About nuclear fuels on MARS

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FROM RESEARCH TO INDUSTRY

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ABOUT NUCLEAR FUELS ON MARS

P. Martin[1], R. Bès[1,4], E. Geiger[1], V. Pennisi[1], P. Matheron[1], Y. Pontillon[1], B. Arab-Chapelet[2], M. Rivenet[3], P.-L. Solari[4], S. Schultig[4], C. Martial[1], M. Strach[1], R. Belin[1], D. Prieur[5]

[1]CEA, DEN, DEC, Centre d'études nucléaires de Cadarache, Saint Paul Lez Durance, 13108, France

[2] CEA, DEN, DRCP, Centre d'études nucléaires de Marcoule, Bagnols-sur-Cèze, 30207, France

[3] Univ. Lille Nord de France, Unité de Catalyse et de Chimie du Solide, UCCS, UMR CNRS 8181, ENSCL-USTL, BP 90108, 59652 Villeneuve d'Ascq Cedex, France

[4] Synchrotron SOLEIL, Ligne de lumière MARS, L'Orme des Merisiers, Saint Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

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

2015 SOLEIL USER MEETING

CONTEXT

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

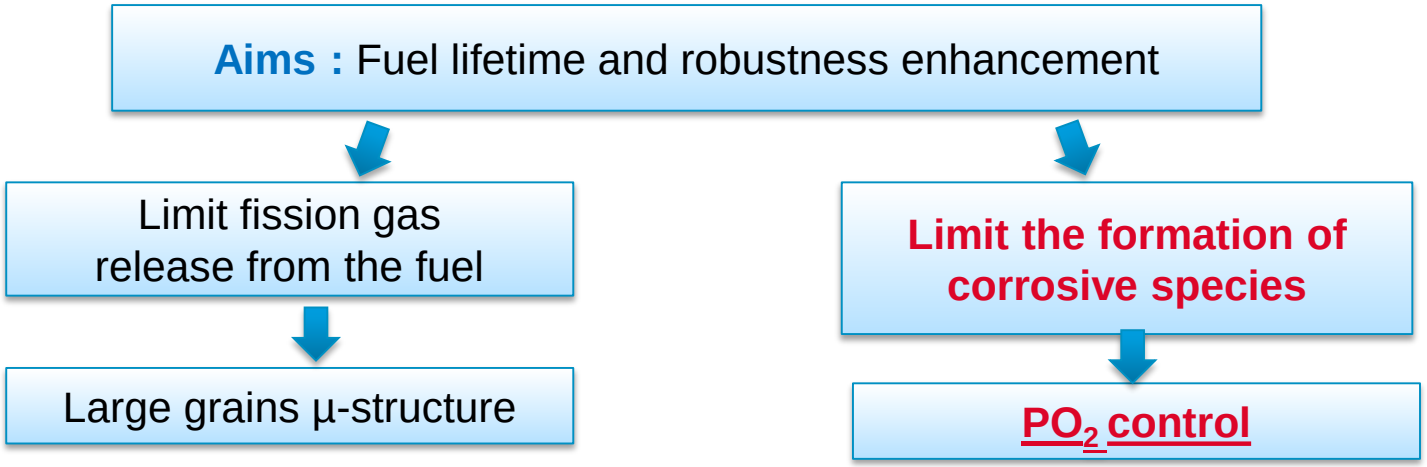
   ➔ Study of (U,Pu(Am))O_{2+x} samples = GEN IV - Na fast reactor fuel & U-Pu-O phase diagram ⇔ (Michal Strach's Ph'd & René Bès's post-doc)

3. Fission products behavior in UO_2-SIMFUEL samples (E. Geiger's Ph'd).

UO_2 DOPED WITH NB - CONTEXT

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.

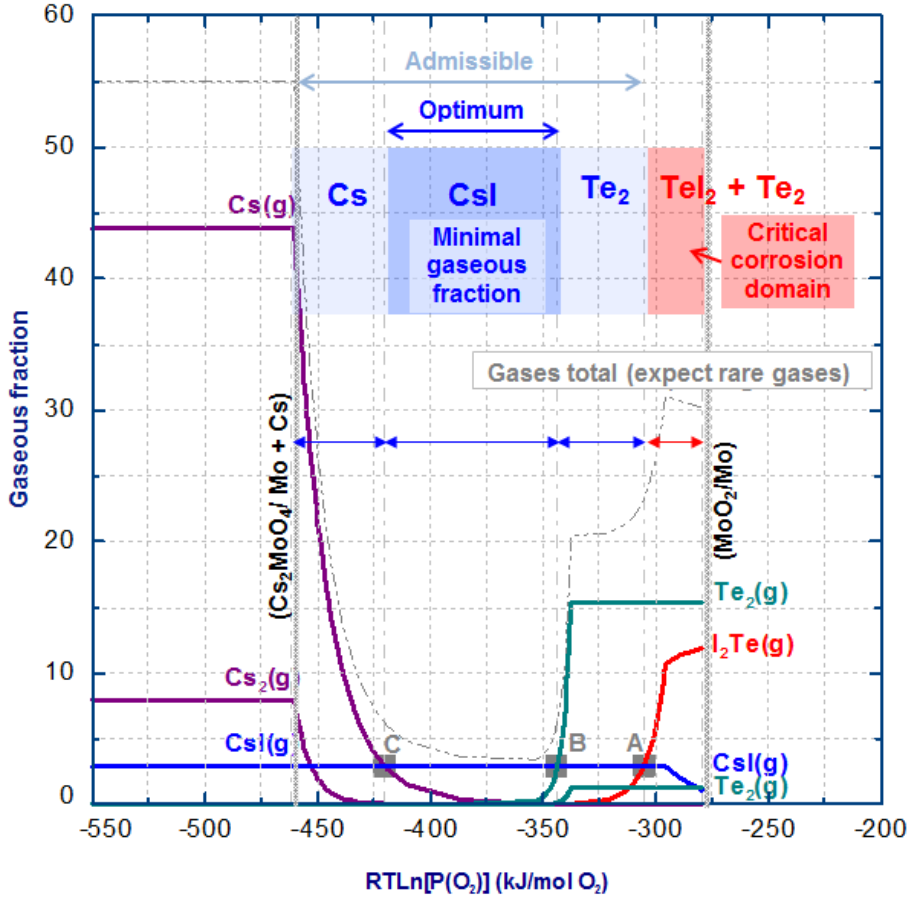


In-situ control of PO_2 thanks to the buffer capacity of an oxido-reductive dopant present under two different oxidation states.

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

DETERMINATION OF THE RANGE OF OXYGEN POTENTIAL

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)



The reactivity of fission gas depends on PO_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.

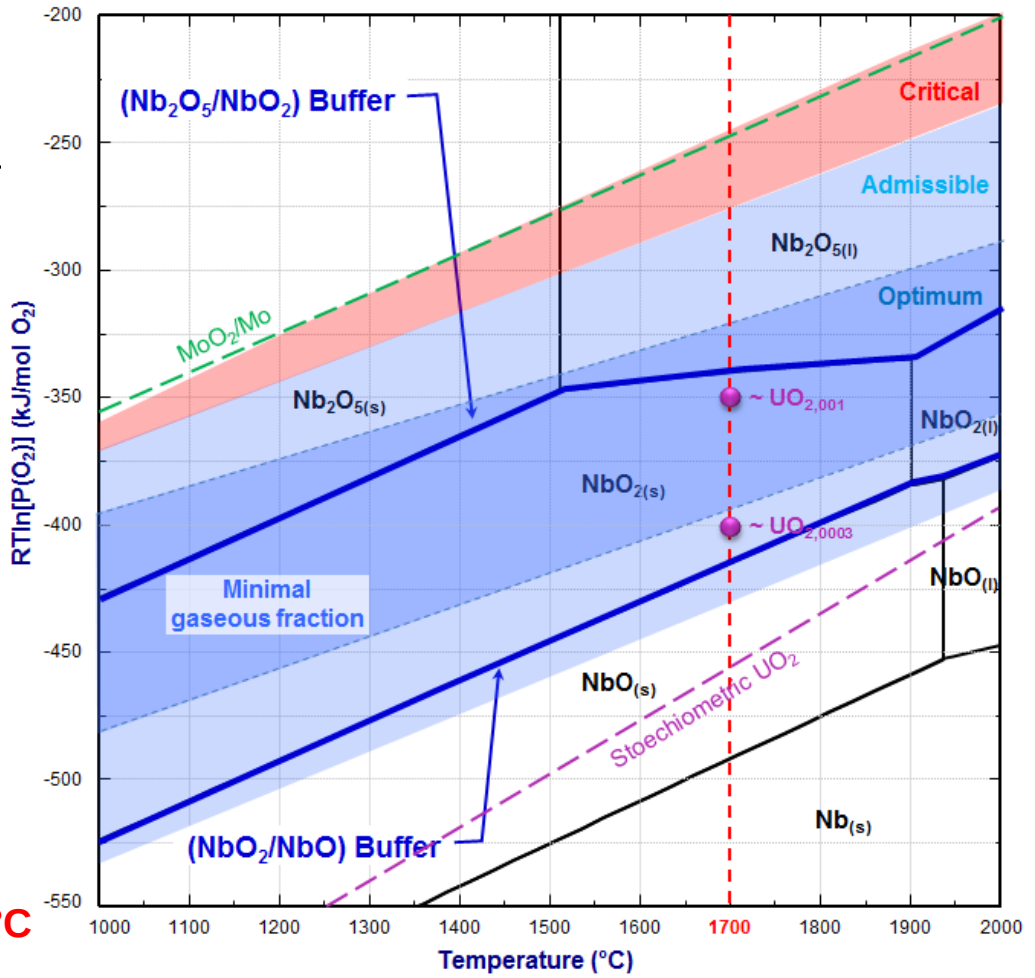
CHOICE OF THE REDOX BUFFER

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



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

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

✓ **Liquid phase Nb_2O_5 at T > 1500°C (→ grain growth)**

MANUFACTURING CONDITIONS

- Batches with different niobium compositions (50/50 %m. for the redox couples) :
  - UO_2 + x wt% (NbO_2 + NbO)
  - UO_2 + x wt% (Nb_2O_5 + NbO_2)

- Niobium doped pellets manufacturing process :

Powders mixture
UO_2 and NbOx

↓

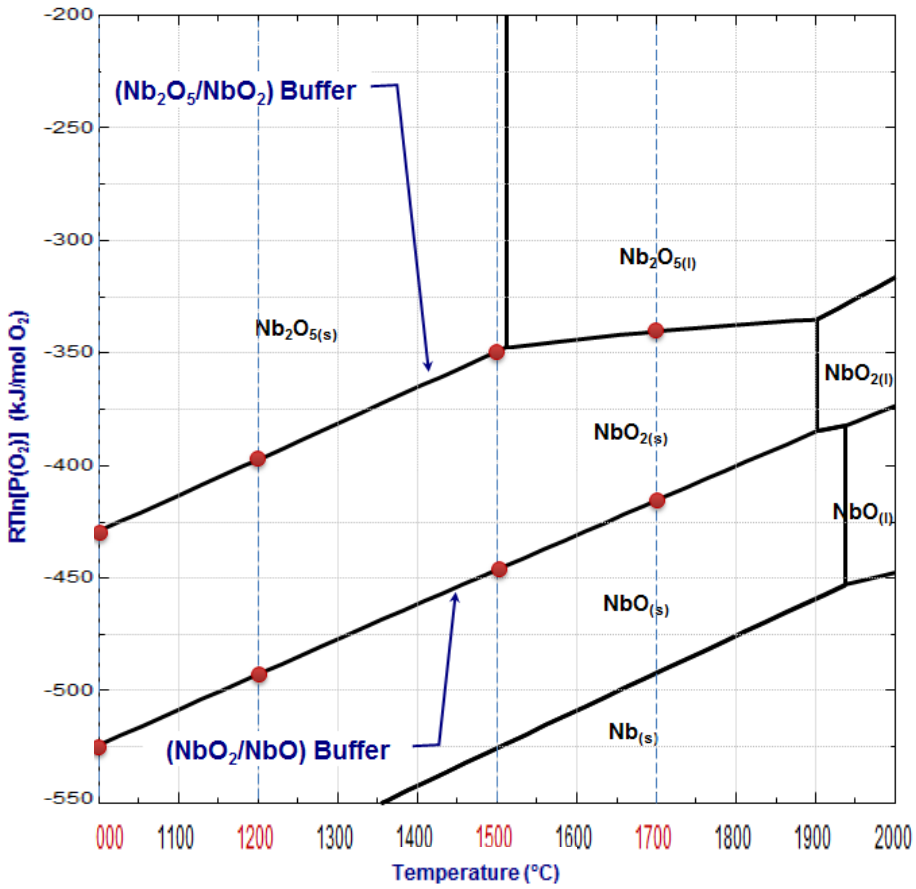
Forming
(uniaxial pressing, 400 MPa)

↓

Reduction (450°C, 2h)
then Sintering (1700°C, 4h)
under Ar/5%H_2

↓

Annealing
1000, 1200, 1500 and 1700°C
1h, under Ar/5%H_2

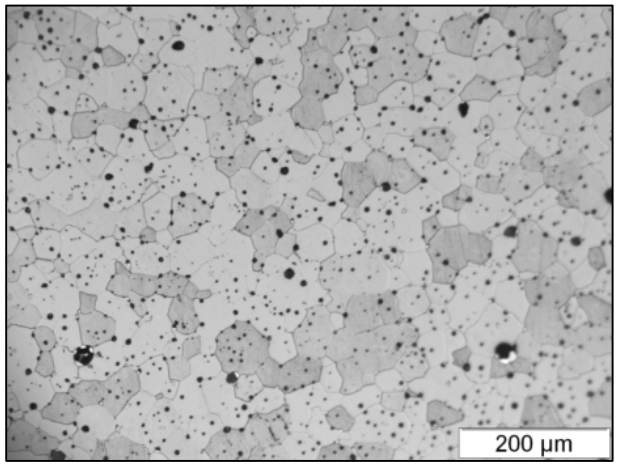


Sintering conditions reported in Nb – U – O phase diagram: *Sintering conditions = red circles*

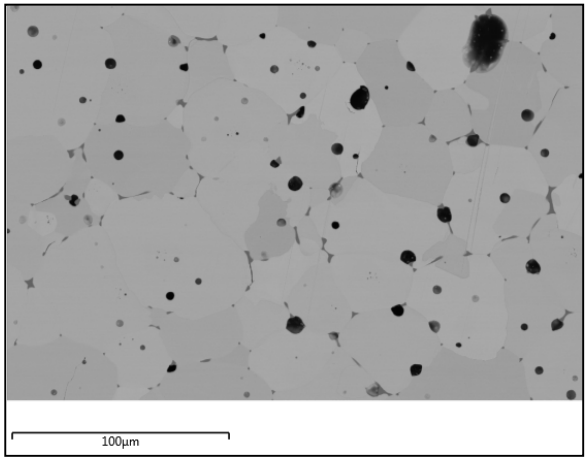
RESULTS - MICROSTRUCTURAL ANALYSIS

Ex: UO_2 + 0.8 wt% (NbO_2 + NbO) pellets

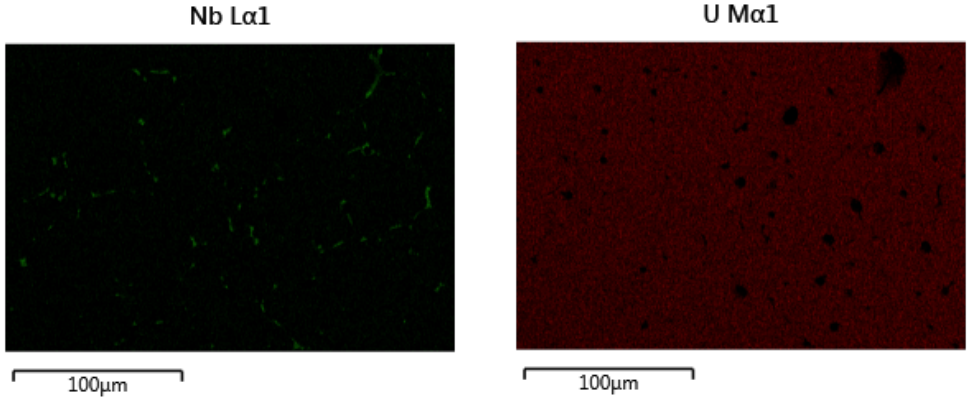
→ Microstructures before annealing



- Healthy pellets (no crack)
- Grain coarsening: grain size about 35 µm (10 µm classical)
- High density: **94.2%Td**



Elemental EDX maps



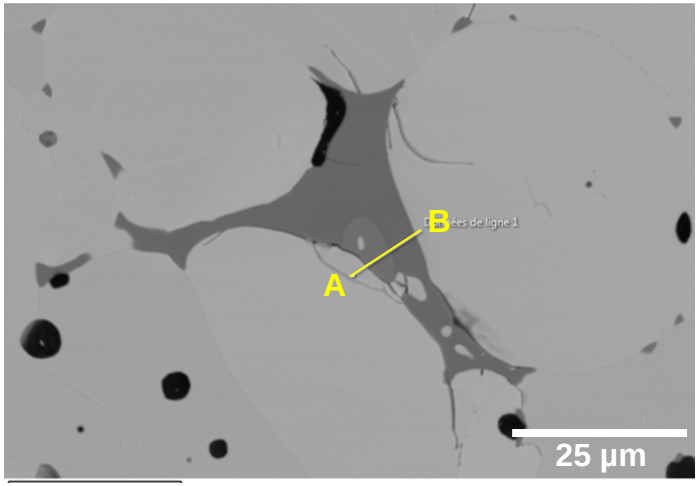
- Micrometer size Nb oxides precipitates at grain boundaries and porosities

RESULTS - MICROSTRUCTURAL ANALYSIS

- Objective: Elemental composition of Nb-O precipitates

→ SEM + EDX analyzes

➢ Sample annealed at **1000°C**



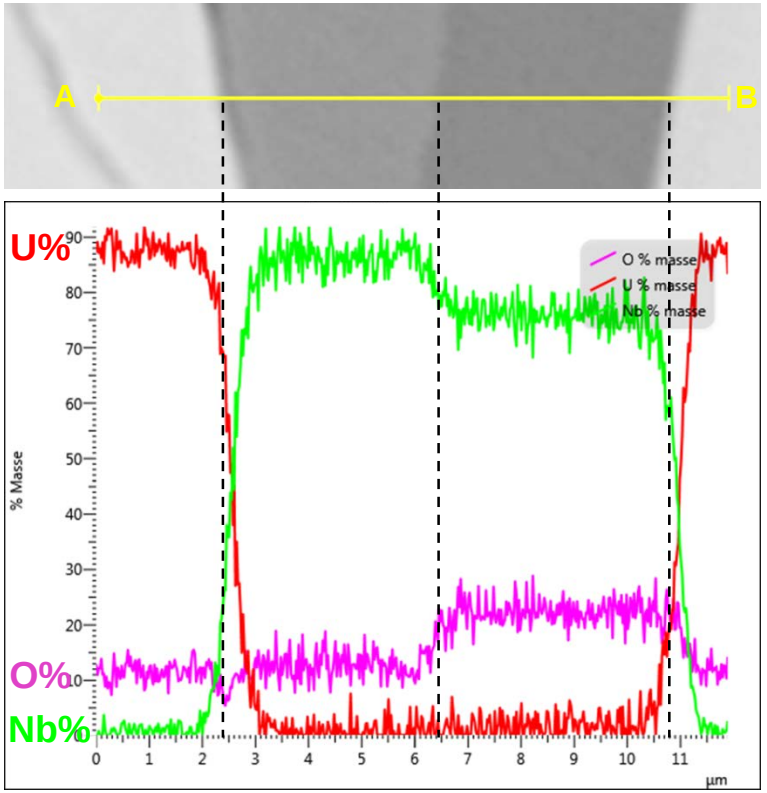
- Two different color contrasts
- Change of the niobium content from one grey to another (composition line)

→ *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)

µ-XRF AND µ-XANES RESULTS

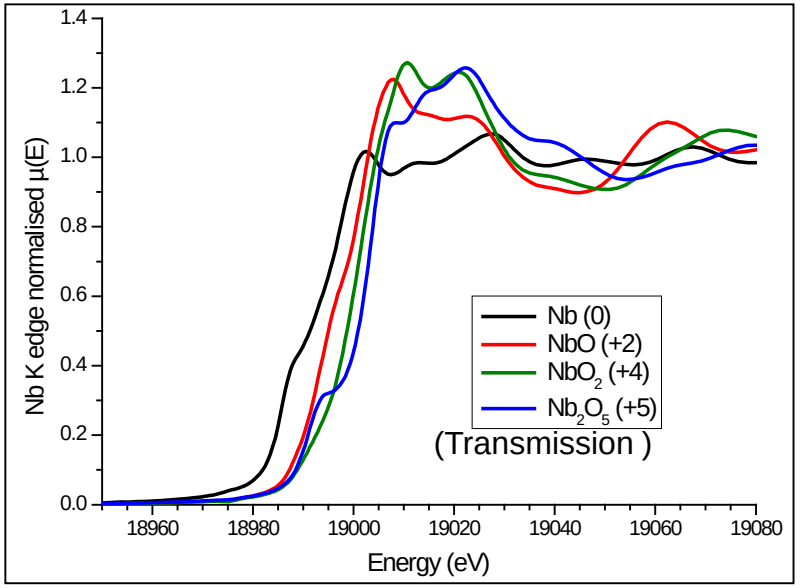
Experiment performed on MARS – 4 days in mid-November

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

⇔ U Lα (13614 eV) & Nb K (16615 eV)

Aims:

- Nb chemical state in precipitates ➔ µ-XANES = buffer effectiveness
- Nb speciation inside UO_2 matrix ➔ µ-XANES + µ-EXAFS



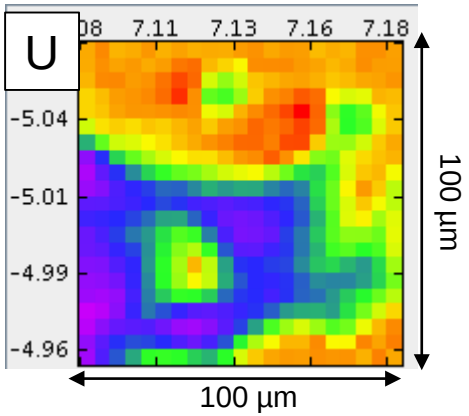
Reference	E_0 (eV)
Nb(0)	18986.0
NbO - Nb(+2)	18994.1
NbO_2 - Nb (+4)	19001.7
Nb_2O_5 - Nb (+5)	19004.0

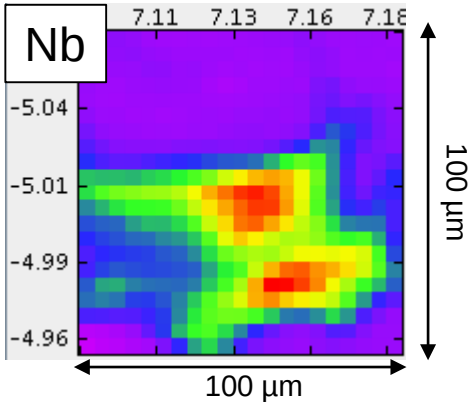
µ-XRF AND µ-XANES RESULTS ON PRECIPITATES

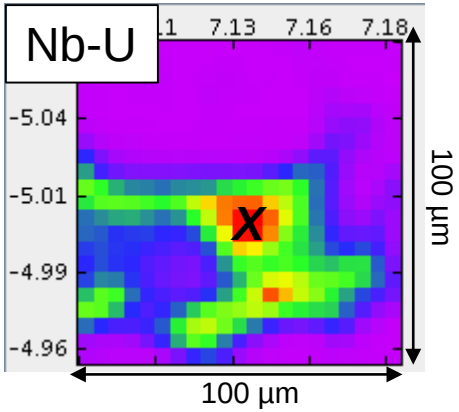
Sample S1: UO_2 + 0.8 wt% (NbO_2 + NbO) as fabricated

2 precipitates studied

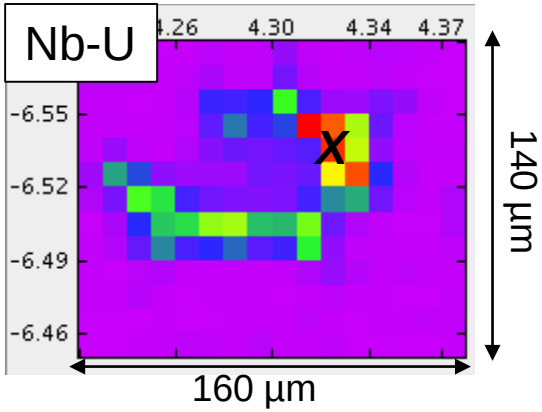
Zone3

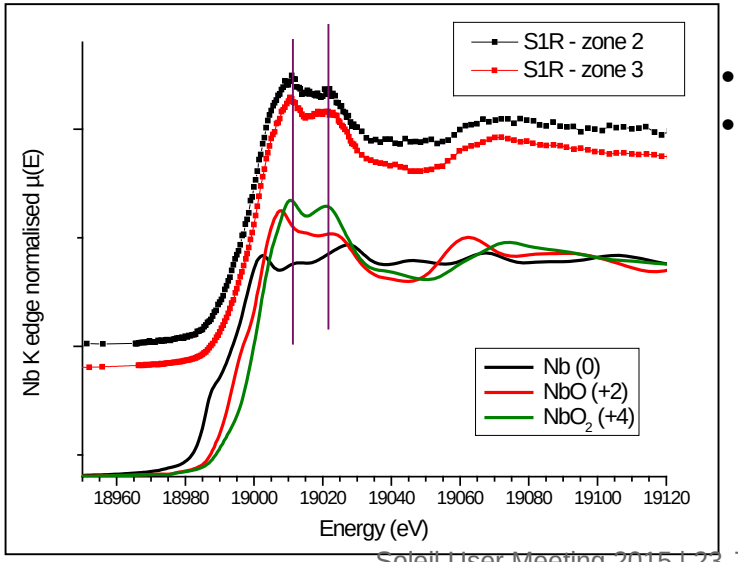






Zone2





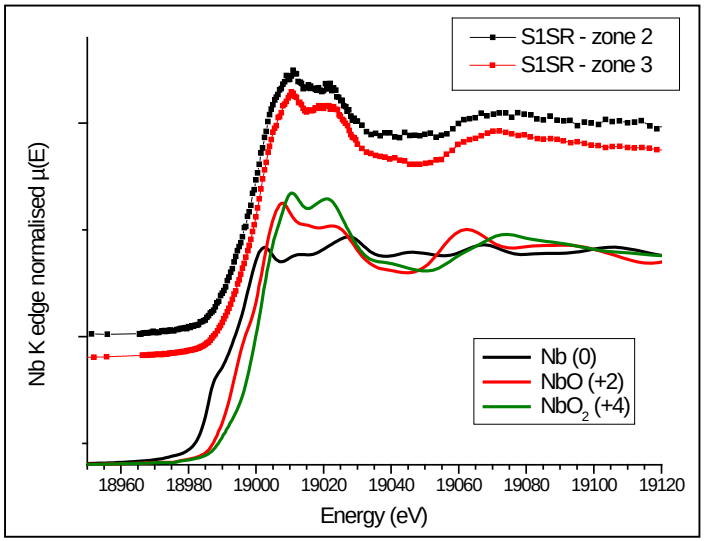
- Spectra similar
- Similarity with NbO_2

Linear combination fit

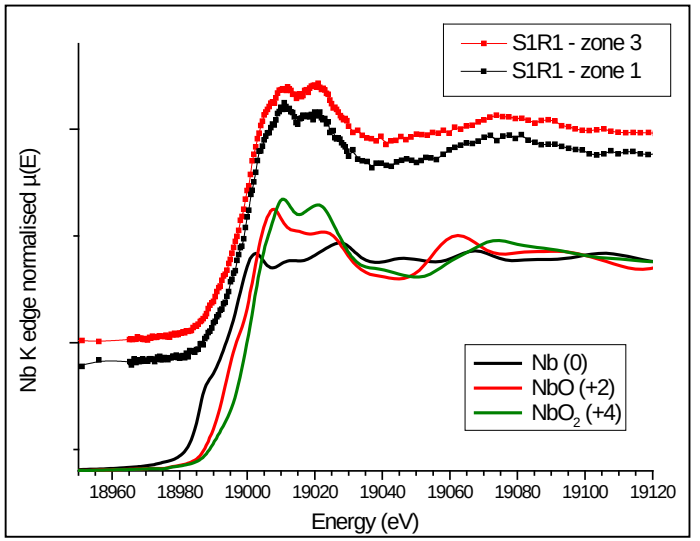
μ-XRF AND μ-XANES RESULTS ON PRECIPITATES

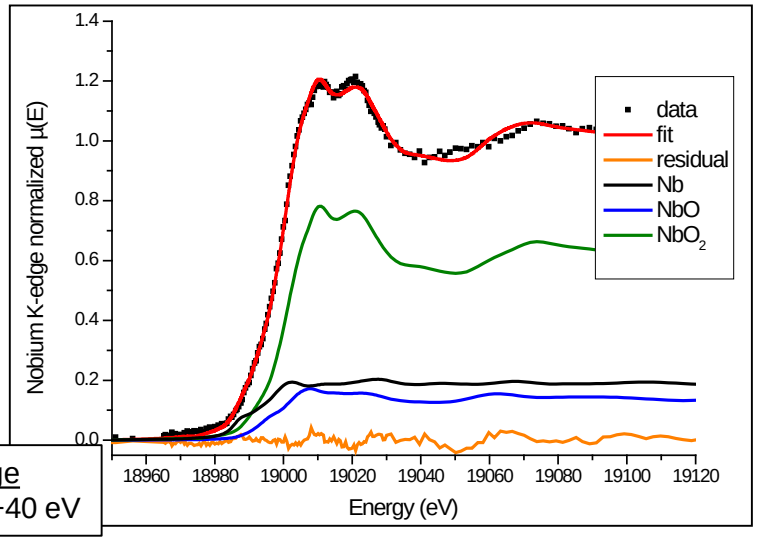
Sample S1: UO_2 + 0.8 wt% (NbO_2 + NbO)

As manufactured



Annealed 1 hour at 1000°C





Range
$-30<E_0<+40$ eV

➔ E_0 systematically between NbO and NbO_2 positions

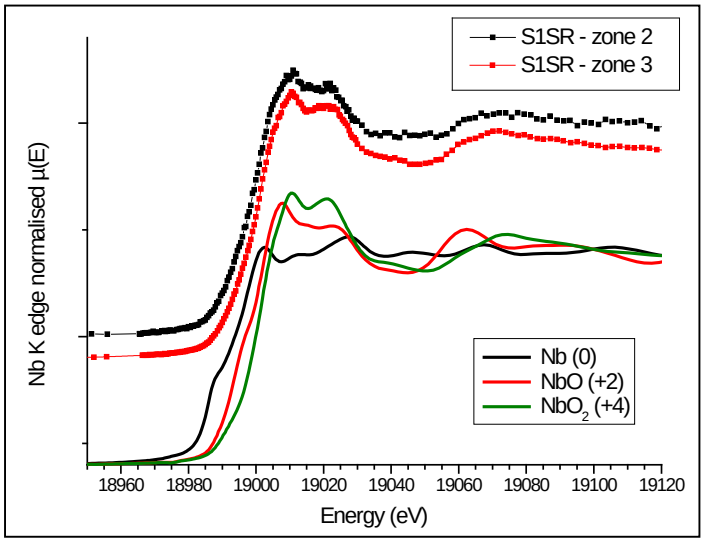
➔ Shoulder at low energy = metallic Nb ?

➔ μ-XANES spectra are reproduced by linear combination of Nb + NbO and NbO_2

µ-XRF AND µ-XANES RESULTS ON PRECIPITATES

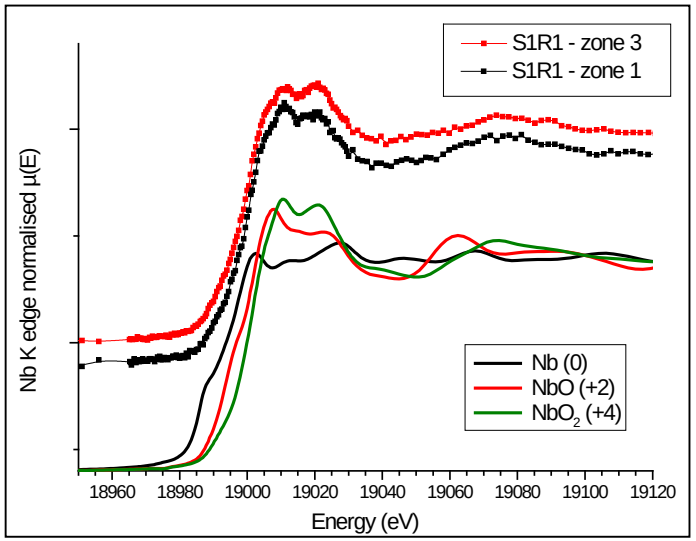
Sample S1: UO_2 + 0.8 wt% (NbO_2 + NbO)

As manufactured



	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

Annealed 1 hour at 1000°C



	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

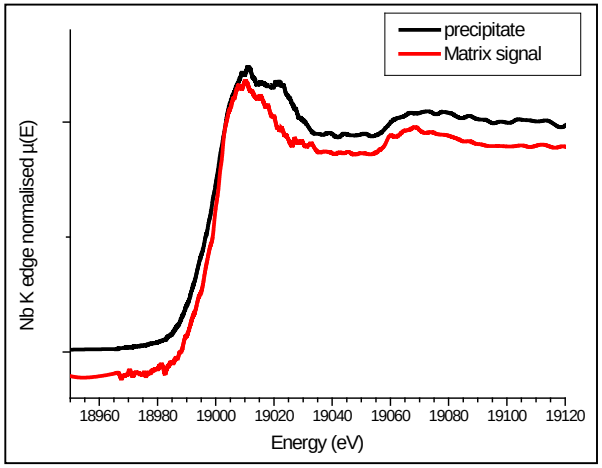
➔ The two phases NbO_2/NbO are observed <=> buffering capacity confirmed

➔ Unexpected metallic Nb signal systematically observed !

µ-XRF AND µ-XANES RESULTS ON MATRIX

µ-XANES & µ-EXAFS on the matrix :

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

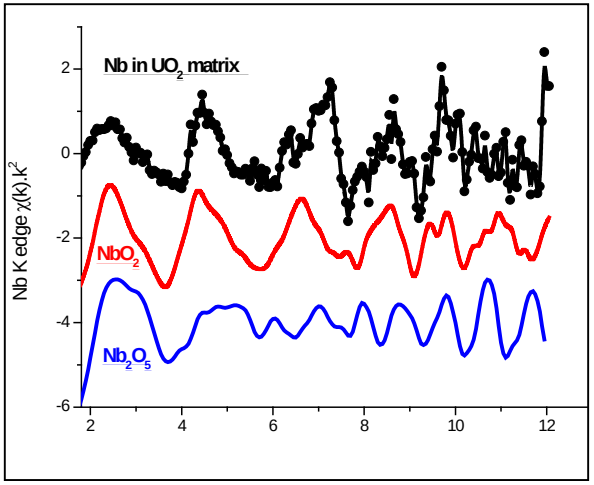


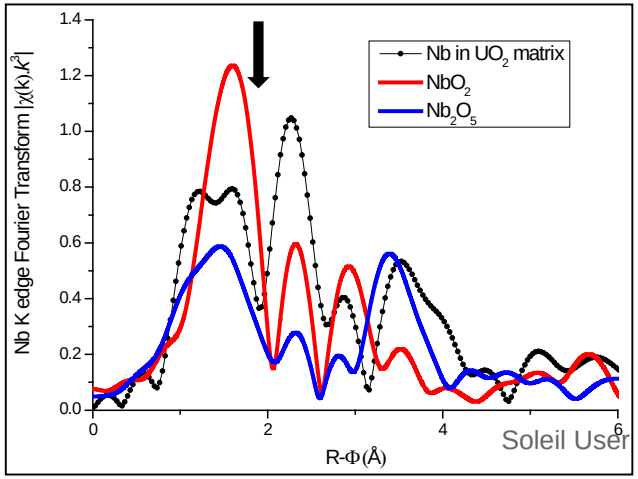
➔ Different with known Nb oxides ⇔ ≠symmetry

➔ Consistent with Nb inside UO_2 fluorite structure ?

➔ E_0 position ~ between Nb^{+4} / Nb^{+5}

µ-EXAFS results => signal up to 11.5 $Å^{-1}$





- Signal from hidden precipitates can not be excluded
- Longer Nb-O distance (Nb-O ≤ 2.15 Å in Nb oxides)

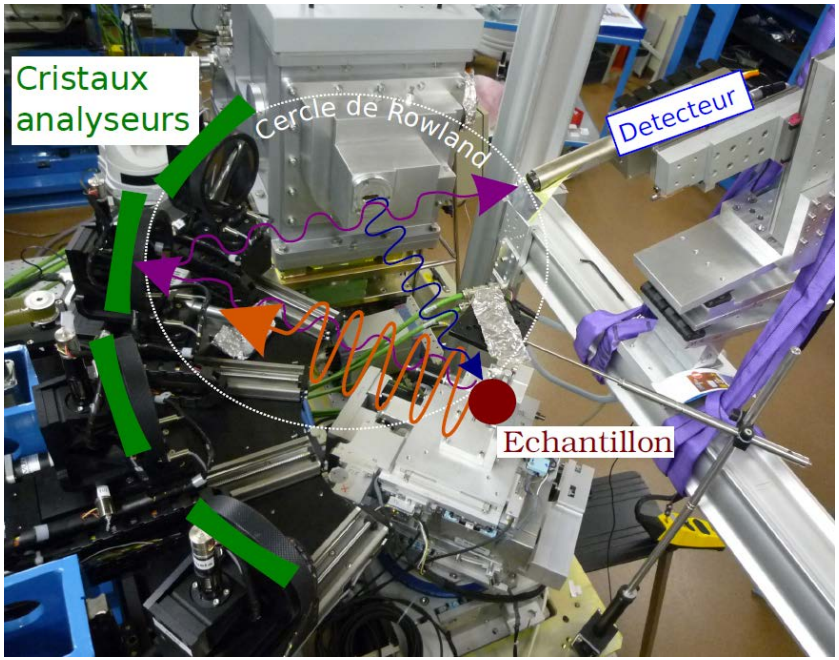
⇒ U-O distance in UO_2 is 2.37 Å.

⇒ **Work in progress**

HERFD - EMISSION SPECTROMETER

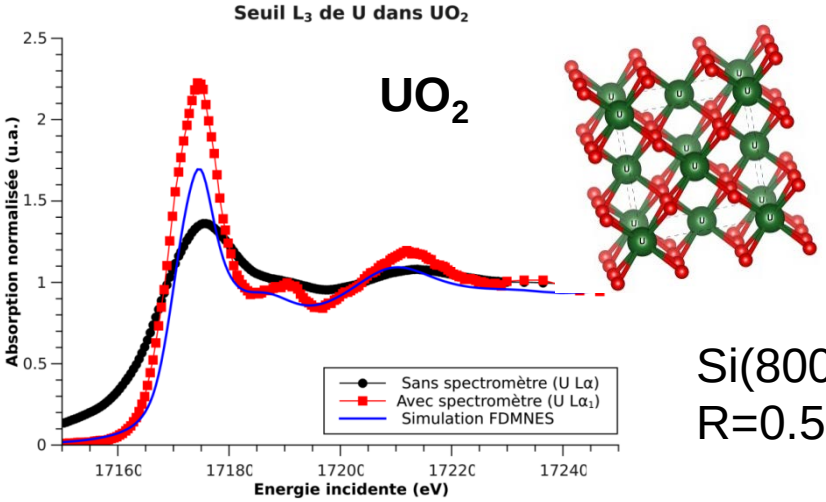
Use of an emission spectrometer with radioactive materials ?

- 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



Si(800)
R=0.5m

L_3 edge (17,166 eV) core-hole = 8.13 eV
$L\alpha1(3d_{5/2} \rightarrow 2p_{3/2})$ => resolution = 3.55 eV

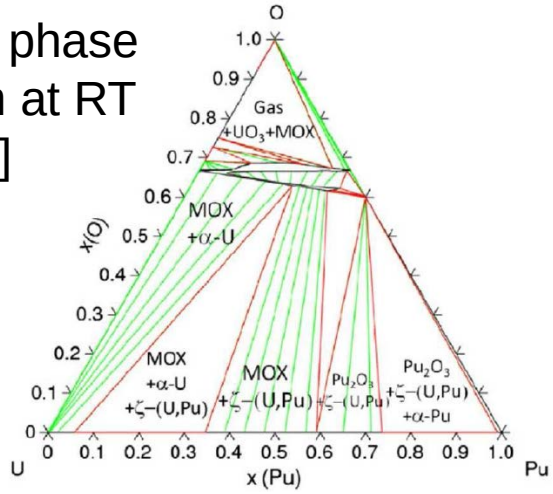
HERFD - EMISSION SPECTROMETER

First experiment on Mixed oxides samples in july 2014

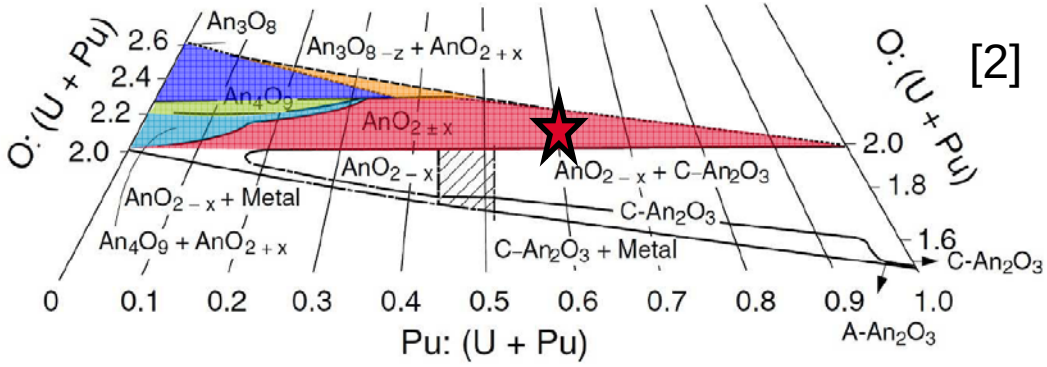
- UO_2, U_3O_8, PuO_2 containing 1.7 % Am (due to ^{241}Pu decay)
- Dense sintered $(U_{0.45}Pu_{0.542}(Am_{0.008}))O_2$ pellets prepared with conventional powder metallurgy process

Context: U-Pu-O phase diagram

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



The hyper-stoichiometric domain at RT [2]



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

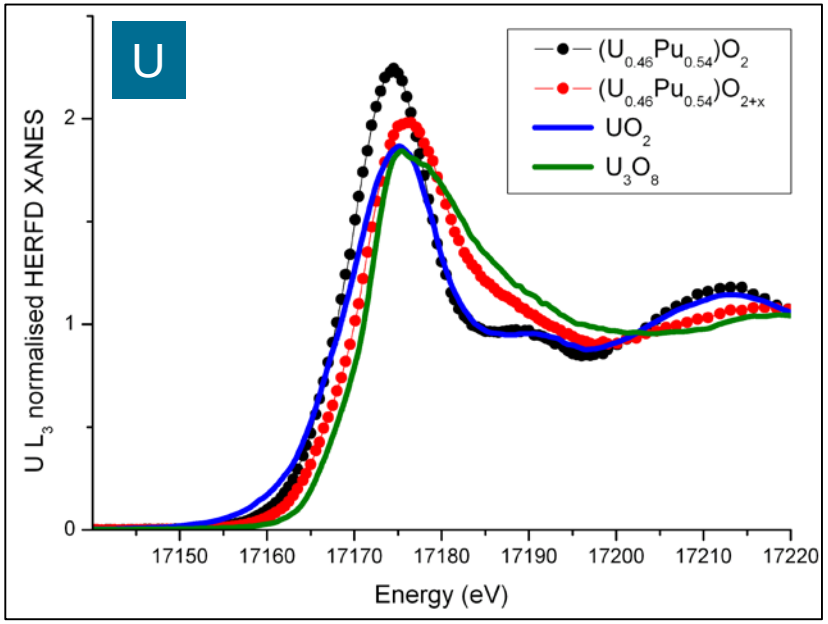
HERFD - EMISSION SPECTROMETER

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



[1] K.O. Kvashnina et al. Phys. Rev. Lett. 111 (2013) 253002

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

- $(U_{0.45}Pu_{0.55})O_2$ => 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

HERFD - EMISSION SPECTROMETER

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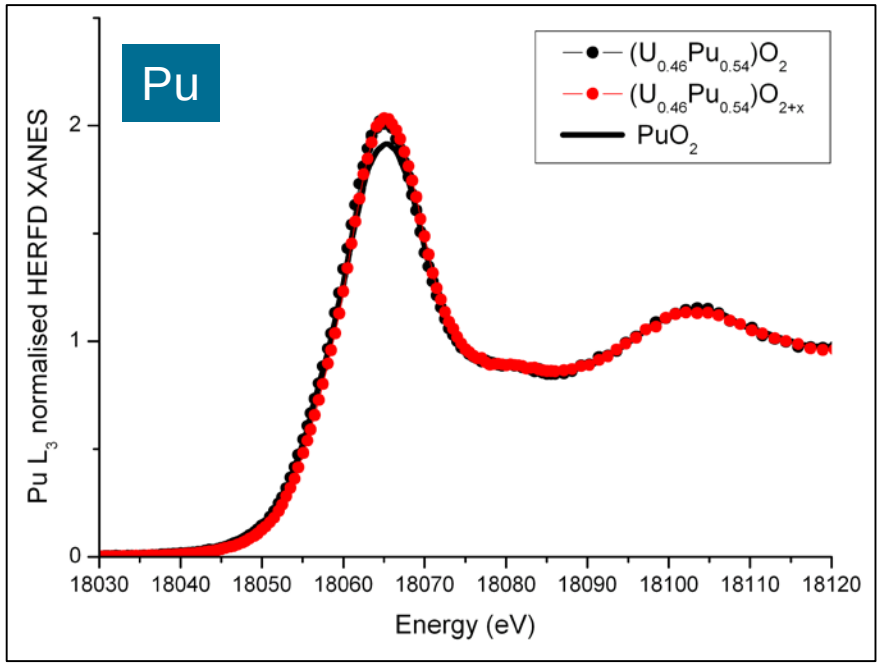
$\Rightarrow$ U, Pu and Am L_3 HERFD XANES



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

HERFD - EMISSION SPECTROMETER

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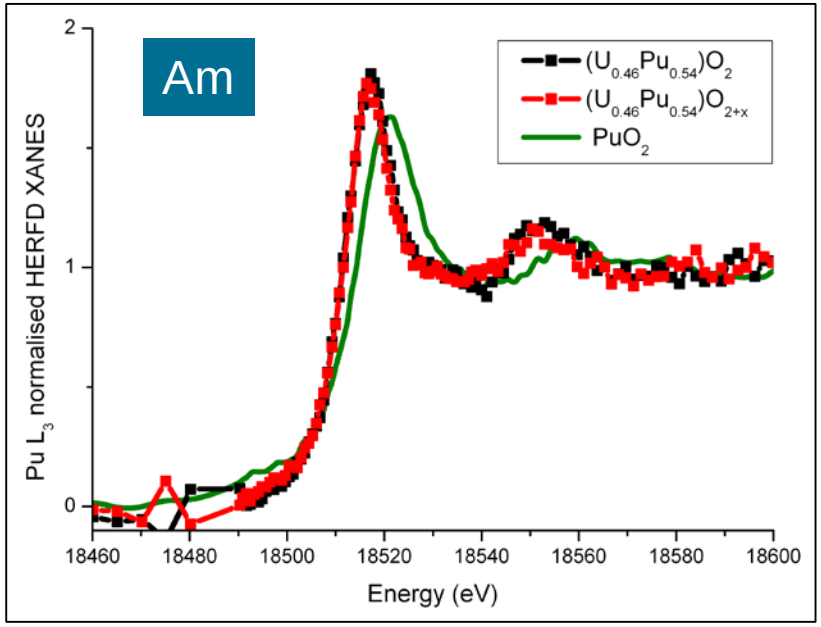

Sample	E_0 (eV)
PuO_2	18515.7
$(U_{0.45}Pu_{0.55})O_2$	18512.1
$(U_{0.45}Pu_{0.55})O_{2+x}$	18512.2

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

Am^{3+} in hyper-stoichiometric MOX

HERFD - EMISSION SPECTROMETER

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- HT-XRD experiments performed at the LEFCA facility (CEA Cadarache)
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$\Rightarrow$ $(U_{0.45}Pu_{0.542}(Am_{0.008}))O_{2+x}$ domain = MO_{2+x} phase at RT

$\Rightarrow$ 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

FISSION PRODUCTS BEHAVIOR

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

➡ UO_2 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/H_2

FISSION PRODUCTS BEHAVIOR

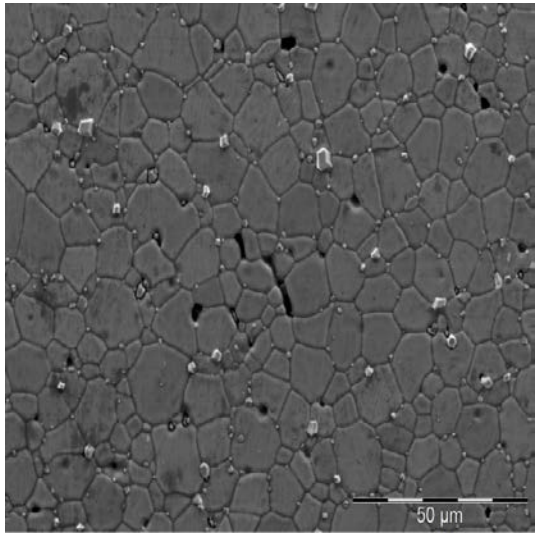
First µ-XANES experiment on MARS = 11/2014

Focused on Mo behavior

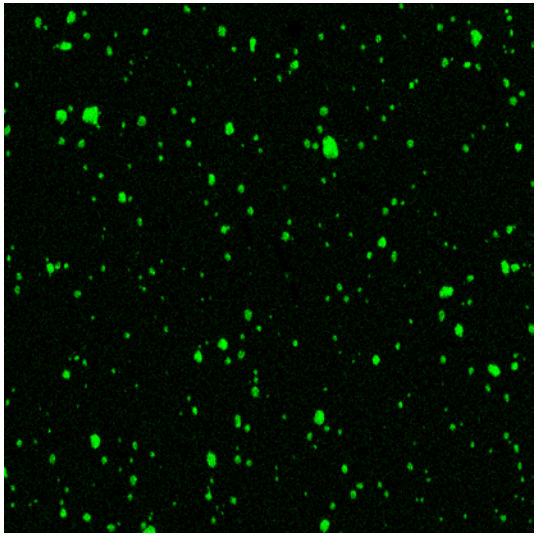
⇒ Mo K edge (20000 keV)

⇒ µ-XRF & µ-XANES ⇔ 6x7 μm^2 with 5.10^8 $ph.s^{-1}$ at 20 keV

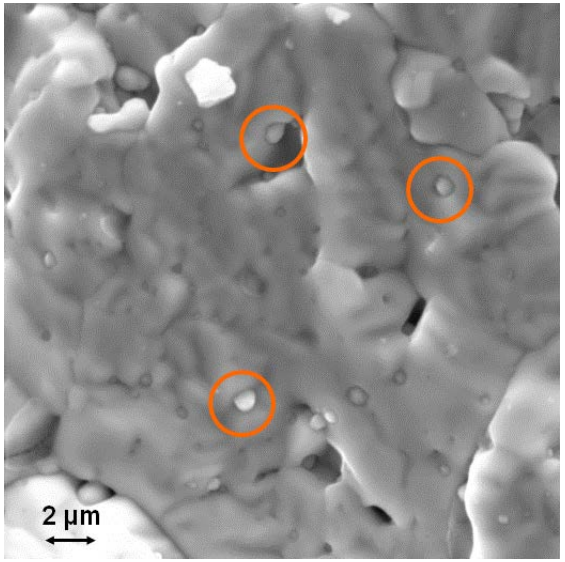
SEM picture



SEM/EDS Mo L_α map



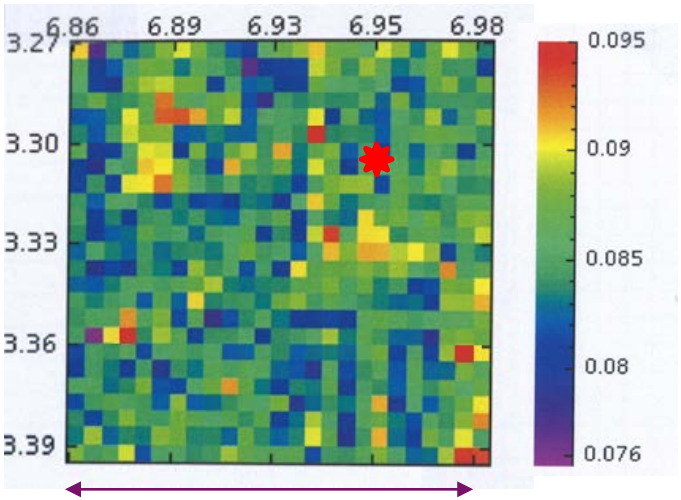
UO_2 spent fuel

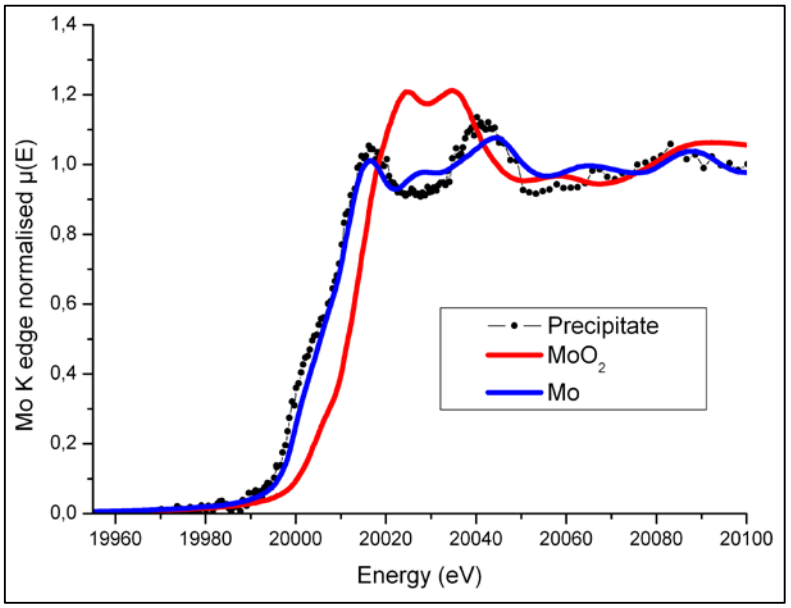


FISSION PRODUCTS BEHAVIOR

First µ-XANES experiment on MARS = 11/2014

Focused on Mo behavior => µ-XRF & µ-XAS (6x7 μm^2 $5x10^8$ Ph/s at 20 keV)





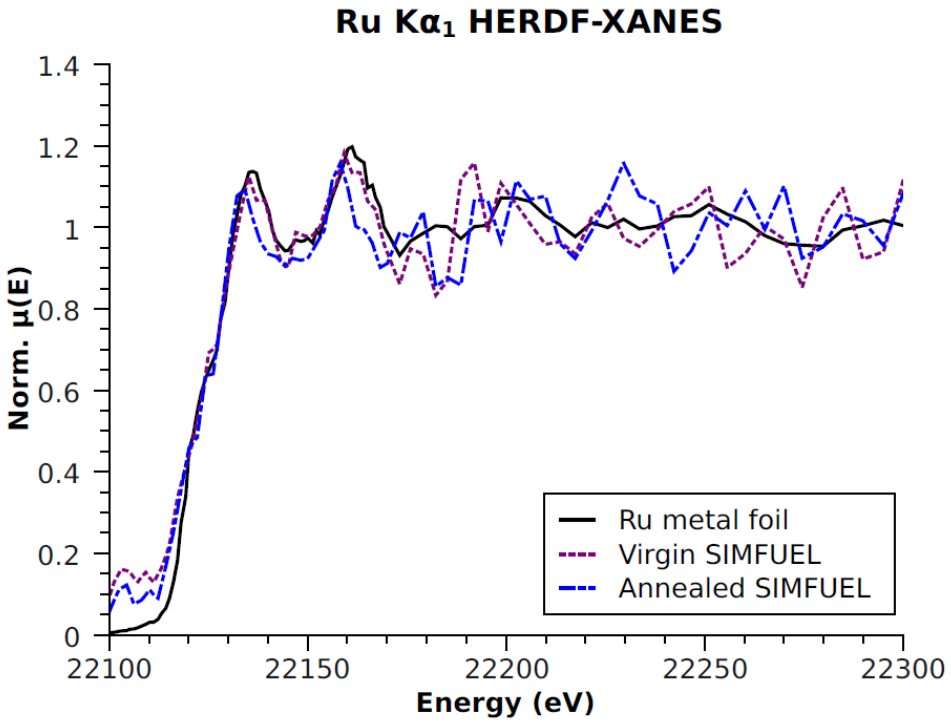
Mo is mostly metallic but difference observed most probably due to association with other fission products (Ru, …)
=> More details during Ernesto Geiger presentation (Chemistry session at 10h30)

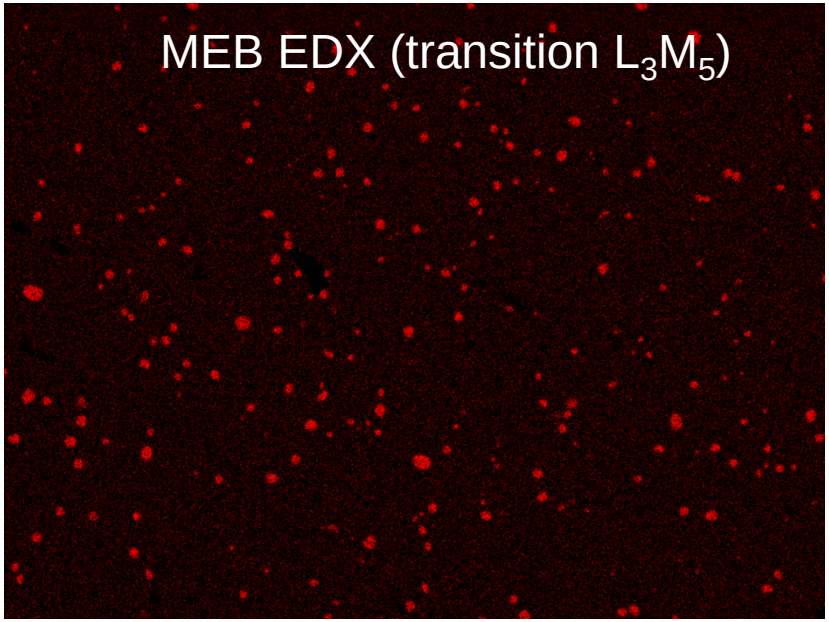
Thank for your attention

FISSION PRODUCT CHEMISTRY ON NUCLEAR FUEL

Ruthenium K-edge

- Form clusters (with Mo)
- 1 transition collected (K-L_3)



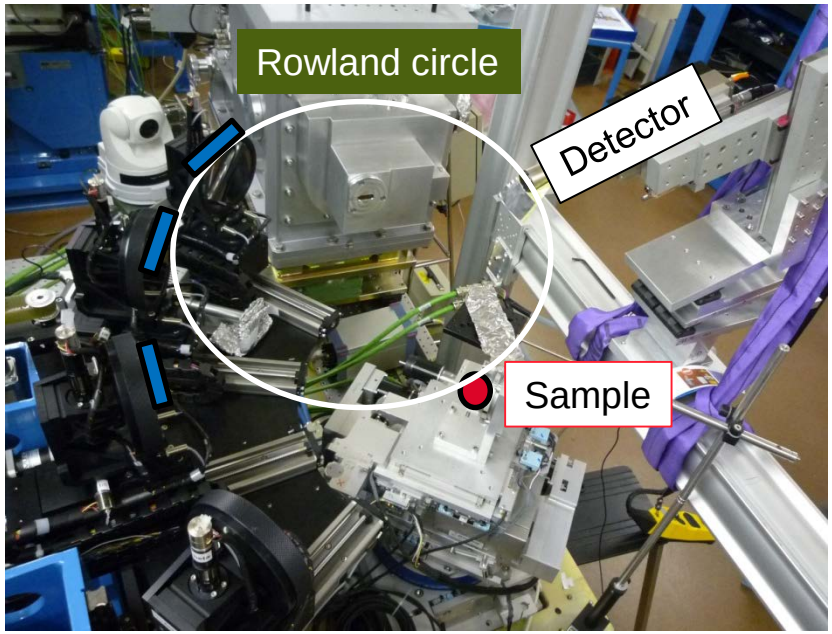


- No evolution of Ru local environment
- Metallic Ru
- Probable mixing of Mo/Ru metals
- Ab initio calculations under progress

HERFD - EMISSION SPECTROMETER

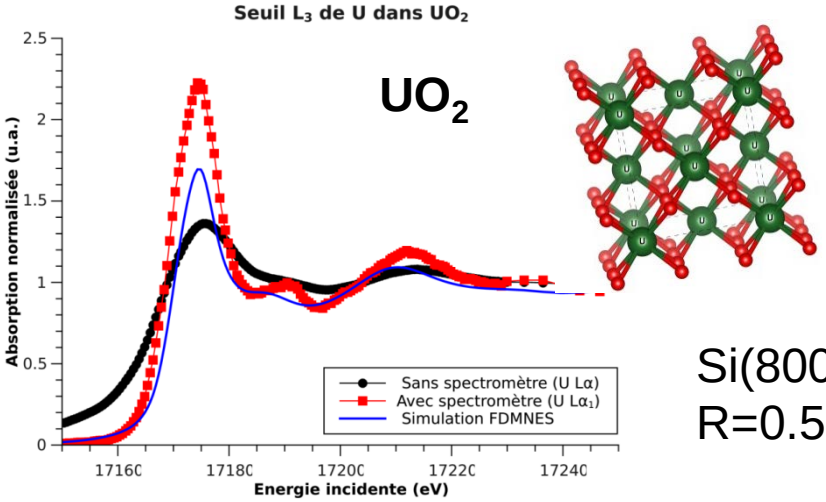
Use of an emission spectrometer with radioactive materials ?

- 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



Si(800)
R=0.5m

L_3 edge (17,166 eV) core-hole = 8.13 eV
$L\alpha1(3d_{5/2} \rightarrow 2p_{3/2})$ => resolution = 3.55 eV