



# Study of niobium in UO<sub>2</sub> advanced fuel doped with NbO<sub>x</sub>

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# STUDY OF NIOBIUM IN $\text{UO}_2$ ADVANCED FUEL DOPED WITH $\text{NbO}_x$

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techniques for future nuclear technologies

# OUTLINE

## ➤ Study principle

- Context and aim
- Determination of the range of oxygen potential
- Choice of the redox buffer

## ➤ Manufacturing conditions

### ➤ First results

- Microstructural analysis
- Precipitates composition analysis

### ➤ Niobium speciation study

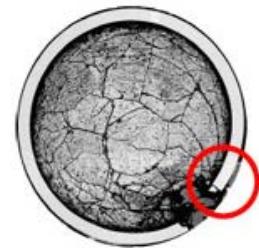
- Synchrotrons presentation
- Precipitates analysis
- Matrix analysis

### ➤ Conclusion and future work

# STUDY PRINCIPLE

## Context and aim

Pressurized Water Reactor (2<sup>nd</sup> generation) → Uranium Dioxide fuel (*reference fuel*)



Cross section of a failed fuel rod

**Aim** : Fuel lifetime and manoeuvrability enhancement

Limit fission gas release from the fuel

**Limit the presence of corrosive species**

Thermo-mechanical evolution of the irradiated material  
 → Governed by the **temperature** and the **oxygen partial pressure** (i.e. oxygen potential)

Grain coarsening

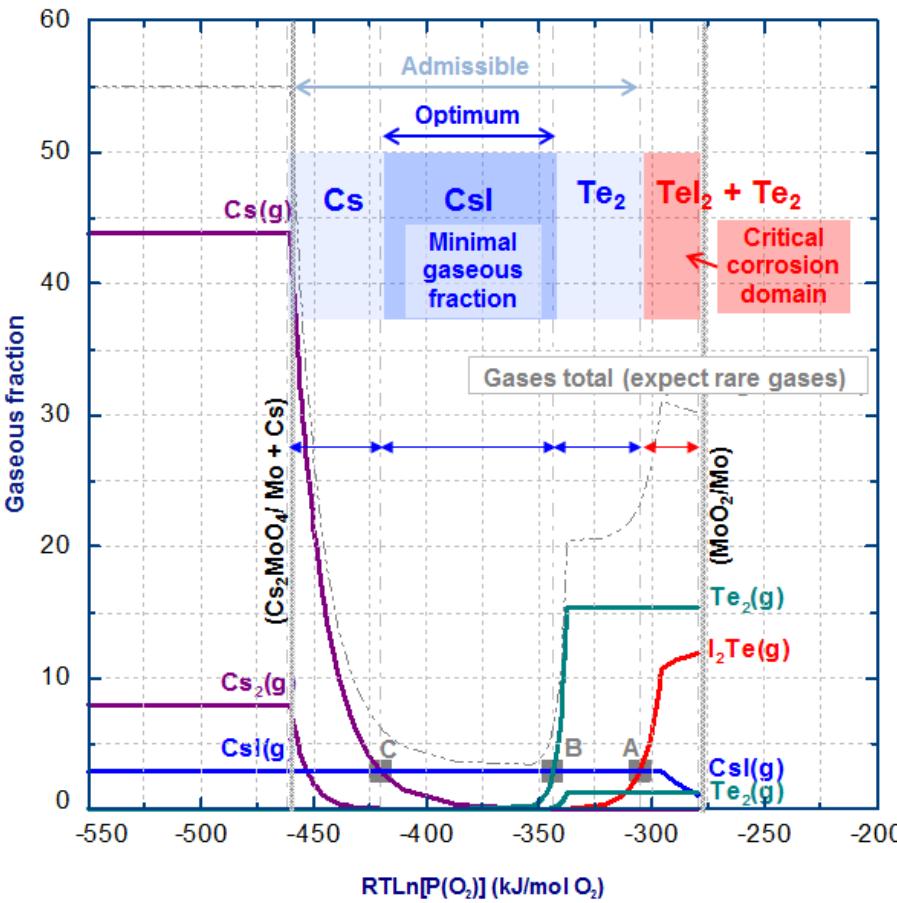
PO<sub>2</sub> control

In situ control of PO<sub>2</sub> in the nuclear fuel thanks to the buffer capacity of an oxido-reductive dopant present under two different oxidation degrees.

→ Study of the doping and fission products chemistry

# STUDY PRINCIPLE

## Determination of the range of oxygen potential



Fugacity profiles and major gaseous speciation in a UO<sub>2</sub> 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 reactive fission gas speciation depends on PO<sub>2</sub>.

# STUDY PRINCIPLE

## Choice of the redox buffer

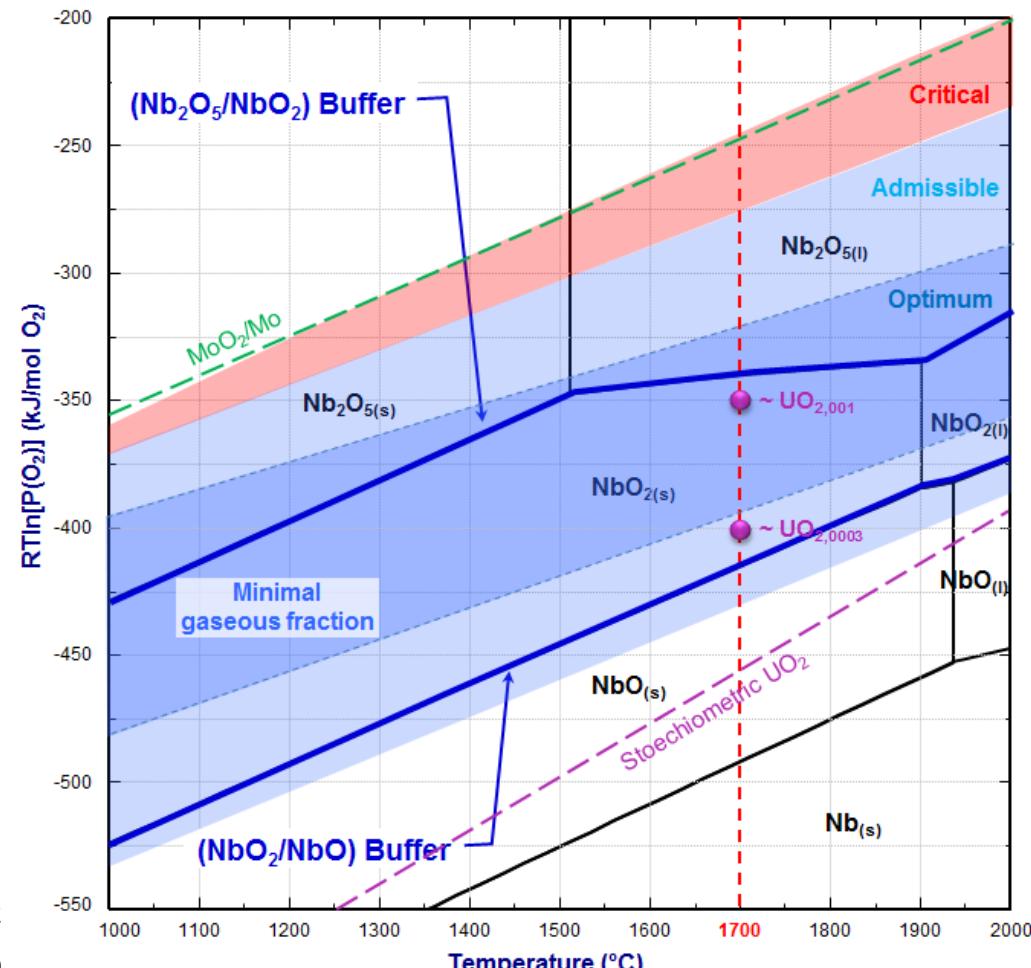
### Criteria for the choice of the redox buffer :

Temperature range, buffering capacity, cross section, final properties of the unirradiated fuel...

#### Selected dopant : NIOBIUM

Potential redox buffers	Buffering capacity (mole O / mole Nb)
$\text{Nb}_2\text{O}_5/\text{NbO}_2$	0,5
$\text{NbO}_2/\text{NbO}$	1
$\text{Nb}_2\text{O}_5/\text{NbO}_2/\text{NbO}$	1,5

- ✓ Redox reactions likely to be thermodynamically activated above 1000°C
- ✓ Liquid phase  $\text{Nb}_2\text{O}_5$  at  $T > 1500^\circ\text{C}$  ( $\rightarrow$  grain growth)

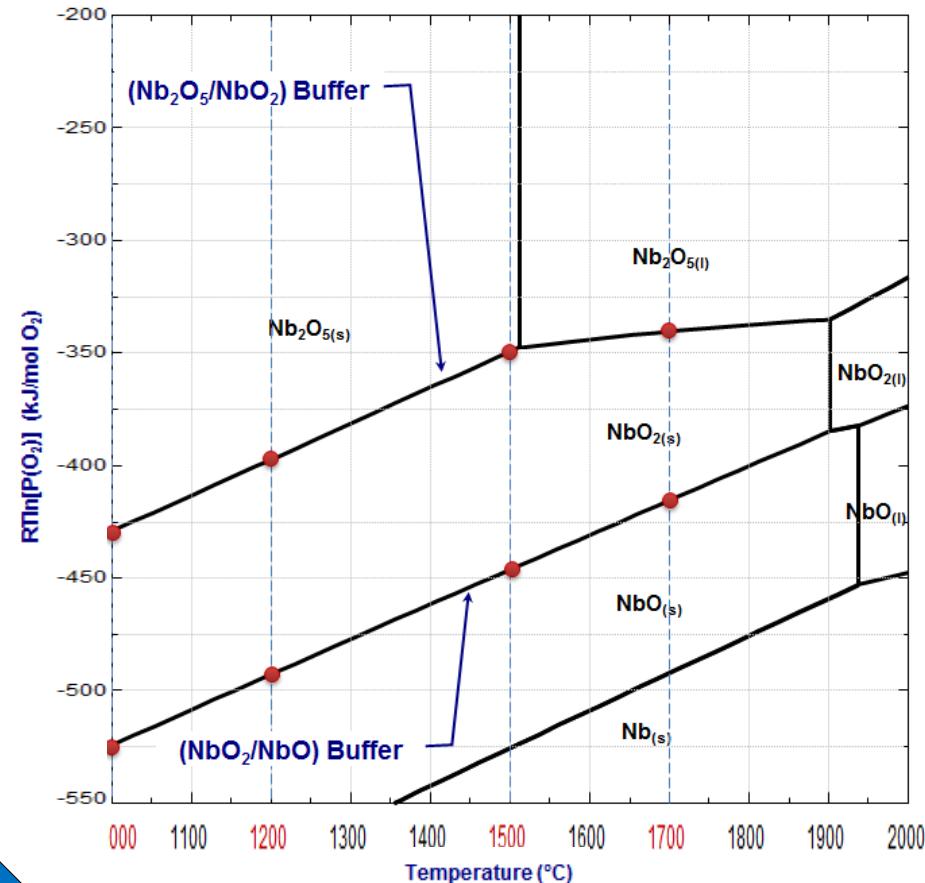
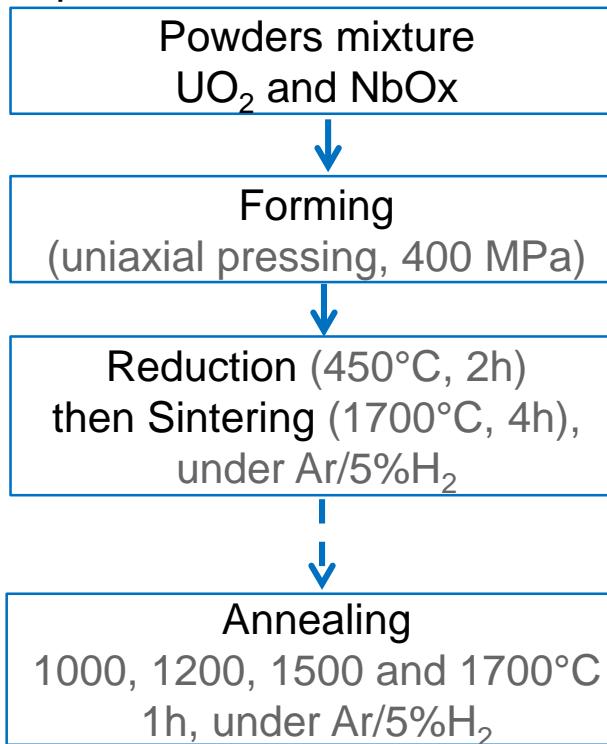


Niobium buffering systems position compared to the stability areas of the corrosive species

# MANUFACTURING CONDITIONS

- Batches with different niobium compositions (50/50 wt.% for the redox couples) :
  - $\text{UO}_2 + 0.8 \text{ wt.\% } (\text{NbO}_2 + \text{NbO})$
  - $\text{UO}_2 + 0.8 \text{ wt.\% } (\text{Nb}_2\text{O}_5 + \text{NbO}_2)$

- Niobium doped pellets manufacturing process :



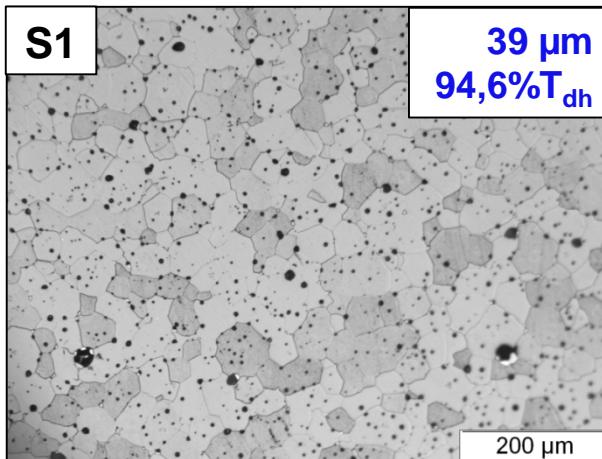
Sintering conditions reported in Nb – O phase diagram.  
Sintering conditions studied are given by red circles

# FIRST RESULTS

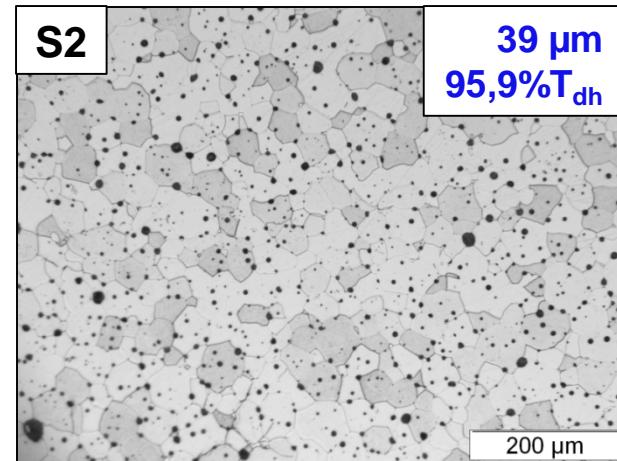
## Microstructural analysis

- **Objective:** Analysis of the doped pellets state

→ Microstructures :



$\text{UO}_2 + 0,8\text{wt.} (\text{NbO}_2+\text{NbO}) - 1700^\circ\text{C}$   
 $T_d = 10.90 \text{ g.cm}^{-3}$



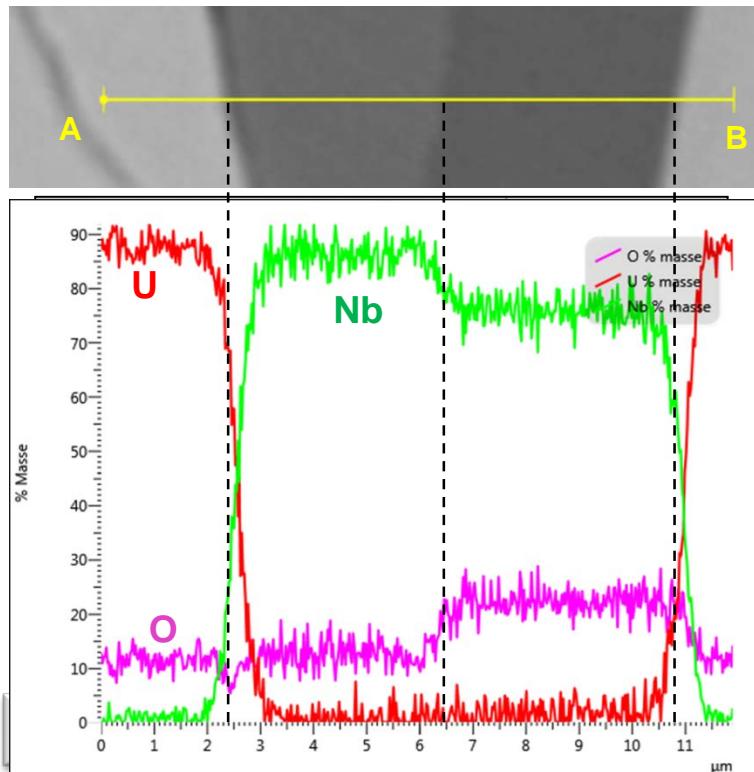
$\text{UO}_2 + 0,8\text{wt.} (\text{Nb}_2\text{O}_5+\text{NbO}_2) - 1700^\circ\text{C}$   
 $T_d = 10.86 \text{ g.cm}^{-3}$

- Healthy pellets (no crack)
- Grain coarsening : grain size about 39 µm (10 µm classical)
- Micrometer size Nb oxides precipitates at grain boundaries

# FIRST RESULTS

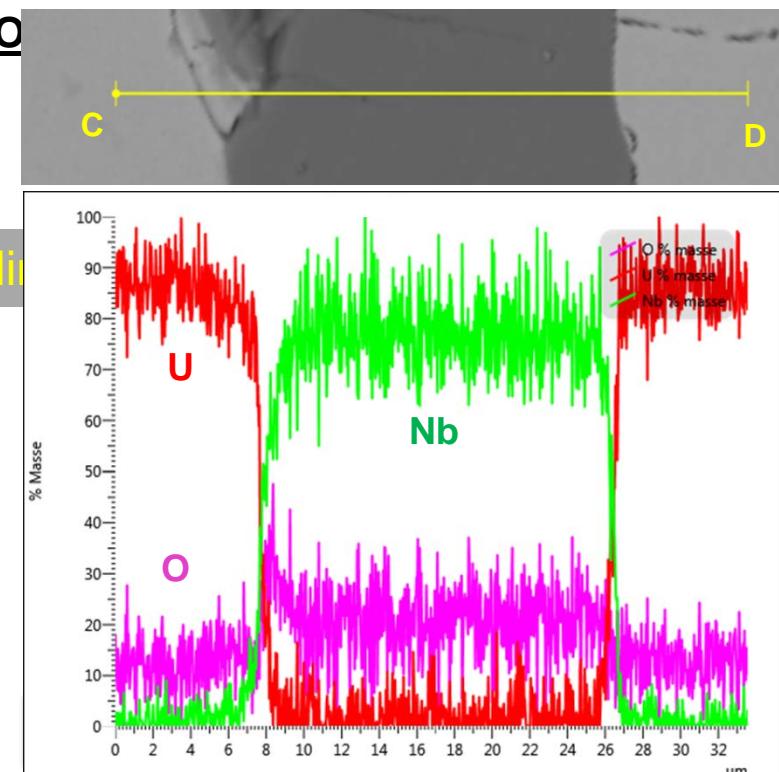
## Precipitates composition analysis

- Objective : Check of elemental composition of NbO precipitates



Profile and element contents

Change of the Nb/O ratio



Profile and element contents

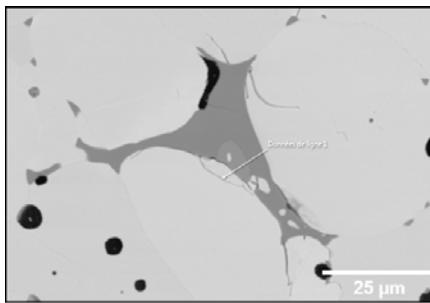
No change of the Nb/O ratio

# FIRST RESULTS

## Precipitates composition analysis

→ SEM + EDX analysis on  $\text{UO}_2 + 0.8\%\text{wt.} (\text{NbO}_2 + \text{NbO})$  pellets  
*Same results observed for  $\text{UO}_2 + 0.8\%\text{m.} (\text{Nb}_2\text{O}_5 + \text{NbO}_2)$*

➤ Annealing at 1000°C (same for 1200°C)  
*« low temperature » annealing*

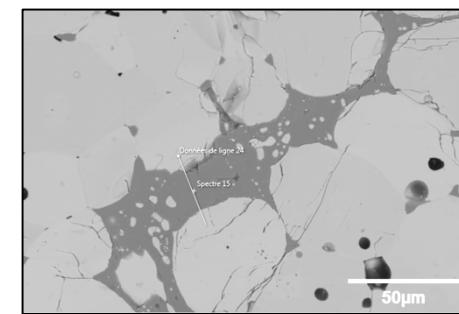


Observation of a grey contrast

Change of the Nb/O ratio

→ *Hypothesis : Presence of two niobium oxide phases or more complex system*

➤ Annealing at 1700°C (same for 1500°C)  
*« high temperature » annealing*



Observation of a single grey

No change of the Nb/O ratio

→ *Hypothesis : Presence of a single niobium oxide phase*

→  $\mu$ -XANES experiments

# NIOBIUM SPECIATION STUDY

- **Objective :** Identify the niobium valence state in the precipitates to check the presence of the two  $\text{NbO}_x$  phases

→ Experiences performed on two Synchrotrons :

## SOLEIL - MARS beamline

- Nb K edge (18 986 eV)
- 12x13  $\mu\text{m}^2$  beam
- Depth interaction : ~10 $\mu\text{m}$



$\mu$ -EXAFS spectrum  
*Local environment*

## ESRF - ID21 beamline

- Niobium L<sub>3</sub> edge (2 371 eV)
- 1x1  $\mu\text{m}^2$  beam
- Depth interaction : entre 0,3 et 1  $\mu\text{m}$



$\mu$ -XRF cartographies  
*Nb localisation*  
 $\mu$ -XANES spectrum  
*Nb chemical form*

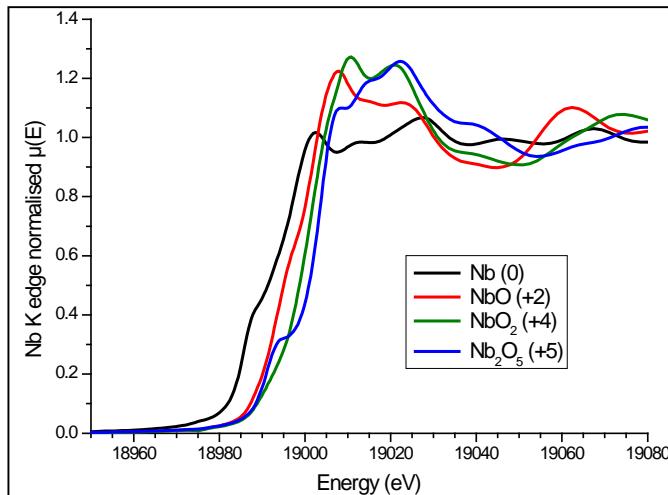


# NIOBIUM SPECIATION STUDY

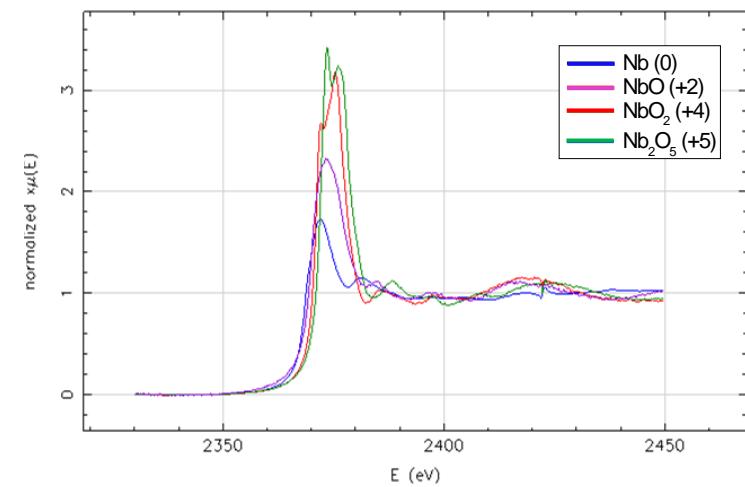
→ Reference components :

4 references : Nb, NbO, NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>

**SOLEIL – MARS beamline**



**ESRF - ID21 beamline**



References	Nb	NbO	NbO <sub>2</sub>	Nb <sub>2</sub> O <sub>5</sub>
E <sub>0</sub> (eV)	18986,0	18994,1	19001,7	19004,0

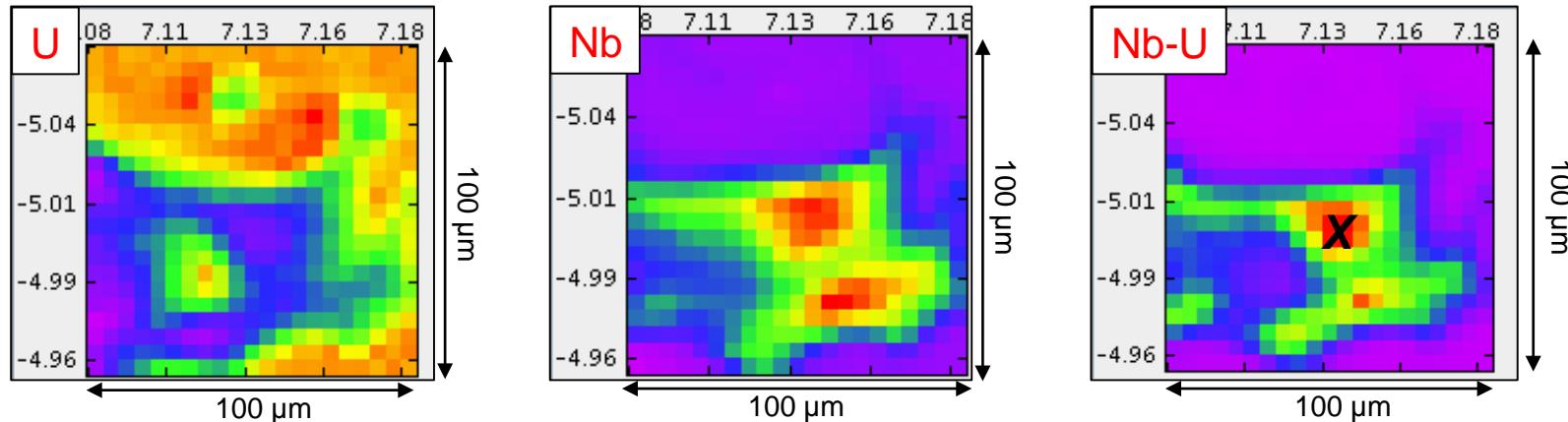
References	Nb	NbO	NbO <sub>2</sub>	Nb <sub>2</sub> O <sub>5</sub>
E <sub>0</sub> (eV)	2368,6	2370,1	2371,2	2372,4

# NIOBIUM SPECIATION STUDY – PRECIPITATES ANALYSIS

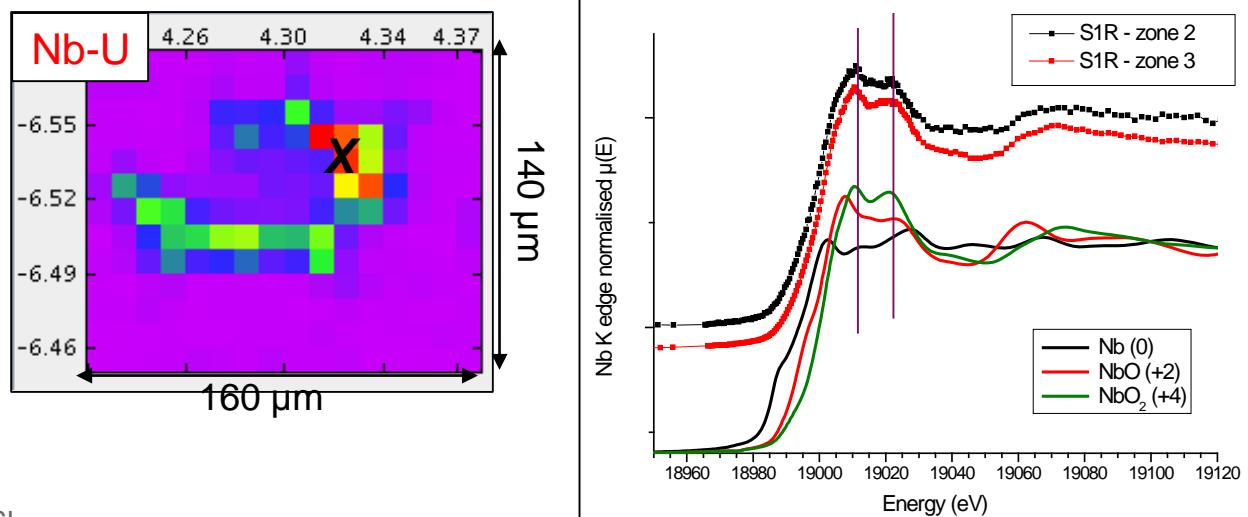
## $\mu$ -XRF and $\mu$ -XANES on MARS beamline

→ Study of the sample  $\text{UO}_2 + 0.8 \text{ wt.\%} (\text{NbO}_2 + \text{NbO})$   
 2 precipitates studied (intensive Nb zone)

Zone 3



Zone 2



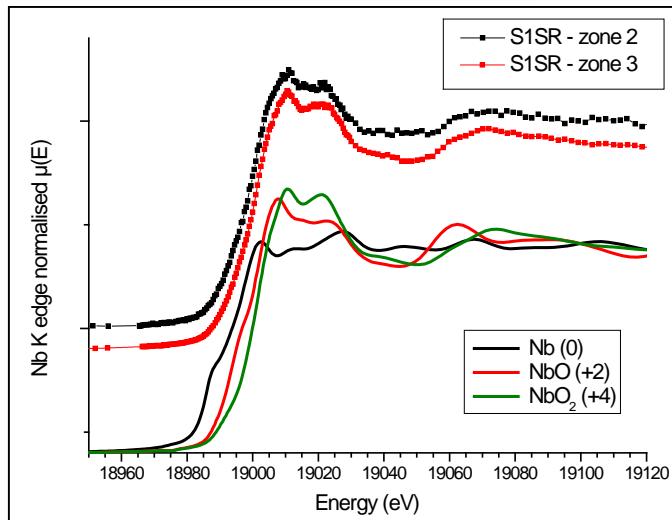
- Similar spectra
- Similarity with  $\text{NbO}_2$

# NIOBIUM SPECIATION STUDY – PRECIPITATES ANALYSIS

## $\mu$ -XANES on MARS beamline

→ Study of the sample  $\text{UO}_2 + 0.8 \text{ wt.\%} (\text{NbO}_2 + \text{NbO})$

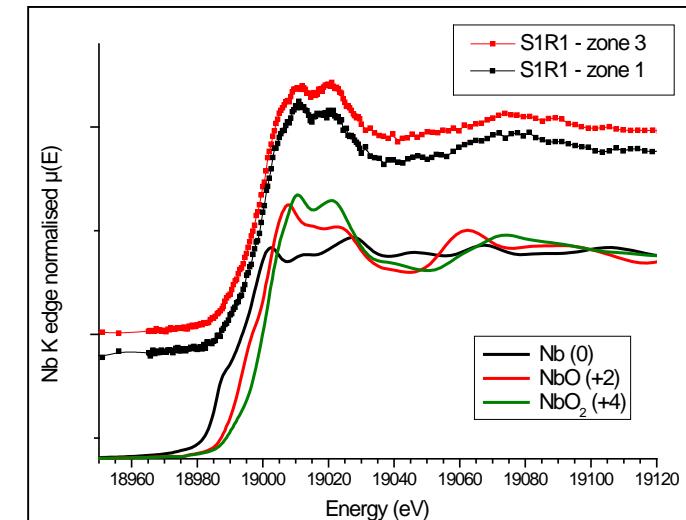
Before annealing



$E_0$  between NbO  
and  $\text{NbO}_2$  positions



Annealing at 1000°C



Linear  
combination



	Nb	NbO	$\text{NbO}_2$	$R_{\text{factor}}$
Zone 2	0,12	0,43	0,45	1,0e-3
Zone 3	0,07	0,27	0,67	4,0e-4

	Nb	NbO	$\text{NbO}_2$	$R_{\text{factor}}$
Zone 3	0,19	0,19	0,62	1,0e-3
Zone 1	0,14	0,23	0,64	2,0e-3

Uncertainties  $\pm 0,03 \text{ eV}$

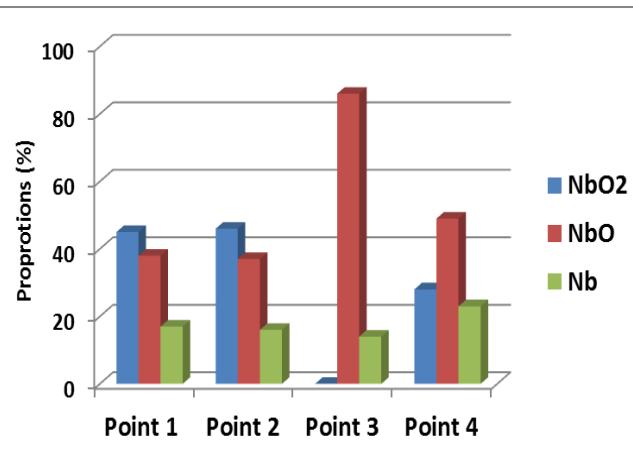
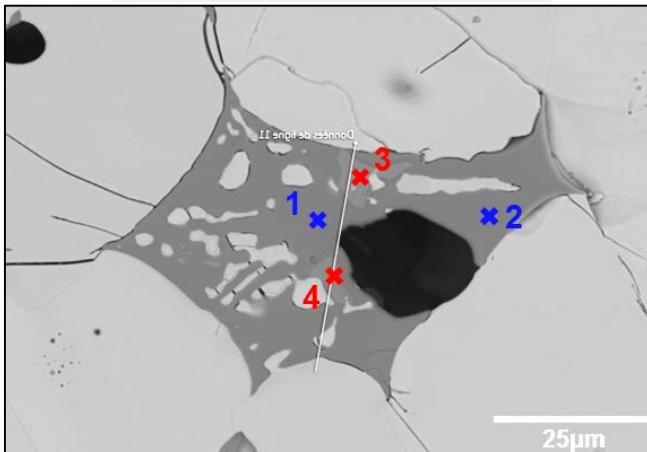
- Presence of the two phases  $\text{NbO}_2$  et NbO
- Unexpected presence of metallic Nb

# NIOBIUM SPECIATION STUDY – PRECIPITATES ANALYSIS

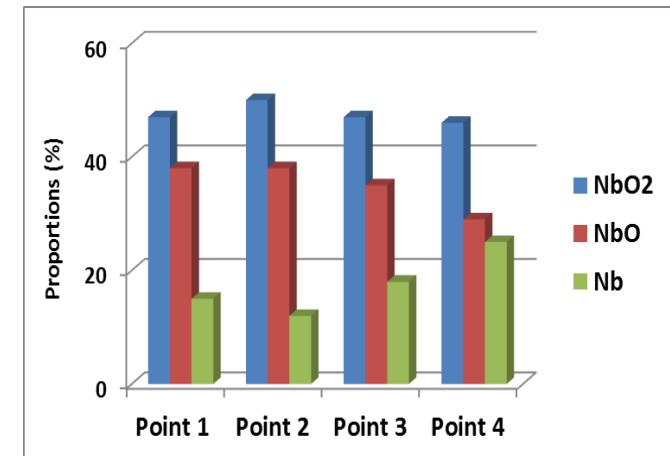
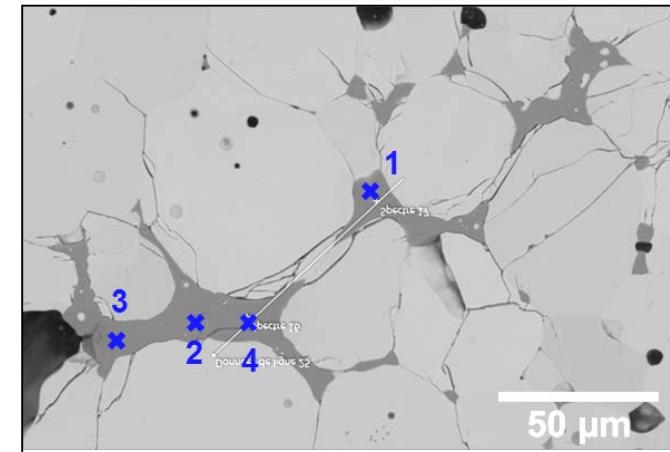
## $\mu$ -XANES on ID21 beamline

→ Study of the sample  $\text{UO}_2 + 0.8 \text{ wt.\%} (\text{NbO}_2 + \text{NbO})$

Annealing at 1000°C



Annealing at 1700°C



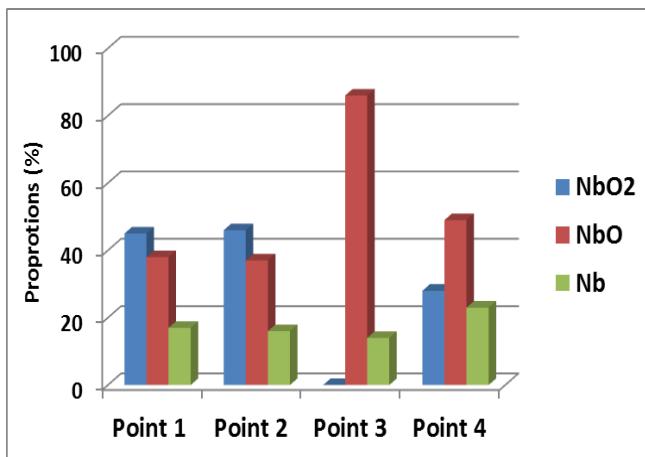
$\mu$ -XANES

# NIOBIUM SPECIATION STUDY – PRECIPITATES ANALYSIS

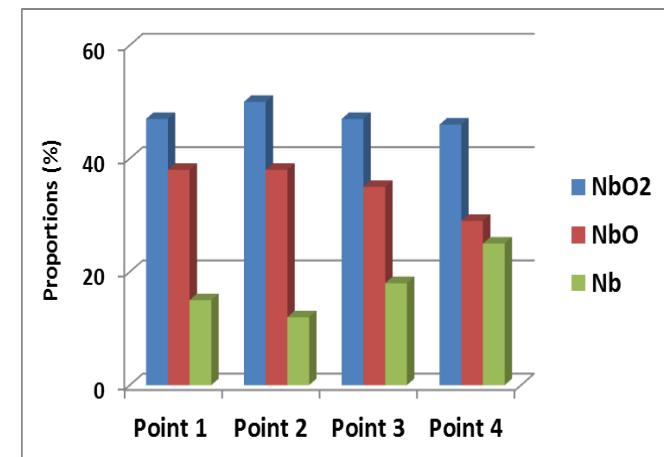
## $\mu$ -XANES on ID21 beamline

→ Study of the sample  $\text{UO}_2 + 0.8 \text{ wt.\%} (\text{NbO}_2 + \text{NbO})$

Annealing at 1000°C



Annealing at 1700°C



- ➔ Presence of the two phases  $\text{NbO}_2$  and  $\text{NbO}$
- ➔ Unexpected presence of metallic Nb
- ➔ Homogenization of the precipitates for the sample annealed at 1700°C

# NIOBIUM SPECIATION STUDY – PRECIPITATES ANALYSIS

## Conclusion

### μ-XRD and μ-XANES analyzes (on MARS and ID21 beamlines)

- Whatever the starting redox couple and the annealing temperature, three niobium phases are present in the precipitates : **Nb, NbO and NbO<sub>2</sub>**.
- Absence of the Nb<sub>2</sub>O<sub>5</sub> species (*initially present*) in UO<sub>2</sub> + 0,8% m. (Nb<sub>2</sub>O<sub>5</sub>+NbO<sub>2</sub>)
- Unexpected presence of metallic niobium in all the S1 and S2 precipitates.
- Precipitates homogenization at high temperature (1500 and 1700°C).



Reduction of the initially introduced NbO<sub>x</sub> species

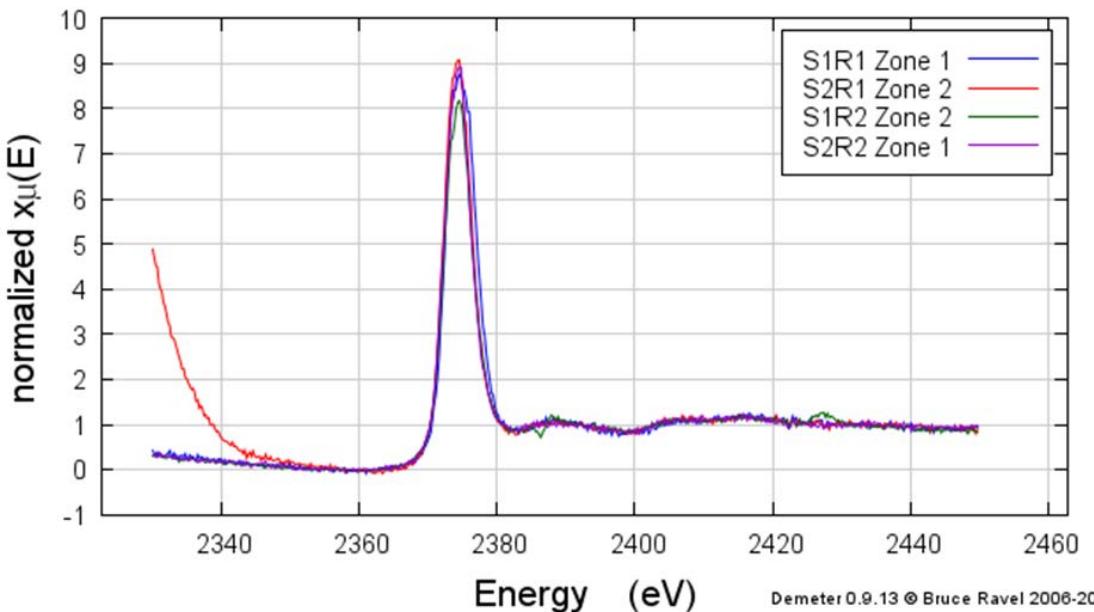
- Ar/5%H<sub>2</sub> too much reducer
- Change of the annealing atmosphere necessary

# NIOBIUM SPECIATION STUDY – MATRIX ANALYSIS

## $\mu$ -XANES on ID21 beamline

■ **Objective :** Characterize the soluble form of Nb in  $\text{UO}_2$  matrix

→ Sample  $\text{UO}_2 + 0.8 \text{ m.\% } (\text{NbO}_2 + \text{NbO})$  and  $\text{UO}_2 + 0.8 \text{ m.\% } (\text{Nb}_2\text{O}_5 + \text{NbO}_2)$  for 1000 and 1200°C annealings



$$E_0 (\text{Nb}_2\text{O}_5) = 2372,4 \text{ eV}$$

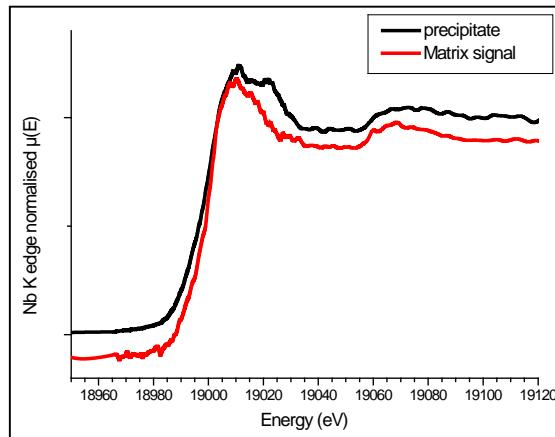
$$2372,5 < E_0 \text{ (matrix)} < 2372,6 \text{ eV}$$

Similar matrix for all the samples  
 → The soluble form of Nb in  $\text{UO}_2$  matrix is  $\text{Nb}^{5+}$ .

# NIOBIUM SPECIATION STUDY – MATRIX ANALYSIS

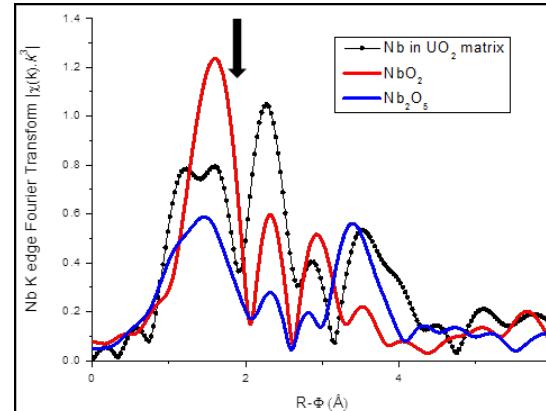
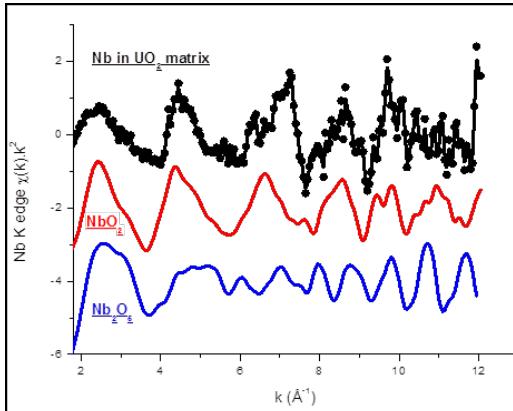
## $\mu$ -XANES ans $\mu$ -EXAFS on MARS beamline

- **Objective :** Characterize the physical form of the matrix and Nb speciation inside  $\text{UO}_2$  matrix
- $\mu$ -XANES on the matrix :



- Same spectra observed on every sample (S1 and S2, annealed or not)
- Different with known  $\text{NbO}_x \Leftrightarrow$  Different symmetry
  - $E_0$  position : between  $\text{Nb}^{4+}$  /  $\text{Nb}^{5+}$
- Hypothesis :  
Contribution of the matrix and the precipitates

- $\mu$ -EXAFS on the matrix :



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→ signal up to  $11.5 \text{\AA}^{-1}$

- Signal from hidden precipitates can not be excluded

→ Work in progress

# CONCLUSION ET PERSPECTIVES

## CONCLUSION

- Influence of the sintering atmosphere (reduction of the dopants during the process)
  - Whatever the starting redox couple and the annealing temperature, coexistence of two niobium oxides ( $\text{NbO}_2$  and  $\text{NbO}$ ) inside the precipitates  $\Leftrightarrow$  Presence of two different valence states
- Possible existence of an in-situ oxygen buffer effect due to niobium

## FUTURE WORK

- New experiments using less reductive annealing atmospheres
  - Preserve the initial redox composition of the dopants
- Solubility limit of niobium in  $\text{UO}_2$  (Electronic Probe MicroAnalysis)
  - Establish a solubility model of niobium in  $\text{UO}_2$

# Thank you for your attention

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