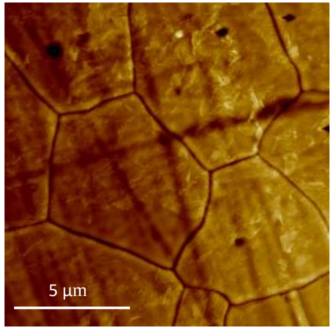
PHENIICS FEST 2023

Impact of irradiation on the chemical durability of UO_2, $U_{0,9}Th_{0,1}O_2$ et $U_{0,9}Nd_{0,1}O_2$ sintered pellets



Mathis Hitier
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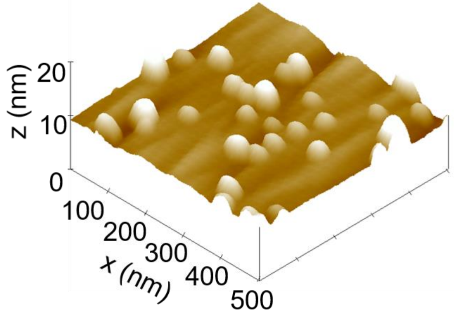

NEEDS : Nucléaire : Energie, Environnement, Déchets, Société

1st Axis of the R3C project : Radiochimie et Chimie du Cycle du Combustible

Team 3 : IJCLab
CNRS – IN2P3, Univ. Paris-Saclay

Team 1 : ICSM
UMR 5257, CNRS – INC, CEA, Univ. Montpellier, ENSCM

Team 4 : IP2I
UMR 5822, CNRS – IN2P3, Univ. de Lyon 1

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Irradiation of materials

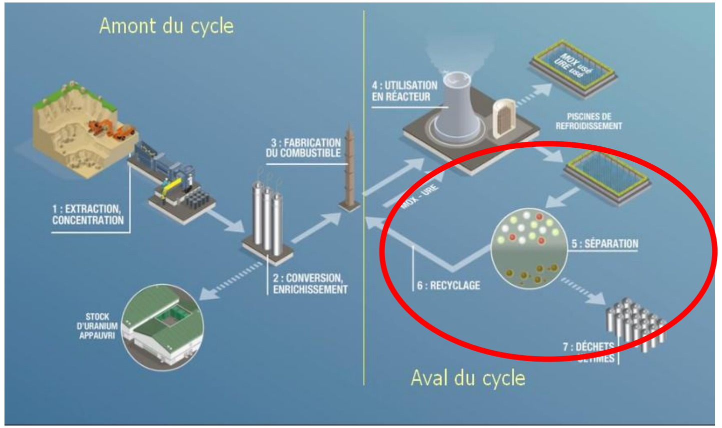
Clotilde GAILLARD
Raman Spectroscopy

Doctoral school
PHENIICS

PUREX Process : the front end of the nuclear fuel cycle

Spent Nuclear Fuel → U (95 wt.%) – Pu (1 wt.%)

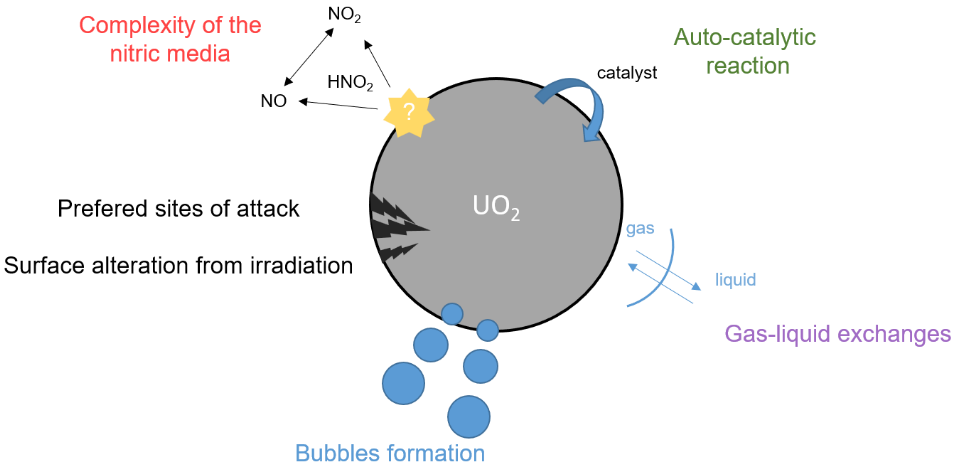
MA (0.1 wt.%) – FP (4 wt.%)



Nuclear Fuel Cycle © CEA/Com Ci Com Ca

- **Harsh reprocessing conditions (nitric acid 3 to 6 mol/L - T > 90°C)**

Necessity to better discriminate the reactions and parameters driving the dissolution…

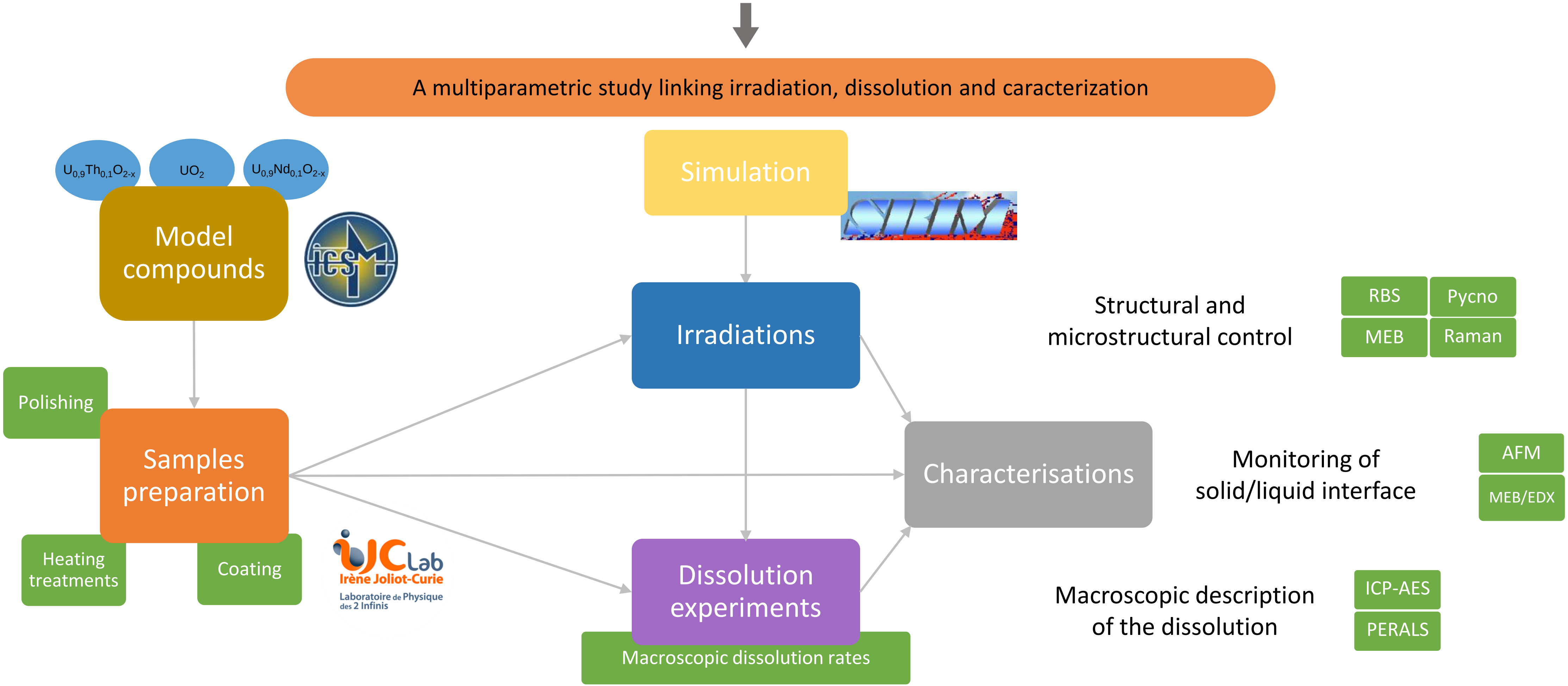


Synoptic diagram representing the different phenomena involved in the dissolution of a UO2 pellet in nitric medium, from the work of S. Bertolotto

… to optimize the PUREX process and extend it to MOX Fuel and new thorium-based nuclear fuels

Objectives and approches

How to discriminate all the paramaters implied in the spent nuclear fuel reprocessing ?

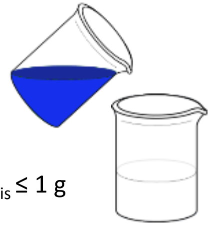


Oxalate precipitation

4h, 700°C
Ar/H_2 (4%)

Thermal conversion to oxide

U(IV) + M^{x+}
HCl



$m_{synthesis} \leq 1$ g

Hydroxyde

$U(OH)_4$
$(U_{1-x}Nd_x)(OH)_4$
$(U_{1-x}Th_x)(OH)_4$

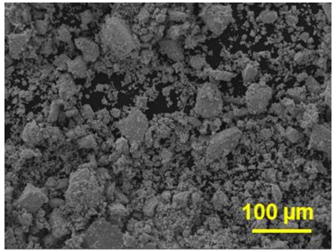
Room temperature
Excess NH_3 (aq) (400%)

Washing
(H_2O - EtOH)

Drying (T_{amb})

Oxyde

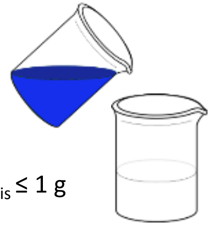
UO_2
$(U_{1-x}Nd_x)O_2$
$(U_{1-x}Th_x)O_2$



Preparation of the sintered pellets

Oxalate precipitation → Thermal conversion to oxide → Shaping / Sintering

U(IV) + M^{x+}
HCl



$m_{synthesis} \leq 1$ g

4h, 700°C
Ar/H_2 (4%)

Hydroxyde

U$(OH)_4$
$(U_{1-x}Nd_x)(OH)_4$
$(U_{1-x}Th_x)(OH)_4$

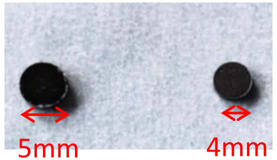
Room temperature
Excess NH_3 (aq) (400%)

Oxyde

UO_2
$(U_{1-x}Nd_x)O_2$
$(U_{1-x}Th_x)O_2$

Sintered pellets
Densification rate (d_{geom}/d_{calc})

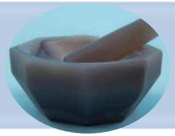
- $UO_2 \approx 91$ %
- $U_{0,9}Nd_{0,1}O_{2-x} \approx 91 - 95\%$
- $U_{0,9}Th_{0,1}O_{2-x} \approx 88 - 92$ %



Washing
(H_2O - EtOH)

→

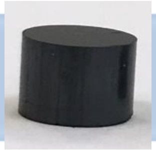
Drying (T_{amb})



Grinding

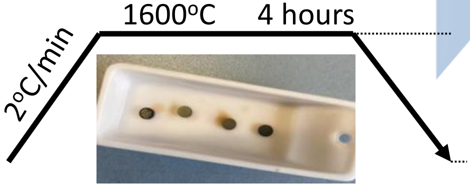
Unixial pressing
Ø 5 mm, 500 MPa

Pellets

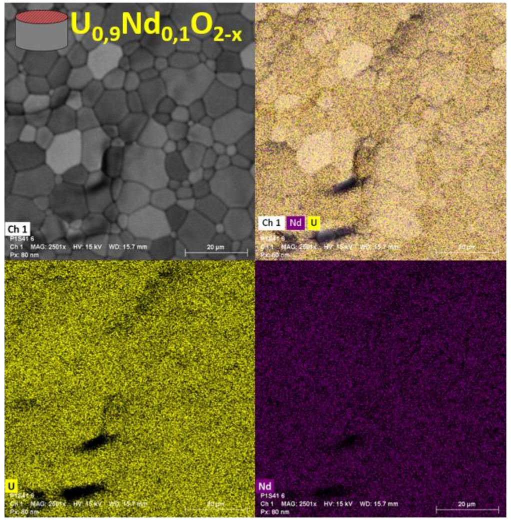


Calcination

Ar/H_2 (4%)

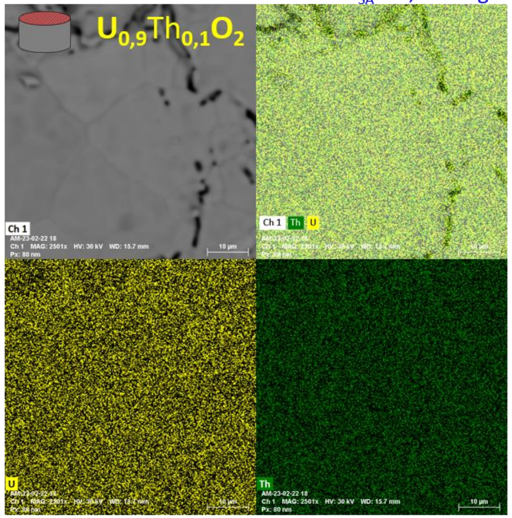


MEB /EDX Characterisation



Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Neodymium	60	L-Serie	83723	5.56	5.42	8.65	0.19
Uranium	92	M-Serie	2277791	96.94	94.58	91.35	2.99
			Sum	102.50	100.00	100.00	

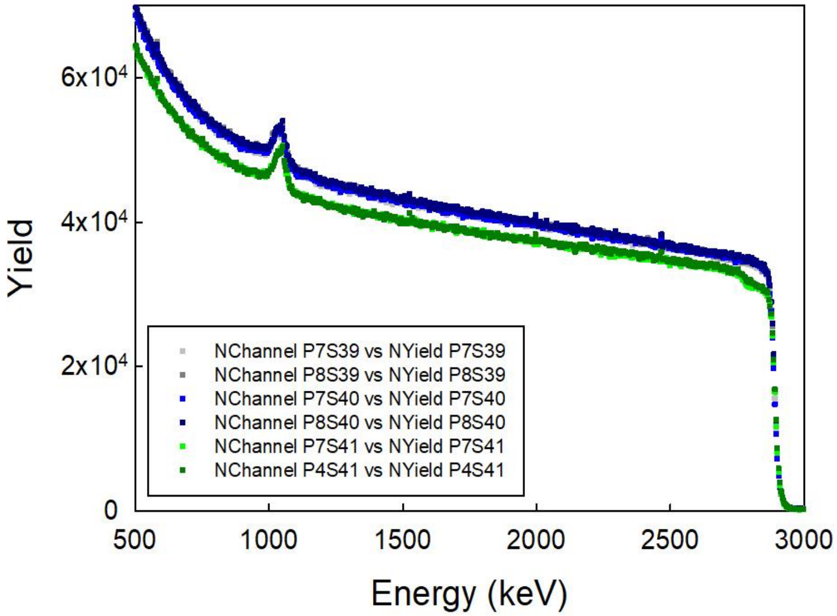
S_{SA} = 0,08 $m^2.g^{-1}$



Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Thorium	90	L-Serie	43510	8.81	9.37	9.59	0.25
Uranium	92	L-Serie	282084	85.21	90.63	90.41	2.19
			Sum	94.03	100.00	100.00	

Good cationic homogeneity

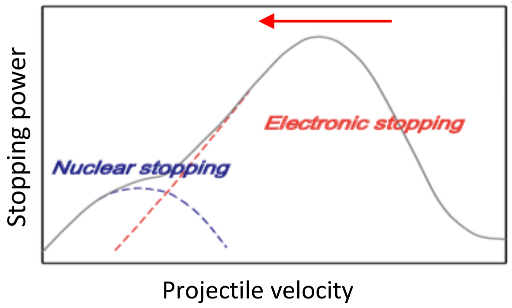
RBS Characterisation



RBS spectra for each sample composition

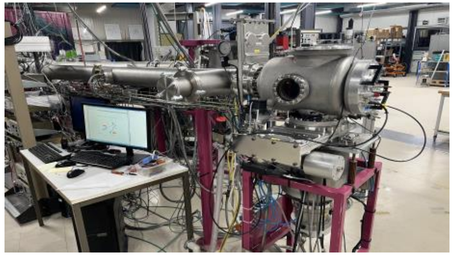
Expected composition achieved

Two kinds of interactions : two distinct effects



Nuclear stopping

The projectile is slowed down by atomic collision. Cascades of collision are observed.



Au
1; 2 and 7MeV

Gold projectiles simulates the radiation damage induced by atomic collisions from fission fragments (close to their range).

Electronic stopping

The projectile has a high velocity. It is slowed down by interaction with the electron clouds of the atoms of the target.

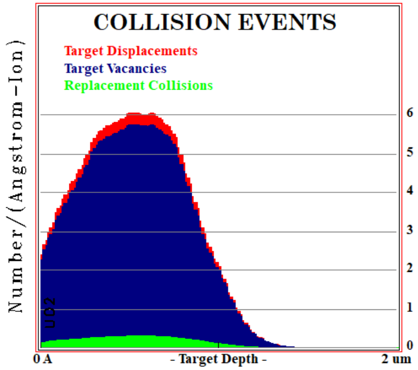
Xe and **Pb**
1GeV

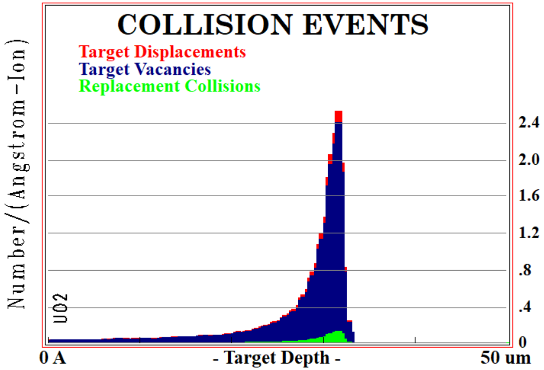
Xenon is an accessible fission fragment with the highest stopping power ($37keV.nm^{-1}$).
Lead is used to maximise the effect of the electronic stopping due to its high atomic number ($55keV.nm^{-1}$).

Irradiation simulations – comparison between nuclear and electronic stopping

Displacements created by collision cascades

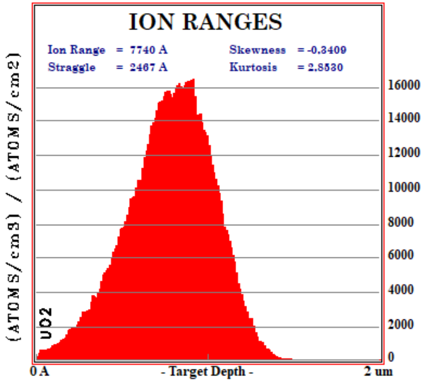
Au – 7MeV **UO_2** Xe – 1GeV

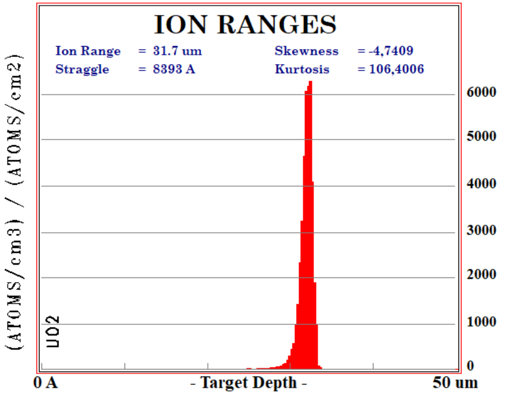




Penetration depths of the projectile

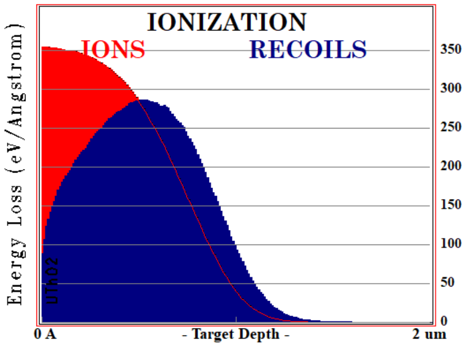
Au – 7MeV **UO_2** Xe – 1GeV

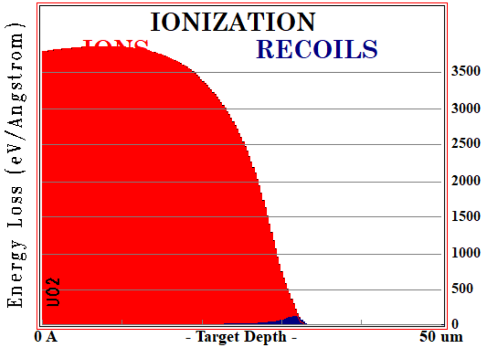




Ionization of the target material

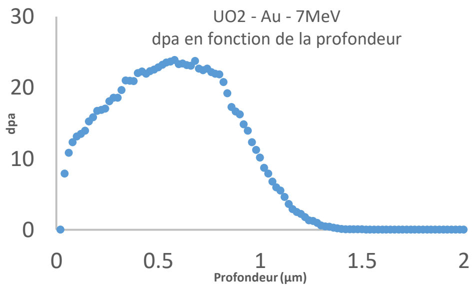
Au – 7MeV **UO_2** Xe – 1GeV

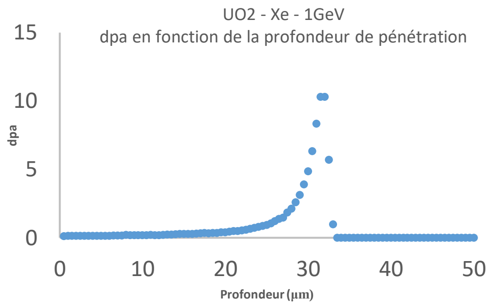




Displacements per atom

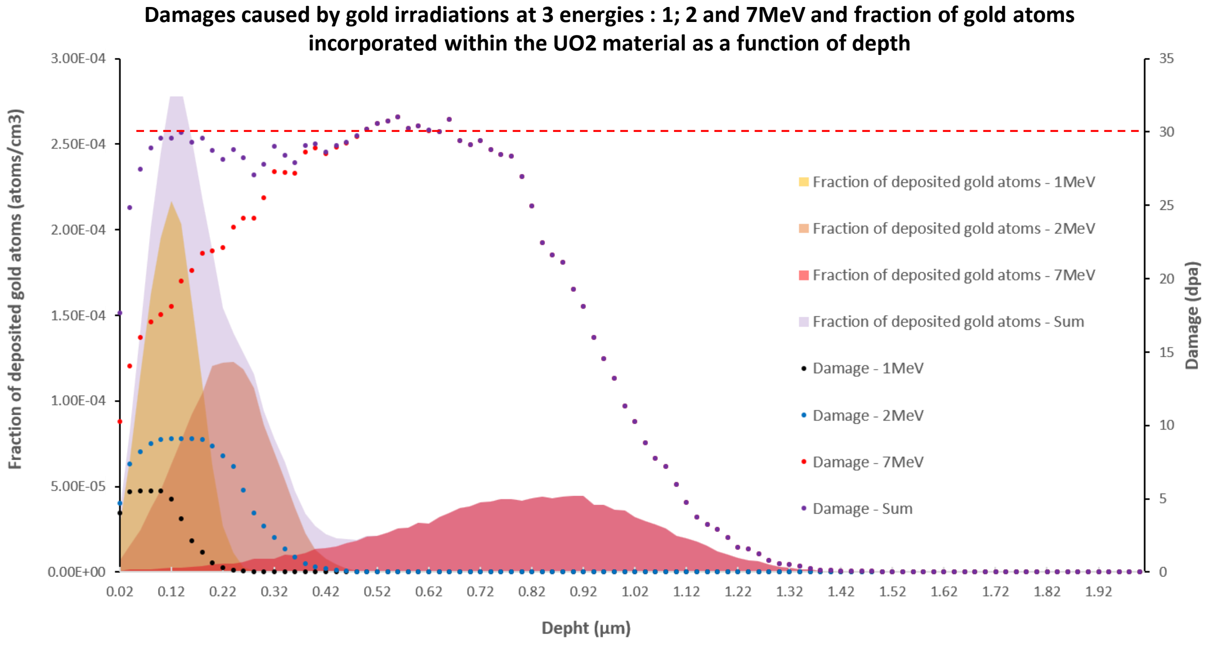
Au – 7MeV **UO_2** Xe – 1GeV





Simulation results

Optimization of the gold irradiation conditions



Choice of irradiation energies

- Maximizing of the penetration depth
- Maximizing of dpa to achieve the formation of a dislocation network.

Max dpa is fixed at 30

Selected fluences

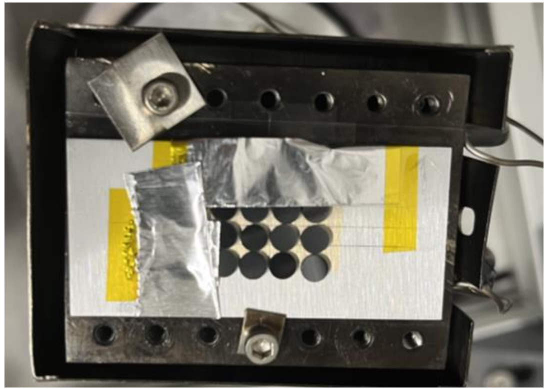
$$\begin{cases} \phi_{1MeV,Au} = 2.10^{14}\ ions.cm^{-2} \\ \phi_{2MeV,Au} = 3{,}2.10^{14}\ ions.cm^{-2} \\ \phi_{7MeV,Au} = 1{,}3.10^{15}\ ions.cm^{-2} \end{cases}$$

Irradiation experiments – atomic collision

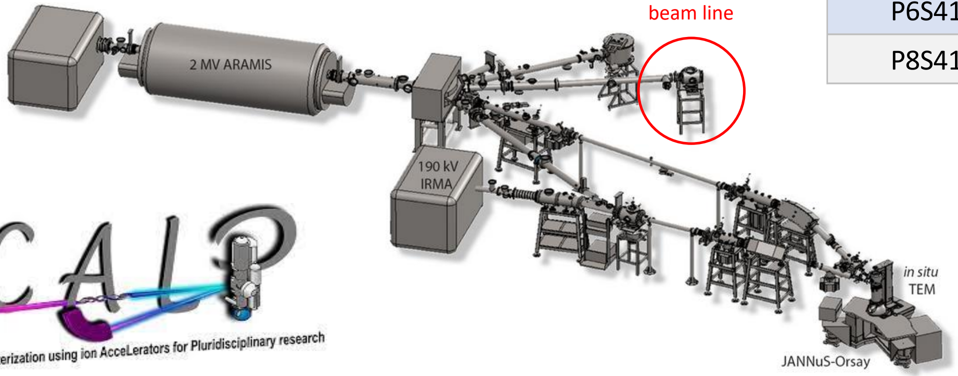
Gold implantation

Irradiation

$$\begin{cases} \phi_{7MeV,Au} = 1{,}3.10^{15}\ cm^{-2} \\ \phi_{2MeV,Au} = 3{,}2.10^{14}\ cm^{-2} \\ \phi_{1MeV,Au} = 2.10^{14}\ cm^{-2} \end{cases}$$



- A mask is placed on half the surface to determine the effect of surface irradiation.
- About 4 hours of irradiation



SCALP
Synthesis & Characterization using ion AcceLerators for Pluridisciplinary research

Pellet code	Composition	Irradiation
P2S39	UO2	**100%**
P4S39	UO2	**100%**
P5S39	UO2	**50,62%**
P6S39	UO2	**70,85%**
P1S40	UTh10%O2	**59,45%**
P2S40	UTh10%O2	**100%**
P4S40	UTh10%O2	**65,63%**
P5S40	UTh10%O2	**100%**
P4S41	UNd10%O2	**65,96%**
P5S41	UNd10%O2	**100%**
P6S41	UNd10%O2	**100%**
P8S41	UNd10%O2	**52,52%**

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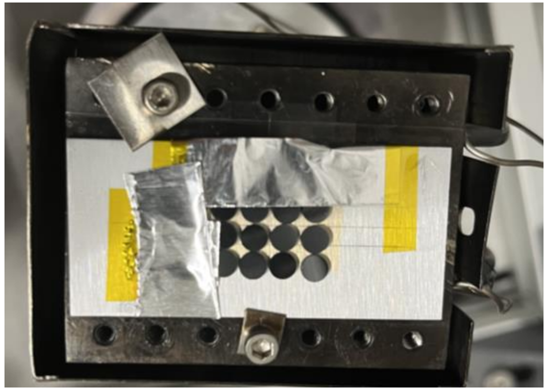
Irradiation experiments – atomic collision

Gold implantation

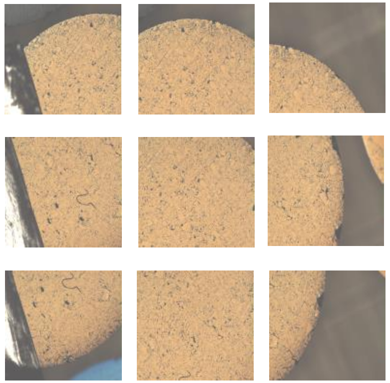
Irradiation

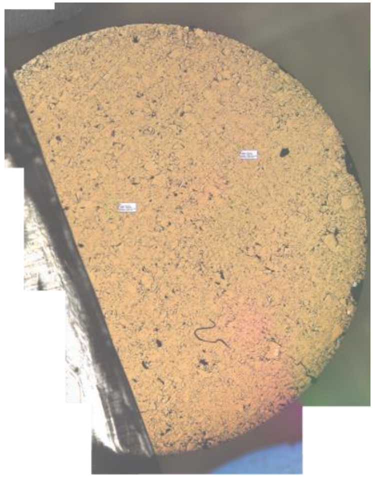
$$\begin{cases} \phi_{7MeV,Au} = 1{,}3.10^{15}\ cm^{-2} \\ \phi_{2MeV,Au} = 3{,}2.10^{14}\ cm^{-2} \\ \phi_{1MeV,Au} = 2.10^{14}\ cm^{-2} \end{cases}$$

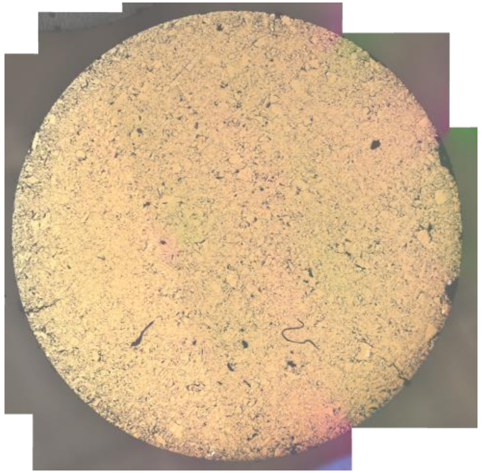


Imaging the surface

Images are taken by optical microscopy







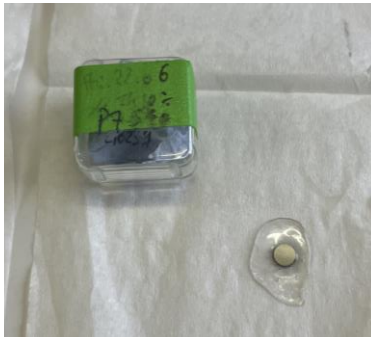
- Hugin & Gimp are used to obtain a complete mesure of the surface (px and µm).

Static dissolution experiments

Coating

Only the irradiated surface is of interest

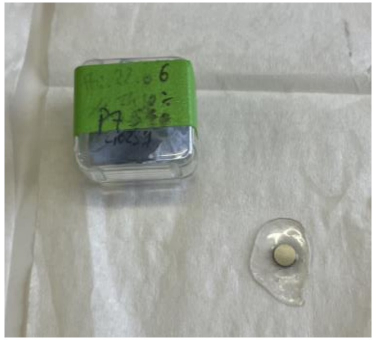
- Epoxy Resin
- Coating after 2 hours
- Drying : 8 hours



Static dissolution experiments

Coating

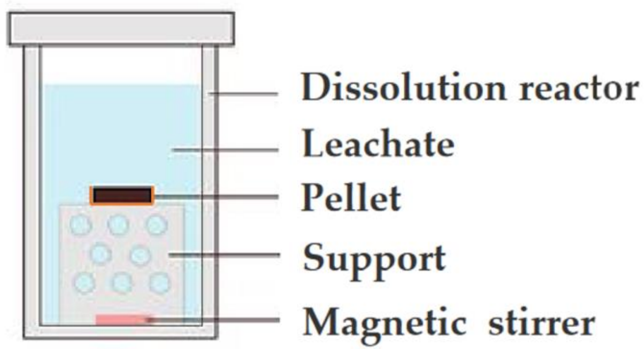
- Epoxy Resin
- Coating after 2 hours
- Drying : 8 hours



Dissolution test

Static dissolution condition

- Sampling of 15% of the total volume (4.5mL)
- Diluted by 2 (9mL)



First parameters

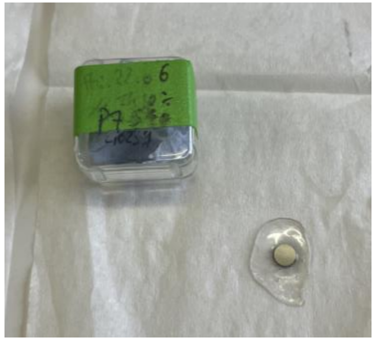
- Room temperature
- 0,1 mol/L nitric acid concentration

Static dissolution experiments

Coating → **Dissolution test** → **Analysis of elements released in the solution**

Coating

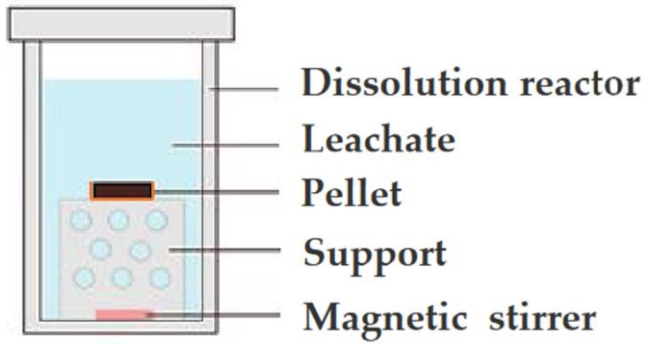
- Epoxy Resin
- Coating after 2 hours
- Drying : 8 hours



Dissolution test

Static dissolution condition

- Room Temperature
- 0,1 mol/L nitric acid concentration



Analysis of elements released in the solution

Elementary concentration determination

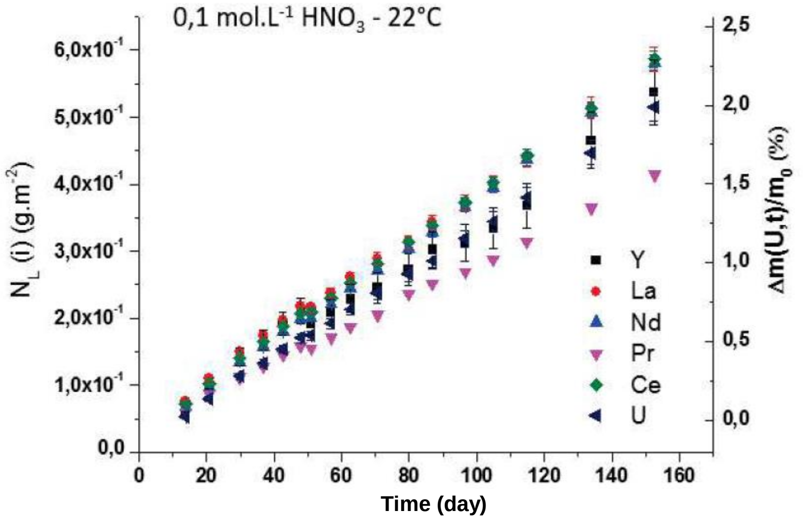
- ICP – AES
- α scintillation

Characterisation of the solution

$$N_L(i) = \frac{m_i}{f_i . S}$$

$$\begin{cases} m_i : amount\ of\ (i) in\ solution\ (g) \\ S : Reactive\ surface\ area\ (m^2) \\ f_i : mass\ ratio\ of\ (i)\ in\ the\ solid \end{cases}$$

- ICP – AES
- α scintillation



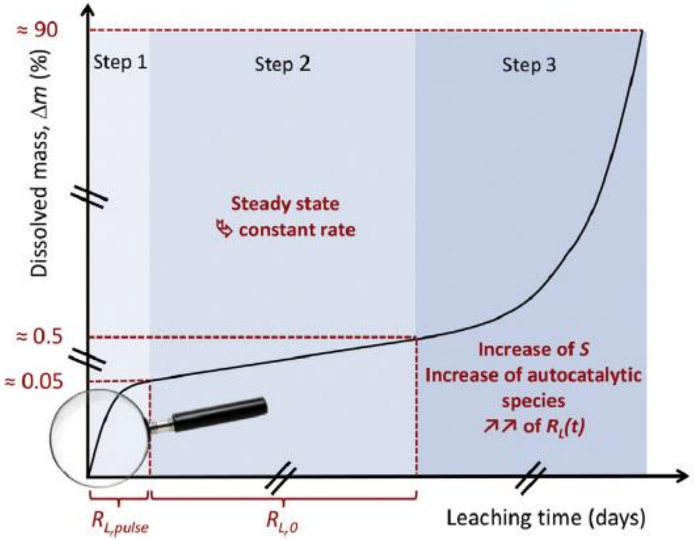
Evolution of normalized mass losses $N_L(i)$ ($g.m^{-2}$) (left axis) and relative masses of dissolved UO_2 ($\Delta m(U,t)/m_0$ in %) (right axis) recorded during dissolution of sintered samples of formula $U_{0,8}Ln_{0,2}O_{1,9}$ at 22°C

How the first step and steady state are modified by irradiation ?

$$R_L(i) = \frac{dN_L(i)}{dt} = \frac{1}{f_i . S}\frac{dm_i}{dt}$$

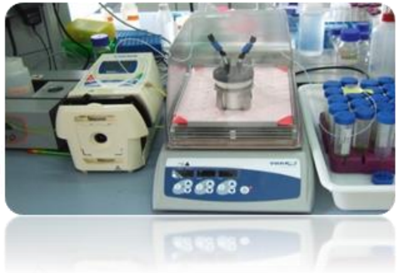
$R_L(i) \approx R_L(j)$: **congruent dissolution**

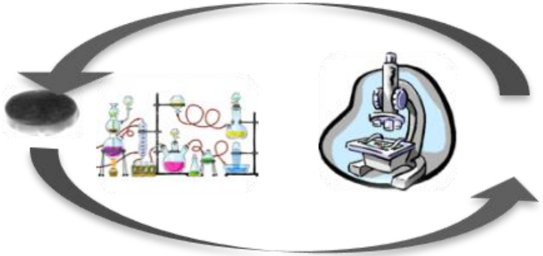
$R_L(i) \neq R_L(j)$: **incongruent dissolution**

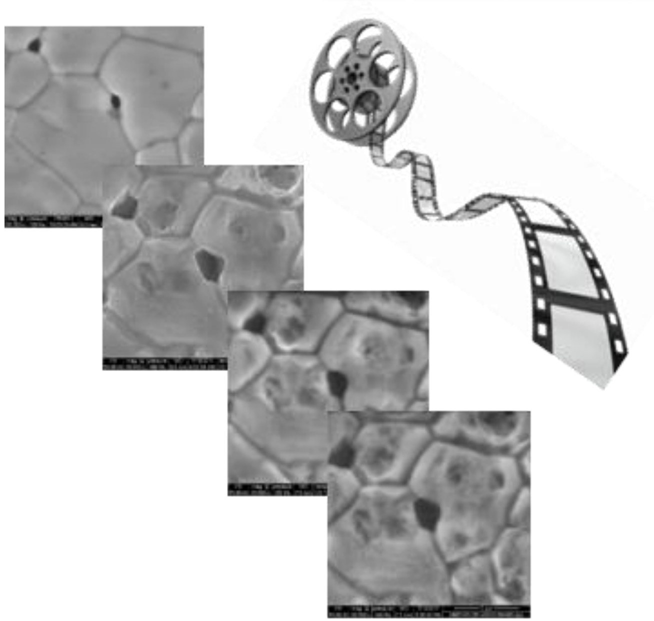


T. Cordara et al., J. Nucl. Mater. 2017, 496, 251-264
T. Dalger et al., J. Nucl. Mater. 2018, 510, 109-122

Operando study of evolving interface during dissolution







Taking and assembling images at different dissolution times

Making of a video Fiji/ImageJ

Images taken by Environmental SEM (ICSM) and AFM (IJCLab)

Conclusions

- All protocols have been optimized so that results will flow in the next couple of months.
- The first gold irradiation campain has been succesfully concluded.
- Long dissolution times means the results take time to be usable but first observations show the necessity to increase nitric acid concentration.

Perspectives

- An internship student, **Kevin LEBAY** will start on 24th of April to conduct AFM experiments for operando study and surface characterization of samples.

Future experiments

Lead and Xenon irradiation at 1GeV

GANIL spiral2 – laboratoire commun CEA/DRF CNRS/IN2P3

Early July 2023

Raman spectrometry

iP2i – LES 2 INFINIS LYON

May / June 2023

Operando study by Environmental SEM

ICSM

October 2023

Acknowledgments

ICSM

Stéphanie SZENKNECT

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Paul-Henri IMBERT

Renaud PODOR

IJCLab

Frédérico GARRIDO

Claire LE NAOUR

Melody MALOUBIER

Florian PALLIER

IP2I

Natalie MONCOFFRE

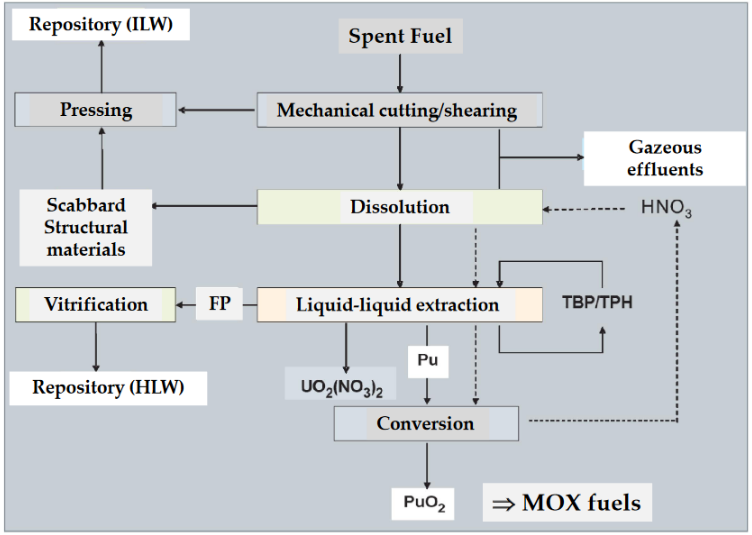
Clothilde GAILLARD

The JANNuS-SCALP plateform staff

Thank you for your attention !

Goal of the PUREX process

"to recover the plutonium and uranium contained in irradiated fuel with the highest possible yields and to purify them in such a way as to allow their reuse, and to condition the various wastes in a form compatible with storage, while having the lowest possible impact on the environment".



Monographie CEA, Ed. Le Moniteur,, 2008

[1]Lecomte, M., & Bonin, B. (2008). Traitement-recyclage du combustible nucléaire usé.

Appendix 2 – Nitric acid media

Main equation used to define the oxidation of uranium* :

$$UO_2(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow UO_2^{2+}(aq) + 2NO_2(aq) + 2H_2O$$

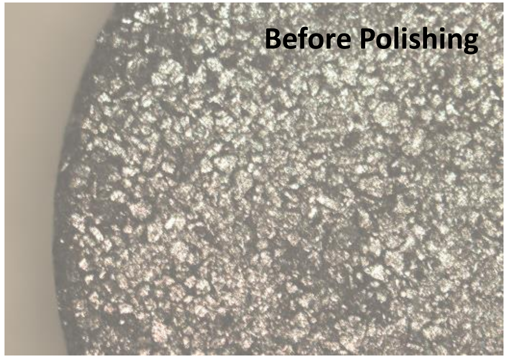
Equations defining the formation of nitrous acid :

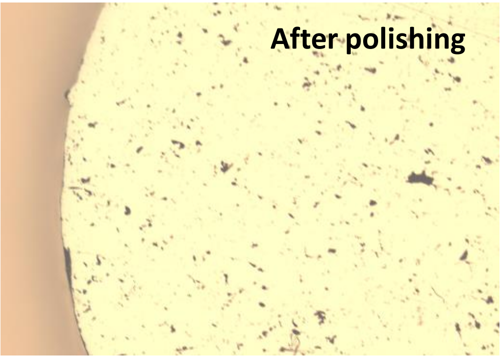
$$UO_2(s) + 2NO_2(aq) + 2H^+(aq) \rightarrow UO_2^{2+}(aq) + 2NO(aq) + 2H_2O$$

$$2NO(aq) + HNO_3(aq) + 2H_2O \rightarrow 3HNO_2(aq)$$

Nom	Formule chimique	Degrés d'oxydation de l'azote	État physique à T=25°C et P = 1 atm	Remarques
Anhydride nitrique	N_2O_5	+V	gaz	
Acide nitrique	HNO_3	+V	liquide pur ou dissous	Initialement présent
Ion nitrate	NO_3^-	+V	dissous	
Ion nitronium	NO_2^+	+V	dissous	
Ion peroxynitrite	ONO_2^-	+V	dissous	
Dioxyde d'azote	NO_2	+IV	gaz	*(Teb = 21,4°C)*
Tétroxyde d'azote	N_2O_4	+IV	gaz	*(Teb = 21,4°C)*
Anhydride nitreux	N_2O3	+III	gaz	
Acide nitreux	HNO_2	+III	dissous	
Ion nitrite	NO_2^-	+III	dissous	
Ion nitrosonium	NO^+	+III	dissous	
Ion nitroacidium	$H_2NO_2^+$	+III	dissous	
Monoxyde d'azote	NO	+II	gaz	
Acide hypoazoteux	$H_2N_2O_2$	+I	dissous	
Ion hypoazotite	NO^-	+I	dissous	
Ion hyponitrite	$N_2O_2^{2-}$	+I	dissous	
Protoxyde d'azote	NO_2	+I	gaz	
Azote	N_2	0	gaz	
Hydroxylamine	NH_2OH	-I	gaz	
Imine	NH	-I	gaz ou dissous	
Ion hydroxylamonium	NH_2OH^+	-I	dissous	
Hydrazine	N_2H_4	-II	dissous	
Ion hydrazinium	$N_2H_5^+$	-II	gaz ou dissous	
Ammoniaque	NH_3	-III	gaz ou dissous	

Polishing by diamond disk

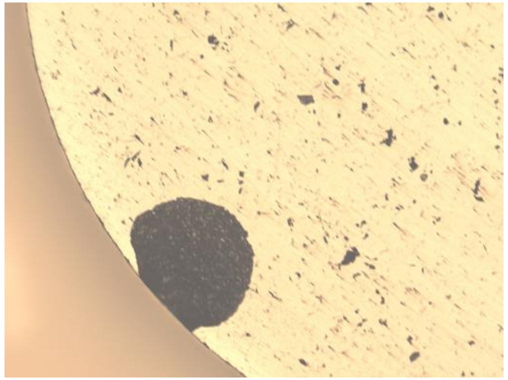


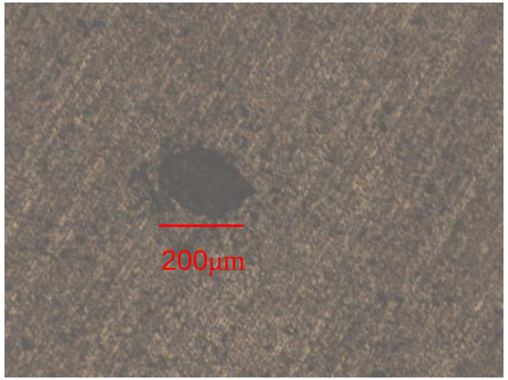


Sintered pellets
Densification rate (d_{geom}/d_{calc})

- $UO_2 \approx 91$ %
- $U_{0,9}Nd_{0,1}O_{2-x} \approx 91 - 95\%$
- $U_{0,9}Th_{0,1}O_{2-x} \approx 88 - 92$ %

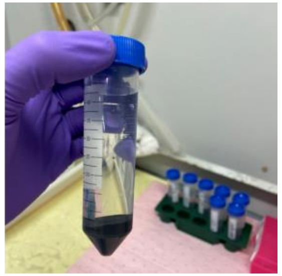
Structural imperfections : presence of cavities

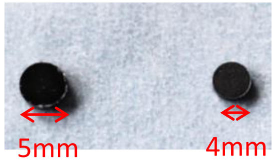




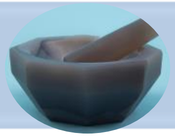
Appendix 4 – preparation of the sintered pellets

Oxalate precipitation → Thermal conversion to oxide → Polishing





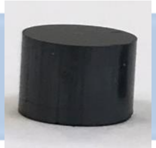
Washing (H_2O - EtOH) → Drying (T_{amb})



Grinding

Unixial pressing
Ø 5 mm, 500 MPa

Pellets



Calcination

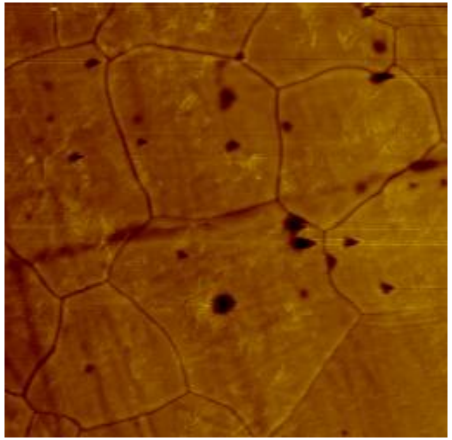
Ar/H_2 (4%)

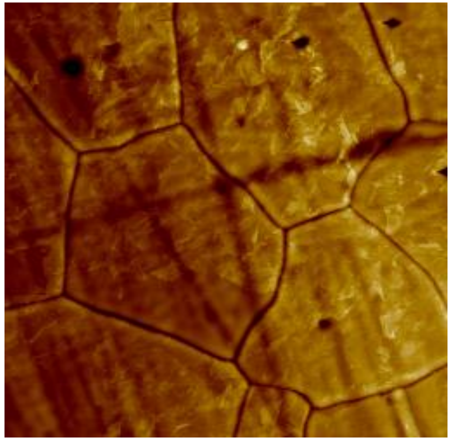
1600°C 4 hours

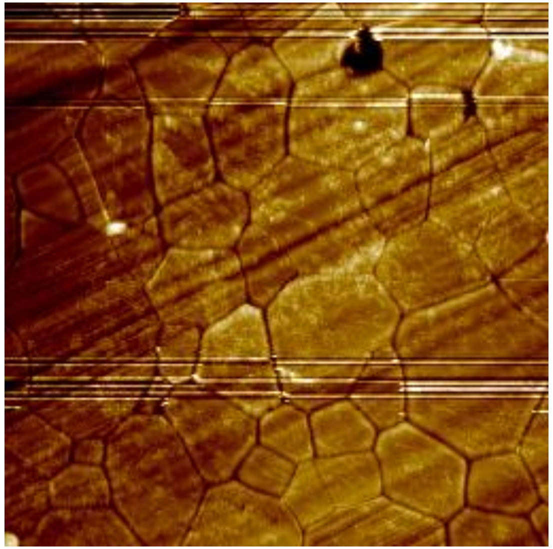
2°C/min

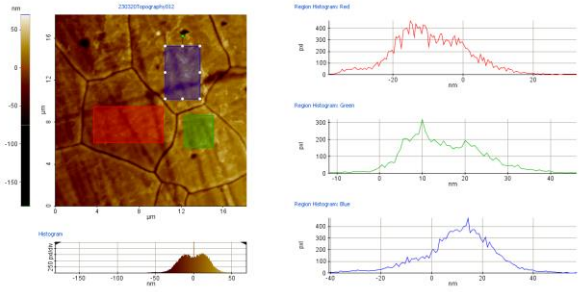
T_{Amb}

Appendix 5 : AFM characterization and roughness



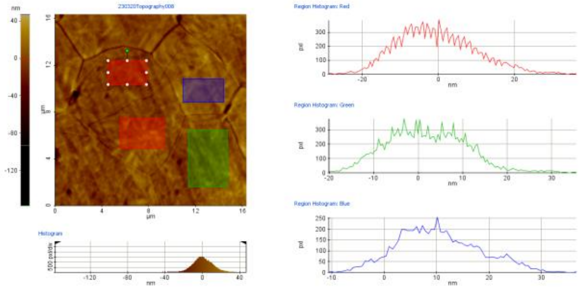






Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-38.252	32.205	-3.024	-9.727	70.458	10.164	8.131	68.770	-0.186	3.149
Green	-11.813	45.987	17.087	14.579	57.801	8.750	7.135	55.044	-0.382	3.007
Blue	-40.503	56.957	8.227	9.772	97.459	13.553	10.378	91.609	0.533	3.749
R-G	-26.439	-13.782	-20.111	-24.306	12.657	1.414	0.996	13.726	0.196	0.142
R-B	2.250	-24.752	-11.251	-19.499	-27.002	-3.389	-2.247	-22.839	-0.719	-0.600
G-B	28.689	-10.969	8.860	4.807	-39.659	-4.803	-3.243	-36.565	-0.915	-0.742



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-28.830	36.143	3.656	-0.839	64.973	10.141	8.182	62.301	-0.412	2.933
Green	-20.111	35.440	7.665	1.492	55.550	8.742	7.127	53.947	-0.286	2.980
Blue	-10.548	36.565	13.009	9.999	47.112	7.684	6.207	42.978	-0.300	2.660
R-G	-8.719	0.703	-4.008	-2.331	9.422	1.400	1.055	8.354	-0.116	-0.046
R-B	-18.282	-0.422	-9.352	-10.839	17.861	2.457	1.975	19.323	-0.112	0.274
G-B	-9.563	-1.125	-5.344	-8.507	8.438	1.057	0.920	10.969	0.004	0.320