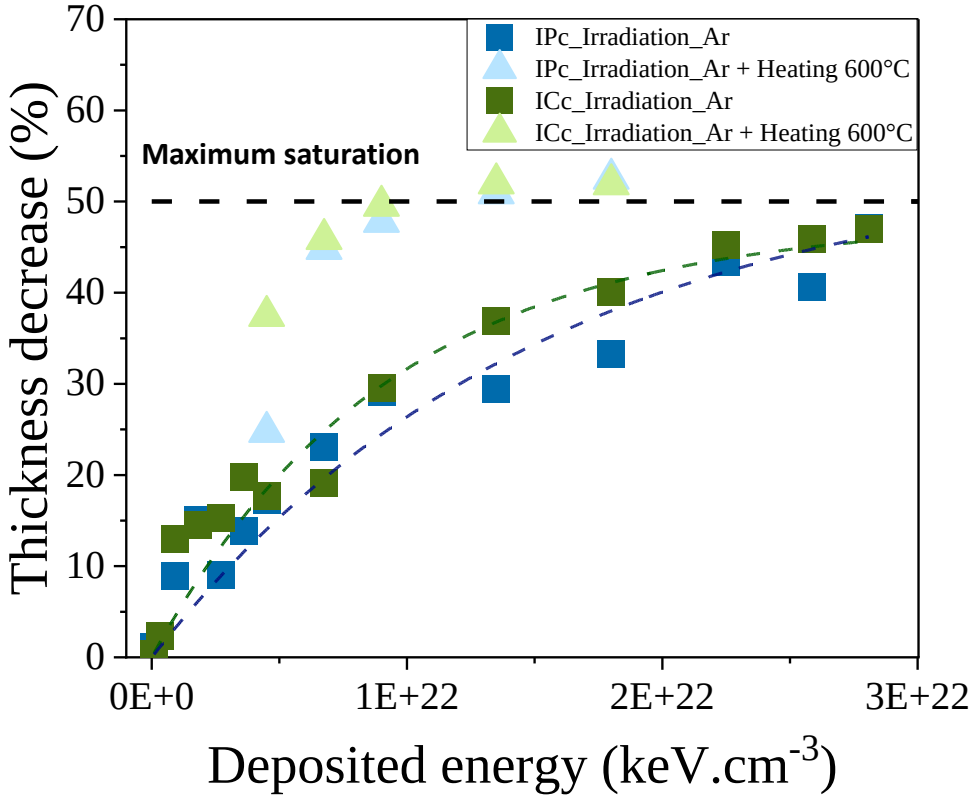
- **Same trend in densification processes**
  - ✓ **Similar deposited energy to reach saturation**
  - ✓ **Similar densification shift due to heating effect**

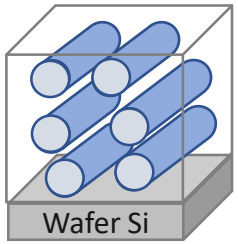
Irradiation ICc VS IPc



ICc

3D Spherical pore diameter 2-3 nm





IPc

2D Cylindrical pore diameter 4 nm

No change with the structure

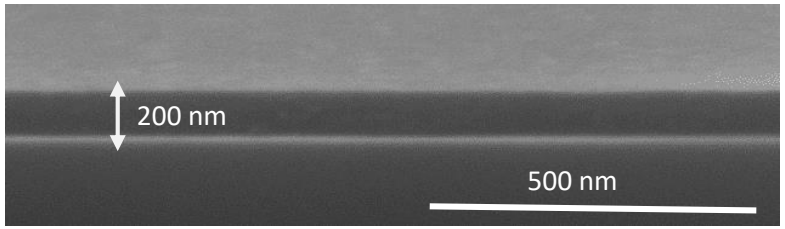
Outlook : mesoporous carbon, TiO_2…

Preliminary results on mesoporous carbon

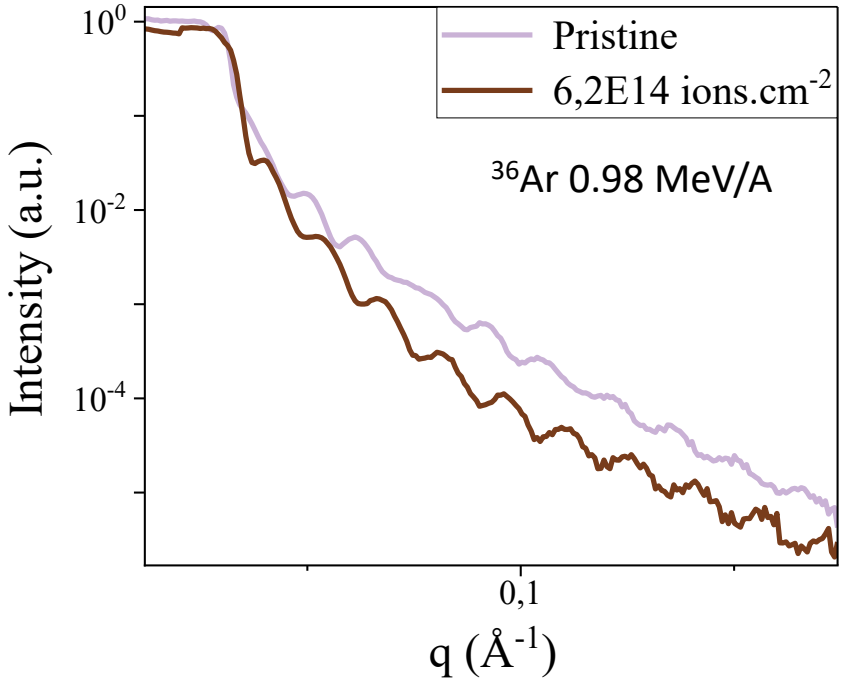
- First step : mesoporous carbon powder

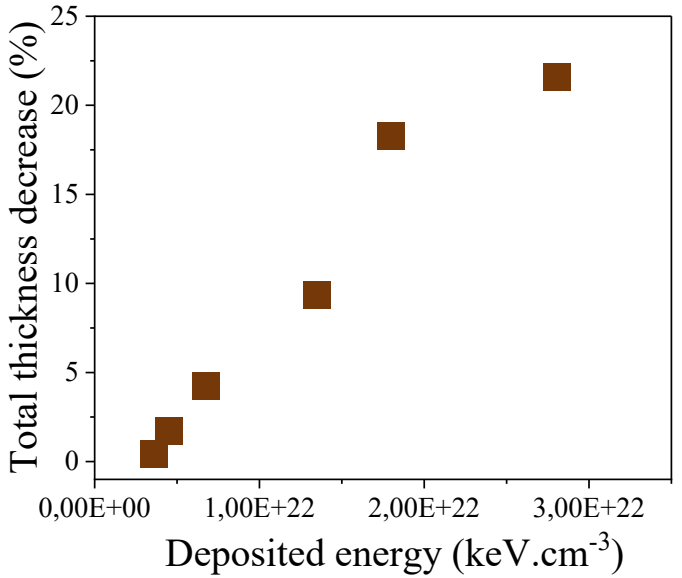
  → Study of specific surface area = 560 m²/g

- Second step : adaptation of the protocol to thin films



Cross-section SEM



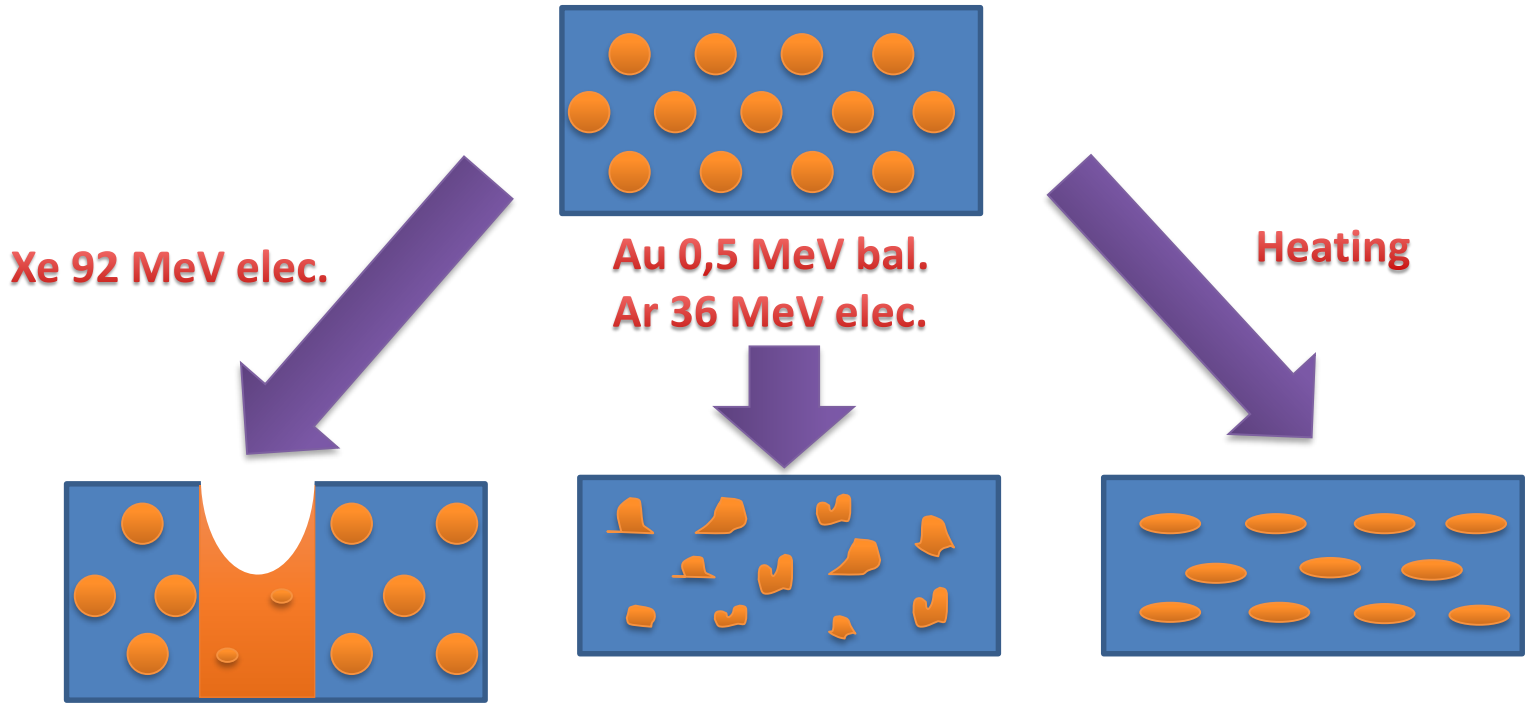


Conclusion

Mesoporous silica

- Ion irradiation makes **collapse** and **densification** of mesoporous silica
- Irradiation + heating → **cumulative processes**
- Same behavior with regard to densification during irradiation in ballistic and electronic regimes → **Possible mechanism** : "low temperature sintering" in relation with diffusion under irradiation

Illustration showing pore collapse due to stress (Irradiation/Heating)

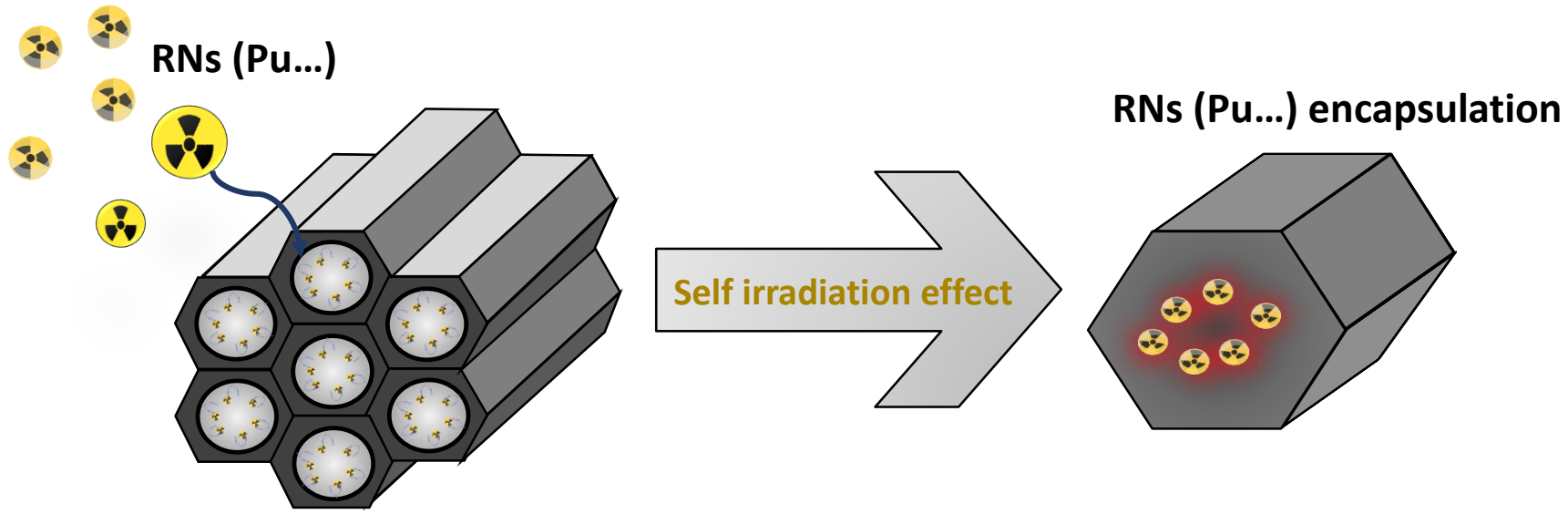


Conclusion

Application :

- Decontamination of radioactive effluents by a two-in-one process “Separation/Conditioning”

- ANR project **AUTOMACT** https://anr.fr/Project-ANR-18-CE05-0016
  “Solid fixation and AUTO-conditioning of ACTinide elements coming from contaminated liquid outflows”



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Thanks for listening !

Any question ?