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FROM RESEARCH TO INDUSTRY

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ABOUT NUCLEAR FUELS ON MARS

P. Martin¹, R. Bès^{1,4}, E. Geiger¹, V. Pennisi¹, P. Matheron¹, Y. Pontillon¹, B. Arab-Chapelet², M. Rivenet³, P.-L. Solari⁴, S. Schultig⁴, C. Martial¹, M. Strach¹, R. Belin¹, D. Prieur⁵

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⁵European Commission, Joint Research Centre, ITU, P.O. Box 2340, 76125 Karlsruhe, Germany

2015 SOLEIL USER MEETING

The MARS beamline is dedicated to the study of radioactive materials

⇒ in the future: Active sample (α , β , γ) up to 18.5 GBq (185 GBq per experiment)

⇒ Experimental station shielding (OK for XRD)

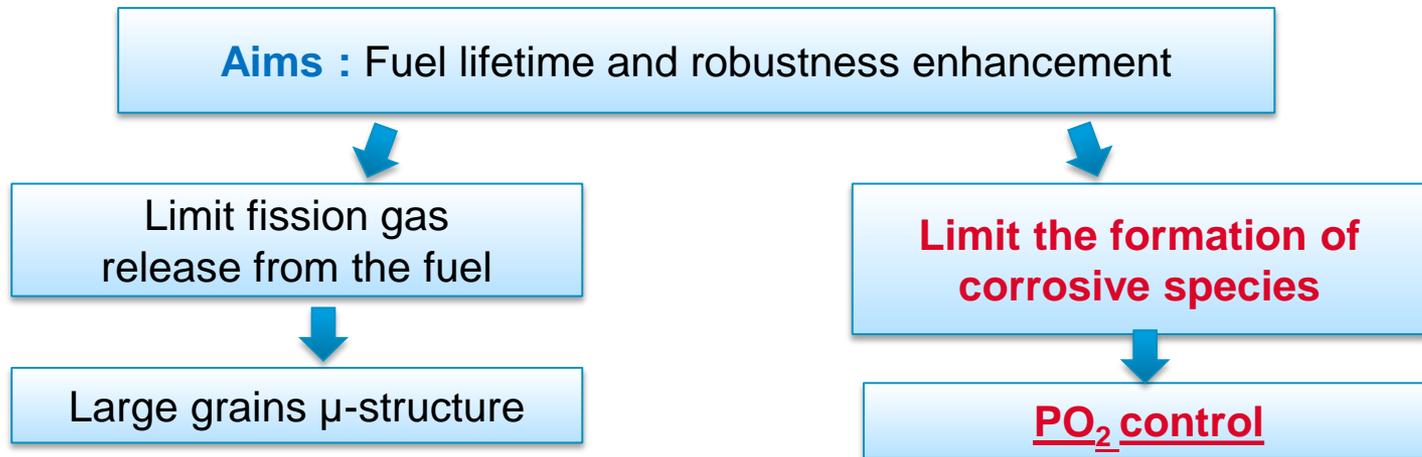
➔ Characterization (XRD & XAS) of irradiated fuel samples

XAS is a powerful tool to enhance the understanding of processes encountered in nuclear fuels ⇔ 3 examples of studies related to nuclear fuels:

1. Development of advanced nuclear fuel : UO_2 doped with Nb – *in situ* control of oxygen potential ⇔ (Vanessa Pennisi's Ph'd)
2. Mixed oxide samples – application of emission spectrometer
➔ Study of $(\text{U,Pu(Am)})\text{O}_{2+x}$ samples = GEN IV - Na fast reactor fuel & U-Pu-O phase diagram ⇔ (Michal Strach's Ph'd & René Bès's post-doc)
3. Fission products behavior in UO_2 -SIMFUEL samples (E. Geiger's Ph'd).

Pressurized Water Reactor (2nd generation) → Uranium Dioxide fuel

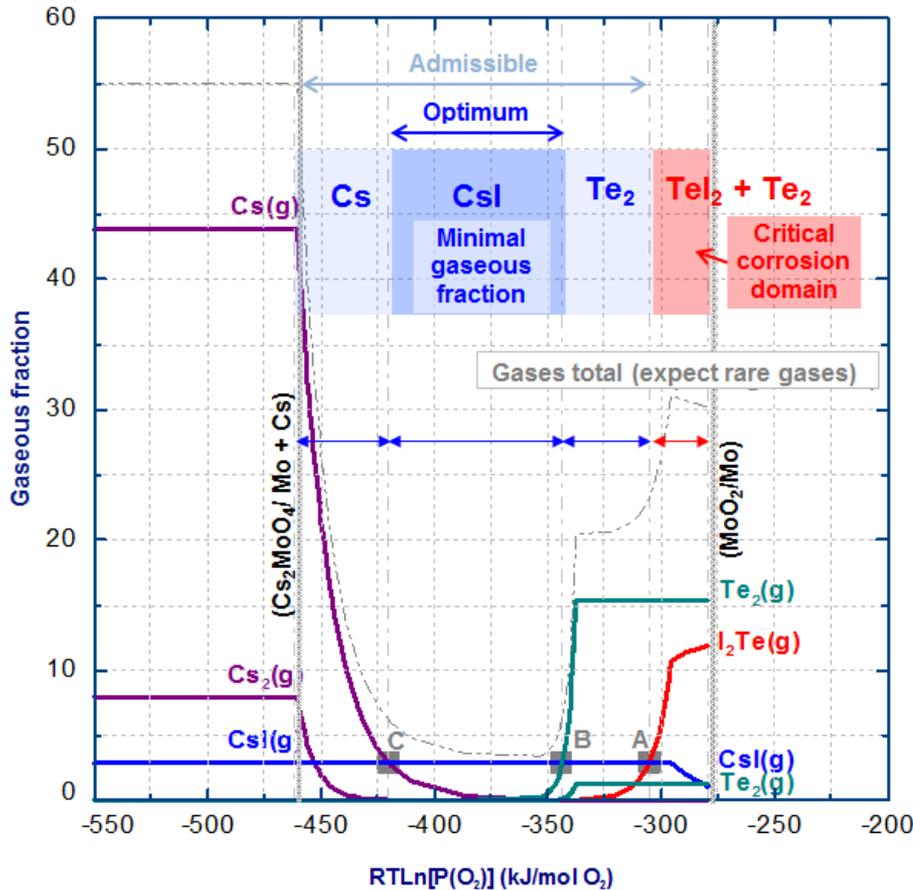
In nuclear oxide fuels, the **temperature** and the **oxygen partial pressure** (i.e. the oxygen potential) are essential parameters governing the thermo-mechanical evolution of the irradiated material.



In-situ control of PO₂ thanks to the buffer capacity of an oxido-reductive dopant present under two different oxidation states.

➔ **Study of the doping and fission products thermochemistry**

Fugacity profiles and speciation of major gaseous species in a UO_2 fuel as a function of oxygen potential
30 GWd/t U, 1500°C (FactSage 6.2)



Objective: Fuel operating in the most favorable oxygen potential area.

→ **Two selection criteria :**

- **Main :** Minimal gaseous fraction of corrosive Fission Products (FP)
- **Secondary :** Highest FP immobilization

➔ **Three areas are delimited :**

- An **unfavorable area**
 - Highest risk of corrosion.
- An **optimum area**
 - Minimal fraction of gaseous corrosive FP.
 - Maximal immobilization of the FP.
- An **intermediate area**
 - Limited risk of corrosion.

The reactivity of fission gas depends on PO_2

Criteria for the choice of the redox buffer:

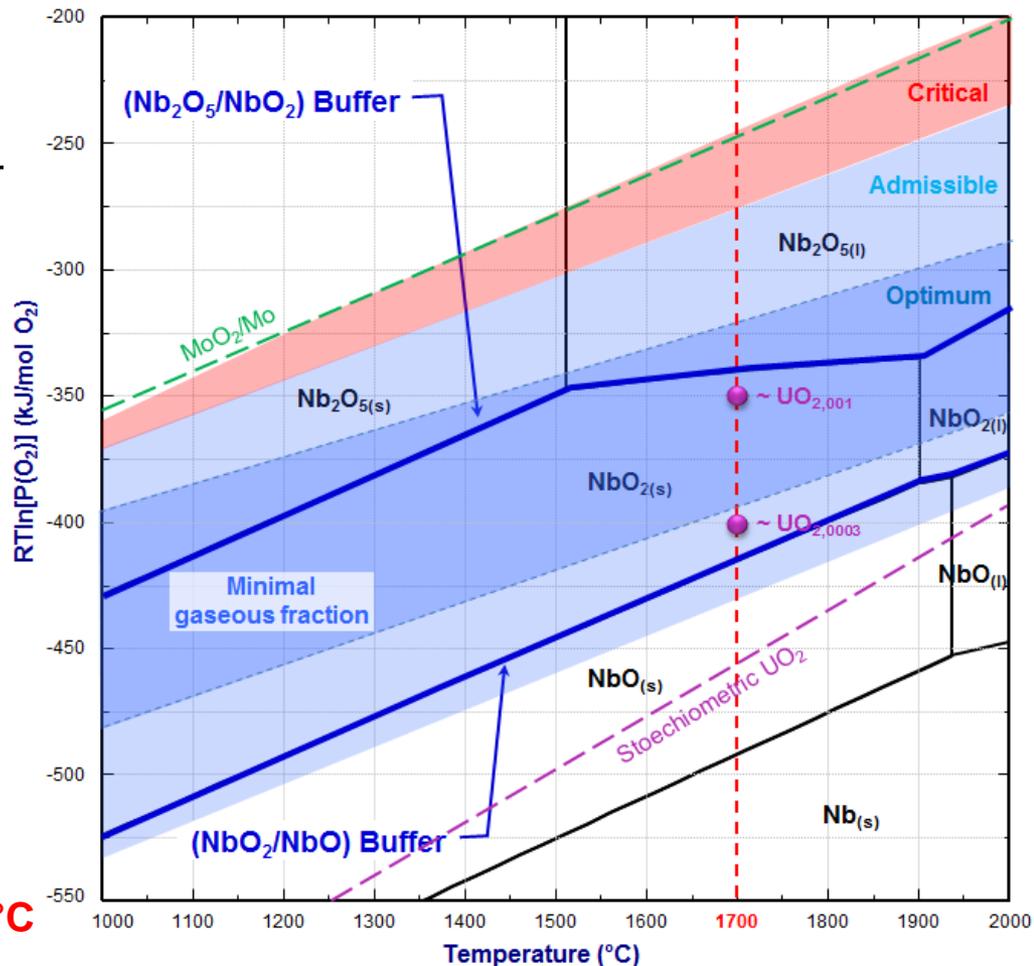
- Temperature range
- Buffering capacity
- Limited solubility in the UO_2 matrix (~1000-2000 ppm),
- Final properties of the un-irradiated fuel,...

Selected dopant : NIOBIUM

Potential redox buffers	Buffering capacity (mole O / mole Nb)
Nb_2O_5/NbO_2	0.5
NbO_2/NbO	1
$Nb_2O_5/NbO_2/NbO$	1.5

✓ **Redox reactions likely to be thermodynamically activated above 1000°C**

✓ **Liquid phase Nb_2O_5 at $T > 1500^\circ C$ (→ grain growth)**

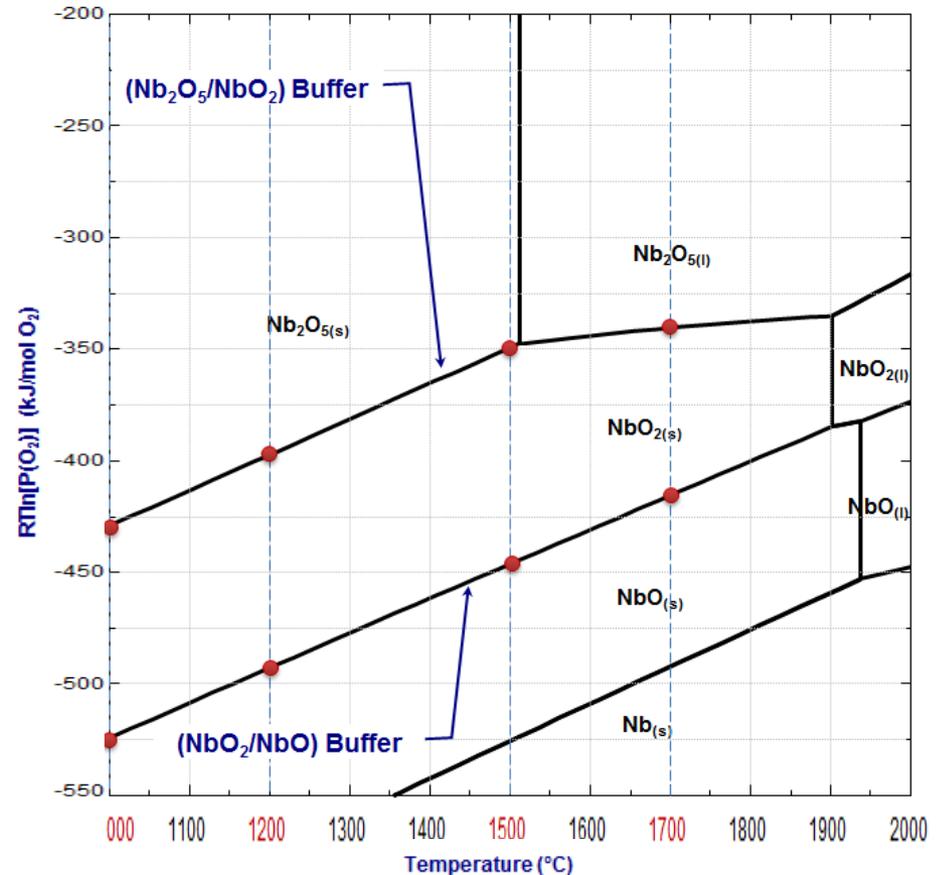
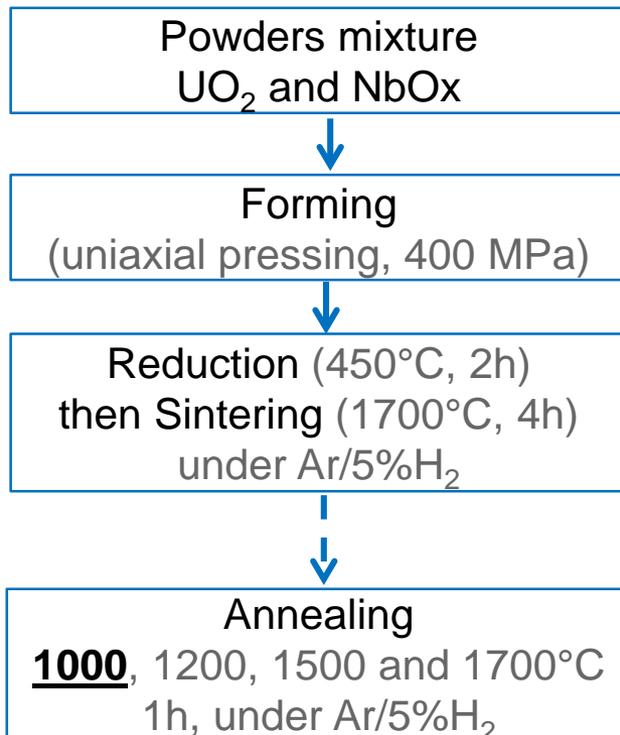


Niobium buffering systems position compared to the stability areas of the corrosive species

MANUFACTURING CONDITIONS

- Batches with different niobium compositions (50/50 %m. for the redox couples) :
 - $UO_2 + x \text{ wt\% (NbO}_2 + \text{NbO)}$
 - $UO_2 + x \text{ wt\% (Nb}_2\text{O}_5 + \text{NbO}_2)$

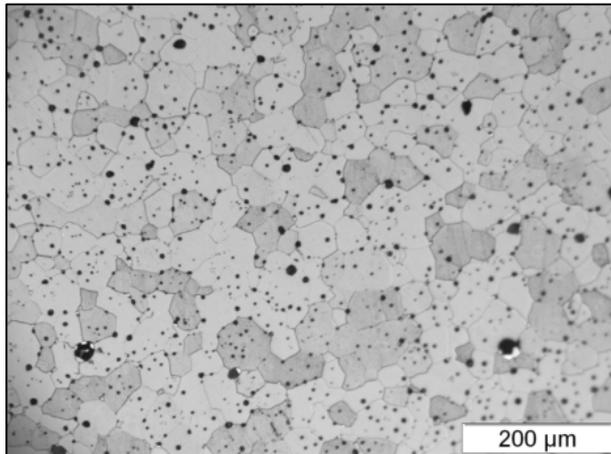
■ Niobium doped pellets manufacturing process :



Sintering conditions reported in Nb – U – O phase diagram: *Sintering conditions = red circles*

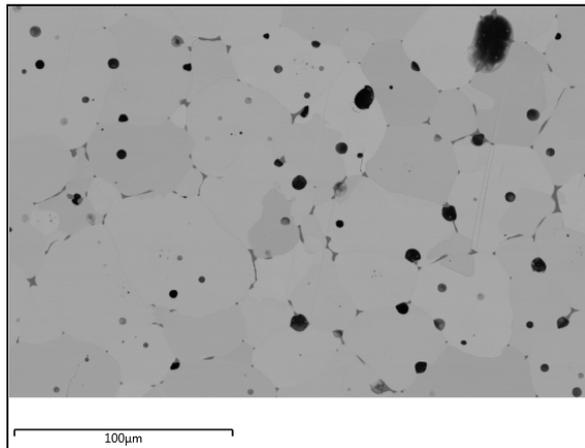
Ex: $\text{UO}_2 + 0.8 \text{ wt\% (NbO}_2 + \text{NbO)}$ pellets

→ Microstructures before annealing

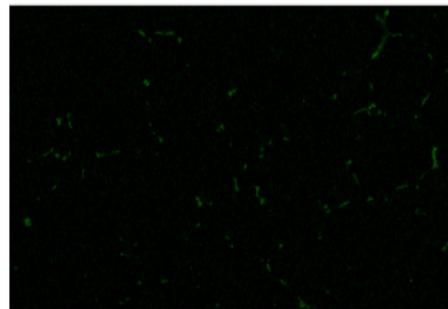


- Healthy pellets (no crack)
- Grain coarsening: grain size about $35 \mu\text{m}$ ($10 \mu\text{m}$ classical)
- High density: **94.2%Td**

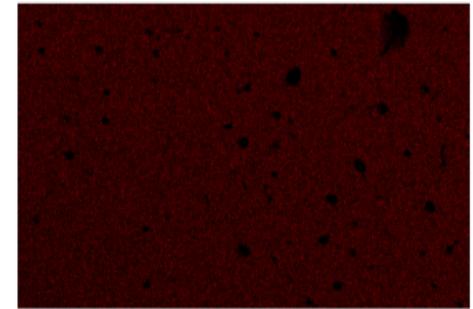
Elemental EDX maps



Nb L α 1



U M α 1

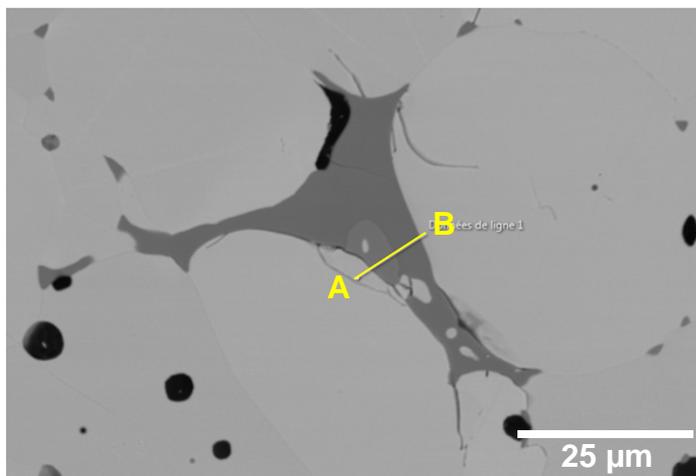


- Micrometer size Nb oxides precipitates at grain boundaries and porosities

Objective: Elemental composition of Nb-O precipitates

→ SEM + EDX analyzes

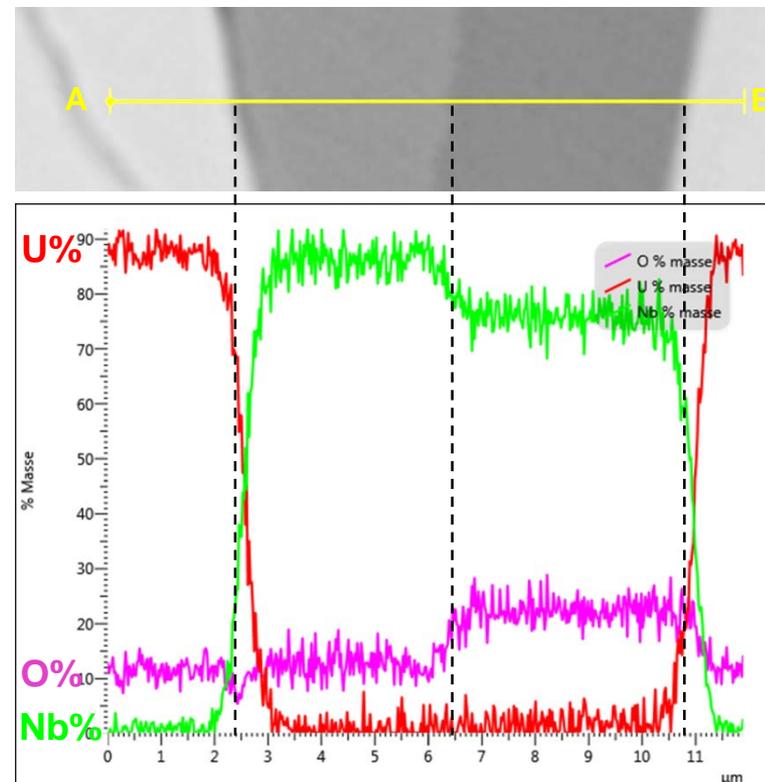
➤ Sample annealed at **1000°C**



- Two different color contrasts
- Change of the niobium content from one grey to another (composition line)
- *Presence of two different niobium/oxide ratio domains*
- *2 phases or more complex system ?*

➔ **μ-XAS experiment**

Profile and element contents



Same conclusion for annealing at **1200°C**
(two different niobium oxide phases)

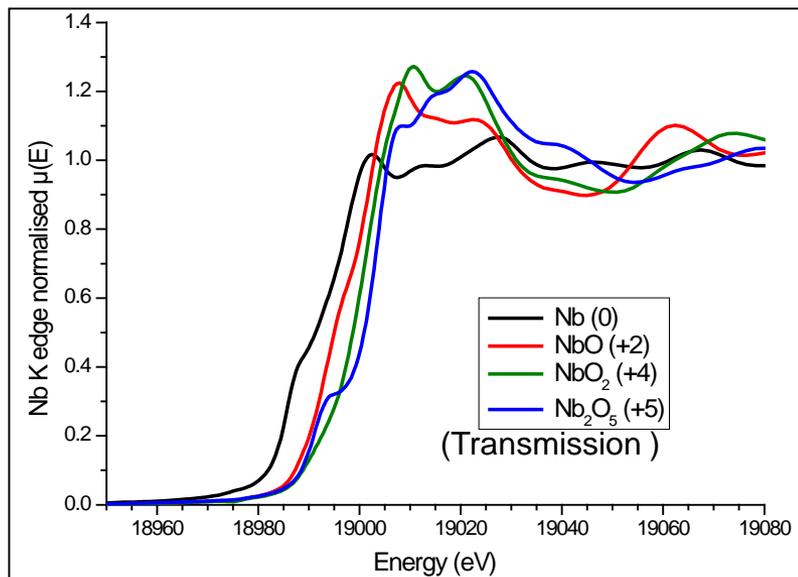
Experiment performed on MARS – 4 days in mid-November

- Nb K edge (18986 eV)
- Micro-focussing using 2 mirrors in K&B geometry $\rightarrow 10^9$ ph.s⁻¹ at 19000 eV
- μ -XRF elemental mapping & μ -XAS using a beam 12x13 μm^2

\Leftrightarrow U L α (13614 eV) & Nb K (16615 eV)

Aims:

- Nb chemical state in precipitates $\rightarrow \mu$ -XANES = buffer effectiveness
- Nb speciation inside UO₂ matrix $\rightarrow \mu$ -XANES + μ -EXAFS

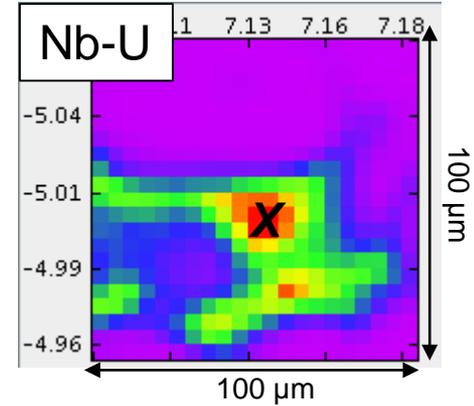
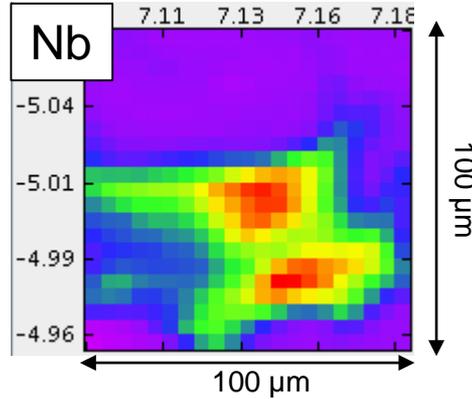
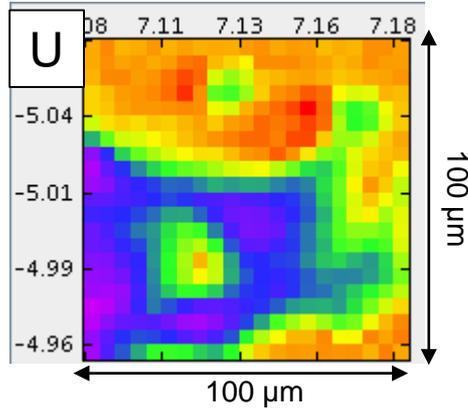


Reference	E_0 (eV)
Nb(0)	18986.0
NbO - Nb(+2)	18994.1
NbO ₂ - Nb (+4)	19001.7
Nb ₂ O ₅ - Nb (+5)	19004.0

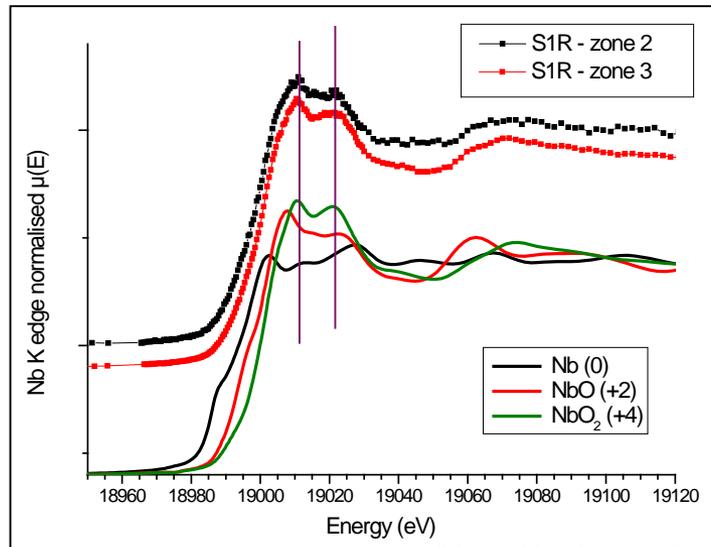
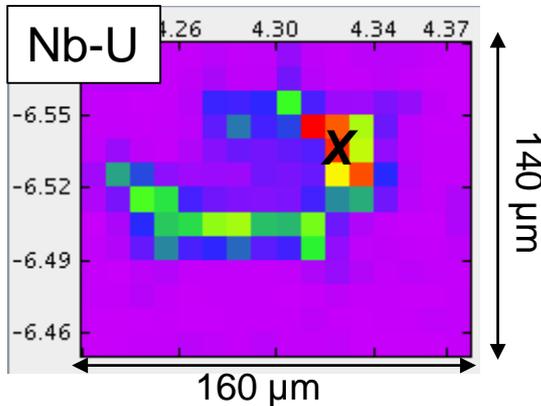
Sample S1: $\text{UO}_2 + 0.8 \text{ wt\% (NbO}_2 + \text{NbO)}$ as fabricated

2 precipitates studied

Zone3



Zone2



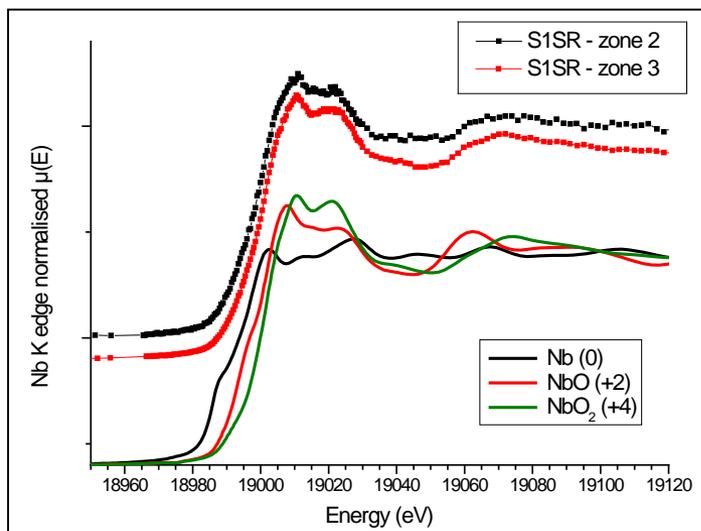
- Spectra similar
- Similarity with NbO_2



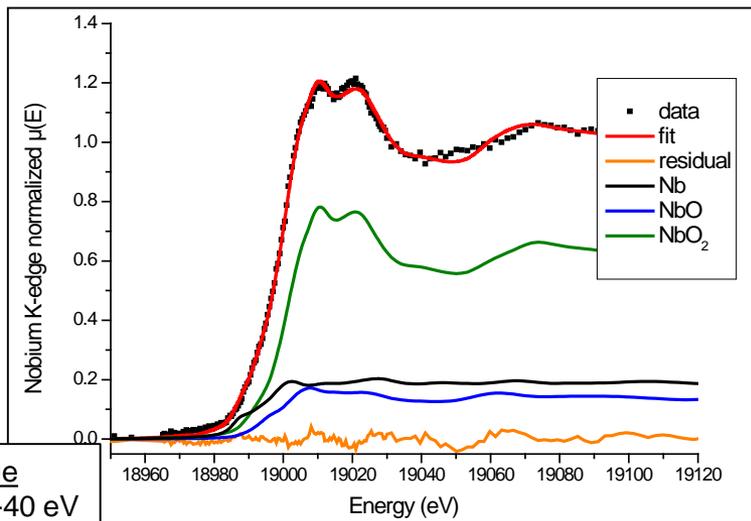
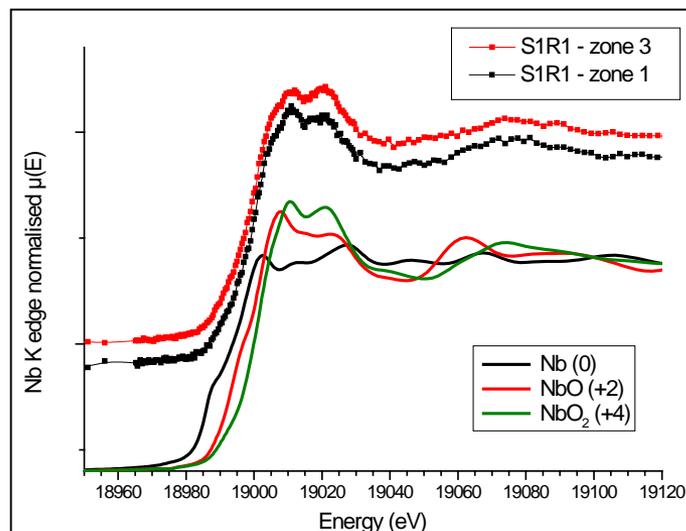
Linear combination fit

Sample S1: UO₂ + 0.8 wt% (NbO₂ + NbO)

As manufactured



Annealed 1 hour at 1000°C

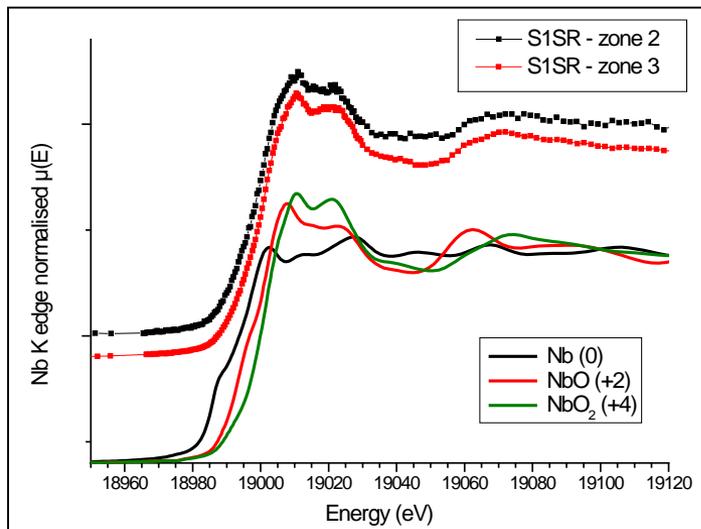


Range
-30 < E₀ < +40 eV

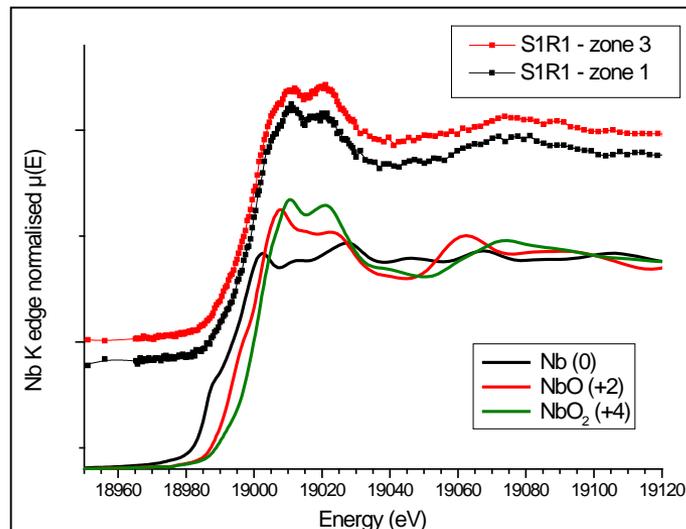
- ➔ E₀ systematically between NbO and NbO₂ positions
- ➔ Shoulder at low energy = metallic Nb ?
- ➔ μ-XANES spectra are reproduced by linear combination of Nb + NbO and NbO₂

Sample S1: UO₂ + 0.8 wt% (NbO₂ + NbO)

As manufactured



Annealed 1 hour at 1000°C



	Nb	NbO	NbO ₂	R _{factor}
Zone 2	0.12	0.43	0.45	1.0e-3
Zone 3	0.07	0.27	0.67	4.0e-4

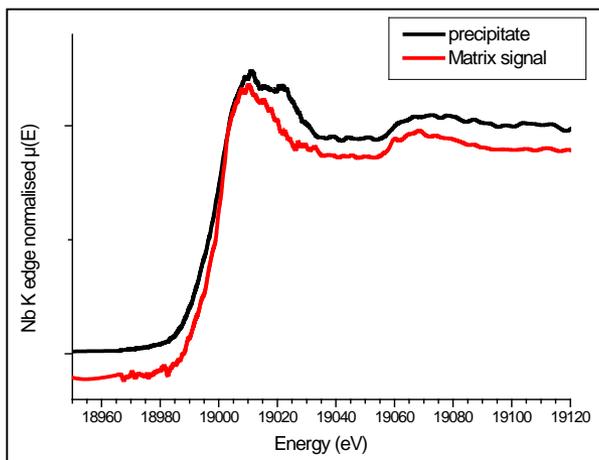
	Nb	NbO	NbO ₂	R _{factor}
Zone 3	0.19	0.19	0.62	1.0e-3
Zone 1	0.14	0.23	0.64	2.0e-3

Uncertainties
0.03

- ➔ The two phases NbO₂/NbO are observed <=> buffering capacity confirmed
- ➔ Unexpected metallic Nb signal systematically observed !

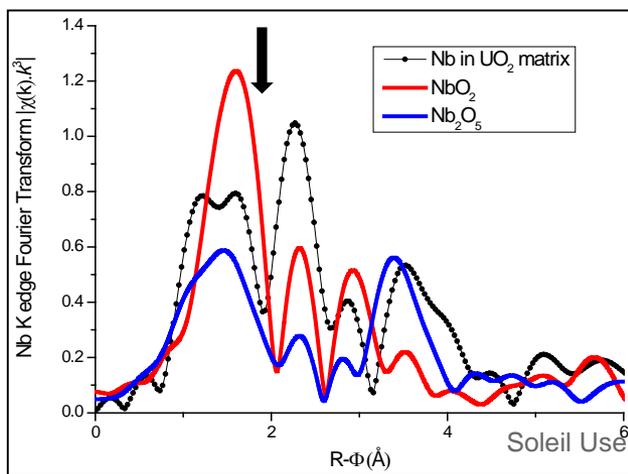
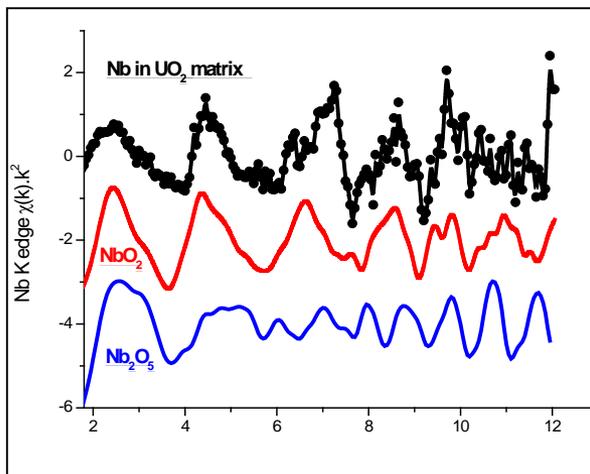
μ -XANES & μ -EXAFS on the matrix :

- same spectra observed on every sample (S1 and S2, annealed or not)



- ➔ Different with known Nb oxides \Leftrightarrow \neq symmetry
- ➔ Consistent with Nb inside UO_2 fluorite structure ?
- ➔ E_0 position \sim between Nb^{+4} / Nb^{+5}

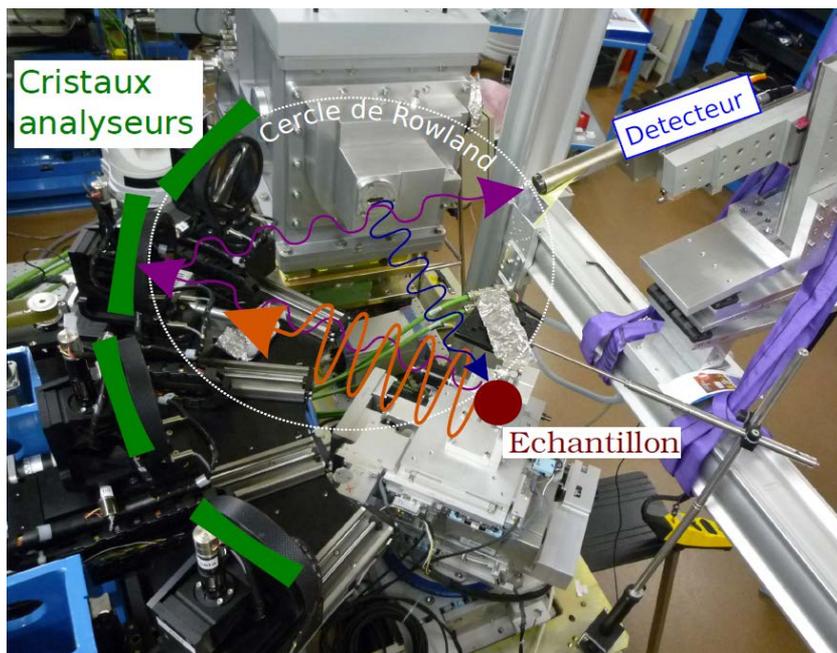
μ -EXAFS results \Rightarrow signal up to 11.5 \AA^{-1}



- Signal from hidden precipitates can not be excluded
- Longer Nb-O distance (Nb-O $\leq 2.15 \text{ \AA}$ in Nb oxides)
- \Rightarrow U-O distance in UO_2 is 2.37 \AA .
- \Rightarrow **Work in progress**

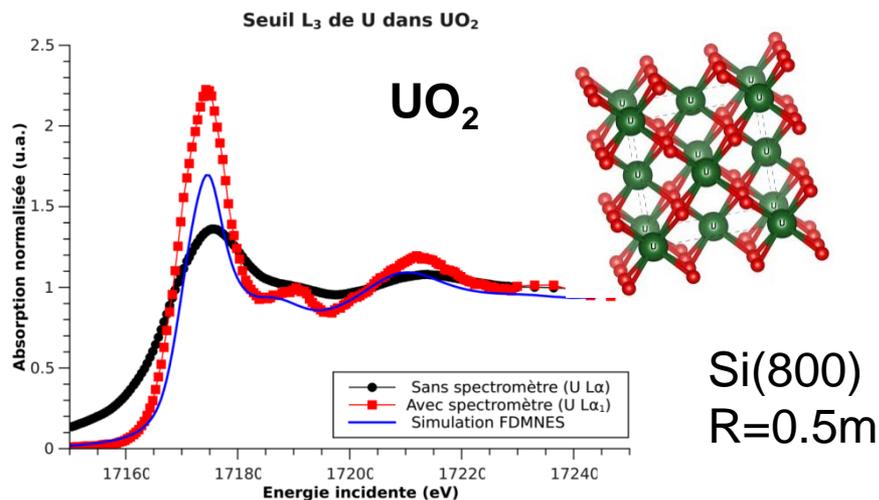
Use of an emission spectrometer with radioactive materials ?

- Remove Bragg peaks and isolate emission lines for diluted elements in fuels: dopant (Cr, Gd), fission products (Xe, Kr, Cs, Ba, ...)
- Radioactive background, emission lines due to other elements



Up to 4 crystals (Si, Ge)

Lifetime broadening reduced ⇔ XANES resolution enhancement



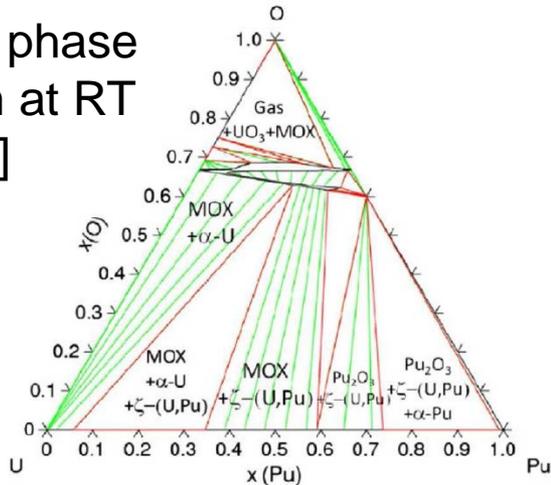
L_3 edge (17,166 eV) core-hole = 8.13 eV
 $L\alpha_1(3d_{5/2} \rightarrow 2p_{3/2}) \Rightarrow$ resolution = 3.55 eV

First experiment on Mixed oxides samples in July 2014

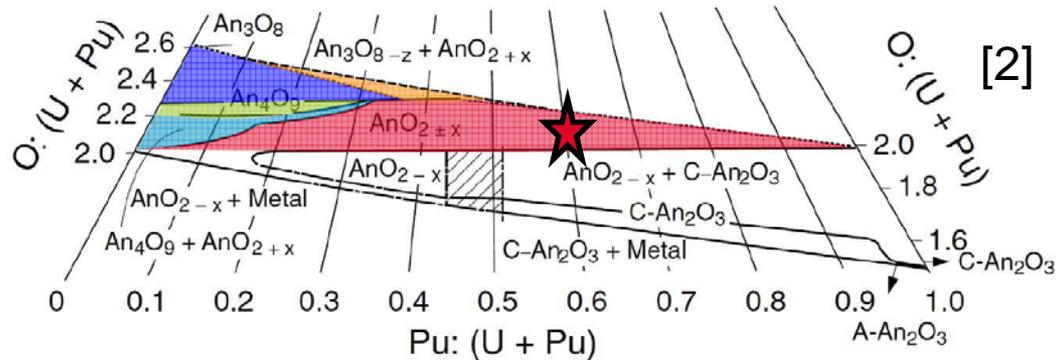
- UO_2 , U_3O_8 , PuO_2 containing 1.7 % Am (due to ^{241}Pu decay)
- Dense sintered $(\text{U}_{0.45}\text{Pu}_{0.542}(\text{Am}_{0.008}))\text{O}_2$ pellets prepared with conventional powder metallurgy process

Context: U-Pu-O phase diagram

U-Pu-O phase diagram at RT [1]



The hyper-stoichiometric domain at RT



M_4O_9 + hexagonal M_3O_8 biphasic domain – Boundaries ?

Pu content in M_3O_8 controversial

M_3O_8 + MO_{2+x} biphasic domain ?

[1] C. Guéneau et al., J. Nucl. Mater. 419 (2011) 145-167

[2] Sari et al. , J. Nucl. Mater. 35 (1970) 267-77

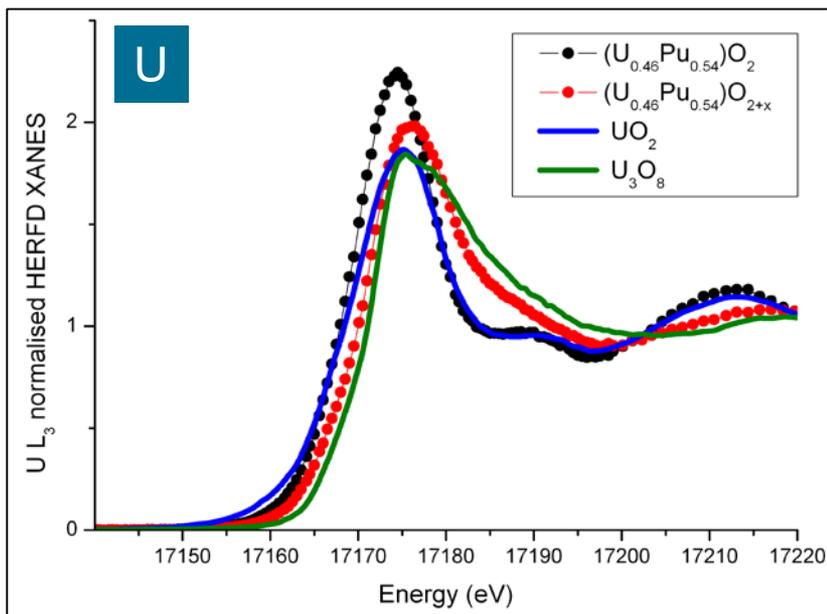
Study of U-Pu-O phase diagram

- HT-XRD experiments performed at the LEFCA facility (CEA Cadarache)

- Hyper-stoichiometric domain : up to 1500°C under air

⇒ $(U_{0.45}Pu_{0.542}(Am_{0.008}))O_{2+x}$ domain = MO_{2+x} phase at RT

⇒ U, Pu and Am L_3 HERFD XANES



Sample	E_0 (eV)
$UO_2 - U^{4+}$	17170.3
$U_3O_8 - U^{5+}+U^{6+}$ [1]	17172.2
$(U_{0.45}Pu_{0.55})O_2$	17170.2
$(U_{0.45}Pu_{0.55})O_{2+x}$	17171.5

- $(U_{0.45}Pu_{0.55})O_2 \Rightarrow UO_2 = U^{4+}$
- $(U_{0.45}Pu_{0.55})O_{2+x}$
 ⇒ between UO_2 & U_3O_8
 ⇒ Mixed U valence = +4/+5/+6

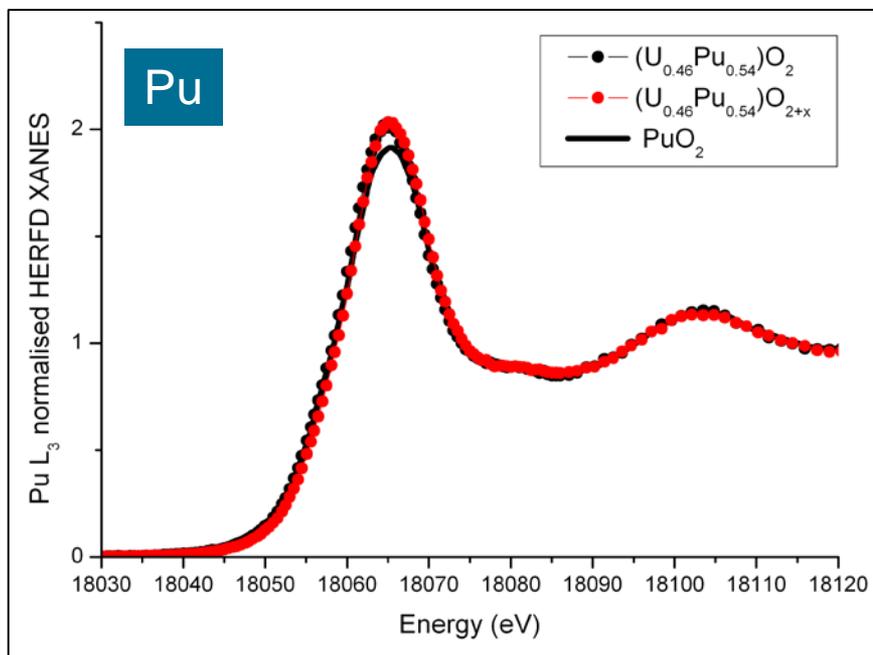
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⇒ U, Pu and Am L_3 HERFD XANES



- No modification = PuO_2 position
- As expected Pu^{+4}
- Cubic fluorite symmetry around Pu is not modified \Leftrightarrow different compared to U

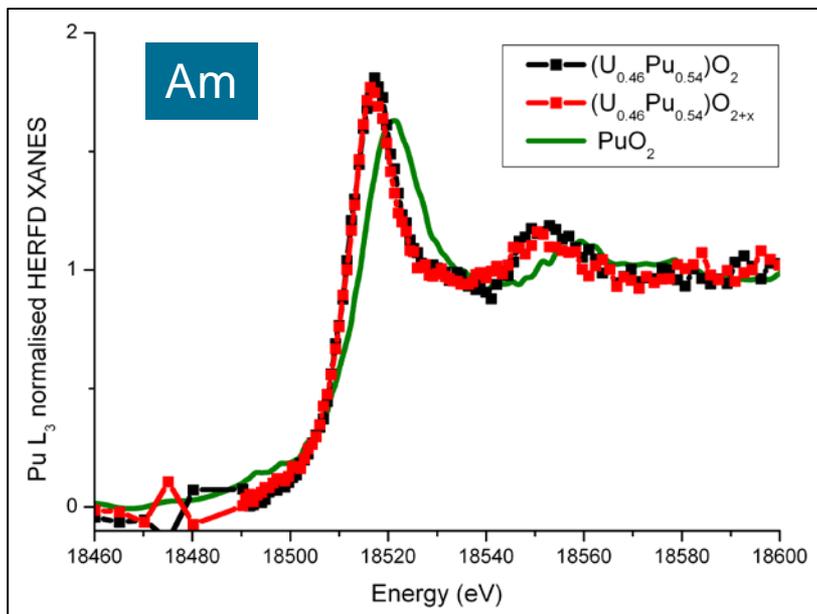
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⇒ U, Pu and Am L_3 HERFD XANES



Sample	E_0 (eV)
PuO_2	18515.7
$(U_{0.45}Pu_{0.55})O_2$	18512.1
$(U_{0.45}Pu_{0.55})O_{2+x}$	18512.2

- Ref = Am in PuO_2 (^{241}Pu decay)
- Reduction to Am^{+3}
- Am not modified by oxidation process !!

Am^{3+} in hyper-stoichiometric MOX

Study of U-Pu-O phase diagram

- HT-XRD experiments performed at the LEFCA facility (CEA Cadarache)

- Hyper-stoichiometric domain : up to 1500 °C under air

⇒ $(U_{0.45}Pu_{0.542}(Am_{0.008}))O_{2+x}$ domain = MO_{2+x} phase at RT

⇒ U, Pu and Am L_3 HERFD

Conclusion

- Actinides emission line of each actinide was successfully isolated
- The stoichiometric MOX = fluorine structure $MO_2 = U^{+4} - Pu^{+4} + Am^{+3}$
- The hyper-stoichiometric is more complex than expected compared to XRD
=> mixed valence $U^{+4} - U^{+5} - U^{+6} / Pu^{+4} / Am^{+3} \Leftrightarrow MO_{2+x}$ domain
- Study of different Pu content => M_3O_8 domain

During a severe accident, irradiated nuclear fuels are submitted to High Temperature (>3000K) + Oxidizing/reducing atmosphere
ex: Fukushima Daiichi (Japan 2011)

The determination of the term source (amount of radionuclide released from the core) is directly connected to the fission products (FP) behavior

- FP chemical state evolution during the accident and identification of intermediary phases
- ➔ UO₂ sample doped with stable non volatile FP during manufacturing
➔ Preparation of future experiment on spent fuels

Sample composition

Burnup (GWd/t)	Composition (At. %)										
	Ba	Ce	La	Mo	Sr	Y	Zr	Rh	Pd	Ru	Nd
76	0.26	0.61	0.20	0.51	0.13	0.06	0.60	0.03	0.42	0.64	0.91

Sample annealed 1 hour at 1700°C under Ar/H₂

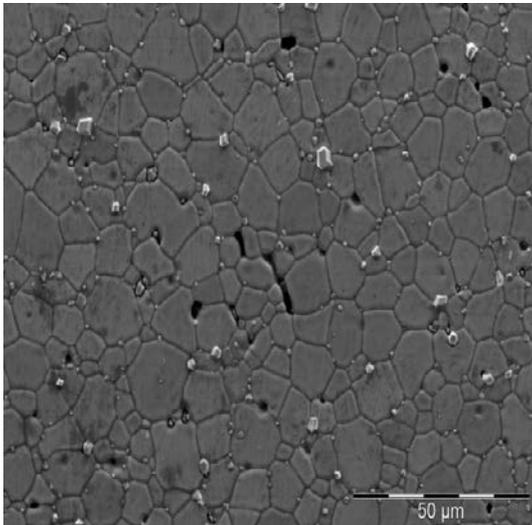
First μ -XANES experiment on MARS = 11/2014

Focused on Mo behavior

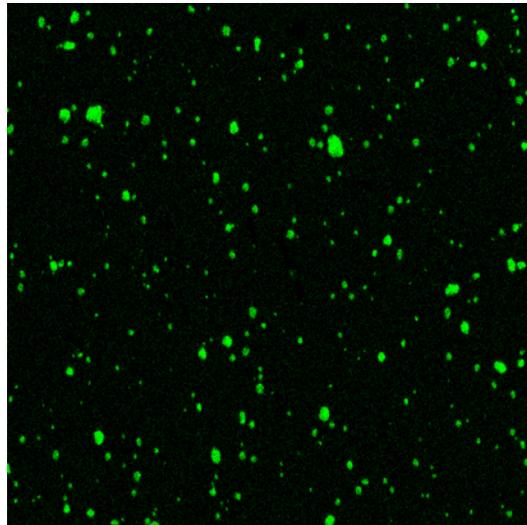
\Rightarrow Mo K edge (20000 keV)

\Rightarrow μ -XRF & μ -XANES \Leftrightarrow $6 \times 7 \mu\text{m}^2$ with $5 \cdot 10^8 \text{ ph.s}^{-1}$ at 20 keV

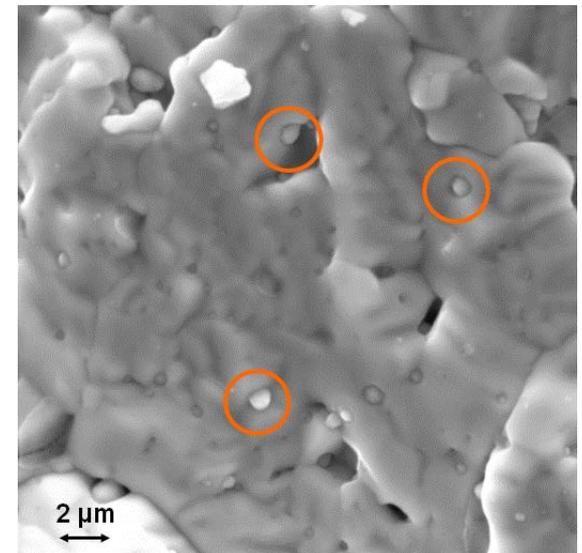
SEM picture



SEM/EDS Mo L α map

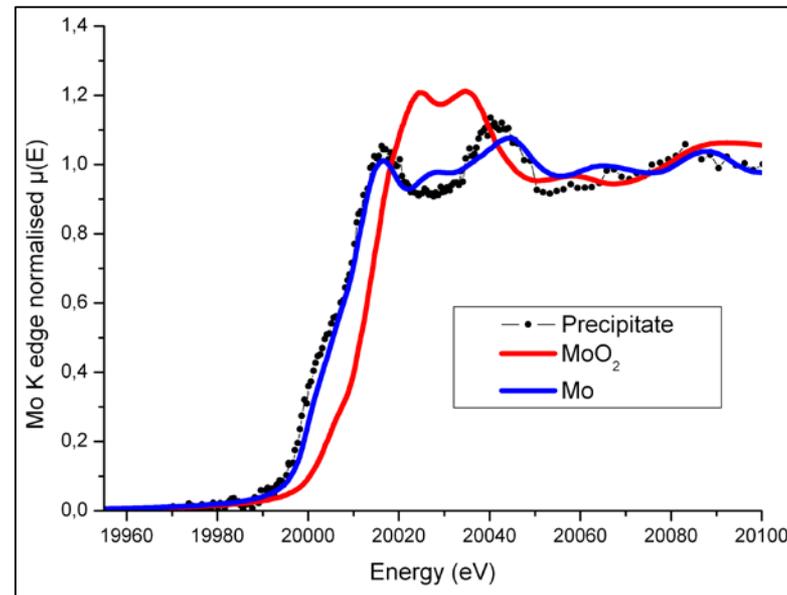
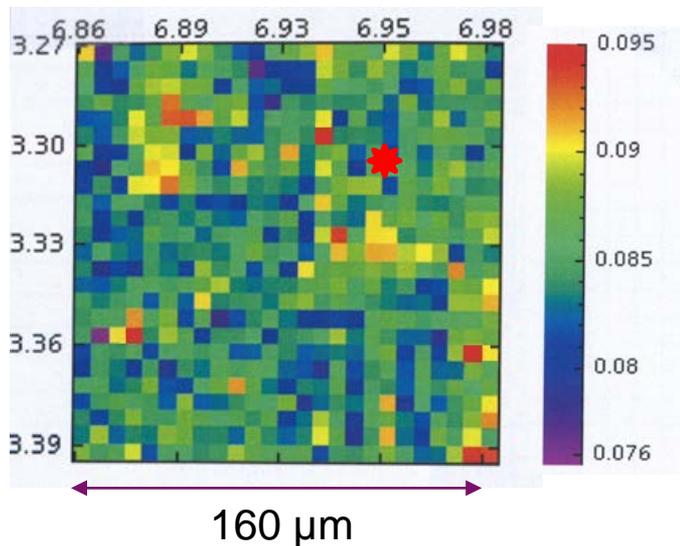


UO $_2$ spent fuel



First μ -XANES experiment on MARS = 11/2014

Focused on Mo behavior => μ -XRF & μ -XAS ($6 \times 7 \mu\text{m}^2$ 5×10^8 Ph/s at 20 keV)



Mo is mostly metallic but difference observed most probably due to association with other fission products (Ru, ...)

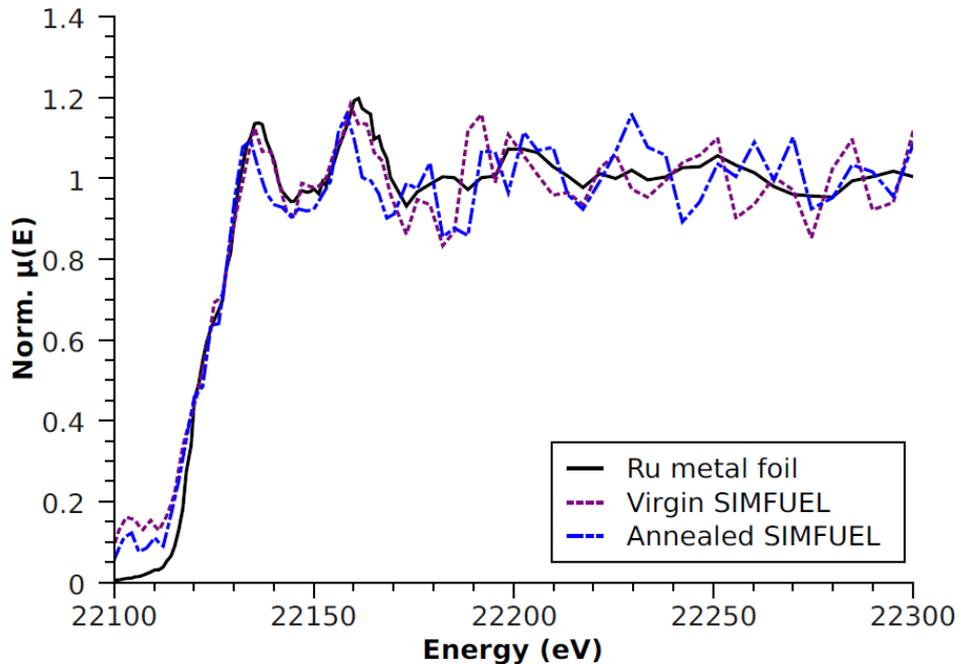
=> More details during Ernesto Geiger presentation (Chemistry session at 10h30)

Thank for your attention

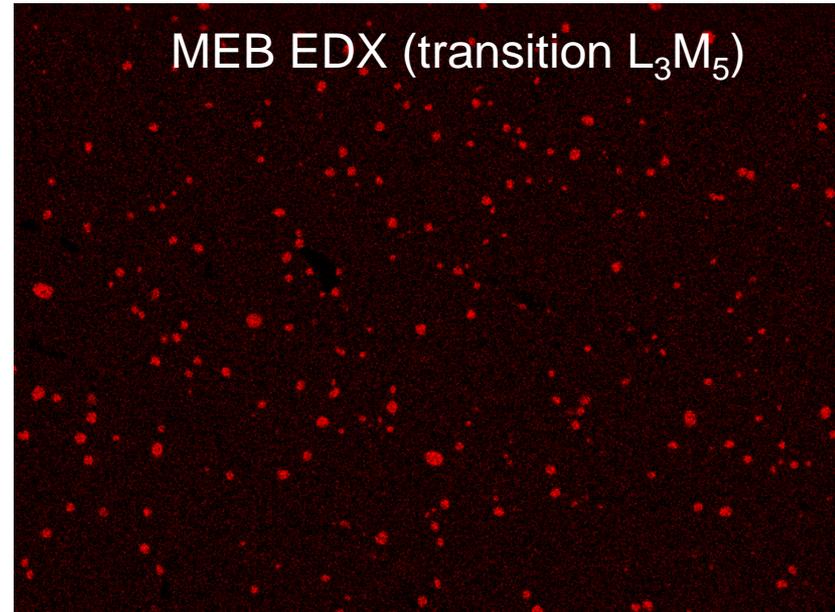
Ruthenium K-edge

- Form clusters (with Mo)
- 1 transition collected (K-L₃)

Ru K α_1 HERDF-XANES



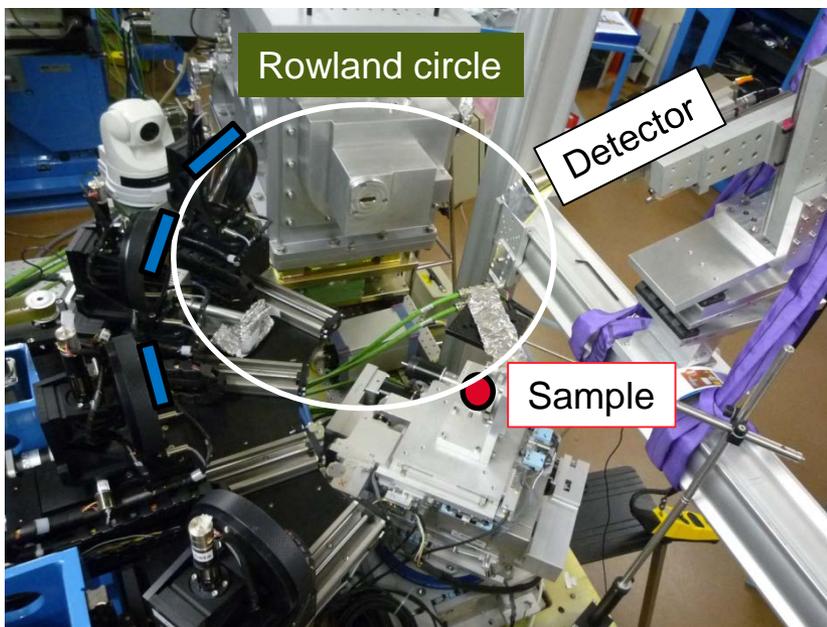
MEB EDX (transition L₃M₅)



- No evolution of Ru local environment
- **Metallic Ru**
- Probable mixing of **Mo/Ru metals**
- Ab initio calculations under progress

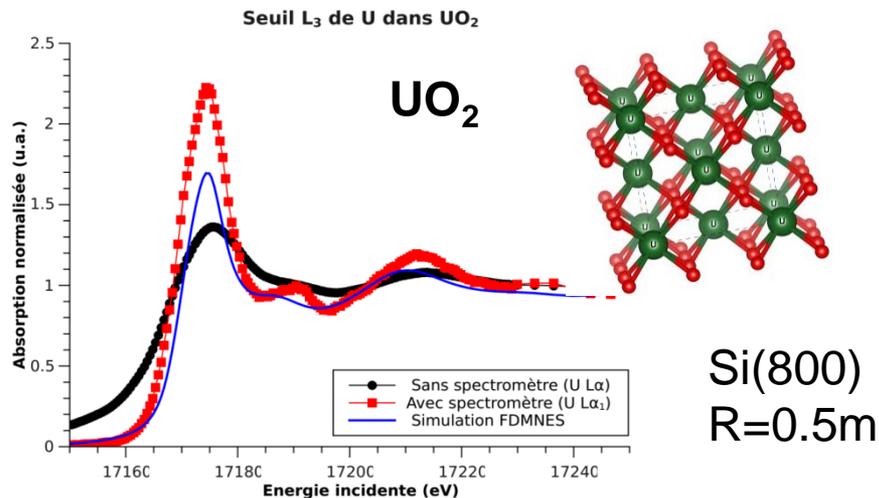
Use of an emission spectrometer with radioactive materials ?

- Remove Bragg peaks and isolate emission lines for diluted elements in fuels: dopant (Cr, Gd), fission products (Xe, Kr, Cs, Ba, ...)
- Radioactive background, emission lines due to other elements



Up to 4 crystals (Si, Ge)

Lifetime broadening reduced ⇔ XANES resolution enhancement



L_3 edge (17,166 eV) core-hole = 8.13 eV
 $L\alpha_1(3d_{5/2} \rightarrow 2p_{3/2}) \Rightarrow$ resolution = 3.55 eV